KINETIC ISOTOPE EFFECTS IN THE $CH_4 + H \underset{\leftarrow}{\rightarrow} CH_3 + H_2$

SYSTEM. PREDICTIONS OF THE LMR SIX-BODY

POTENTIAL-ENERGY REACTION HYPERSURFACE

By

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CHAPTER I

INTRODUCTION

Within the limits of the Born-Oppenheimer approximation, the equilibrium molecular configuration and the hypersurface expressing the electronic potential energy for nuclear motion as a function of inter-nuclear coordinates are independent of isotopic substitution. However, the kinetics of nuclear motion on the potential-energy surface are affected by isotopic substitution. This phenomenon leads to isotope effects on equilibria and rates of chemical reactions. Since kinetic isotope effects (KIEs) can be treated within the framework of transition-state (absolute rate) theory,[1] experimental kinetic isotope effects can be either predicted from or used to extract information about the potential-energy reaction hypersurface. This research is concerned with experimental and theoretically calculated KIEs in the following reactions.

$$CH_4 + H\cdot \rightarrow CH_3\cdot + H_2 \qquad\qquad (I\text{-}1)$$

$$CH_3\cdot + H_2 \rightarrow CH_4 + H\cdot \qquad\qquad (I\text{-}2)$$

The purpose of this theoretical investigation is two-fold. First, it serves to test in part the usefulness of the LMR six-body potential-energy surface (LMR-PES) for the thermal reactions (I-1) and (I-2).[2] In this regard the agreement between experimental and theoretical KIEs,

if the former values are assumed to be accurate, provides information concerning the accuracy of the curvature of the potential-energy surface for motion both parallel and perpendicular to the reaction coordinate. Second, these isotope effects were used to assess the validity of a number of the qualitative interpretations of KIEs developed in physical organic chemistry. It should be pointed out that this research is meant to augment the extensive theoretical studies of KIEs on model systems[3] and/or the deduction of transition-state parameters from experimental KIEs.[36,3h,4] Klein has most recently published a literature review of current isotope-effect publications.[5]

The KIEs for various labelled reactants in equations (I-1) and (I-2) were computed within the framework of absolute-reaction-rate theory. The exact equations are expressed in equations (I-3) and (I-4) using the simplified notation of Wolfsberg and Stern,[3b,6] where

$$ \text{KIE} = \frac{k_1}{k_2} \left(\frac{s_2 s_1^{\ddagger}}{s_1 s_2^{\ddagger}} \right) = \text{(MMI)(EXC)(ZPE)} \qquad (I-3) $$

$$ \text{KIE} = \frac{k_1}{k_2} \left(\frac{s_2 s_1^{\ddagger}}{s_1 s_2^{\ddagger}} \right) = \frac{\nu_{1L}^{\ddagger}}{\nu_{2L}^{\ddagger}} \text{(VP)(EXC)(ZPE)} \qquad (I-4) $$

k_1/k_2 is the isotopic rate constant ratio and $\left(\dfrac{s_2 s_1^{\ddagger}}{s_1 s_2^{\ddagger}} \right)$ is the ratio of symmetry numbers associated with the isotopic configurations.[7] MMI is the mass moment of inertia term composed of the molecular weights, M_j, and the moments of inertia, I_{A_j}, I_{B_j} and I_{C_j}, about the three principal axes of the labelled and unlabelled reactants and transition states, see

equation (I-5).[7] The vibrational excitation term, EXC, and the zero

$$MMI = \frac{\left(M_2/M_1\right)^{3/2} \left(\dfrac{I_{A_2} I_{B_2} I_{C_2}}{I_{A_1} I_{B_1} I_{C_1}}\right)^{1/2}}{\left(M_2^{\ddagger}/M_1^{\ddagger}\right)^{3/2} \left(\dfrac{I_{A_2}^{\ddagger} I_{B_2}^{\ddagger} I_{C_2}^{\ddagger}}{I_{A_1}^{\ddagger} I_{B_1}^{\ddagger} I_{C_1}^{\ddagger}}\right)^{1/2}} \qquad (I-5)$$

point energy term, ZPE, are given by (I-6) and (I-7), respectively,

$$EXC = \frac{\displaystyle\prod_{i=1}^{3n-6} \frac{1 - \exp(-u_{1i})}{1 - \exp(-u_{2i})}}{\displaystyle\prod_{i=1}^{3n^{\ddagger}-7} \frac{1 - \exp(-u_{1i}^{\ddagger})}{1 - \exp(-u_{2i}^{\ddagger})}} \qquad (I-6)$$

$$ZPE = \frac{\exp\left[\displaystyle\sum_{i=1}^{3n-6} (u_{1i} - u_{2i})/2\right]}{\exp\left[\displaystyle\sum_{i=1}^{3n^{\ddagger}-7} (u_{1i}^{\ddagger} - u_{2i}^{\ddagger})/2\right]} \qquad (I-7)$$

where $u_{ji} = hc\nu_{ji}/kT$; h is Planck's constant; c is the velocity of

light; k is Boltzmann's constant; T is the temperature in °K; and

ν_{ji} is the ith normal mode frequency in cm^{-1} for the jth isotopic

species.[7] By the Teller-Redlich product theorem, MMI can be equated

to the vibrational product term, VP, times the ratio $\nu_{1L}^{\ddagger}/\nu_{2L}^{\ddagger}$, $\nu_{1L}^{\ddagger}$ and

$\nu_{2L}^{\ddagger}$ are the imaginary frequencies representing motion of the light and

heavy isotopic species, respectively, along the reaction coordinate

in the transition-state configuration, see (I-8).[8] Therefore,

$$
\text{MMI} \;=\; \nu_{1L}^{\ddagger}/\nu_{2L}^{\ddagger}\;\text{VP} \;=\; \nu_{1L}^{\ddagger}/\nu_{2L}^{\ddagger}\;\;\frac{\displaystyle\prod_{i=1}^{3n-6} u_{2i}/u_{1i}}{\displaystyle\prod_{i=1}^{3n-7} u_{2i}^{\ddagger}/u_{1i}^{\ddagger}}
\tag{I-8}
$$

equations (I-3) and (I-4) are completely equivalent.

The normal mode frequencies and the moments of inertia for the variously labelled species were calculated using force constants and geometries computed from the LMR-PES in the Wolfsberg-Stern modification of the Schachtschneider (WMS) normal mode frequency computer program.[9] In this way, the theoretically calculated KIEs are expressed as a function of the LMR-PES.

In the reaction represented by (I-1), quasiclassical-trajectory analysis has shown that the LMR-PES reasonably reproduces the isotopic yield ratio $(HT/CH_4)/(DT/CD_4)$ obtained by Chou and Rowland using translationally hot (2.8 eV) tritium atoms.[10] Chou and Rowland report a value for the yield ratio isotope effect $(HT/CH_4)/(DT/CD_4)$ of 1.43[10] compared to the computed value of 1.18.[2] This agreement indicates that the LMR-PES predicted relative isotopic reaction cross sections are reasonably accurate.[2]

The high temperature limit for KIEs calculated using transition-state theory corresponds to $\nu_{1L}^{\ddagger}/\nu_{2L}^{\ddagger}$.[11] The 2.8 eV of translational energy contained by the tritium atoms used in the LMR-PES trajectory analysis computation of the isotopic yield ratio $(HT/CH_4)/(DT/CD_4)$ corresponds to an ideal gas temperature of approximately 22,000°K. These high-energy tritium atoms collide with room temperature (~300°K

or approximately stationary relative to the tritium atoms) isotopic

methane molecules. Even though the tritium atoms translational energies

will be moderated to some extent prior to their reactions with methane,

their energy distribution will not be Boltzmann. However, as a first

approximation translationally hot tritium atoms might exhibit an

isotope effect similar to the KIE for the reactions represented by

(I-9) and (I-10) at high temperature.

$$CH_4 + T\cdot \rightarrow CH_3\cdot + HT \qquad\qquad (I-9)$$

$$CD_4 + T\cdot \rightarrow CD_3\cdot + DT \qquad\qquad (I-10)$$

Comparison of the $v_{1L}^{\ddagger}/v_{2L}^{\ddagger}$ ratio for (I-9) and (I-10) to the isotopic

yield ratio $(HT/CH_4)/(DT/CD_4)$ is discussed in Chapter III.

Abstraction is the only reaction observed between thermalized

hydrogen atoms and thermalized methane molecules, see (I-1). However,

translationally hot hydrogen (tritium) atoms also react with methane

via substitution as shown in (I-11).

$$CH_4 + T\cdot^* \rightarrow CH_3T + H\cdot \qquad\qquad (I-11)$$

where T^* represents a translationally hot tritium atom.[10] Since

transition-state theory assumes a Maxwellian distribution of atom and

molecule energies, it is only applicable to computation of KIEs for

reactions that occur at thermal energies, for example (I-1) and (I-2).

Kurylo, Hollinden and Timmons have investigated the temperature

dependence of the hydrogen (deuterium) atom abstraction from methane.[12]

$$CH_4 + D\cdot \rightarrow CH_3\cdot + HD \qquad\qquad (I-12)$$

The isotopic reactions, see (I-1) and (I-12), were run independently and monitored by following the hydrogen or deuterium atom decay with ESR spectroscopy as a function of flow rate and distance down the fast flow reactor tube. Equation (I-13) gives the experimentally observed temperature dependence of k_H/k_D which corresponds to a value of

$$k_H/k_D = 1.38 \ exp[(-500 \pm 150)/RT] \qquad (I-13)$$

$k_H/k_D = 0.762$ at 424°K.[12] Analysis of the data is complicated by the fact that the deuterium atoms react at a measurable rate with the product CH_3 radicals to give CH_2D and H atoms as well as abstracting H from methane; see equations (I-14) and (I-12).[12]

$$CH_3 \cdot + D \cdot \rightarrow CH_2D \cdot + H \cdot \qquad (I-14)$$

Due to the error introduced into the experimental determination of the rate constant for (I-12) by (I-14), Kurylo, Hollinden and Timmons found it necessary to approximate the preexponential factor, 1.38, in (I-13) using a simple collision theory calculation.[12]

Kurylo, Hollinden and Timmons compared their experimental results to KIEs calculated using London-Eyring-Polanyi-Sato (LEPS) and bond-energy-bond-order (BEBO) potential-energy surfaces using a computational approach developed by Weston.[3] These results are compared to the corresponding transition-state theory computations on the LMR-PES.

The experimental KIEs for the variously isotopically labelled reactants in equation (I-2) are given in Table I. Table II gives the temperature dependences of these results. The different KIEs in Tables I and II are designated according to the isotopic ratio of the

TABLE I

EXPERIMENTAL KIEs

Isotopic Rate Constant Ratio	Temperature °K	k_1/k_2	Source
$\dfrac{k(CH_3, H_2)}{k(CH_3, D_2)}$	296	2.12	a
	399	4.80	b
	403	4.79	c
	403	5.50	d
$\dfrac{k(CD_3, H_2)}{k(CD_3, D_2)}$	296	0.465	a
	402	3.33	b
	403	2.98	c
	403	4.11	d
$\dfrac{k(CH_3, \underline{H}D)^f}{k(CH_3, \underline{D}H)}$	296	6.37[e]	a
	403	2.33	c
	467	2.08	b
$\dfrac{k(CD_3, \underline{H}D)^f}{k(CD_3, \underline{D}H)}$	402	1.81	b
	402	1.76	c

[a] See Reference 13.

[b] See Reference 14.

[c] See Reference 15.

[d] See Reference 16.

[e] Ting and Weston state that this value is probably excessively high due to the effect of the high HD pressures required for the hot methyl radical reaction. See Reference 13.

[f] The atom underlined is the one being abstracted by the methyl group.

TABLE II

TEMPERATURE DEPENDENCE OF EXPERIMENTAL KIEs

KIE	A_1/A_2	ΔE cal./mole	Temperature Range °K	Source
$\dfrac{k(CH_3, H_2)}{k(CH_3, D_2)}$	0.911	1327	399-645	b
	0.194	1760	403-564[e]	c
	0.246	2516	408-571[e]	d
		1100	409-591	e
$\dfrac{k(CD_3, H_2)}{k(CD_3, D_2)}$	1.592	588	402-611	b
	3.724	-201	410-572[e]	c
	1.727	701	407-570[e]	d
$\dfrac{k(CH_3, \underset{\sim}{H}D)}{k(CH_3, \underset{\sim}{D}H)}$	0.283	1929	467-651	b
	0.452	1350	408-569	c
$\dfrac{k(CD_3, \underset{\sim}{H}D)}{k(CD_3, \underset{\sim}{D}H)}$	0.932	546	402-611	b
	1.73	0	410-572	c

[a]KIEs were fit to the Arrhenius equation of the form $\ln(k_1/k_2) = \ln(A_1/A_2) + \Delta E/RT$.

[b]See Reference 14.

[c]See Reference 15.

[d]See Reference 16.

[e]Davison and Burton assumed a steric factor of $S_1/S_2 = 1$ in their calculation of ΔE from their data. See Reference 17.

[f]Since Whittle and Steacie and Majury and Steacie did not run simultaneous isotopic reactions the temperatures indicate the smallest range encompassing both isotopic reactions.

corresponding reactants. For example, the KIE designated $k(CD_3, HD)/$ $k(CD_3, DH)$ refers to the k_1/k_2 rate constant ratio for the reactions represented by equation (I-15) and (I-16).

$$CD_3 + HD \xrightarrow{k_1} CD_3H + D \qquad (I-15)$$

$$CD_3 + DH \xrightarrow{k_2} CD_3D + H \qquad (I-16)$$
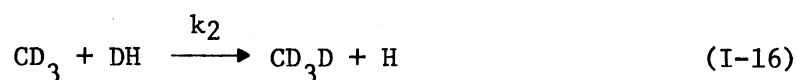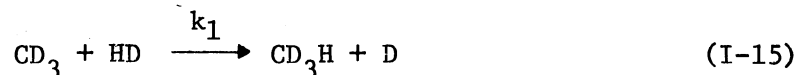
Theoretical KIEs were computed for a comparison to the experimental values in Tables I and II and are discussed relative to each other in Chapter III.

Except in the studies done by Ting and Weston,[13] methyl radicals were generated by photolysis of acetone or acetone-d_6 using a mercury-vapor lamp.[14,15,16,17] The intensity of the 253.7 nm radiation was minimized in order to reduce the mercury sensitized decomposition and scrambling of isotopic reactants.[14,15,16,17] Only a small percentage of the initial acetone was photolyzed (Shapiro and Weston,[14] 1-2%; Whittle and Steacie,[15] ≤ 5%; Majury and Steacie,[16] < 10%) in order to reduce the occurrence of secondary reactions of methyl radicals with the product methanes. The experimental KIE rate constant ratios in Table I were calculated in terms of the initial concentrations of the isotopic reactants, molecular hydrogen and acetone,[13b] and the final concentrations of the products, methane[13-17] and ethane.[15,16] Shapiro and Weston used competitive techniques to determine the KIEs for CH_3 and CD_3 abstraction from H_2/D_2 mixtures.[14] Majury and Steacie[16] and Whittle and Steacie[15] determined these KIEs by measuring the individual rate constants. As seen in Table I, the Shapiro values appear to agree reasonably well with those of Whittle and Steacie.

However, the temperature dependence data in Table II show that the agreement is somewhat fortuitous. Due to the effect of identical isotopic reaction conditions the KIEs determined by competitive techniques should be the more accurate over the temperature range reported, other factors being equal. Indeed the ensemble of experimental data is contradictory in nature and indicates the necessity for precise evaluation of the status of experimental procedures.

Shapiro and Weston used LEPS and BEBO methods together with their experimental results in an attempt to deduce the transition-state geometry and force constants for reaction (I-2).[14] One deficiency in the LEPS and BEBO functions is that they do not include valence bending force constants between the nonreacting methyl hydrogens and between the nonreacting methyl hydrogens and the hydrogen being abstracted. Therefore, Shapiro and Weston used bending force constants from spectroscopic methane data for the HCH bending coordinates not directly associated with the reaction coordinate motion.[14] These authors investigated the dependence of the KIEs on the assumed magnitudes of the HCH valence bending force constants, F_β, associated with the partially formed C-H bond in the transition state.[14] The results from these calculations are discussed in detail in Chapter III. However, it is worth noting that a self-consistent set of transition-state parameters cannot be deduced from the various isotope effects measured for reaction (I-2). It can be seen in Tables I and II that there is considerable difference between the corresponding CH_3 and CD_3 KIE results. This difference must be associated with the transition state force constants. By adjusting the HCH bending force constant in the transition state, Shapiro and Weston could approximately fit either the CH_3 or the CD_3 KIE results, but not both.

Ting and Weston generated hot methyl radicals by photolyzing CH_3Br and CD_3Br with 185 nm light.[13] The KIE determined for reaction of hot CH_3 with H_2 or D_2 was normal (k_H/k_D = 2.12) while the corresponding KIE for CD_3 was inverse (k_H/k_D = 0.465); see Table I. Ting and Weston attempted to explain these unusual results using activated-complex theory to calculate the average cross sections for reaction as a function of total energy. The resultant KIEs, $k(CH_3, H_2)/k(CH_3, D_2)$ = 1.30 and $k(CD_3, H_2)/k(CD_3, D_2)$ = 1.79, are not close to the experimental values.[13] Chapman and Bunker[18] calculated relative cross sections for reaction of both CH_3 and CD_3 with H_2 and D_2, that is, $\sigma(CH_3, H_2)/\sigma(CH_3, D_2)$ = 1.84 and $\sigma(CD_3, H_2)/\sigma(CD_3, D_2)$ = 0.70, which correlate with Ting and Weston's experimental isotope effects.[13] The significance of this result is not clear since a cross section ratio is not the same measured or calculated quantity as a KIE. These isotope effects were indicated to occur only for ground state vibrational energy in the methyl radical.[18] However, the Chapman and Bunker results show that vibrational excitation of $H_2(D_2)$ tended to preserve this unusual isotope effect and enhance the reaction rates. This enhancement of reaction rates is in agreement with the experimental data of Sims and others for reactions of halogen atoms with H_2.[19]

The transition-state configuration for reactions (I-1) and (I-2) is treated as being linear along the two bonds directly involved in the hydrogen transfer reactions, see (I-17), where $r_1^{\ddagger}$ is the $C-H_1$ bondlength,

$$CH_3 \cdots \overset{\overset{\ddagger}{r_1}}{H_1} \cdots \overset{\overset{\ddagger}{r_2}}{H_2} \qquad (I-17)$$

$r_2^{\ddagger}$ is the H_1-H_2 bond length and $r_1^{\ddagger}$ and $r_2^{\ddagger}$ are collinear. If the CH_3

moiety is treated as a point group, then there are four normal mode frequencies associated with the linear configuration (I-17); $\nu_S^{\ddagger}$ is the symmetric stretching frequency, $\nu_L^{\ddagger}$ is the imaginary asymmetric stretching frequency representing translational motion along the reaction coordinate and $\nu_B^{\ddagger}$ corresponds to the doubly degenerate linear bending frequency. Theoretical treatments of the linear three-center transition-state configuration have often neglected the linear-bending frequencies on the assumption that the sum of the two frequencies compensates for the loss in reactant-state bending frequencies. (That is, in passing from the reactant state to the activated complex no net change in vibrational energy due to the normal vibrational bending modes is associated with the H(D) being transferred.) This allowed the isotope effect to be rationalized as a result of the normal mode stretching vibrations $\nu_S^{\ddagger}$ and $\nu_L^{\ddagger}$. The transition state harmonic potential energy expression for this simplified configuration is given in (I-18),

$$2V = f_1^{\ddagger} \Delta r_1^{\ddagger} + f_2^{\ddagger} \Delta r_2^{\ddagger} + 2 f_{12}^{\ddagger} \Delta r_1^{\ddagger} \Delta r_2^{\ddagger} \qquad (I\text{-}18)$$

where $f_1^{\ddagger}$ and $f_2^{\ddagger}$ are the stretching force constants associated with $r_1^{\ddagger}$ and $r_2^{\ddagger}$, respectively, $f_{12}^{\ddagger}$ is the stretching interaction force constant, and $\Delta r_1^{\ddagger}$ and $\Delta r_2^{\ddagger}$ are deviations from the equilibrium values for $r_1^{\ddagger}$ and $r_2^{\ddagger}$, respectively.[20] Bigeleisen[20] and Willi and Wolfsberg[21] have shown that the primary hydrogen (deuterium) KIE is a maximum for a symmetric transition-state configuration where $r_1^{\ddagger} \simeq r_2^{\ddagger}$ and $f_1^{\ddagger} \simeq f_2^{\ddagger}$ when $\nu_L^{\ddagger} = 0$. (That is, the PES is flat at the top of the barrier along the reaction coordinate.) However, Willi and Wolfsberg have demonstrated that if $\nu_L^{\ddagger}$ has an imaginary value then the transition-state bond orders can be

very unequal and still yield a KIE value that is almost identical to the KIE calculated for the symmetric transition-state configuration.[21] This shows that knowledge of the temperature independent factor, $\nu_{1L}^{\ddagger}/\nu_{2L}^{\ddagger}$, is really essential in determining the transition-state configuration. Thus, insight into the transition-state bonding and geometry requires comparison of $\nu_{1L}^{\ddagger}/\nu_{2L}^{\ddagger}$ ratios and KIEs calculated from a complete and reasonably accurate potential-energy surface with experimental KIEs and their temperature dependency data.

The approximation of neglecting all bending frequencies associated with the isotopic atom being transferred in a reaction proceeding via a linear three-center activated complex may have some validity at least in certain instances. Kresge and Chiang determined a KIE for a proton transfer reaction involving the hydrolysis of ethyl vinylether by HF (or DF). These reactions assumably proceed through a linear transition-state configuration.[22] The magnitude of this KIE was considerably less than the value expected. Kresge and Chiang attributed the low KIE to the existence of a doubly degenerate linear-bending frequency in the transition-state configuration which tends to compensate for the loss in the HF (DF) stretching vibration. The magnitude of the bending vibration necessary to cause the observed lowering of the KIE was about $1100 \, \text{cm}^{-1}$.[22] Kresge and Chiang noted that since $1100 \, \text{cm}^{-1}$ is not very different from HCX bending frequencies in many molecules this could account for the reasonable success in predicting maximum KIEs with neglect of the bending frequencies associated with the atom being transferred in the activated complex.[22] A semi-quantitative estimate of the effect on the KIEs of the C-H-H linear bend in the six-body transition-state configuration, CH_3-H-H, was

made on the basis of a normal mode frequency analysis using force
constants obtained from the LMR-PES. This normal mode frequency
analysis allowed an estimate of the inaccuracy that would be
incurred by neglecting bending frequencies in the calculation of
KIEs for (I-1) and (I-2).

The Swain-Schaad relationship, see (I-19), provides a simple
method of relating primary deuterium and tritium KIEs.[23] The

$$k_H/k_T = (k_H/k_D)^{1.442} \qquad\qquad (I-19)$$

Swain-Schaad relationship takes advantage of the fact that at low
temperatures primary hydrogen isotope effects principally reflect
changes in the zero-point energy associated with the hydrogen
(deuterium or tritium) being transferred in passing from the reactant
state to the transition state. The assumptions basic to the Swain-
Schaad relationship are as follows. First, in a reaction like (I-1)
the isotopic H being transferred is bonded to a polyatomic and
relatively heavy molecular entity. Thus, as a reasonable first approx-
imation isotopic substitution affects only the harmonic frequencies
associated with the bond to the isotopically substituted atom. Second,
no tunneling is assumed to occur.[23] Consequently, the KIE is
effectively equated to the ZPE term, see (I-7), involving only the
vibrations associated with the H being transferred. For high temper-
atures Swain and others included a vibrational excitation correction
factor, α, based on the temperature dependency of EXC, see (I-6), such
that $k_H/k_T = \alpha(k_H/k_D)^{1.442}$.[23]

Bigeleisen, using a more complete transition-state theory approach, predicted a range of $1.33 \leq r \leq 1.58$ for the relative deuterium to tritium KIEs where r is defined by (I-20) and $r = 1.442$ is

$$r = \frac{\ln(k_H/k_T)}{\ln(k_H/k_D)} \qquad \text{(I-20)}$$

equivalent to the Swain-Schaad equation (I-19).[24] Stern and Vogel calculated the temperature dependences for r in a large number of model calculations and agreed with Bigeleisen's observation that an experimental value for r lower than 1.33 would be evidence for the existence of tunneling provided that the isotope effects are large primary (or mixed secondary-primary) normal individual isotope effects exhibiting a monotonic temperature dependence.[25] However, in a more recent paper Stern and Weston found that there was no direct general correlation between the magnitude of r and the extent of tunneling.[26]

In this research values of r as a function of temperature were obtained from the calculated KIEs for reaction (I-1) relative to (I-21) and (I-22). Correspondingly similar calculations of r were also

$$CH_4 + D(T) \rightarrow CH_3 + HD(HT) \qquad \text{(I-21)}$$

$$CH_3D(T) + H\cdot \rightarrow CH_3 + DH(TH) \qquad \text{(I-22)}$$
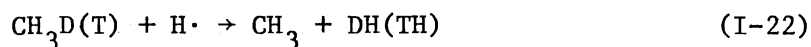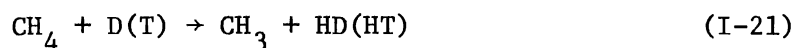
made for the isotopic reactions of equation (I-2). These values are discussed in Chapter III.

A relationship similar to the Swain-Schaad equation has been developed for relating carbon-13 and carbon-14 KIEs. This relationship was tested relative to the transition-state theory

calculated KIEs in a manner similar to that used for the tritium-deuterium relationship.

Bigeleisen has developed equations for relating, $S_2/S_1 f(\frac{2}{1})$, the vibrational partition function ratios of isotopically substituted molecules which are commonly referred to as the rule of the geometric mean (RGM).[27] These equations were developed from the relationship between the vibrational frequency sum rules of Decius and Wilson[27c] and the approximation of the Bigeleisen $S_2/S_1 f(\frac{2}{1})$ factor by the truncated expansion in powers of u_i, see (I-23), where u_i is as

$$\ln[S_2/S_1 f(\tfrac{2}{1})] \stackrel{\sim}{=} 1/24 \sum_i u_{1i}^2 - u_{2i}^2 \qquad \text{(I-23)}$$

previously defined, see (I-7), and S_2/S_1 is the symmetry number ratio.[7b] Equation (I-23) is the first-order approximation to the exact equation for $S_2/S_1 f(\frac{2}{1})$, see (I-24), and is valid at sufficiently high tempera-

$$S_2/S_1 f(\tfrac{2}{1}) = \prod_i \frac{u_{2i}}{u_{1i}} \frac{\left(\dfrac{e^{-u_{2i}/2}}{1 - e^{-u_{2i}}} \right)}{\left(\dfrac{e^{-u_{1i}/2}}{1 - e^{-u_{1i}}} \right)} \qquad \text{(I-24)}$$

ture that $u_{1i} << 2\Pi$. The sum-rule relationships between isotopically different $S_2/S_1 f(\frac{2}{1})$ values approximated by (I-23) require the involvement of three or more different isotopic molecular species.[27c] Bigeleisen has given a general expression for higher order approximations to $S_2/S_1 f(\frac{2}{1})$, see (I-25), where the B's are Bernoulli numbers

$$\ln(S_2/S_1 f(\tfrac{2}{1})) = \sum_{i}^{3n-6} \sum_{j=1}^{m} (-1)^{j+1} \frac{B_{2j-1}}{2j(2j!)} \delta u_i^{2j} \tag{I-25}$$

$(B_1 = \tfrac{1}{6}, \; B_3 = \tfrac{1}{30}, \; B_5 = \tfrac{1}{42}, \text{ et cetera})$, and $\delta u_i = u_{1i} - u_{2i}$ for $u_{1i} < 2\pi.$[27b]

Bigeleisen has stated that systems that obey sum rules through the order $\underset{\sim}{m}$ will obey the RGM through the order of δu_i^{2m}.[27b] Some examples of RGM relationships given by Bigeleisen are exhibited in (I-26) through (I-28).[27b]

$$[S_2/S_1 f(\frac{CH_2D_2}{CH_3D})]^3 = S_2/S_1 f(\frac{CHD_3}{CH_4}) \tag{I-26}$$

$$[S_2/S_1 f(\frac{CHD_3}{CH_2D_2})]^3 = S_2/S_1 f(\frac{CD_4}{CH_3D}) \tag{I-27}$$

$$[S_2/S_1 f(\frac{CHD_3}{CH_3D})]^2 = S_2/S_1 f \frac{CD_4}{CH_4} \tag{I-28}$$

The Bigeleisen $S_2/S_1 f$ factors are also defined in terms of equation (I-29), where VP·EXC·ZPE are as previously defined, see (I-4).[7] Using

$$\frac{S_2/S_1 f(\tfrac{2}{1})}{S_2^{\ddagger}/S_1^{\ddagger} f^{\ddagger}(\tfrac{2}{1})} = \text{VP·EXC·ZPE} \tag{I-29}$$

(I-29), calculations similar to (I-26) through (I-28) were done using the normal mode frequencies obtained from the LMR-PES, see (I-30) through (I-33). The results of these relationships are discussed in Chapter III.

$$\left[\frac{S_2/S_1\,f\left(\dfrac{CH_3D}{CH_4}\right)}{S_2^{\ddagger}/S_1^{\ddagger}\,f^{\ddagger}\left(\dfrac{CH_2D-H-H}{CH_3-H-H}\right)}\right]^3 = \frac{S_2/S_1\,f\left(\dfrac{CHD_3}{CH_4}\right)}{S_2^{\ddagger}/S_1^{\ddagger}\,f^{\ddagger}\left(\dfrac{CD_3-H-H}{CH_3-H-H}\right)} \qquad (I\text{-}30)$$

$$\left[\frac{S_2/S_1\,f\left(\dfrac{CH_3D}{CH_4}\right)}{S_2^{\ddagger}/S_1^{\ddagger}\,f^{\ddagger}\left(\dfrac{CH_2D-H-H}{CH_3-H-H}\right)}\right]^2 = \frac{S_2/S_1\,f\left(\dfrac{CH_2D_2}{CH_4}\right)}{S_2^{\ddagger}/S_1^{\ddagger}\,f^{\ddagger}\left(\dfrac{CHD_2-H-H}{CH_3-H-H}\right)} \qquad (I\text{-}31)$$

$$\left[\frac{S_2/S_1\,f\left(\dfrac{CH_2D}{CH_3}\right)}{S_2^{\ddagger}/S_1^{\ddagger}\,f^{\ddagger}\left(\dfrac{CH_2D-H-H}{CH_3-H-H}\right)}\right]^3 = \frac{S_2/S_1\,f\left(\dfrac{CD_3}{CH_3}\right)}{S_2^{\ddagger}/S_1^{\ddagger}\,f^{\ddagger}\left(\dfrac{CD_3-H-H}{CH_3-H-H}\right)}$$

$$\left[\frac{S_2/S_1\,f\left(\dfrac{CH_2D}{CH_3}\right)}{S_2^{\ddagger}/S_1^{\ddagger}\,f^{\ddagger}\left(\dfrac{CH_2D-H-H}{CH_3-H-H}\right)}\right]^2 = \frac{S_2/S_1\,f\left(\dfrac{CHD_2}{CH_3}\right)}{S_2^{\ddagger}/S_1^{\ddagger}\,f^{\ddagger}\left(\dfrac{CHD_2-H-H}{CH_3-H-H}\right)} \qquad (I\text{-}33)$$

CHAPTER II

COMPUTATIONAL PROCEDURES

Calculation of Force Constants and Geometries

General

The application of transition-state theory to the calculation of
kinetic isotope effects for reactions (I-1) and (I-2) by equations
(I-3) and (I-4) requires the normal-mode vibrational frequencies
associated with the isotopic reactant and transition-state molecular
species. Calculation of these normal mode frequencies requires the
force constant description of the bonding in the various molecular
species and the associated geometry and atomic masses. The harmonic
force-constant description is calculated as the second derivative of
the internal energy of a molecular species with respect to an
internal coordinate motion.[28] For example, molecular hydrogen, H_2,
has the bond stretching internal coordinate defined by r_H. If V is
the internal potential function for H_2, then the force constant F_H is
given by $\left. \dfrac{\partial^2 V}{\partial r_H^2} \right|_{r_H = (r_H)_{eq}}$. The normal-mode frequency for this simple
molecule is calculated by $\nu_H = 2\pi \left(\dfrac{F_H}{\mu_H} \right)^{1/2}$, where μ_H is the reduced mass
of the H_2 molecule. Normal-mode frequencies for large molecular species
are calculated using the WMS program method described in Appendix B.[9]

Description of the LMR-PES

The LMR-PES is defined as a sum of three-body interactions plus harmonic bond-bond interactions, where the three-body terms,

$$V(R_i, \theta_j) = T(r_1, r_5, r_6) + T(r_2, r_5, r_7) + T(r_3, r_5, r_8)$$
$$+ T(r_4, r_5, r_9) + \frac{1}{2} \sum_{j=1}^{6} k_j (\theta_j - \theta_j^\circ)^2 \tag{II-1}$$

$T(r_{AB}, r_{AC}, r_{BC})$, and the harmonic bond-bond terms $k_j (\theta_j - \theta_j^\circ)^2$ are defined in terms of the LMR-PES internal coordinates shown in Figure 1 and/or designated in Table III. Values of the internal coordinates for the $CH_4 + H$ and $CH_3 + H_2$ reactant states are also presented in Table III. Each of the three-body terms in equation (II-1) are defined in terms of the interaction energies between the two atoms in the diatomic pairs represented by the interatomic distances r_i, r_j, and r_k,

$$T(r_i, r_j, r_k) = Q_{AB} + Q_{AC} + Q_{BC} \tag{II-2a}$$

$$1/2[(J_{AB} - J_{BC})^2 + (J_{AC} - J_{AB})^2 + (J_{BC} - J_{AC})^2]^{1/2}$$

$$Q_{\alpha\beta} = [{}^1E_{\alpha\beta} + {}^3E_{\alpha\beta}]/2 \tag{II-2b}$$

$$J_{\alpha\beta} = [{}^1E_{\alpha\beta} - {}^3E_{\alpha\beta}]/2 \tag{II-2c}$$

where ${}^1E_{\alpha\beta}$ and ${}^3E_{\alpha\beta}$ are the singlet and triplet state energies, respectively, for each $\alpha\beta$ diatomic system. The singlet state energy is represented by a Morse function, see(II-3), where r_n is the interatomic
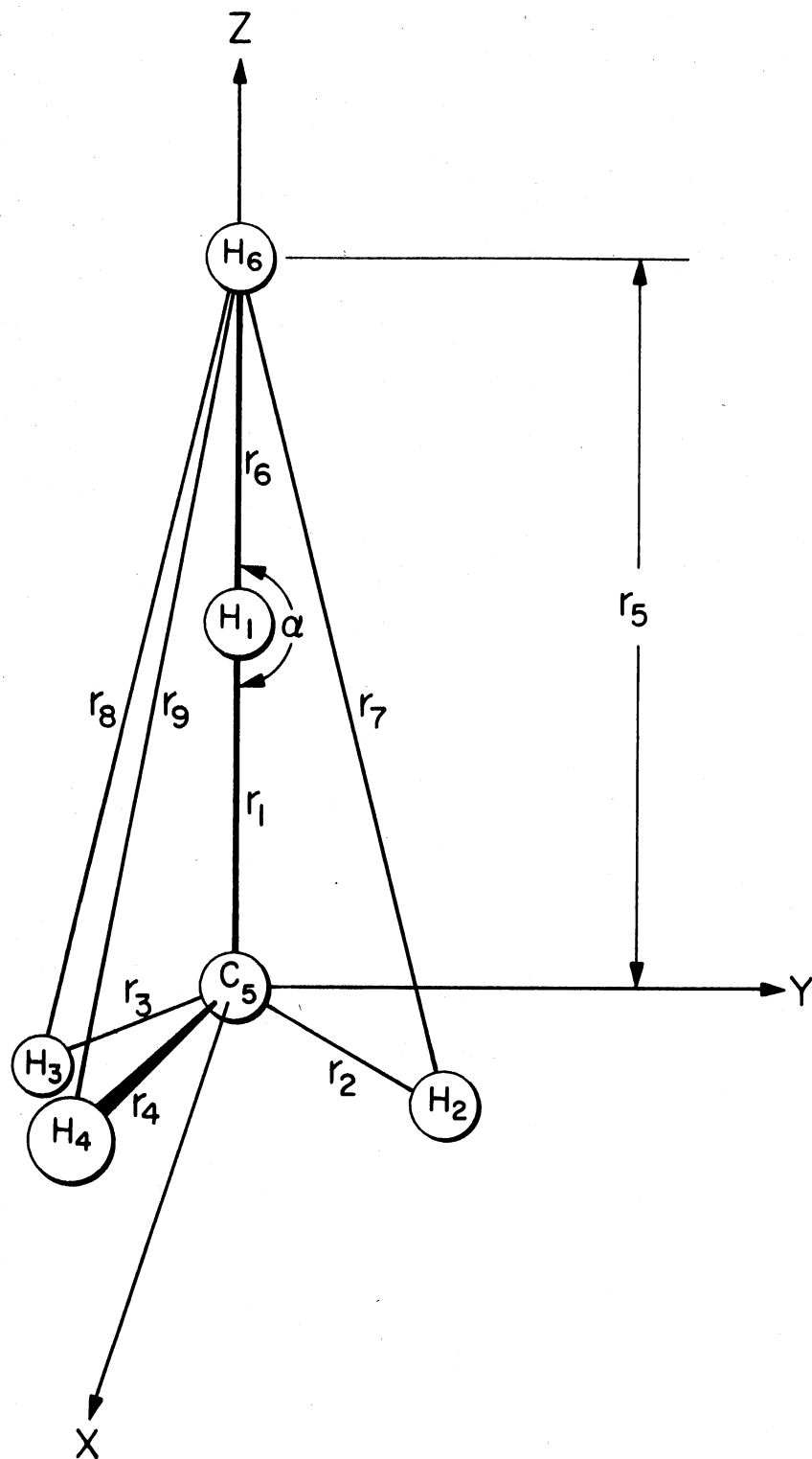
Figure 1.   Interatomic Distances Used in the LMR-
PES

TABLE III

LMR-PES AND VALENCE INTERNAL COORDINATES
DESIGNATIONS AND VALUES FOR REACTANTS

Atoms in Coordinate	LMR-PES Designation	Equilibrium Values and Valence Coordinates Designations for			
		$CH_4 + H$		$CH_3 + H_2$	
		Value[a]	Coordinate[b]	Value[a]	Coordinate[b]
CH_1	r_1	2.0673	R_1	20.0000	
CH_2	r_2	2.0673	R_2	2.0673	R_1
CH_3	r_3	2.0673	R_3	2.0673	R_2
CH_4	r_4	2.0673	R_4	2.0673	R_3
CH_6	r_5	1002.0673		21.4020	
H_1H_6	r_6	1000.0000		1.4020	R_1[c]
H_2H_6	r_7	1002.7583		21.5016	
H_3H_6	r_8	1002.7583		21.5016	
H_4H_6	r_9	1002.7583		21.5016	
H_1CH_2	θ_1	109.4712	ϕ_1	90	
H_1CH_3	θ_2	109.4712	ϕ_2	90	
H_1CH_4	θ_3	109.4712	ϕ_3	90	
H_2CH_3	θ_4	109.4712	ϕ_4	120	ϕ_1
H_2CH_4	θ_5	109.4712	ϕ_5	120	ϕ_2
H_3CH_4	θ_6	109.4712	ϕ_6	120	ϕ_3

[a]Bond lengths and interatomic distances in atomic units and bond angles are in degrees.

[b]Out-of-plane bending valence coordinate for CH_3 is not defined by the LMR-PES.

[c]Specifies the vibrational motion of H_2.

$$^1E_{\alpha\beta} = D[\exp\{-2\alpha(r_n - r_e)\} - 2\exp\{-\alpha(r_n - r_e)\}] \qquad \text{(II-3)}$$

distance between one of the nine $\alpha\beta$ diatomic pairs in Table III, r_e is

the equilibrium $\alpha\beta$ bond distance, D is the bond dissociation energy

plus the zero-point energy, and α is the exponential Morse parameter.[2]

As shown in equation (II-4), the triplet state energy is given by a

$$E^3_{\alpha\beta} = {}^3D[\exp\{-2\beta(r_n - r_e)\} + 2\exp\{-\beta(r_n - r_e)\}] \qquad \text{(II-4)}$$

similar functional representation for the condition that all $r_n \leq r^*$.

If $r_n > r^*$ then $^3E_{\alpha\beta}$ is represented by (II-5). Thus, r^* is the

$$E^3_{\alpha\beta} = C[r_n + A]\exp(\sigma r_n) \qquad \text{(II-5)}$$

changeover point between the functional forms (II-4) and (II-5). Values

for the triplet state parameters in (II-4) and (II-5) are given in

Table IV. These parameters were empirically determined by a procedure

previously described by Raff and coworkers.[2,29] The harmonic bond-bond

interaction terms, $1/2 \sum_{j=1}^{6} k_j(\theta_j - \theta_j^o)^2$, are a function of the six HCH

angles described in Table III, where the θ_j^o are the angles character-

istic of the equilibrium molecular configuration and the θ_j and k_j are

the angles and bending force constants, respectively, for a specified

molecular configuration. The force constant values are determined by

(II-6),

$$k_j = k_j^o f(r_{C-H_i}, r_{H_i-H_6}) f(r_{C-H_\ell}, r_{H_\ell-H_6}) \qquad \text{(II-6)}$$

with $i = 1,2,3,4$, $\ell = 1,2,3,4$ and $\ell \neq i$. The equilibrium bending force

TABLE IV

LMR-PES PARAMETERS

Parameter	Diatomic Pair		
	C–H	C–H'[a]	H–H
D^{b}	4.5808	1.1452	4.7466
α^{c}	0.98058	0.98058	1.04435
r_{e}^{d}	2.0673	2.0673	1.402
D_{e}^{b}	1.63	0.4075	1.9668
β^{c}	0.60	0.60	1.000122
C^{b}	3675.92	918.98	25.55301785
A^{d}	−2.360263	−2.360263	1.0
σ^{c}	2.296479	2.296479	1.6756385
r_{*}^{d}	3.0	3.0	1.6
a_{1}^{e}	0.8999975		
a_{2}^{e}	0.448035		
a_{3}^{e}	0.606528		
a_{4}^{e}	3.239921		
a_{5}^{e}	0.080768		

[a]Corresponds to the two atoms describing r_{5} in Table III.

[b]In units of electron volts (eV).

[c]In (atomic units (a.u.))$^{-1}$.

[d]In a.u.

[e]In (a.u.)$^{-2}$.

constant k_j^o equals 3.4436 eV/rad.[2] Each $f(r_{C-H}, r_{H-H_6})$ term is a function of one of the C-H bonds defining the angle θ_j and the corresponding interatomic distance between the hydrogen bonded to the carbon and the abstracting hydrogen, H_6. The form of the $f(r_{C-H}, r_{H-H_6})$ function was determined by a nonlinear least squares fit to INDO calculated results as given by (II-7),

$$f(r_{C-H}, r_{H-H_6}) = k_i/k_i^o = A_1 \exp\{-A_2[r_{C-H} - r_e(C-H)]^2\} \qquad \text{(II-7a)}$$

$$A_1 = 1.0 - \exp(-a_1 r_{H-H_6}^2) \qquad \text{(II-7b)}$$

$$A_2 = a_2 + a_3 \exp\{-a_4[r_{H-H_6} - r_e(H-H)]^2\} \qquad \text{(II-7c)}$$

where the coefficients A_1, A_2, a_1, a_2, a_3, and a_4 were all determined by nonlinear least squares procedures and $r_e(C-H)$ in (II-7a) and $r_e(H-H)$ in (II-7c) refer to the equilibrium C-H and H-H bond lengths, respectively.[2] The equilibrium frontside angles, $\theta_f(f=1,2,3)$, are determined by the functional relationship given by (II-8),

$$\theta_f^o = \tau - a_5[r^+ - r_e(C-H)], \quad (r^+ \leq 6.274 \text{ a.u.}) \qquad \text{(II-8a)}$$

$$\theta_f^o = 90°, \quad (r^+ > 6.274 \text{ a.u.}) \qquad \text{(II-8b)}$$

where τ is the tetrahedral angle in radians, and a_5 and the value 6.274 were determined from INDO computational results. The longest C-H bond length in the five atom CH_4 methane configuration is designated as r^+ (in the transition state $r^+ = r_1$), and r_e is the equilibrium C-H bond

length. The equilibrium backside angles, θ_b (b=4,5,6), are functions of the frontside angles, see (II-9). The values of the constants used in

$$\theta_b^\circ = \arccos(1.0 - 1.5\sin^2\theta_f^\circ) \tag{II-9}$$

the LMR-PES function calculations are given in Table IV. It should be noted that the energy parameters, D, D_3, and C, for the C-H' values are 25 percent of the C-H values because the C-H' interaction is counted once in each of the four three-body terms in (II-1).

Reactant and Product Geometries and Coordinates

The general six-atom configuration is given by Figure 1. Table III compares the LMR-PES internal coordinate designations and geometry values for the reactants and products in equations (I-1) and (I-2) to the corresponding internal valence coordinates designations for which force constants are calculated. The two-atom internal valence coordinate designations describe bond stretching vibrational motion and the three-atom designations describe bond bending vibrational motion. It should be noted that in Table III the internal valence coordinates for the reactants and products are direct functions of the corresponding LMR-PES internal coordinates except for the out-of-plane bending valence coordinate which is not defined by the functional form of the LMR-PES. By equation (II-8), the LMR-PES predicts a planar CH_3 geometry. However, by (II-6) and (II-7) when CH_3 is planar then the k_j (j=1,2,3) force constant terms in the LMR-PES which describe the out-of-plane bending motion in CH_3 are effectively zero. For this reason the calculation of the out-of-plane bending force constant value is handled separately from the LMR-PES force constant calculations which follow.

Transition-State Geometry and Coordinates

The transition-state geometry values are given in Table V for the LMR-PES coordinates. Unlike the reactants and products coordinates, all of the transition-state LMR-PES coordinates contribute significantly to the calculated energy. Therefore, since not all the LMR-PES coordinates correspond to a valence coordinate, the valence coordinates were expressed as a function of the appropriate LMR-PES coordinates involved in each internal valence coordinate designation. Force constants were calculated with respect to these designated internal valence coordinates.

The transition-state geometry values in Table V were obtained by scanning the LMR-PES for the top of the barrier along the reaction coordinate. The coordinates r_1 and r_6 were initialized at values greater and less than their corresponding equilibrium values from Table IV, respectively. The r_1 coordinate is then decremented 100 times (or until a minimum energy is found) at each r_6 incremented coordinate value. These minimum energy configurations describe the reaction coordinate for reactions (I-1) and (I-2). The maximum energy along the reaction coordinate corresponds to the top of the barrier. The barrier height energy is obtained by subtracting the reactant $CH_4 + H$ internal energy from the configuration energy at the top of the barrier. Table VI shows the results of a consecutive series of concurrent scans of the LMR-PES to find the top of the barrier.

TABLE V

LMR-PES AND VALENCE INTERNAL COORDINATES DESIGNATIONS
AND VALUES FOR THE TRANSITION STATE

LMR-PES Coordinates			Valence Coordinates	
Atoms in Coordinate	Designation	Equilibrium[a] Value	Atoms in Coordinate	Designation
CH_1	r_1	3.0178	CH_1	$R_1 = f(r_1, r_5, r_7, r_8, r_9)$
CH_2	r_2	2.0673	CH_2	$R_2 = f(r_2, r_7)$
CH_3	r_3	2.0673	CH_3	$R_3 = f(r_3, r_8)$
CH_4	r_4	2.0673	CH_4	$R_4 = f(r_4, r_9)$
CH_6	r_5	4.4982	H_1H_6	$R_5 = f(r_5, r_6, r_7, r_8, r_9)$
H_1H_6	r_6	1.4804	H_1CH_2	$\phi_1 = f(\theta_1, r_7)$
H_2H_6	r_7	5.4170	H_1CH_3	$\phi_2 = f(\theta_2, r_8)$
H_3H_6	r_8	5.4170	H_1CH_4	$\phi_3 = f(\theta_3, r_9)$
H_4H_6	r_9	5.4170	H_2CH_3	$\phi_4 = f(\theta_4, r_7, r_8)$
H_1CH_2	θ_1	105.0726	H_2CH_4	$\phi_5 = f(\theta_5, r_7, r_9)$
H_1CH_3	θ_2	105.0726	H_3CH_4	$\phi_6 = f(\theta_6, r_8, r_9)$
H_1CH_4	θ_3	105.0726	$(CH_1H_6)_{xz}^{b}$	$\alpha_x = f(r_5, r_7, r_8, r_9)$
H_2CH_3	θ_4	113.4886	$(CH_1H_6)_{yz}^{c}$	$\alpha_y = f(r_5, r_7, r_8, r_9)$
H_2CH_4	θ_5	113.4886		
H_3CH_4	θ_6	113.4886		

[a]Bond lengths and interatomic distances in atomic units and bond angles in degrees.

[b]Specifies linear bending in the xz plane.

[c]Specifies linear bending in the yz plane.

TABLE VI

TRANSITION-STATE SCANNING RESULTS

Scan Number	$r_1{}^a$	$r_6{}^a$	Increment Size[a]	Barrier Height Energy[b]
Start 1[c]	3.5	1.25	7.5×10^{-3}	
End 1[d]	3.02	1.49		5.60624735710553
Start 2[c]	3.0275	1.475	1.5×10^{-4}	
End 2[d]	3.0179	1.48055		5.59759021152999
Start 3[c]	3.0182	1.48025	6.0×10^{-6}	
End 3[d]	3.017804	1.480382		5.59758731815947
Start 4[c]	3.017816	1.48037	2.4×10^{-7}	
End 4[d]	3.0177992	1.4803774		5.59758731610498
Start 5[c]	3.01779968	1.48037696	9.6×10^{-9}	
End 5[d]	3.0177991232	1.4803772096		5.59758731609884
Start 6[c]	3.0177991424	1.4803771904	3.84×10^{-10}	
End 6[d]	3.017799132032	1.480377204608		5.59758731609884

[a]Values in atomic units (a.u.).

[b]Values in kilocalories per mole for reaction (I-1).

[c]Values at the start of the scan.

[d]Values at the end of the scan.

Numerical Methods of Force Constant

Determination

Force constants were calculated numerically for each of the internal valence coordinates described in Tables III and V. Additionally, off-diagonal cross term force constants were calculated. These force constants determine the amount of interaction between any two of the valence coordinates in a particular molecular species. These force constants are defined by the value of $(\frac{\partial}{\partial q_i} \frac{\partial}{\partial q_j})_{q_k \neq q_i, q_j}$, where q_i and q_j are valence coordinates of a molecular species defined in Table III or Table V. If $q_i = q_j$, then the second derivative is a diagonal force constant, but if $q_j \neq q_i$, it is an interaction force constant.

The simplest numerical partial differentiation technique used is the two function-point definition of a derivative,

$$\lim_{h \to 0} \frac{f(x+h,y)-f(x,y)}{h} = f_1(x,y) = \frac{\partial f(x,y)}{\partial x} \qquad (II-10)$$

where $f(x,y)$ is a function of variables x and y, and h is the increment size.[30] Equation (II-10) was used to generate the three-point second derivative method given by (II-11).[30]

$$\lim_{h \to 0} \left[\frac{\left(\frac{f(x+h,y)-f(x,y)}{h}\right) - \left(\frac{f(x,y)-f(x-h,y)}{h}\right)}{h} \right] =$$

$$\lim_{h \to 0} \frac{f(x+h,y)+f(x-h,y)-2f(x,y)}{h^2} = f_{1,1}(x,y) = \frac{\partial^2 f(x,y)}{\partial x^2}$$

$$f_{1,1}(x,y) \cong \frac{f(x+h,y)+f(x-h,y)-2f(x,y)}{h^2} \qquad (II-11)$$

The error in (II-11) is equal to

$$E_d = -\frac{h^2}{12} f^{IV}(\xi) \tag{II-12}$$

where h is the increment size and $f^{IV}(\xi)$ is the fourth derivative of the function being differentiated with $|\xi-x| < |h|$.[30] This error is referred to as the discretization error due to the method of finite differences and is in addition to any round-off error.[30] For double precision accuracy on the IBM 360/65 used for these calculations, the relative round-off error is approximately 1×10^{-16}. An estimate of the error involved in the calculation of (II-11) with $f(x,y) = [g(x)+k(y)]$, where $g(x) = C^2 e^{-2x} - 2Ce^{-x}$, $C = e^2$, $x = 2$, $h = 1 \times 10^{-4}$ and $k(y) = 0$ is given by

$$E = (E_d + \frac{4E_r}{h^2}) = [\frac{-(1 \times 10^{-4})^2}{12}(16C^2 e^{-2x} - 2Ce^{-x}) + \frac{4E_r}{(1 \times 10^{-4})^2}] \tag{II-13}$$

where E_r is the approximate round-off error in each of the four function values in (II-11). If $E_r \cong 1 \times 10^{-16}$ then the relative error in the evaluation of (II-11) for $f(x,y)$ is given by $E_{Rel} = E/f(x,y) \cong$ -1.4×10^{-8}. Although the exact error involved in numerical differentiation of (II-1) is not calculated, the functional form is composed primarily of negative exponential terms with relatively small exponents. Therefore, the relative error involved in applying (II-11) to (II-1) should be close to that for (II-13) within two or three orders of magnitude. The following difference method for cross-terms should have comparably small error.

A computational method was derived for calculation of the off-diagonal (cross term) second derivatives of the form $\frac{\partial}{\partial x}(\frac{\partial f(x,y)}{\partial y})_x =$ $f_{1,2}(x,y)$. For purposes of derivation, a function of the incremented coordinates was defined by

$$Q_{h,k}(\delta) = f(x + \delta h, y + \delta k) \tag{II-14}$$

where δ/x and $\delta/y \ll 1$ and h and k are unit directional coefficients of δ having possible values of 1, 0, or -1. By deriving a functional form for the second derivative of $Q_{h,k}(\delta)$ it was possible to obtain a numerical approximation to $f_{1,2}(x,y)$. The first derivative of $Q_{h,k}(\delta)$ is defined by (II-15),

$$Q'_{h,k}(\delta) = \frac{\partial f(x + \delta h, y + \delta k)}{\partial \delta}$$

$$Q'_{h,k}(\delta) = \frac{\partial f(x + \delta h, y + \delta k)}{\partial (x + \delta h)} \cdot \frac{\partial (x + \delta h)}{\partial \delta} + \frac{\partial f(x + \delta h, y + \delta k)}{\partial (y + \delta k)} \cdot \frac{\partial (y + \delta k)}{\partial \delta}$$

$$Q'_{h,k}(\delta) = hf_1(x + \delta h, y + \delta k) + kf_2(x + \delta h, y + \delta k) \tag{II-15}$$

where $f_2(x + \delta h, y + \delta k) = \dfrac{\partial f(x + \delta h, y + \delta k)}{\partial (y + \delta k)}$, f_1 is defined by (II-10), $h = \dfrac{\partial (x + \delta h)}{\partial \delta}$ and $k = \dfrac{\partial (y + \delta k)}{\partial \delta}$. Therefore, the second derivative of $Q_{h,k}(\delta)$ is given by (II-16),

$$Q''_{h,k}(\delta) = h \left[\frac{\partial f_1(x + \delta h, y + \delta k)}{\partial (x + \delta h)} \cdot \frac{\partial (x + \delta h)}{\partial \delta} + \frac{\partial f_1(x + \delta h, y + \delta k)}{\partial (y + \delta k)} \cdot \frac{\partial (y + \delta k)}{\partial \delta} \right]$$

$$+ \; k \left[\frac{\partial f_2(x + \delta h, y + \delta k)}{\partial (x + \delta h)} \cdot \frac{\partial (x + \delta h)}{\partial \delta} + \frac{\partial f_2(x + \delta h, y + \delta k)}{\partial (y + \delta k)} \cdot \frac{\partial (y + \delta k)}{\partial \delta} \right]$$

$$Q''_{h,k}(\delta) = h^2 f_{1,1}(x + \delta h, y + \delta k) + 2hk f_{1,2}(x + \delta h, y + \delta k) + k^2 f_{2,2}(x + \delta h, y + \delta k)$$

$$\tag{II-16}$$

where $f_{2,2}(x + \delta h, y + \delta k) = \dfrac{\partial^2 f(x + \delta h, y + \delta k)}{[\partial (y + \delta k)]^2}$ and $f_{1,2}(x + \delta h, y + \delta k) =$

$f_{2,1}(x+\delta h), y+\delta k)$. Therefore, the second derivative, $Q''_{h,k}(\delta)$, for $\delta = 0$ is given by (II-17).

$$Q''_{h,k}(0) = h^2 f_{1,1}(x,y) + 2hk f_{1,2}(x,y) + k^2 f_{2,2}(x,y) \qquad \text{(II-17)}$$

Using the definition of $Q_{h,k}(\delta)$ in equation (II-14), $Q''_{h,k}(0)$ is also defined by (II-18).

$$Q''_{h,k}(0) = \lim_{\delta \to 0} \frac{Q_{h,k}(\delta) - 2Q_{h,k}(0) + Q_{h,k}(-\delta)}{\delta^2} \qquad \text{(II-18)}$$

The difference equations used to calculate the second derivatives of the form of $f_{1,2}(x,y)$ were obtained by combining (II-14), (II-17) and (II-18) for various pairs of (h,k) values. For example, one difference equation is given by substituting $h = 1$, $k = 0$ into (II-17), see (II-19a); then equating (II-19a) to (II-18) in (II-19b). The specific form of (II-19b) used to obtain the numerical second derivative is given by substitution of (II-14) with (h,k) = (1,0) into (II-19b), see (II-19c).

$$Q''_{h,k}(0) = Q''_{1,0}(0) = (1)^2 f_{1,1}(x,y) + 2(1)(0) f_{1,2}(x,y) + (0)^2 f_{2,2}(x,y)$$
$$\text{(II-19a)}$$

$$Q''_{1,0}(0) = f_{1,1}(x,y) = \lim_{\delta \to 0} \frac{Q_{1,0}(\delta) - 2Q_{1,0}(0) + Q_{1,0}(-\delta)}{\delta^2} \qquad \text{(II-19b)}$$

$$Q''_{1,0}(0) = f_{1,1}(x,y) = \lim_{\delta \to 0} \frac{f(x+\delta,y) - 2f(x,y) + f(x-\delta,y)}{\delta^2} \qquad \text{(II-19c)}$$

Similarly for (h,k) = (0,1), equations (II-14) and (II-18) lead to equation (II-20) which defines $f_{2,2}(x,y)$.

$$Q''_{0,1}(0) = \lim_{\delta \to 0} \frac{f(x,y+\delta) - 2f(x,y) + f(x,y-\delta)}{\delta^2} \qquad \text{(II-20)}$$

Finally, substitution of $(h,k) = (1,1)$ into (II-17), (II-18) and (II-14) produces an expression which includes the desired cross term $f_{1,2}(x,y)$, see (II-21).

$$Q''_{1,1}(0) = (1)^2 f_{1,1}(x,y) + 2(1)(1) f_{1,2}(x,y) + (1)^2 f_{2,2}(x,y)$$

$$Q''_{1,1}(0) = f_{1,1}(x,y) + 2f_{1,2}(x,y) + f_{2,2}(x,y) \qquad \text{(II-21a)}$$

$$Q''_{1,1}(0) = \lim_{\delta \to 0} \frac{Q_{1,1}(\delta) - 2Q_{1,1}(0) + Q_{1,1}(-\delta)}{\delta^2}$$

$$Q''_{1,1}(0) = \lim_{\delta \to 0} \frac{f(x+\delta,y+\delta) - 2f(x,y) + f(x-\delta,y-\delta)}{\delta^2} \qquad \text{(II-21b)}$$

By rearrangement of (II-21a), $f_{1,2}(x,y) = [Q''_{1,1}(0) - f_{1,1}(x,y) - f_{2,2}(x,y)]/2$. This result and the definition of $f_{1,1}(x,y)$ and $f_{2,2}(x,y)$ in (II-19) and (II-20), respectively, led to equation (II-22) which defines the cross term second derivative.

$$f_{1,2}(x,y) = \frac{Q''_{1,1}(0) - Q''_{1,0}(0) - Q''_{0,1}(0)}{2} \qquad \text{(II-22)}$$

The general difference method equations are summarized in Table VII. The symbols A, B, C, D and E in Table VII represent second derivatives in the limit as the increment size δ approaches zero. Thus for a given δ, A and B constitute numerical approximations to the diagonal force constants (second derivatives), $(\delta^2 f(x,y)/\delta x^2)y$ and

TABLE VII

SUMMARY OF THREE-POINT CROSS-TERM DIFFERENCE EQUATIONS[a]

Unit[b] Increment Pair	Definition of[c] Second Derivative	Difference Method Approximation[d] to the Second Derivative
$(h,k) = (1,0)$	$f_{1,1}(x,y) = \lim_{\delta \to 0} A$	$A = \dfrac{f(x+\delta,y) - 2f(x,y) + f(x-\delta,y)}{\delta^2}$
$(h,k) = (0,1)$	$f_{2,2}(x,y) = \lim_{\delta \to 0} B$	$B = \dfrac{f(x,y+\delta) - 2f(x,y) + f(x,y-\delta)}{\delta^2}$
$(h,k) = (1,1)$	$Q''_{1,1}(0) = \lim_{\delta \to 0} D$	$D = \dfrac{f(x+\delta,y+\delta) - 2f(x,y) + f(x-\delta,y-\delta)}{\delta^2}$
$(h,k) = (1,-1)$	$Q''_{1,-1}(0) = \lim_{\delta \to 0} E$	$E = \dfrac{f(x+\delta,y-\delta) - 2f(x,y) + f(x-\delta,y+\delta)}{\delta^2}$
	$f_{1,2}(x,y) = \lim_{\delta \to 0} C$	$C = \dfrac{D-A-B}{2} = \dfrac{A+B-E}{2} = \dfrac{D-E}{4}$

[a]See Reference 31.

[b]See Equations (II-19), (II-20), and (II-21).

[c]Definitions based on combination of Equations (II-14), (II-17), and (II-18).

[d]Difference methods based on Equations (II-14) and (II-18). Note Equation C is only definable as a combination of other difference methods. Also, the increment size δ should be identical in all equations used for each calculation of C.

$(\partial^2 f(x,y)/\partial y^2)_x$, respectively. For a given δ, D is the numerical

estimate of $\partial^2 Q_{1,1}(0)/\partial \delta^2$. Therefore, given a specific δ the numerical

approximation to the off-diagonal force constant, $\partial^2 f(x,y)/\partial x \partial y$, is

obtained by substituting A, B, and D into (II-22). The symbol E in

Table VII is defined in the same manner as D, except for (h,k) = (1,-1).

Thus for a given δ, E is the numerical estimate of $\partial^2 Q_{1,-1}(0)/\partial \delta^2$. By

substituting the numerical approximations A, B, and C for the appro-

priate analytical second derivatives in (II-17) with (h,k) = (1,-1), E

is defined as the quantity $(A - 2C + B)$. This definition of E leads to

the last two quantities equated to C in Table VII which constitute two

additional numerical approximations to the off-diagonal force constant

(or cross-term second derivative).

The energy values obtained from six equal increments and decrements

about a particular cartesian coordinate were least squares fitted to a

quadratic equation, see (II-23).[32] A numerical estimate of the

$$V = Kx^2 + Lx + M \qquad \qquad (II-23)$$

cartesian coordinate force constant is then provided by the analytic

second derivative of this quadratic equation, $\partial^2 V/\partial x^2 = 2K$.

A seven point difference method based on the differentiation of a

Langrangian interpolation function was also used to calculate force

constants for comparison to the three-point and polynomial least-

squares methods.[33] As shown in Equation (II-24) the derivative is

$$V'_o = \frac{\partial V_o}{\partial q_i} = \frac{1}{60h} \left[45(V_1 - V_{-1}) - 9(V_2 - V_{-2}) + (V_3 - V_{-3}) \right] \qquad (II-24)$$

calculated at the center (equilibrium) point, $V_o = f(q_i)$, using

energies $V_\ell = f(q_i + \ell h)$ for three equally incremented and decremented (that is $\ell = \pm3, \pm2, \pm1$) points, where h is the increment size and q_i is the coordinate being incremented. Thus a particular force constant V_j'' was evaluated as follows. For a given h, potential energies V_j were computed for $j = 0$ and ±1 to ±6. Equation (II-24) and these V_j were used to obtain first derivatives V_j' at $j = \pm3, \pm2, \pm1$. Equation (II-24) and these V_j' values were then used to calculate V_j'' at $j = 0$. The error in the seven-point difference method, E, is given by (II-25),

$$E = -\frac{h^6}{140} f^{VII}(\xi) \qquad \text{(II-25)}$$

where h is the increment size and $f^{VII}(\xi)$ is the seventh derivative of the function being differentiated for $(q_i - 3h) \leq \xi \leq (q_i + 3h)$. An accurate estimate of this error cannot be made but it can be seen that a sufficiently small increment size, h, will tend to overshadow the $f^{VII}(\xi)$ function. Since $h \leq 1 \times 10^{-4}$ was used then $f^{VII}(\xi)$ must exceed 1×10^{22} to significantly affect the calculated force constant. In view of the functional form of (II-1) this is unlikely.

Values for the cross-term second derivative force constants were calculated using the seven point difference method. This method requires a seven by seven point grid of energy values. These were obtained by concomitantly incrementing two different coordinates q_i and q_j. Figure 2 displays the grid of coordinate positions for which energy values were calculated. The calculated energy values falling on a line perpendicular to the q_i axis in Figure 2 were substituted into Equation (II-24) to calculate the first derivatives at $V(q_i + \ell h, q_j)$ for $\ell = \pm1$ to ±3 on the q_i axis. These $V'(q_i + \ell h, q_j)$ for

q_j

$V(q_i-3H,q_j+3h)$ $V(q_i, q_j+3h)$ $V(q_i+3h,q_j+3h)$

q_i

$V(q_i-3h,q_j)$ $V(q_i, q_j)$ $V(q_i+3h,q_j)$

$V(q_i-3h,q_j-3h)$ $V(q_i, q_j-3h)$ $V(q_i+3h,q_j-3h)$
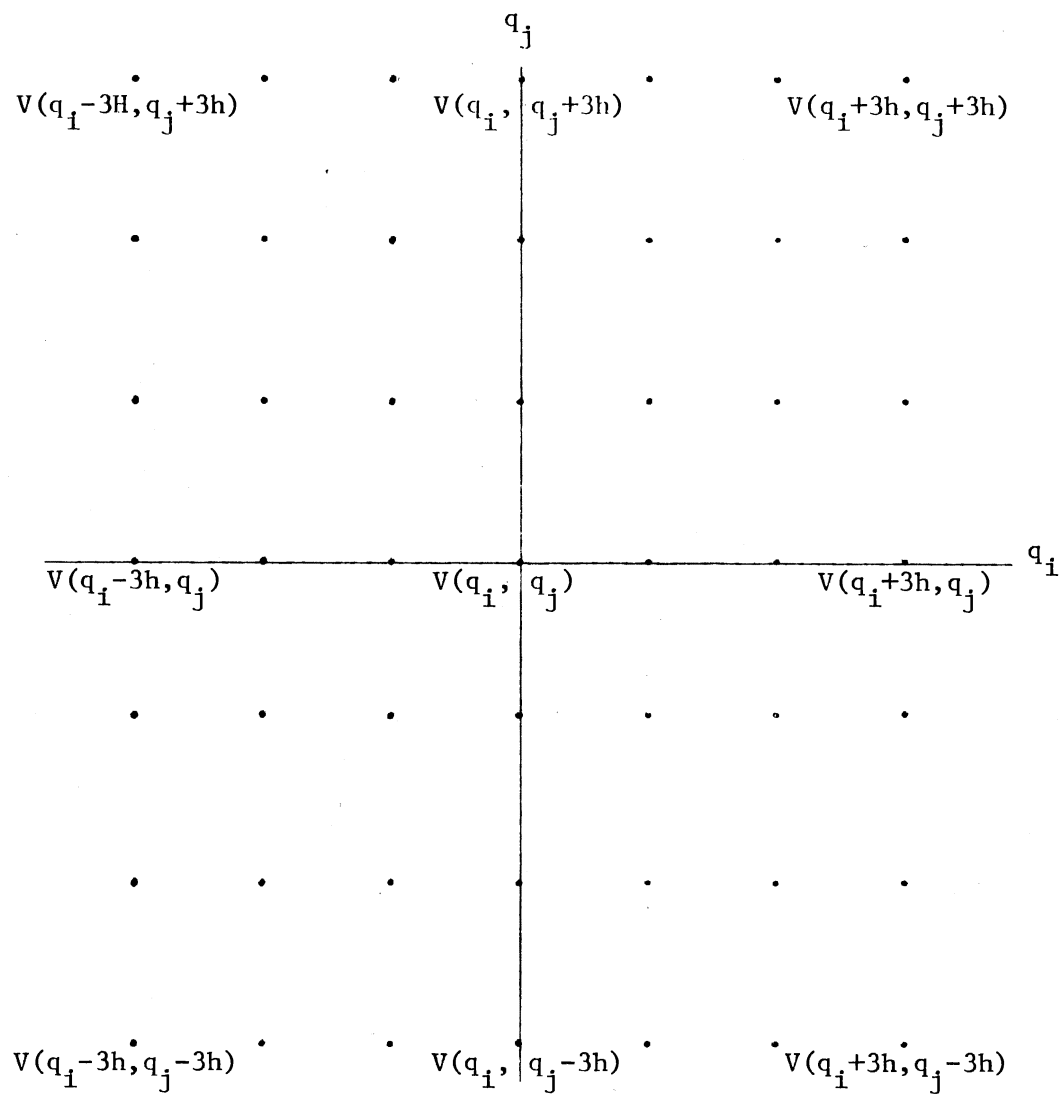
Figure 2. Grid of Incremented Coordinate Positions for Which
Energies were Calculated

$\ell = \pm 1$ to ± 3 were then substituted into Equation (II-24) to obtain $\partial^2 V/\partial q_i \partial q_j$ or $V''(q_i + \ell h, q_j)$ for $\ell = 0$. These interaction force constant values obtained by the seven-point difference method are not based on as sound a theoretical background as those determined by the three-point method summarized in Table VI. For this reason, the three-point method interaction force constants were used to evaluate the isotopic normal mode frequencies for the isotope effect calculations. However, the seven-point method values were very close if not identical to the three-point method values.

Force Constant Calculation

The previously described difference methods were applied to energies obtained from the LMR-PES and its coordinate relationships, see Appendix A, to calculate force constants for the internal valence coordinates described in Tables III and V. The transition-state internal valence coordinate force constants (TS-VFC) were calculated for several increment sizes using both the three-point and seven-point difference methods, see Table VIII. The increment sizes, 1×10^{-4} and 5×10^{-5}, were found to give the best agreement between degenerate force constants. Overall, the best agreement between the force constants calculated by the two difference method techniques is given by an increment size of 1×10^{-4}. The force constants in Table VIII show a lack of consistency between degenerate force constants calculated using increment sizes of 5×10^{-6} and 5×10^{-7}. The validity of both numerical difference methods and the LMR-PES coordinate relationships was established as follows. First, force constants were calculated with respect to the cartesian coordinates of

TABLE VIII

TRANSITION–STATE DIAGONAL INTERNAL COORDINATE FORCE CONSTANT VALUES[a]

Valence Coordinate q_i	Three Point Method[b]		Seven Point Method[c]			
	$\dfrac{\partial^2 V}{\partial q_i^2}$[d]	$\dfrac{\partial^2 V}{\partial q_i^2}$[e]	$\dfrac{\partial^2 V}{\partial q_i^2}$[e]	$\dfrac{\partial^2 V}{\partial q_i^2}$[d]	$\dfrac{\partial^2 V}{\partial q_i^2}$[f]	$\dfrac{\partial^2 V}{\partial q_i^2}$[g]
R_1[h]	-1.5344	-1.5345	-1.5345	-1.5345	-1.5344	-1.5342
R_2[h]	5.0393	5.0395	5.0395	5.0395	5.0394	5.0355
R_3[h]	5.0393	5.0395	5.0395	5.0395	5.0394	5.0392
R_4[h]	5.0393	5.0395	5.0395	5.0395	5.0394	5.0392
R_5[h]	4.4042	4.4043	4.4043	4.4043	4.4043	4.4077
ϕ_1[i]	0.1802	0.1802	0.1802	0.1802	0.1802	0.1813
ϕ_2[i]	0.1802	0.1802	0.1802	0.1802	0.1802	0.1813
ϕ_3[i]	0.1802	0.1802	0.1802	0.1802	0.1802	0.1813
ϕ_4[i]	0.5517	0.5517	0.5517	0.5517	0.5517	0.5530

TABLE VIII (Continued)

Valence Coordinate q_i	Three Point Method[b]		Seven Point Method[c]			
	$\dfrac{\partial^2 V}{\partial q_i^2}$[d]	$\dfrac{\partial^2 V}{\partial q_i^2}$[e]	$\dfrac{\partial^2 V}{\partial q_i^2}$[e]	$\dfrac{\partial^2 V}{\partial q_i^2}$[d]	$\dfrac{\partial^2 V}{\partial q_i^2}$[f]	$\dfrac{\partial^2 V}{\partial q_i^2}$[g]
ϕ_5^{i}	0.5517	0.5517	0.5517	0.5517	0.5517	0.5530
ϕ_6^{i}	0.5517	0.5517	0.5517	0.5517	0.5517	0.5530
α_x^{i}	0.0270	0.0270	0.0270	0.0270	0.0269	0.0257
α_y^{i}	0.0270	0.0270	0.0270	0.0270	0.0270	0.0256

[a]Force constants calculated for the internal valence coordinates described in Table V.

[b]Values calculated by the three point difference method, see (II-11).

[c]Values calculated by the seven point difference method, see (II-27).

[d]Increment size $h = 5 \times 10^{-5}$.

[e]Increment size $h = 1 \times 10^{-4}$.

[f]Increment size $h = 5 \times 10^{-6}$.

[g]Increment size $h = 5 \times 10^{-7}$.

[h]Stretching force constants in mdyne/Å.

[i]Bending force constants in mdyne-Å.

each atom in the transition-state configuration. These cartesian

coordinate force constants (CCFC) were compared to the CCFC obtained

from conversion of the TS-VFC matrix using the B matrix method

described in Appendix B. It can be seen in Table IX that the agreement

is reasonably good but not quantitative. Second, transition-state

normal mode frequencies were calculated using the VFC, converted CCFC,

and directly calculated CCFC. These values are compared in Table X.

When the CCFC are used to calculate normal-mode frequencies there are

six degrees of freedom in the eigenvalues in addition to those

corresponding to the normal-mode frequencies. These six extra degrees

of freedom correspond to the translation and rotation of the transition-

state molecular configuration. It can be seen that the directly

calculated CCFC generate some small residual values that correspond to

rotational and translational degrees of freedom. Theoretically these

rotational and translational values should be zero but the directly

calculated CCFC were not normalized with respect to the internal

coordinates. Due to the form of the ICFC normal mode frequency

calculation, the six extra degrees of freedom are not allowed. Also,

the method of converting the ICFC to CCFC normalizes the converted

CCFC to the internal coordinates. Therefore, only zero or negligibly

small values for the translational and rotational degrees of freedom

are obtained. Neglecting the rotational and translational degrees of

freedom, it can be observed that the various sets of normal-mode

frequencies in Table X agree very well; the largest deviation being

about 2.5 cm^{-1}. This indicates the validity of the LMR-PES coordinate

relationships and the numerical difference methods.

TABLE IX

TRANSITION-STATE DIAGONAL CARTESIAN COORDINATE FORCE CONSTANTS
CALCULATED BY DIFFERENT NUMERICAL METHODS[a]

Cartesian Coordinate[b]	Seven Point[c]	Three Point[d]	Quadratic[e]	Converted[f]
x_1	0.2112	0.2112	0.2112	0.2095
y_1	0.2112	0.2112	0.2112	0.2095
z_1	1.2552	1.2552	1.2552	1.2552
x_2	0.7680	0.7680	0.7680	0.7665
y_2	4.7208	4.7208	4.7208	4.7190
z_2	0.6271	0.6271	0.6271	0.6265
x_3	3.7326	3.7326	3.7326	3.7309
y_3	1.7562	1.7562	1.7562	1.7546
z_3	0.6271	0.6271	0.6271	0.6265
x_4	3.7326	3.7326	3.7326	3.7309
y_4	1.7562	1.7562	1.7562	1.7546
z_4	0.6271	0.6271	0.6271	0.6265

TABLE IX (Continued)

Cartesian Coordinate[b]	Seven Point[c]	Three Point[d]	Quadratic[e]	Converted[f]
x_5	8.7621	8.7621	8.7621	8.7640
y_5	8.7621	8.7621	8.7621	8.7640
z_5	0.3412	0.3412	0.3412	0.3394
x_6	0.0439	0.0439	0.0439	0.0439
y_6	0.0439	0.0439	0.0439	0.0439
z_6	4.4043	4.4043	4.4043	4.4043

[a] Force constant values in mdyne/Å. All values calculated using an increment size of 5×10^{-5}.

[b] Coordinate subscript is the atom number, see Figure 1.

[c] Values calculated by the seven point difference method, see (II-27).

[d] Values calculated by the three point difference method, see (II-11).

[e] Values calculated by the quadratic least squares fit method, see (II-23).

[f] Values converted from internal coordinate force constant values by the B-matrix conversion method described in Appendix B.

TABLE X

TRANSITION-STATE NORMAL MODE FREQUENCIES[a]

Normal Mode	Internal[b]	Cartesian[c]	Cartesian[d]	Assignment of the Normal Mode
ν_1[e]	3388.5	3388.5	3388.5	Symmetric C-H-H stretching
ν_2[e]	2937.7	2937.7	2937.6	Symmetric CH_3 stretching
ν_3[e]	964.7	964.7	967.2	CH_3 bending deformation
ν_4[e]	1479.3i	1479.3i	1479.3i	Antisymmetric C-H-H stretching
ν_5[f]	3085.7	3085.7	3085.7	Antisymmetric CH_3 stretching
ν_6[f]	1502.9	1502.9	1503.7	Degenerate CH_3 bending deformation
ν_7[f]	752.3	752.3	754.5	Linear bending + CH_3 bending
ν_8[f]	367.3	367.3	369.8	Linear bending - CH_3 bending
R_1[g]		0	50.8	Rotation about Z-axis
R_2[g]		0	39.4	Rotation about Y-axis

TABLE X (Continued)

Normal Mode	Internal[b]	Cartesian[c]	Cartesian[d]	Assignment of the Normal Mode
$R_3{}^g$		0	39.4	Rotation about X-axis
$T_1{}^h$		0	1.5	
$T_2{}^h$		0	.5	
$T_3{}^h$		0	−.2	

[a] Frequencies in cm^{-1}. Force constants calculated using an increment size of 5×10^{-5}.

[b] Frequencies calculated using the internal coordinate force constants in Table VIII plus all off-diagonal interaction force constants.

[c] Frequencies calculated using cartesian coordinate force constants converted from the internal coordinate force constants described in footnote b.

[d] Frequencies calculated using the three point method cartesian coordinate force constants from Table IX plus all off-diagonal interaction force constants.

[e] Non-degenerate normal mode frequencies.

[f] Doubly degenerate normal mode frequencies.

[g] Rotational degree of freedom.

[h] Translational degree of freedom.

The assignments of the normal modes in Table X are based on the eigenvectors given in Table XI. The cartesian coordinate eigenvectors make assigning a normal mode of motion relatively easy, since each eigenvector value represents relative motion along or parallel to the cartesian coordinates for each atom in Figure 1. The rotational assignments are particularly easy. For example, the R_1 eigenvector shows that atom two has motion in the positive x direction, atom three has motion in the negative x and positive y directions, and atom four has motion in the negative x and negative y directions. Thus, R_1 is an eigenvector representing rotation about the Z axis in Figure 1.

Force constants were calculated for the reactant molecular species in reactions (I-1) and (I-2) with respect to the internal valence coordinates described in Table III. Normal-mode frequencies calculated using these force constants are compared with spectroscopic values in Tables XII and XIII. The CH_4 frequency values from the LMR-PES VFC agree well with those calculated from the diagonal Herzberg VFC matrix in Table XII.[34] However, the numerically determined VFC matrix from the LMR-PES is not a diagonal matrix due to strong internal coupling between the CH stretching and HCH bending VFC. The diagonal Herzberg force constants,[34] 5.04 mdyne/Å and 0.5517 mdyne-Å for CH stretching and HCH bending, respectively, appear implicitly and explicitly, respectively, in the LMR-PES.[2] However, the numerically determined CH stretching VFC from the LMR-PES is 5.08 mdyne/Å. The agreement between frequencies predicted by the LMR-PES and Herzberg VFC reflects the fact that the C-H stretching modes are coupled, 1) between themselves by a small -0.01 mdyne/Å value and 2) to the HCH bending VFC by a larger ±0.042 mdyne value (+0.042 coupled to adjacent C-H bonds and

TABLE XI

TRANSITION–STATE CARTESIAN COORDINATE EIGENVECTORS[a]

Cartesian Coordinate	Transition-State Normal Modes[b]								Rotation[c]			Translation[d]
	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6	ν_7	ν_8	R_1	R_2	R_3	T_1
x_1	0	0	0	0	-.003	.010	-.758	.087	0	-.450	.007	.241
y_1	0	0	0	0	0	.015	.087	-.374	0	-.007	-.450	.022
z_1	.547	-.018	.117	.787	0	0	0	0	0	0	0	.004
x_2	0	0	0	0	-.023	-.405	-.080	-.023	.575	.149	-.002	.241
y_2	.018	.550	-.116	.025	.016	.126	.006	.092	0	.002	.150	.002
z_2	-.013	-.150	-.499	.005	-.004	.152	.052	.507	0	.005	.333	.004
x_3	-.015	-.476	.144	-.021	-.553	.287	-.060	-.026	-.288	.149	-.002	.241
y_3	-.009	-.275	.083	-.012	-.306	-.232	.020	.099	.498	.003	.149	.022
z_3	-.013	-.150	-.499	.005	-.173	-.160	.365	-.152	0	-.290	-.162	.004
x_4	.015	.476	-.144	.021	-.567	-.369	-.058	-.018	-.288	.149	-.003	.241
y_4	-.009	-.275	.083	-.012	.314	-.653	-.004	.098	-.498	.001	.149	.022
z_4	-.013	-.150	-.499	.005	.177	.008	-.417	-.355	0	.285	-.171	.004

TABLE XI (Continued)

Cartesian Coordinate	Transition-State Normal Modes[b]								Rotation[c]			Translation[d]
	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6	ν_7	ν_8	R_1	R_2	R_3	T_1
x_5	0	0	0	0	.096	.040	.065	.010	0	.060	−.001	.241
y_5	0	0	0	0	−.002	.062	−.007	−.004	0	.001	.060	.022
z_5	.027	.036	.105	−.108	0	0	0	0	0	0	0	.004
x_6	0	0	0	0	.001	.001	.186	−.140	.001	−.716	.011	.241
y_6	0	0	0	0	0	.001	−.021	.605	0	−.011	−.716	.022
z_6	−.826	.045	.132	.481	0	0	0	0	0	0	0	.004

[a] The values are relative potential motion vectors along or parallel to the cartesian coordinates for each numbered atom in Figure 1.

[b] Normal modes correspond to those in Table X.

[c] Represent nonzero rotational contributions from cartesian force constant frequency calculation, see Table X.

[d] Typical eigenvector for the negligibly small translational energy contribution from cartesian force constant frequency calculation, see Table X.

TABLE XII

TETRAHEDRAL CH_4 NORMAL MODE FREQUENCIES[a]

Normal Mode	Calculated LMR-PES Force Constants	Herzberg Calculated	Herzberg Spectroscopic	Shimanouchi[c] Spectroscopic
ν_1	2917	2914	2914	2917
ν_2[d]	1527	1527	1526	1534
ν_3[e]	3080	3080	3020	3019
ν_4[e]	1366	1363	1306	1306

[a] All values in cm^{-1}.

[b] See Reference 34.

[c] See Reference 35.

[d] Doubly degenerate.

[e] Triply degenerate.

TABLE XIII

PLANAR CH_3 AND H_2 FREQUENCIES[a]

Normal Mode	Snelson[b]	MJ[c]	TWP[d]	LMR-PES[e]	Gaussian 70[f]	Herzberg[g]
ν_1	3044			2914	3251	
ν_2	617	611	607	847	847	
ν_3[h]	3162			3100	3455	
ν_4[h]	1396			1606	1538	
sum[i] $\nu(CH_3)$	12777			13173	14084	
sum[j] $\nu(CH_3)$	12160			12326	13237	
$\nu(H_2)$				4468		4395

[a]All values in cm^{-1}.

[b]See Reference 36. Since ν_1 is infrared inactive, the value corresponds to Snelson's calculated value.

[c]See Reference 37.

[d]See Reference 38.

[e]Calculated using LMR-PES valence force constants except for the $\nu_2(CH_3)$ obtained from Gaussian 70, see Reference 39.

[f]Calculated from Gaussian 70, 6-31G basis set force constants.

[g]See Reference 40.

[h]Doubly degenerate frequencies.

[i]Sum includes the ν_2 value.

[j]Sum excludes the ν_2 value.

-0.042 coupled to non-adjacent C-H bonds). These interaction VFC values effectively decrease the calculated normal mode frequency values. The diagonal HCH bending VFC from the LMR-PES are identical to the Herzberg values.[34] It can be seen in Table XII that the Shimanouchi spectroscopic values[35] differ somewhat from the Herzberg[34] spectroscopic values and agree somewhat better with the calculated values.

The spectroscopic CH_3 frequencies in Table XIII reported by Snelson for ν_1, ν_3 and ν_4 compare reasonably well with the corresponding LMR-PES values. In terms of KIE calculations it should be noted that differences in the ν_4 values would tend to be offset by opposing differences in the ν_1 and ν_3 values.[36] Thus, the LMR-PES curvatures governing the symmetric and asymmetric CH stretching are realistic. However, the ν_4 in-plane bending VFC may be somewhat large compared to the spectroscopic value. The frequencies calculated from Gaussian 70 VFC are all greater than the corresponding spectroscopic values by about nine percent on the average. The ν_2 out-of-plane bending frequency is about 235 cm^{-1} greater than the corresponding spectroscopic frequencies.[36,37,38] The effect of using either the Gaussian 70 or the spectroscopic isotopic ν_2 frequencies in conjunction with the corresponding LMR-PES calculated frequencies to obtain KIEs from (I-3) and (I-4) is discussed in Chapter III. The H_2 frequency (4468 cm^{-1}) obtained from the LMR-PES VFC (5.924 mdyne/Å) is less than two percent greater than the Herzberg spectroscopic frequency (4395 cm^{-1}) having a VFC of 5.732 mdyne/Å.

The force constants used to calculate the LMR-PES and Gaussian 70 frequencies for CH_3 are compared to the spectroscopically determined

force constants in Table XIV. It can be seen in Table XIV, that the Gaussian 70 in-plane bending VFC agrees well with the LMR-PES value, but the spectroscopic value is somewhat lower. This corresponds to the agreement between ν_4 frequencies in Table XIII. However, the two C-H stretching VFC differ considerably. This difference is reflected in disagreement between the ν_1 and ν_3 values in Table XIII. As discussed earlier in the coordinates section, the LMR-PES predicts no out-of-plane bending force constant. Therefore, the Gaussian 70 ab initio program was used with its 6-31G internal basis set to calculate the value for F_γ in Table XIV.[39] The out-of-plane bending internal coordinate corresponds to bending all three CH bonds out-of-plane simultaneously by the angle γ in radians. The numerical methods discussed earlier were applied to the incremented Gaussian 70 energies to obtain the CH_3 VFC in Table XIV. The Gaussian 70 out-of-plane bending VFC is almost twice as large as the spectroscopically determined value. This difference is clearly reflected in the calculated and spectroscopic ν_2 values.

TABLE XIV

PLANAR CH$_3$ FORCE CONSTANTS AND BONDLENGTHS[a]

Label	LMR-PES[b]	Gaussian 70[c]	Snelson[d]	MJ[e]	TWP[f]
F_{r_i}[g] (i=2,3,4)	5.040	6.273	5.2		
F_{ϕ_i}[h] (i=4,5,6)	0.461	0.422	0.315		
F_γ[i]		0.340	0.179	0.177	0.174
r_i (i=2,3,4)	1.094	1.072	1.079	1.079	1.079

[a] All force constants are in mdyne/Å and the bondlengths, r_i (i=2,3,4) are in Å.

[b] Values calculated from the LMR-PES.

[c] Values calculated using (II-11) and (II-23) methods applied to 6-31G basis set energies from Gaussian 70, see Reference 39.

[d] See Reference 36. In-plane force constants are calculated Urey-Bradley force constants.

[e] See Reference 37.

[f] See Reference 38.

[g] C-H stretching force constant.

[h] HCH in-plane bending force constant.

[i] Out-of-plane bending force constant.

CHAPTER III

THEORETICAL KINETIC ISOTOPE EFFECTS FOR THE

REACTION $CH_4 + H \overset{\rightarrow}{\underset{\leftarrow}{\rightleftharpoons}} CH_3 + H_2$
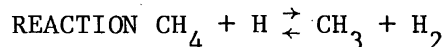
Results and Discussion

Comparison of Theoretical Vibrational
Frequencies and Force Constants

The activated complex normal mode frequencies calculated for the

LMR-PES and the various BEBO and LEPS models reported by Kurylo,

Hollinden, and Timmons[12] and Shapiro and Weston[14] are compared in

Table XV. It should be noted that most of these normal mode

frequencies are of comparable magnitude except for the symmetric

stretching frequency for motion along the reaction coordinate, ν_1, and

the linear bending modes, ν_7 and ν_8. Also, the imaginary frequency, ν_4,

for the LMR-PES is considerably smaller in value, than the correspond-

ing BEBO and LEPS values indicating that the former potential-energy

barrier along the reaction coordinate has less curvature than either

of the latter two. This lower degree of curvature in the barrier may

be at least partially the result of the LMR-PES having a somewhat lower

barrier height as can be seen in Table XVI. Table XVI also shows that

the imaginary frequency for the BEBO and LEPS models results from a

large interaction force constant between the $C-H_1$ and H_1-H_6 stretching

force constants. In contrast the imaginary frequency for the LMR-PES

TABLE XV

CH_3-H-H TRANSITION-STATE FREQUENCIES FROM DIFFERENT SOURCES[a]

Normal Mode	LMR-PES[b]	KHT[c]		SW[d]					
		BEBO	LEPS	BEBO3[e]	LEPS2[e]	BEBO3[f]	LEPS2[f]	BEBO3[g]	LEPS2[g]
ν_1	3388	1610	1397	1568	1392	1577	1412	1603	1482
ν_2	2938	2980	2980	3149	3149	3149	3149	3149	3149
ν_3	965	1179	1147	958	954	1156	1142	1337	1279
ν_4	1479i	1689i	2024i	1691i	1839i	1691i	1838i	1690i	1838i
ν_5	3086	3047	3047	3165	3165	3166	3167	3168	3168
ν_6	1503	1459	1458	1473	1472	1480	1480	1527	1535
ν_7	752	1046	1077	623	779	1008	1078	1355	1384
ν_8	367	446	502	14	14	430	500	458	555

[a]All frequencies in cm^{-1}.

[b]Calculated using LMR-PES parameters.

[c]Calculated using the BEBO and LEPS parameters in Reference 12.

[d]Calculated using the BEBO3 and LEPS2 parameters in Reference 14 with the HCH_1 bending force constant value specified in the footnotes.

[e]Calculated with $F^{\ddagger}_{\phi_i}(i=1,2,3) = 0.0001$ mdyne-Å.

[f]Calculated with $F^{\ddagger}_{\phi_i}(i=1,2,3) = 0.26$ mdyne-Å.

[g]Calculated with $F^{\ddagger}_{\phi_i}(i=1,2,3) = 0.568$ mdyne-Å.

TABLE XVI

COMPARISON OF TRANSITION-STATE PARAMETERS[a]

| Value Label | LMR-PES[b] | KHT[c] | | SW[d] | | Units |
		BEBO	LEPS	BEBO3	LEPS2	
$F_{R_1}^{\ddagger}$	-1.534	1.157	0.775	1.096	0.930	mdyne/Å
$F_{R_5}^{\ddagger}$	4.404	1.157	0.565	1.096	0.653	mdyne/Å
$F_{int}^{\ddagger}$	0.807	1.879	1.653	1.818	1.597	mdyne/Å
$F_{\alpha}^{\ddagger}$	0.0270	0.0526	0.0821	0.0486	0.0799	mdyne-Å
$F_{\phi_i}^{\ddagger}$ (i=1,2,3)	0.180	0.280	0.260	---[i]	---[i]	mdyne-Å
$F_{\phi_i}^{\ddagger}$ (i=4,5,6)	0.552	0.568	0.568	0.568	0.568	mdyne/Å
$F_{R_i}^{\ddagger}$ (i=2,3,4)	5.039	5.040	5.040	5.50	5.50	mdyne/Å
$F_{R_i R_j}^{\ddagger}$ (i≠j=2,3,4)	0.0	0.050	0.050	0.124	0.124	mdyne/Å

TABLE XVI (Continued)

Value Label	LMR-PES[b]	Values from KHT[c]		Values from SW[d]		Units
		BEBO	LEPS	BEBO3	LEPS2	
$F^{\ddagger}_{R_i\phi_{i-2}}$ (i-2,3,4)	0.0	0.165	0.165	0.165	0.165	mdyne
$F^{\ddagger}_{R_i\phi_{i-2}}$ (i=2,3,4)	0.0	-.165	-.165	0.0	0.0	mdyne
$F^{\ddagger}_{R_1R_i}$ (i=2,3,4)	-0.0015	0	0	0	0	mdyne/A
$F^{\ddagger}_{R_1\phi_i}$ (i=1,2,3)	0.0268	0	0	0	0	mdyne
$F^{\ddagger}_{\phi_iR_{i+1}}$ (i=1,2,3)	0.0007	0	0	0	0	mdyne
$F^{\ddagger}_{R_5\phi_i}$ (i=1,2,3)	-0.0014	0	0	0	0	mdyne
r_1	1.597	1.27	1.29	1.27	1.28	Å
r_6	0.783	0.92	0.96	0.92	0.95	Å
r_i (i=2,3,4)	1.094	1.091	1.091	1.09	1.09	Å
$V_a(CH_4 + H)^f$	5.60	12.24	12.22			kilocalories/mole

TABLE XVI (Continued)

| Value Label | LMR-PES[b] | KHT[c] | | SW[d] | | Units |
		BEBO	LEPS	BEBO3	LEPS2	
$V_a(CH_3 + H_2)$[f]	9.42			13.46	10.63	kilocalories/mole
$E_a(CH_3 + H_2)$[g]	11.11			13.1[j]	10.9	kilocalories/mole
$E_a(CH_4 + H)$[h]	6.44	11.73	11.53			kilocalories/mole

(Values from header spans KHT, SW groups)

[a]All force constants have subscript designations from Table V. The bondlength designations are also from Table V; see Reference 7.

[b]Values determined from the LMR-PES.

[c]BEBO and LEPS parameters described in Reference 12.

[d]BEBO3 and LEPS2 parameters described in Reference 14.

[e]Interaction force constant between the $C-H_1$ and H_1-H_6 stretching force constants.

[f]Barrier height in kilocalories/mole.

[g]Activation energy calculated at 500°K.

[h]Activation energy calculated at 625°K.

[i]Three different values 0.0001, 0.26, and 0.568 mdyne-Å were used; see Reference 14.

[j]Includes a tunneling correction.

activated complex results from a negative $C-H_1$ stretching force

constant. This difference in force constants is not unreasonable since

the LMR-PES predicts $C-H_1$ and H_1-H_6 bond lengths in the transition

state approximately 0.3 Å longer and 0.15 Å shorter, respectively, than

the BEBO and LEPS models. For this reason, the LMR-PES activated

complex more closely resembles a methyl radical and hydrogen molecule

than the BEBO and LEPS models. This geometry and the large H_1-H_6 force

constant, $F_{R_5}^{\ddagger}$, give rise to the exceptionally large ν_1 value for the

LMR-PES in Table XV. Although the differences in the ν_7 and ν_8

frequencies reflect the differences in the linear-bending force

constant, $F_{\alpha}^{\ddagger}$, differences in these frequencies result primarily from

differences in the HCH_1 bending force constants, $F_{\phi_{1-3}}^{\ddagger} = F_{\phi_i}^{\ddagger}$ $(i=1,2,3)$,

between the surfaces. The frequency changes associated with the

changes in the $F_{\phi_{1-3}}^{\ddagger}$ values can be observed in Table XV. The force

constants in Table XVI and the frequencies in Table XV considered

together show that a BEBO3 and LEPS2 value of $F_{\phi_{1-3}}^{\ddagger} = 0.26$ mdyne-Å[14]

gives the best agreement with the LMR-PES and Kurylo, Hollinden, and

Timmons (KHT)[12] ν_7 and ν_8 frequencies. For the KHT BEBO and LEPS

surfaces the $F_{\alpha}^{\ddagger}$ values in columns three and four of Table XVI vary by

a factor of 1.56 but produce a negligible change in ν_7 and ν_8, see

columns three and four of Table XV. Thus the magnitude of the linear

bending frequencies is not strongly dependent on the magnitude of the

bending force constant, $F_{\alpha}^{\ddagger}$.

For purposes of comparison, the values for the LMR-PES activation

energies were calculated using the method of Kibby and Weston.[41] The

values predicted by the LMR-PES are compared to the BEBO and LEPS E_a

reported by KHT[12] and Shapiro and Weston (SW),[14] which were also

reportedly calculated by this method. The method, as given by Kibby and Weston,[41] follows the approach of Johnston.[42] The experimental activation energy, E_a, is treated as a linear function of the rate constant and temperature.[42]

$$E_a = \frac{-Rd\ln k}{d(T^{-1})} \qquad \text{(III-1)}$$

Integration of (III-1) gives the natural log form of the Arrhenius equation.

$$\ln k = \ln A - \frac{E_a}{RT} \qquad \text{(III-2)}$$

Johnston then gives an equation similar to (III-2) derived from transition-state theory,

$$\ln k = \ln(B(T)) - \dot{V}_a/RT \qquad \text{(III-3)}$$

where V_a is the barrier height along the reaction coordinate in kilocalories per mole, $B(T)$ is a temperature dependent form of the Arrhenius preexponential factor, and R and T are the gas constant and temperature in °K, respectively. The relation between the theoretical $B(T)$ and V_a on the one hand and the A and E_a on the other hand is given by:

$$\Omega = \frac{d\ln B(T)}{d\ln T} \qquad \text{(III-4a)}$$

$$A = B(T)\exp(\Omega) \qquad \text{(III-4b)}$$

$$E_a = V_a + \Omega RT \qquad \text{(III-4c)}$$

The expressions in (III-4) assume that the $(\partial \ln k/\partial T)_p$ for (III-2) and (III-3) are identical and that (III-2) and (III-3) may be equated. Kibby and Weston (KW) then define w_i for each vibrational degree of freedom by

$$w_i = (u_i/2)\coth(u_i/2) - 1 \qquad \text{(III-5)}$$

where u_i is the same as u_{1i} in (I-6) and (I-7).[41] The temperature dependent factor, Ω, is defined by KW as

$$\Omega = w^* + 1/2(d^\ddagger - d_r) + \sum_{i=1}^{d^\ddagger-1} w_i^\ddagger - \sum_{i=1}^{d_r} w_i^r \qquad \text{(III-6)}$$

where w^* is a tunneling correction factor (if used, zero otherwise); $d^\ddagger$ is the number of vibrational degrees of freedom in the activated complex including the imaginary frequency; d_r is the number of vibrational degrees of freedom in the reactants, and $w_i^\ddagger$ and w_i^r have a value for each transition-state and reactant vibrational degree of freedom calculated by (III-5), respectively. As a result of the 3.82 kcalorie/mole (0.1658 eV) difference between the $C-H_1$ (4.5808 eV) and H_1-H_6 (4.7466 eV) bond energies used in the LMR-PES,[2] the V_a (9.42 kilocalories/mole) and E_a (11.11 kilocalories/mole) for reaction of $CH_3 + H_2$ calculated at 500°K are reasonably comparable to the corresponding V_a (13.46 and 10.63 kilocalories/mole for the BEBO3 and LEPS2 models, respectively) and E_a (13.1 and 10.9 kilocalories/mole for the BEBO3 and LEPS2 models, using $F_{\phi_i}^\ddagger$ (i=1,2,3) = 0.26 mdyne-$\overset{\circ}{A}$, respectively) calculated by SW.[14] However, the LMR-PES V_a (5.60 kilocalories/mole) and E_a (6.44 kilocalories/mole) for reaction of

$CH_4 + H$ calculated at 625°K are about five kilocalories per mole smaller

than the corresponding V_a (12.24 and 12.22 kilocalories/mole for the BEBO

and LEPS models, respectively) and E_a (11.73 and 11.53 kilocalories/mole

for the BEBO and LEPS models, respectively) values calculated by KHT.[12] The

difference in the relationships between E_a and V_a for the various models is

primarily the result of the diversity in the magnitude of the $\sum_{i=1}^{d^{\ddagger}-1} w_i^{\ddagger} - \sum_{i=1}^{d_r} w_i^r$

differences in equation (III-6). The $\sum_{i=1}^{d^{\ddagger}-1} w_i^{\ddagger}$ values were easily determined

by (III-5) using the frequencies in Table XV with no tunneling correction.

However, calculation of the $\sum_{i=1}^{d_r} w_i^r$ values requires a full set of reactant

frequencies. For the reaction of CH_4 and H it was determined that KHT[12] used

the spectroscopic frequency values for methane that are reported by

Herzberg,[34] since their reported E_a could be reproduced using these

frequency values. For the reaction of CH_3 and H_2 it is not known what

set of reactant frequencies that SW used to calculate their reported E_a

since they do not specify which of the various spectroscopic of calcu-

lated sets of CH_3 frequency values they used.[14] The LMR-PES E_a values

were calculated using the harmonic methane and CH_3 and H_2 calculated

normal mode frequencies given in Appendix C. Since the $\sum_{i=1}^{d_r} w_i^r$ values at

625°K are 13.89 for the LMR-PES harmonic CH_4 frequencies and 13.52 for

the Herzberg spectroscopic CH_4 frequencies, it can be seen that the

positive deviation between the LMR-PES V_a and E_a values and the

negative deviation between the KHT-BEBO (or LEPS) V_a and E_a values

is the result of the $\sum_{i=1}^{d^{\ddagger}-1} w_i^{\ddagger}$ values. The $\sum_{i=1}^{d^{\ddagger}-1} w_i^{\ddagger}$ values calculated

at 625°K are 13.07 for the LMR-PES activated complex, 11.61 for

the KHT-BEBO activated complex, and 11.47 for the KHT-LEPS activated

complex. By application of equation (III-6), the Ω values 0.68,

-0.41, and -0.55 were calculated for the LMR-PES, KHT-BEBO, and

KHT-LEPS CH_4 + H models, respectively. Therefore, the LMR-PES data generate a larger Ω value than any of the BEBO or LEPS models leading to a greater difference in the corresponding V_a and E_a values. The reason for the larger Ω value can be traced to the very large LMR-PES transition-state $\nu_1^{\ddagger}$ (3388 cm^{-1}) value which is more than twice as large as any of the BEBO and LEPS $\nu_1^{\ddagger}$ values.

Assuming that the curvature parameter for motion perpendicular to the reaction coordinate are essentially independent of the barrier height, then the inadequacies of the LMR-PES in this regard have a negligible effect on the quantum mechanical contribution to the predicted KIEs. However, the curvature of the barrier for motion parallel to the reaction coordinate is not necessarily independent of the barrier height and clearly effects the magnitude of $\nu_L^{\ddagger}$. Consequently, an inaccurate barrier height would affect the classical mechanical contribution to the calculated KIE. The magnitude of the effect should be largest for a primary KIE where isotopic motion is directly considered in the reaction coordinate and much smaller for a secondary KIE.

Since SW report their calculated KIEs only in the form of temperature dependence plots, accurate comparison to the LMR-PES KIEs required recalculation of the SW KIE values. Using the activated complex parameters in Table XVI and tetrahedral geometry for the CH_3 group relative to the linear C-H-H entity, isotopic normal-mode frequencies consistent with the monoisotopic frequencies in Table XV were calculated for the BEBO and LEPS models and are tabulated in Appendix C along with the mass moment of inertia parameters. These frequencies and parameters were combined with the H_2 and D_2 harmonic

frequencies reported by Persky and Klein, that is, 4395.2 and 3109.1 cm^{-1}, respectively, to calculate the SW KIEs.[43] Table XVII presents isotope effects determined experimentally and calculated from the various theoretical models. It should be noted that the H_2 and D_2 frequencies are the only reactant-state frequencies which contribute to the calculated KIEs in Table XVII, since all other reactant contributions to the KIEs cancel out. However, SW[14] report that they used the rotationally corrected H_2 and D_2 quantities reported by Persky and Klein (PK)[43] to calculate the $k(CH_3,H_2)/k(CH_3,D_2)$ and $k(CD_3,H_2)/k(CD_3,D_2)$ values in their data. The transition-state theory equation used by SW[14] is equivalent to (I-4) plus a rotational correction factor added to the reactant ZPE term. The SW reactant and transition state vibrational partition function ratios, $f(H_2,D_2)$ and $f^{\ddagger}$, respectively, are defined in (III-7),

$$k_H/k_D = \nu^{\ddagger}_{1L}/\nu^{\ddagger}_{2L} \; \frac{f(H_2/D_2)}{f^{\ddagger}} = \frac{(m_H/m_D)^{\frac{1}{2}} \exp\left(\dfrac{Z_{H_2} - Z_{D_2}}{T}\right)}{\displaystyle\prod_{i=1}^{11} \frac{u^{\ddagger}_{2i} \sinh(u^{\ddagger}_{1i}/2)}{u^{\ddagger}_{1i} \sinh(u^{\ddagger}_{2i}/2)}} \qquad (III-7)$$

where m_H and m_D are the isotopic masses of hydrogen, 1.007825 and 2.0141 amu, respectively, T is in °K, the u_{ji} terms are the same as in (I-6) and (I-7), and Z_{x_2} equals $(u_{x_2}/2)-(\sigma_{x_2}/3)$. The $\sigma_{x_2}/3$ value is the rotational correction to the $(u_{x_2}/2) = (hc\nu_{x_2})/(2kT)$. The combined ZPE exponent, $(Z_{H_2}-Z_{D_2})/T$, can be expanded to $[(u_{H_2}-u_{D_2})(\frac{1}{2}) - (\sigma_{H_2}-\sigma_{D_2})(1/3)]/T$. Since σ_{H_2} and σ_{D_2} have the values 87.5 and 43.8, respectively, then obviously, the application of the rotational

TABLE XVII

EXPERIMENTAL AND THEORETICAL KINETIC ISOTOPE EFFECTS

Rate Constant Ratio	Temp. K	LMR-PES[a] HF[c]	BT[d]	OF[e]	RC[f]	Experimental KHT[g]	SW[h]	WS[i]	MS[j]	DB[k]	TW[l]	Theoretical[b] BEBO3 $P_\beta=0.0001$	BEBO3 $F_\beta=0.26$	BEBO3 $F_\beta=0.568$	LEPS2 $F_\beta=0.0001$	LEPS2 $F_\beta=0.26$	LEPS2 $F_\beta=0.568$	BEBO	LEPS
$\dfrac{k(CH_4,H)}{k(CH_4,D)}$	500	0.509	0.611		0.834							0.739	0.738	0.738	0.786	0.786	0.786	0.724	0.785
	546	0.554	0.639		0.870							0.773	0.773	0.773	0.818	0.818	0.818	0.763	0.821
$\dfrac{k(CH_3,H_2)}{k(CH_3,D_2)}$	296	1.99	---	1.85	1.67						2.12	7.14	5.40	4.25	6.82	5.26	4.19	5.07	5.32
	399	1.90	5.04	1.80	1.67		4.80					4.85	4.06	3.44	4.77	4.04	3.44	3.91	4.07
	403	1.90	4.87	1.80	1.67			4.79	5.50			4.79	4.03	3.42	4.72	4.00	3.42	3.87	4.04
	409	1.89	4.61	1.79	1.67					5.75		4.71	3.98	3.39	4.65	3.96	3.39	3.82	3.99
	426	1.88	3.98	1.78	1.67					5.32		4.50	3.84	3.30	4.45	3.82	3.31	3.69	3.85
	428	1.88	3.93	1.78	1.67		4.45					4.47	3.82	3.29	4.42	3.81	3.30	3.67	3.83
	482	1.83	3.26	1.75	1.65			2.80	3.33			3.92	3.45	3.04	3.90	3.45	3.05	3.33	3.47
$\dfrac{k(CD_3,H_2)}{k(CD_3,D_2)}$	296	1.98	---	1.83	1.67						0.465	7.13	5.32	4.08	6.82	5.19	4.04	4.99	5.26
	402	1.90	4.89	1.79	1.67	3.33						4.81	4.01	3.36	4.73	3.99	3.37	3.89	4.03
	403	1.90	4.85	1.79	1.67			2.98	4.11			4.79	4.01	3.36	4.72	3.98	3.36	3.85	4.02
	468	1.84	3.18	1.76	1.65	3.07						4.06	3.53	3.07	4.03	3.53	3.08	3.40	3.55
	483	1.83	3.01	1.75	1.65			2.98	3.48			3.92	3.44	3.01	3.90	3.44	3.02	3.32	3.47
$\dfrac{k(CH_3,HD)}{k(CH_3,DH)}$	296	2.02	---								6.37	2.06	1.56	1.23	1.57	1.22	0.972	1.55	1.20
	403	1.73	2.57						2.33			1.77	1.49	1.26	1.47	1.25	1.07	1.48	1.24
	467	1.63	2.07			2.08						1.67	1.46	1.27	1.43	1.26	1.11	1.46	1.25
	483	1.61	2.00						1.79			1.65	1.45	1.28	1.42	1.26	1.12	1.45	1.25
	532	1.55	1.83			1.92						1.60	1.43	1.30	1.40	1.27	1.14	1.43	1.25
$\dfrac{k(CD_3,HD)}{k(CD_3,DH)}$	402	1.73	2.56			1.81						1.77	1.48	1.24	1.47	1.24	1.05	1.48	1.23
	403	1.73	2.55						1.76			1.77	1.48	1.24	1.47	1.24	1.05	1.47	1.23
	468	1.63	2.06			1.71						1.67	1.45	1.26	1.43	1.25	1.10	1.45	1.24
	483	1.61	2.00						1.73			1.65	1.45	1.26	1.42	1.26	1.10	1.44	1.25

[a] Transition-state theory calculated KIEs using the LMR-PES geometries and force constants (plus Guassian 70 out-of-plane bending force constant) except as noted.

[b] Transition-state theory calculated KIE values using the LEPS2 and BEBO3 model parameters from Reference 14 $[F_\beta=F^\ddagger_{\phi_i}(i=1,2,3)]$ and using the BEBO and LEPS model parameters from Reference 12.

[c] Transition-state theory calculated using the harmonic calculated LMR-PES normal mode frequencies.

[d] LMR-PES-HF values including Bell tunneling.

[e] LMR-PES KIEs calculated using the H_2 and D_2 observed frequencies from Reference 40.

[f] LMR-PES-HF values corrected to the rotationally corrected H_2 and D_2 values in Reference 43; see text.

[g] Results from Reference 12.

[h] Results from Reference 14.

[i] Results from Reference 15.

[j] Results from Reference 16.

[k] Results from Reference 17.

[l] Results from Reference 13.

correction in (III-7), reduces the KIE value below that produced by the same set of frequencies used in (I-4).[43] At about 400°K the amount of this reduction is approximately three percent. The interatomic H_2 distance, r_{H_2} = 0.742Å, was used in both the PK[43] and the LMR-PES[2] calculations. Therefore, use of the PK σ_{H_2} and σ_{D_2} values to apply a rotational correction to the LMR-PES KIEs in Table XVII is valid [since, $\sigma_{x_2} = h^2/(8\pi^2 kTur_{x_2}^2)$, where h, k, T, u, and r_{x_2} are the Planck's constant, Boltzmann's constant, temperature in °K, reduced mass of the diatomic molecule, and the interatomic distance, respectively]. The application of a rotational correction to the LMR-PES $k(CH_3,H_2)/k(CH_3,D_2)$ values in the column labeled HF at 296 and 483°K reduces the values 1.99 and 1.83 to 1.89 and 1.78, respectively. Similarly for $k(CD_3,H_2)/k(CD_3,D_2)$ in the column labeled HF the values at 296 and 483°K are reduced by rotational correction from 1.98 and 1.83 to 1.88 and 1.78, respectively.

Since our transition-state-theory computer routine was not designed to handle a rotational correction in the manner of (III-7) directly, the rotationally corrected frequency values reported by PK were used to obtain a temperature dependent correction factor which could be multiplied times the KIEs obtained by (I-3) or (I-4). One factor value was used to correct the SW values and another factor value was used to obtain LMR-PES values which are directly comparable to the rotationally corrected SW values.[14] The SW correction factor is obtained as follows. The reactant exponent in the ZPE term for (I-3) and (I-4) is given by (III-8),

$$\frac{u_{H_2} - u_{D_2}}{2} = \frac{1.4388(4395.2 - 3109.1)}{2T} = \frac{925.2}{T} \qquad \text{(III-8)}$$

where $u_i = \dfrac{hc\nu_i}{kT} = \dfrac{1.4388\nu_i}{T}$ is the conversion factor used in the

computer code. The rotationally corrected exponent reported by Persky

and Klein is $\dfrac{889.4}{T}$.[43] Therefore, the reactant ZPE term using (III-8)

is converted to the PK rotationally corrected ZPE term by multiplying

by (III-9).

$$\frac{\exp(\frac{889.4}{T})}{\exp(\frac{925.2}{T})} = \exp(\frac{889.4 - 925.2}{T}) = \exp(\frac{-35.8}{T}) \qquad \text{(III-9)}$$

The rotationally corrected KIE is given by (III-10) since the

reactant EXC value is to at least five significant digits unity.

$$k_H/k_D \text{(corrected)} = k_H/k_D \cdot \exp(\frac{-35.8}{T}) \qquad \text{(III-10)}$$

All of the BEBO3, LEPS2, BEBO, and LEPS $k(CH_3,H_2)/k(CH_3,D_2)$ and

$k(CD_3,H_2)/k(CD_3,D_2)$ values in Table XVII were calculated by application

of (III-10) to those KIEs calculated using (I-3) and the H_2 and D_2

frequencies in (III-8). The same type correction was applied to the

LMR-PES KIEs; these rotationally corrected LMR-PES KIEs are given in

the column labeled RC in Table XVII. The LMR-PES H_2 and D_2 harmonic

frequencies, 4468.1 and 3160.6 cm^{-1}, respectively, were used to

calculate this correction factor, and the corrected LMR-PES KIE is

given by (III-11c).

$$\frac{u_{H_2} - u_{D_2}}{2} \text{ (LMR-PES)} = \frac{1.4388(4468.1-3160.6)}{2T} = \exp(\frac{940.6}{T}) \quad \text{(III-11a)}$$

$$\frac{\exp(\frac{889.4}{T})}{\exp(\frac{940.6}{T})} = \exp(\frac{889.4-940.6}{T}) = \exp(\frac{-51.2}{T}) \quad \text{(III-11b)}$$

$$k_H/k_D \text{(corrected LMR-PES)} = k_H/k_D \text{(LMR-PES)} \exp(\frac{-51.2}{T}) \quad \text{(III-11c)}$$

Therefore, the values in the column labeled RC in Table XVII are obtained by multiplying the values in the column labeled HF by (III-11b). Obviously, adjusting the LMR-PES reactant ZPE values to the rotationally corrected PK reactant ZPE values does lead to lower calculated KIES and does further increase the disagreement between experiment and theory. However, some of the LEPS2, BEBO3, LEPS, and BEBO KIEs were larger than their corresponding experimental values. Therefore, lowering these theoretical KIEs by application of the rotational correction improved their agreement with experiment. This improvement occurs for the BEBO3 and LEPS2 $k(CH_3,H_2)/k(CH_3,D_2)$ values in columns 13 and 16 only in Table XVII (that is, for the KIEs calculated using $F^{\ddagger}_{\phi_i}(i=1,2,3)=0.0001$ mdyne-$\overset{\circ}{A}$). However, for the $k(CD_3,H_2)/k(CD_3,D_2)$ values the rotational correction improves the agreement with most of the experimental values (that is, most all of the values in columns 13 through 19 in Table XVII exceed or are approximately equal to the corresponding experimental value). One exception to the latter statement for the $k(CD_3,H_2)/k(CD_3,D_2)$ values is that the Majury and Steacie experimental values, 4.11 and 3.48,[16]

exceed the calculated LEPS2 and BEBO3 KIEs using $F^{\ddagger}_{\phi_i}(i=1,2,3) = 0.26$

and 0.568 mdyne-$\overset{o}{A}$[14] and the LEPS and BEBO[12] KIEs.

Columns five and six of Table XVII show that use of the observed

H_2 and D_2 frequencies, 4395.2_4 and 3118.4_6 cm^{-1}, respectively, in

place of the LMR-PES harmonic frequencies leads to KIEs which are about

five percent lower than those calculated using harmonic frequencies.[40]

Clearly, the agreement between theory and experiment is not as strongly

dependent upon the magnitude of the fundamental frequencies for H_2 and

D_2 used in the calculation as upon other factors.

Application of Bell tunneling to the LMR-PES KIEs in the column

labeled HF produces the values in the column labeled BT.[44] Bell

tunneling treats the potential-energy barrier along the reaction

coordinate as being parabolic in shape and is assumably valid for all

$u^{\ddagger}_L = \dfrac{hcv^{\ddagger}_L}{kT} < 2\pi$, where h is Planck's constant, c is the velocity of

light, k is Boltzmann's constant, T is in °K and $v^{\ddagger}_L$ is the imaginary

frequency representing translational motion along the reaction coordi-

nate for the activated complex.[44] The Bell tunneling correction

factor B_t is calculated for the isotopic $u^{\ddagger}_L < 2\pi$ using equation

(III-12).

$$B_t(T) = \frac{u^{\ddagger}_{1L} \sin(u^{\ddagger}_{2L}/2)}{u^{\ddagger}_{2L} \sin(u^{\ddagger}_{1L}/2)} \qquad \text{(III-12)}$$

The condition $u^{\ddagger}_L < 2\pi$ is valid for the LMR-PES above 340°K; for the

BEBO model above ~390°K; and for the LEPS model above ~465°K. The Bell

tunneling correction factor is a function of the absolute temperature

and is simply multiplied by the transition-state theory LMR-PES-HF KIE

at the corresponding temperature to obtain the Bell tunneling corrected KIEs in the column labeled BT. It can be seen that the application of Bell tunneling to the LMR-PES KIEs improves the agreement with the corresponding experimental KIEs with the possible exceptions of the $k(CD_3,\underset{\sim}{H}D)/k(CD_3,\underset{\sim}{D}H)$ and the $k(CD_3,H_2)/k(CD_3,D_2)$ values. This improvement in the agreement between theoretically calculated KIEs and experimental KIEs upon applying a correction for tunneling does not necessarily indicate the presence of tunneling in that reaction. It could also indicate deficiencies in the LMR-PES and/or inaccuracies in the experimentally determined KIE.

The only experimental KIE for reaction of CH_4 + H involves the effect of D atoms versus H atoms on the abstraction rate.[12] The activated complexes principally determine this KIE since the reactants contribution only reflects the momentum of H relative to D along the reaction coordinate. Similarly the intramolecular isotope effects for the reaction of CH_3 and CD_3 with HD are entirely determined by the isotopic properties of the activated complexes. Obviously, the $k(CH_3,\underset{\sim}{H}D)/k(CH_3,\underset{\sim}{D}H)$ and $k(CD_3,\underset{\sim}{H}D)/k(CD_3,\underset{\sim}{D}H)$ values predicted by the LMR-PES KIEs with and without tunneling agree reasonably well, although not quantitatively with the experimental KIEs. This amount of agreement between the LMR-PES and experimental KIEs indicates that the force constants governing vibrational motion both parallel and perpendicular to the reaction coordinate at the top of the barrier (or saddle point) are reasonable.

The various BEBO and LEPS models produce values for $k(CH_4,H)/k(CH_4,D)$ in better agreement with experiment than does the LMR-PES. Also, variation of the HCH_1 bending force constant,

$F^{\ddagger}_{\phi_i}(i=1,2,3)$, from 0.0001 to 0.568 mdyne-Å in the SW BEBO3 and LEPS2

models has no effect on the $k(CH_4,H)/k(CH_4,D)$ KIE values. However,

the LMR-PES $k(CH_3,\underset{\sim}{H}D)/k(CH_3,\underset{\sim}{D}H)$ and $k(CD_3,\underset{\sim}{H}D)/k(CD_3,\underset{\sim}{D}H)$ KIEs agree with

experiment much better than the corresponding BEBO and LEPS KIEs

except for the BEBO3 model with the unrealistically small HCH_1 bending

force constant $F^{\ddagger}_{\phi_i}(i=1,2,3)$ = 0.0001 mdyne-Å. Comparison of the BEBO3

and LEPS2 $k(CH_3,\underset{\sim}{H}D)/k(CD_3,\underset{\sim}{D}H)$ and $k(CD_3,\underset{\sim}{H}D)/k(CD_3,\underset{\sim}{D}H)$ values as a

function of the $F^{\ddagger}_{\phi_i}(i=1,2,3)$ values shows that as the HCH_1 force

constant becomes larger, these intramolecular isotope effects become

smaller and hence the agreement between theory and experiment worsens.

The LMR-PES predicts a value for the $F^{\ddagger}_{\phi_i}(i=1,2,3)$ of 0.18 mdyne-Å which

is comparable to but slightly smaller than both the median value used

by SW and the value assumed by KHT, see Table XVI.

In view of the results in Table XVII, the KIEs for the reactions

CH_4 + H(D), CH_3 + $H_2(D_2)$ and CD_3 + $H_2(D_2)$ could be construed as

indicating inadequacies in the LMR-PES compared to the BEBO and LEPS

models relative to experiment. However, the results for the reactions

CH_3 + HD and CD_3 + HD in Table XVII could be taken to suggest that the

BEBO and LEPS models are inadequate relative to the LMR-PES when

compared to experiment. These contradictory results are indicative of

one or more of the following. First, both the LMR-PES and the BEBO3,

LEPS2, BEBO, and LEPS models contain inadequacies specific to a

certain type of calculated KIE. Absolute reaction rate theory

requires that the correct potential energy hypersurface reproduce all

experimental KIEs assuming that the latter are accurate and precise.

Therefore, it seems illogical that a model could reasonably predict

results for only one of two related experiments. Second, the

experimental determination of one type of KIE is subject to errors and

and the correction of these errors would lead to agreement between only

one theoretical model and experiment. Although this is not

inconceivable, it is impossible to tell which model (BEBO3, LEPS2,

BEBO, LEPS, or the LMR-PES) if any would best fit a set of revised

experimental results, provided the present results were found to be in

error. Empirical variation of various LMR-PES transition-state force

constants was attempted, but no completely self-consistent set of

isotopic frequencies could be found to reproduce the experimental

differences between the CH_3 and CD_3 reactions with $H_2(D_2)$ and HD. A

similar conclusion was reached by Shapiro and Weston.[14]

As seen in Table XVII, Ting and Weston observed normal inter-

molecular and intramolecular isotope effects on the abstraction of

hydrogen from H_2 by hot CH_3^*; that is, $k(CH_3,H_2)/k(CH_3,D_2) = 2.12$ and

$k(CH_3,HD)/k(CH_3,DH) = 6.37$ at 296°K.[13] However, reaction of hot CD_3

with $H_2(D_2)$ produced an inverse isotope effect, $k(CD_3,H_2)/k(CD_3,D_2)$ of

0.465.[13] As discussed in Chapter I, these results are difficult to

interpret either qualitatively or quantitatively. Since a thermal

distribution of reactant energies is a prerequisite to the use of

absolute-reaction-rate theory, kinetic isotope effects can not be

calculated for these reactions by this approach.

For the hot-atom reactions $T^* + CH_4 \rightarrow CH_3 + TD$ and $T^* + CD_4 \rightarrow$

$CD_3 + TD$ the hot atom yield ratios, $[(HT/CH_4)/(DT/CD_4)]$, found

experimentally by Chou and Rowland[10] and calculated by Raff[2] are 1.43

and 1.18, respectively. The calculated yield ratio was obtained using

the LMR-PES, an integrated reaction probability equation, and reactant

and Br_2 moderator concentrations equivalent to those used by Chou and

Rowland.[2,10] Both the calculated and experimental yield ratios assumably reflect the reaction of thermalized (or relatively stationary with respect to H and T atoms) CH_4 and CD_4 with tritium atoms possessing translational energies $\leq$ 65 kilocalories/mole. The temperature equivalent of these translational energies is $\leq$ 22,000 °K. In terms of equation (I-4) it is important to note that as T in °K approaches infinity VPxEXC approaches ZPE-1.[3a,b,11] Thus, in the limit of high temperature the isotope effect for a given reaction equals $\nu_{1L}^{\ddagger}/\nu_{2L}^{\ddagger}$; that is, the observed KIE is classical mechanical in origin. It is thus interesting to note, that for the abstraction reactions of thermalized tritium atoms with CH_4 and CD_4, the LMR-PES predicts an "infinite"-temperature isotope effect, $\nu_{1L}^{\ddagger}/\nu_{2L}^{\ddagger}$, of 1.19. This value is in good agreement with both the experimental and hot atom yield ratios. Thus, this agreement maybe tentatively taken to suggest that in a reactive collision between T^{*} and CH_4 and T^{*} and CD_4, the T^{*} atom translational energies are on the average sufficiently large to obscure the differences in quantum mechanical effects for the two reactions.

However, for the reactions $CH_3^{*} + H_2(D_2)$ and $CD_3^{*} + H_2(D_2)$ using hot methyl radicals, the isotope effects reported by Ting and Weston, k_H/k_D = 2.12 and 0.465, respectively, are not approximated by the $\nu_{1L}^{\ddagger}/\nu_{2L}^{\ddagger}$ ratios calculated for the corresponding thermal reactions, $\nu_{1L}^{\ddagger}/\nu_{2L}^{\ddagger}$ = 1.327 and 1.328, respectively. The following comments are thus pertinent. First, the agreement between the hot atom yield ratios and the $\nu_{1L}^{\ddagger}/\nu_{2L}^{\ddagger}$ ratio is merely fortuitous. Second, the CH_3 and CD_3 excitation energy involves principally internal rather than translational modes of the radicals. It is to be noted that Chapman

and Bunker[18] claim isotope effects of 1.84 and 0.70 on the ratios of

reactive cross sections, $\sigma(CH_3,H_2)/\sigma(CH_3,D_2)$ and $\sigma(CD_3,H_2)/\sigma(CD_3,D_2)$,

respectively. These results supposedly reproduce the corresponding

normal and inverse isotope effects reported by Ting and Weston[12] for

$CH_3^* + H_2(D_2)$ and $CD_3^* + H_2(D_2)$. Chapman and Bunker (CB) also claim

that these isotope effects do not reflect vibrational excitation in CH_3

and CD_3.[18] However, their data does appear to show that vibrational

excitation of H_2 (or D_2) does enhance the reaction rate and preserve

the unusual isotope effect, as previously mentioned in Chapter I.[18]

However, these conclusions could be fortuitous, since each normal mode

frequency is assigned an apparently arbitrary dynamic energy which is

used to obtain and then adjust the internal coordinates of the molecule

to obtain some specified total energy for the molecule. It is not

clear whether this adjustment procedure or the method of choosing the

initial energies allows for the proper representation of the CB

potential energy surface in these calculations. Also, the validity of

comparing isotopic reactive cross sections with the experimental

isotope effects of Ting and Weston is unclear.

Theoretical and Experimental
Temperature Dependences

The temperature dependences for the experimental KIEs in Table

XVII are compared to the temperature dependences of the corresponding

LMR-PES, BEBO, BEBO3, LEPS, and LEPS2 theoretically calculated KIEs

summarized in Tables XVIII through XXII. The ratio of the preexponen-

tial factors, A_H/A_D, and the difference in activation energies for

labeled and unlabeled reactions, ΔE, was determined for each isotope

TABLE XVIII

EXPERIMENTAL AND THEORETICAL TEMPERATURE DEPENDENCES FOR $k(CH_4,H)/k(CH_4,D)$[a]

A_H/A_D	ΔE (calories/mole)	Temperature Range (°K)	Reference[b] Source	Source[c] Label
1.391 ± 0.003	−1000 ± 2	396–969	2	LMR-PES
0.903 ± 0.053	−355 ± 59	396–696	2,44	LMR-PES + Bell Tunneling
1.38	−500 ± 300	500–732	12	KHT experimental result
1.268 ± 0.008	−541 ± 6	396–696	14	BEBO3 $F_\phi^\ddagger = 0.0001$ mdyne-Å[d]
1.269 ± 0.008	−541 ± 6	396–696	14	BEBO3 $F_\phi^\ddagger = 0.26$ mdyne-Å[d]
1.269 ± 0.008	−541 ± 6	396–696	14	BEBO3 $F_\phi^\ddagger = 0.658$ mdyne-Å[d]
1.263 ± 0.008	−475 ± 6	396–696	14	LEPS2 $F_\phi^\ddagger = 0.0001$ mdyne-Å[d]
1.264 ± 0.008	−476 ± 6	396–696	14	LEPS2 $F_\phi^\ddagger = 0.26$ mdyne-Å[d]
1.265 ± 0.008	−477 ± 6	396–696	14	LEPS2 $F_\phi^\ddagger = 0.568$ mdyne-Å[d]

TABLE XVIII (Continued)

A_H/A_D	ΔE (calories/mole)	Temperature Range (°K)	Reference[b] Source	Source[c] Label
1.224 ± 0.007	−561 ± 6	396−696	12	BEBO
1.261 ± 0.008	−469 ± 6	396−696	12	LEPS

[a] All results except experimental results are from the least squares fits to equation (III-13) for 12 temperatures over the specified range. All deviations are standard deviations.

[b] References from which the experimental values and/or the force constants and geometries used for the theoretical calculations were obtained.

[c] Describes information obtained from the references.

[d] $F_\phi^{\ddagger} = F_{\phi_i}^{\ddagger} (i=1,2,3)$, see Table XVI.

TABLE XIX

EXPERIMENTAL AND THEORETICAL TEMPERATURE DEPENDENCES FOR $k(CH_3,H_2)/k(CH_3,D_2)$[a]

A_H/A_D	ΔE (calories/mole)	Temperature Range (°K)	Reference[b] Source	Source[c] Label
1.483 ± 0.009	201 ± 6	396-696	2	LMR-PES
0.612 ± 0.064	1584 ± 102	396-696	2,44	LMR-PES + Bell Tunneling
0.911 ± 0.020	1327 ± 24	399-645	14	SW experimental
0.194 (0.659)[d]	1760 (707)[d]	403-564	15	WS experimental
0.246 ± 0.134 (0.809 ± 0.673)[d]	2516 ± 613 (1560 ± 1693)[d]	408-571	16	MS experimental
	1100	409-591	17	DB experimental
1.337 ± 0.013	1028 ± 10	396-696	14	BEBO3 $F_\phi^{\ddagger}$ = 0.0001 mdyne-Å[e]
1.455 ± 0.018	822 ± 12	396-696	14	BEBO3 $F_\phi^{\ddagger}$ = 0.26 mdyne-Å[e]
1.540 ± 0.019	646 ± 13	396-696	14	BEBO3 $F_\phi^{\ddagger}$ = 0.568 mdyne-Å[e]

TABLE XIX (Continued)

A_H/A_D	ΔE (calories/mole)	Temperature Range (°K)	Reference[b] Source	Source[c] Label
1.379 ± 0.016	993 ± 12	396-696	14	LEPS2 $F_\phi^\ddagger = 0.0001$ mdyne-Å[e]
1.488 ± 0.020	801 ± 14	396-696	14	LEPS2 $F_\phi^\ddagger = 0.26$ mdyne-Å[e]
1.566 ± 0.021	635 ± 14	396-696	14	LEPS2 $F_\phi^\ddagger = 0.568$ mdyne-Å[e]
1.533 ± 0.019	777 ± 13	396-696	12	BEBO
1.484 ± 0.020	809 ± 14	396-696	12	LEPS

[a]All results except experimental results are from the least squares fits to equation (III-13) for 12 temperatures over the specified range. All deviations are standard deviations.

[b]References from which the experimental values and/or the force constants and geometries used for the theoretical calculations were obtained.

[c]Describes information obtained from the references.

[d]Values in parentheses are calculated by a different method, see text.

[e]$F_\phi^\ddagger = F_{\phi_i}^\ddagger$ (i=1,2,3), see Table XVI.

TABLE XX

EXPERIMENTAL AND THEORETICAL TEMPERATURE DEPENDENCES FOR $k(CD_3, H_2)/k(CD_3, D_2)$

A_H/A_D	ΔE (calories/mole)	Temperature Range (°K)	Reference[b] Source	Source[c] Label
1.488 ± 0.010	197 ± 7	396-696	2	LMR-PES
0.616 ± 0.064	1576 ± 101	396-696	2,44	LMR-PES + Bell Tunneling
1.592 ± 0.124	588 ± 70	402-611	14	SW experimental
$3.724 \ (1.702)[d]$	$-201 \ (714)[d]$	410-572	15	WS experimental
1.727 ± 0.279 $(1.062 \pm 0.699)[d]$	701 ± 462 $(1100 \pm 480)[d]$	407-570	16	MS experimental
1.339 ± 0.013	1027 ± 10	396-696	14	BEBO3 $F_\phi^\ddagger = 0.0001$ mdyne-$\overset{\circ}{A}$[e]
1.466 ± 0.018	813 ± 13	396-696	14	BEBO3 $F_\phi^\ddagger = 0.26$ mdyne-$\overset{\circ}{A}$[e]
1.572 ± 0.021	616 ± 14	396-696	14	BEBO3 $F_\phi^\ddagger = 0.568$ mdyne-$\overset{\circ}{A}$[e]

TABLE XX (Continued)

A_H/A_D	ΔE (calories/mole)	Temperature Range (°K)	Reference[b] Source	Source[c] Label
1.380 ± 0.016	992 ± 12	396–696	14	LEPS2 $F_\phi^\ddagger = 0.001$ mdyne-$\mathring{A}$[e]
1.497 ± 0.021	792 ± 14	396–696	14	LEPS2 $F_\phi^\ddagger = 0.26$ mdyne-$\mathring{A}$[e]
1.595 ± 0.023	607 ± 15	396–696	14	LEPS2 $F_\phi^\ddagger = 0.568$ mdyne-$\mathring{A}$[e]
1.490 ± 0.019	777 ± 13	396–696	12	BEBO
1.493 ± 0.021	800 ± 14	396–696	12	LEPS

[a]All results except experimental results are from the least squares fits to equation (III-13) for 12 temperatures over the specified range. All deviations are standard deviations.

[b]References from which the experimental values and/or the force constants and geometries used for the theoretical calculations were obtained.

[c]Describes information obtained from the references.

[d]Values in parentheses are calculated by a different method, see text.

[e]$F_\phi^\ddagger = F_{\phi_i}^\ddagger (i=1,2,3)$, see Table XVI.

TABLE XXI

EXPERIMENTAL AND THEORETICAL TEMPERATURE DEPENDENCES FOR $k(CH_3,\underset{\sim}{H}D)/k(CH_3,\underset{\sim}{D}H)$ [a]

A_H/A_D	ΔE (calories/mole)	Temperature Range (°K)	Reference[b] Source	Source[c] Label
1.083 ± 0.003	379 ± 3	396–969	2	LMR-PES
0.761 ± 0.027	945 ± 36	396–696	2,44	LMR-PES + Bell Tunneling
0.283 ± 0.258	1929 ± 690	367–651	14	SW experimental
0.452[d]	1350[d]	408–569	15	WS experimental
1.170 ± 0.002	330 ± 2	396–696	14	BEBO3 $F_\phi^\ddagger = 0.0001$ mdyne-Å[e]
1.273 ± 0.001	125 ± 1	396–696	14	BEBO3 $F_\phi^\ddagger = 0.26$ mdyne-Å[e]
1.346 ± 0.001	−51 ± 1	396–696	14	BEBO3 $F_\phi^\ddagger = 0.568$ mdyne-Å[e]
1.213 ± 0.001	154 ± 1	396–696	14	LEPS2 $F_\phi^\ddagger = 0.0001$ mdyne-Å[e]

TABLE XXI (Continued)

A_H/A_D	ΔE (calories/mole)	Temperature Range (°K)	Reference[b] Source	Source[c] Label
1.308 ± 0.002	-362 ± 1	396-696	14	LEPS2 $F_\phi^\ddagger = 0.26$ mdyne-$\overset{o}{A}$[e]
1.375 ± 0.002	-201 ± 1	396-696	14	LEPS2 $F_\phi^\ddagger = 0.568$ mdyne $\overset{o}{A}$[e]
1.278 ± 0.001	120 ± 1	396-696	12	BEBO
1.309 ± 0.002	-44 ± 1	396-696	12	LEPS

[a] All results except experimental results are from the least squares fits to equation (III-13) for 12 temperatures over the specified range. All deviations are standard deviations.

[b] References from which the experimental values and/or the force constants and geometries used for the theoretical calculations were obtained.

[c] Describes information obtained from the references.

[d] Average of the results at two different reactant pressures.

[e] $F_\phi^\ddagger = F_{\phi_i}^\ddagger (i=1,2,3)$, see Table XVI.

TABLE XXII

EXPERIMENTAL AND THEORETICAL TEMPERATURE DEPENDENCES FOR $k(CD_3,HD)/k(CD_3,DH)$[a]

A_H/A_D	ΔE (calories/mole)	Temperature Range (°K)	Reference[b] Source	Source[c] Label
1.085 ± 0.003	375 ± 3	396-696	2	LMR-PES
0.764 ± 0.027	939 ± 35	396-696	2,44	LMR-PES + Bell Tunneling
0.932 ± 0.133	546 ± 131	402-611	14	SW experimental
1.698	0	410-572	15	WS experimental
1.171 ± 0.002	329 ± 2	396-696	14	BEBO3 $F_\phi^\ddagger = 0.0001$ mdyne-Å[d]
1.282 ± 0.001	115 ± 1	396-696	14	BEBO3 $F_\phi^\ddagger = 0.26$ mdyne-Å[d]
1.374 ± 0.002	-82 ± 2	296-696	14	BEBO3 $F_\phi^\ddagger = 0.568$ mdyne-Å[d]
1.214 ± 0.001	153 ± 1	396-696	14	LEPS2 $F_\phi^\ddagger = 0.0001$ mdyne-Å[d]
1.316 ± 0.002	-46 ± 1	396-696	14	LEPS2 $F_\phi^\ddagger = 0.26$ mdyne-Å[d]

TABLE XXII (Continued)

A_H/A_D	ΔE (calories/mole)	Temperature Range (°K)	Reference[b] Source	Source[c] Label
1.401 ± 0.003	−230 ± 2	396–696	14	LEPS $F_\phi^\ddagger$ = 0.568 mdyne-Å[d]
1.289 ± 0.001	109 ± 1	396–696	12	BEBO
1.317 ± 0.002	−54 ± 2	396–696	12	LEPS

[a]All results except experimental results are from the least squares fits to equation (III-13) for 12 temperatures over the specified range. All deviations are standard deviations. The atom underlined is being abstracted.

[b]References from which the experimental values and/or the force constants and geometries used for the theoretical calculations were obtained.

[c]Describes information obtained from the references.

[d]$F_\phi^\ddagger = F_{\phi_i}^\ddagger$ (i=1,2,3), see Table XVI.

effect by applying equation (III-13) to the KIE data using the method
of least squares.

$$\ln(k_1/k_2) = \ln(A_1/A_2) + \Delta E/RT \qquad \text{(III-13)}$$

In (III-13) the subscripts 1 and 2 refer to the light and heavy
isotopes, respectively, and k_1/k_2 is the KIE at a specific temperature
T in °K.

For the isotope effect $k(CH_4,H)/k(CH_4,D)$, the data in Table XVIII
shows that the error in the KHT experimental ΔE value encompasses all
but the LMR-PES ΔE value. The application of Bell tunneling to the
LMR-PES KIEs apparently over-corrects the LMR-PES ΔE value, but
it does cause the value to fall within the error bounds of the
experimental value. However, inclusion of the Bell tunneling correc-
tion produces a calculated A_H/A_D value of 0.903 which is lower than
either the experimental value, 1.38, or the values obtained from the
various BEBO and LEPS models. As previously mentioned the improve-
ment in the agreement with experiment by application of tunneling
may be more indicative of inadequacies in either one or more of
the theoretical models or in the experimental results or both than
the existence of tunneling. The maximum error in the experimental
A_H/A_D value, 1.38, is estimated by KHT to probably be within ± 0.14.[12]
However, due to the experimental problems discussed in Chapter I, this
A_H/A_D value, 1.38, and the associated error were estimated
using simple collision theory.[12] It should be noted that
changes in the value of $F^{\ddagger}_{\phi_i}(i=1,2,3)$ has no more

effect on the calculated Arrhenius equation parameters than it does

on the $k(CH_4,H)/k(CH_4,D)$ values in Table XVII.

As seen in Table XIX, the ΔE for the reaction $CH_3 + H_2(D_2)$ calculated from the experimental KIEs is greater than the values obtained from the isotope effects calculated without inclusion of tunneling; the lowest value being that from the LMR-PES data. For the LMR-PES, inclusion of Bell tunneling into the isotope effects significantly improves the agreement between predicted and experimental ΔE values. However, this result does not necessarily indicate that tunneling is present. Precise comparison between theory and experiment is necessarily precluded by the considerable discrepancies between the experimental ΔE values. The individual experimental ΔE values differ by more than the uncertainties measured for any one reported value. The experimental A_H/A_D values in Table XIX seem too low except for the value reported by SW.[14] The differences in these experimental A_H/A_D values may be at least partially due to the experimental technique. Davison and Burton[17] and SW[14] determined their KIE values for the reaction of methyl radicals with a mixture of H_2 and D_2, whereas Whittle and Steacie[15] and Majury and Steacie[16] reacted methyl radicals with H_2 or D_2 separately. Davison and Burton (DB) determined their ΔE value by fitting a line to their KIE values assuming a steric factor ratio of unity. The collision theory equation used by DB is equivalent to the Arrhenius equation used by SW except that the steric factor ratio (S_1/S_2) must be multiplied by a collision number ratio (C_1/C_2) to obtain a value equivalent to the A_H/A_D values given by fitting data to (III-13). The collision number ratio, C_1/C_2, is given by

$$C_1/C_2 = \left[\frac{\sigma(CH_3,H_2)}{\sigma(CH_3,D_2)}\right]^2 \frac{1/M_{CH_3} + 1/M_{H_2}}{1/M_{CH_3} + 1/M_{D_2}} \qquad \text{(III-14)}$$

where the M values are molecular weights of the species specified in the subscript and the σ values are the collision diameters of the reactant species.[17] Assuming the same collision diameter for H_2 and D_2, a C_1/C_2 value of 1.337 is obtained from (III-14) using the masses (in amu): C= 12; H = 1.007825; D = 2.0141. Therefore, the S_1C_1/S_2C_2 value 1.337 could be taken as the A_H/A_D associated with the DB ΔE value of 1100 calories/mole and could be compared to the other A_H/A_D values in Table XIX. The Arrhenius parameters reported by Whittle and Steacie (WS)[15] and by Majury and Steacie (MS)[16] were calculated from rate constants obtained by two methods. These two different methods are only applicable to the determination of the individual rate constants for the reactions $CH_3 + D_2$ and $CD_3 + H_2$ which are used to calculate the Arrhenius parameters in Table XIX and Table XX, respectively. The values obtained by using method I rate constants are given in parentheses in Tables XIX and XX. For method I the rate constants were calculated by subtracting the concentration of methane obtained from photolysis of acetone alone from the total concentration of isotopic methanes obtained from photolysis of acetone or acetone-d_6 in the presence of D_2 or H_2 to obtain the concentration of CH_3D or CD_3H, respectively. These concentrations are needed to determine the individual rate constants for formation of CH_3D or CD_3H, respectively.[15,16] For method II, rate constants were obtained from mass spectrometric determination of the ratios $[CH_3D]/[CH_4]$ or

$[CD_3H]/[CD_4]$ in the product gases from photolysis of acetone or acetone-d_6 in the presence of either D_2 or H_2, repectively.[15,16] The individual $k(CH_3,H_2)/k(CH_3,D_2)$ and $k(CD_3,H_2)/k(CD_3,D_2)$ values that were reported in Table XVII and attributed to MS were calculated by us using the rate constants reported by MS in a summary table and are averages of the method I and method II rate constant values.[16] However, WS considered the method II rate constants to be the more accurate. Therefore, the $k(CH_3,H_2)/k(CH_3,D_2)$ and $k(CD_3,H_2/k(CD_3,D_2)$ values reported in Table XVII in the column labeled WS were calculated using the method II rate constants $k(CH_3,D_2)$ and $k(CD_3,H_2)$.[15] WS did not report individual method I rate constant values in their summary table from which the other WS values in Table XVII were calculated.[15] It should be noted that the rate constants for reaction of $CH_3 + H_2$ and $CD_3 + D_2$ could only be determined by method I. Therefore, the generally better agreement between the method I Arrhenius equation parameters given in parentheses in Tables XIX and XX for MS[16] and WS[15], and the parameter values reported by Shapiro and Weston[14] and by Davison and Burton[17] reflects the probable cancellation of consistent errors in the method I values yielding reasonably accurate KIEs. Although, the method II rate constants determined by MS[16] and WS[15] may be more accurate, by themselves, the KIEs determined by a ratio of one method I and one method II rate constant may actually compound the error of each rate constant into a greater error in the resultant KIE value.

The data in Tables XIX and XX clearly show that transition state theory predicts only negligible differences between the $k(CH_3,H_2)/k(CH_3,D_2)$ and $k(CD_3,H_2)/k(CD_3,D_2)$ Arrhenius parameters

are in serious disagreement with this prediction. Furthermore, for

the reactions of CH_3 and CD_3 with H_2 and D_2 the LMR-PES and SW

transition-state force constants could not be arbitrarily adjusted to

produce a single set that would produce a variation in the KIEs and

Arrhenius parameters comparable to the variation in the experimental

values. It can be seen that decreasing the $F^\ddagger_{\phi_i}(i=1,2,3)$ force

constants from 0.568 to 0.0001 mdyne-$\overset{o}{A}$ increases the calculated ΔE

values and decreases the A_H/A_D values. Therefore, the BEBO3 and

LEPS2 Arrhenius parameters calculated using $F^\ddagger_{\phi_i}(i=1,2,3) = 0.0001$

mdyne-$\overset{o}{A}$ are in much better agreement with the Table XIX experimental

results than those using larger $F^\ddagger_{\phi_i}(i=1,2,3)$ values. However, a force

constant value of $F^\ddagger_{\phi_i}(i=1,2,3) = 0.568$ mdyne-$\overset{o}{A}$ produces BEBO3 and

LEPS2 theoretically calculated Arrhenius parameters in best agreement

with the experimental values in Table XX. Similarly for the LMR-PES,

other transition-state force constants including off-diagonal cross-

term force constants can be adjusted to produce KIEs and Arrhenius

parameters which are in agreement with one but not both of the

$CH_3 + H_2(D_2)$ or $CD_3 + H_2(D_2)$ experimental values.

The $k(CH_3,\underset{\sim}{H}D)/k(CH_3,D\underset{\sim}{H})$ and $k(CD_3,\underset{\sim}{H}D)/k(CD_3,D\underset{\sim}{H})$ Arrhenius para-

meters are given in Tables XXI and XXII, respectively. The LMR-PES

gives k_H/k_D values which lead to A_H/A_D and ΔE values in much better

agreement with experiment than are the values predicted by the BEBO3,

LEPS2, BEBO and LEPS models. This result is opposite to that

observed for the reaction of CH_3 and CD_3 with H_2 and D_2. As can be

seen, the reproducibility in the A_H/A_D and ΔE values derived from

experiment leaves much to be desired. Also, as in Tables XVIII

through XX the addition of Bell tunneling to the LMR-PES values

improves the agreement with experiment for reactions involving CH_4 or CH_3 radicals but tends to over-correct those values obtained for reactions involving CD_3 radicals. The differences in the values reported by both SW[14] and WS[15] between the experimental ΔE values in Table XXI and the corresponding values in Table XXII are about 1.4 kilocalories/mole. However, for each isotope effect the ΔE value reported by SW[14] is about 500 calories/mole greater than the ΔE values reported by WS[15]. This latter difference is most pronounced in Table XXII where WS report the isotope effect is temperature independent. Since the rate determining step involves transfer of either H or D, the result is clearly incorrect and casts doubt upon the experimental results obtained by Whittle and Steacie[15]. For the theoretically calculated Arrhenius parameters, it can be seen that the LEPS2 and BEBO3 models predict increasingly large A_H/A_D values and decreasing ΔE values which actually become negative as $F_{\phi i}^{\ddagger}$ (i=1,2,3) increases. It should also be noted that the error bounds on the SW ΔE values do not encompass any of the theoretically calculated ΔE values, although the LMR-PES ΔE and A_H/A_D values are closer to the SW experimental result than any other theoretical result.

Theoretical Primary Carbon Effects

Tables XXIII and XXIV tabulate 13-carbon isotope effects and their temperature dependences based upon the LMR-PES. These tables also present 13-carbon KIEs based upon BEBO[12] and BEBO3[14] models. These latter values are based upon force constants and geometry that were also used to calculate secondary α-deuterium isotope effects (see below). Although k_{12}/k_{13} for both reactions are no where maximal, the $k(CH_4,H)/k(^{13}CH_4,H)$ are much larger than $k(CH_3,H_2)/k(^{13}CH_3,H_2)$. This result is

TABLE XXIII

COMPARISON OF $k(CH_4,H)/k(^{13}CH_4,H)$ RESULTS[a]

Activated Complex Used	Transition State Theory Results					Arrhenius Results[b]		
	Temperature °K	MMI	EXC	ZPE	KIE	A_1/A_2	ΔE	Temperature Range °K
LMR-PES[c]	296	1.002	0.999	1.034	1.035			
	546	1.002	0.998	1.018	1.018	$0.999 \pm 3 \times 10^{-5}$	21.1 ± 0.02	273-546
BEBO[d]	296	1.003	0.999	1.020	1.022			
	546	1.003	0.998	1.010	1.011	$0.999 \pm 7 \times 10^{-5}$	13.0 ± 0.06	273-546
BEBO3[e]	296	1.003	0.993	1.032	1.028			
	546	1.003	0.993	1.017	1.013	$0.995 \pm 4 \times 10^{-5}$	19.0 ± 0.03	273-546
BEBO3[f]	296	1.003	0.999	1.006	1.008			
	546	1.003	0.999	1.003	1.005	$1.001 \pm 3 \times 10^{-5}$	3.9 ± 0.03	273-546

[a] For purposes of comparison all results were calculated using the LMR-PES reactant data with the activated complex parameters from the specified source.

[b] Results obtained by linear least squares fit of $\ln(k_{12}/k_{13})$ versus T^{-1} for 12 values over the specified temperature range. See Appendix D. ΔE is in calories per mole.

[c] Calculated using the LMR-PES data.

[d] Calculated using the BEBO activated complex data from Reference 12.

[e] Calculated using the BEBO3 activated complex data with $F^{\ddagger}_{\phi_i}$ (i=1,2,3) =0.0001 mdyne-Å from Reference 14.

[f] Calculated using the BEBO3 activated complex data with $F^{\ddagger}_{\phi_i}$ (i=1,2,3) =0.568 mdyne-Å from Reference 14.

TABLE XXIV

COMPARISON OF $k(CH_3,H_2)/k(^{13}CH_3,H_2)$ RESULTS[a]

| Activated Complex Used | Transition State Theory Results | | | | | Arrhenius Results[b] | | Temperature Range °K |
	Temperature °K	MMI	EXC	ZPE	KIE	A_1/A_2	ΔE	
LMR-PES[c]	296	1.008	0.999	0.999	1.006	$1.006 \pm 4 \times 10^{-5}$	0.4 ± 0.03	273–546
	546	1.008	0.998	1.000	1.006			
BEBO[d]	296	1.009	0.999	0.985	0.993	$1.007 \pm 1 \times 10^{-4}$	-7.7 ± 0.09	273–546
	546	1.009	0.998	0.992	0.999			
BEBO3[e]	296	1.009	0.993	0.997	0.999	$1.002 \pm 1 \times 10^{-5}$	-1.8 ± 0.01	273–546
	546	1.009	0.993	0.999	1.001			
BEBO3[f]	296	1.009	1.000	0.972	0.979	$1.008 \pm 9 \times 10^{-5}$	-16.8 ± 0.07	273–546
	546	1.009	1.000	0.984	0.993			

TABLE XXIV (Continued)

Activated Complex Used	Transition State Theory Results					Arrhenius Results[b]		
	Temperature °K	MMI	EXC	ZPE	KIE	A_1/A_2	ΔE	Temperature Range °K
Pimentel[g]	296	1.008	1.000	0.995	1.003	$1.007 \pm 7 \times 10^{-5}$	-2.7 ± 0.05	273–546
	546	1.008	1.000	0.997	1.005			

[a]For purposes of comparison all results were calculated using the LMR–PES reactant data with the activated complex parameters from the specified source.

[b]Results obtained by linear least squares fit $\ln(k_{12}/k_{13})$ vs. T^{-1} for 12 values over the specified temperature range. See Appendix D. ΔE is in calories per mole.

[c]Calculated using the LMR–PES data with Gaussian 70 out-of-plane bending frequency values.

[d]Calculated using the BEBO activated complex data from Reference 12.

[e]Calculated using the BEBO3 activated complex data with $F^{\ddagger}_{\phi_i}(i=1,2,3)=0.0001$ mdyne-$\overset{\circ}{A}$ from Reference 14.

[f]Calculated using the BEBO3 activated complex data with $F^{\ddagger}_{\phi_i}(i=1,2,3)=0.568$ mdyne-$\overset{\circ}{A}$ from Reference 14.

[g]Calculated using the LMR–PES data with out-of-plane bending frequency values corresponding to the harmonic values from Reference 38.

not unreasonable qualitatively since reaction (I-1) involves almost total breaking of the C-H$_1$ bond in passing from reactant-state to the transition state (that is, the transition-state configuration for (I-1) is very product-like). However, the small primary carbon effect for H atom abstraction on CH$_4$ reflects the fact that the loss in the frequencies associated with the C-H$_1$ bond being broken is compensated to a large extent by the frequencies associated with the H$_1$-H$_6$ bond being formed. Conversely, for reaction (I-2) passing from the reactant state to the transition state involves very little of both H$_1$-H$_6$ bond breaking and C-H$_1$ bond making (that is the transition state for reaction (I-2) is very reactant-like). Since the 13-carbon KIE is largely dependent on frequency changes associated with the C-H$_1$ bond and reaction (I-2) involves less of a change in the C-H$_1$ bonding in passing from reactant state to transition state than reaction (I-1), then the Table XXIV KIEs for reaction (I-2) tend to be less than the corresponding KIEs for reaction (I-1). Also, the BEBO3 13-carbon effect using $F_{\phi i}^{\ddagger}$ (i=1,2,3) = 0.568 mdyne-$\overset{\circ}{A}$ gives an inverse KIE for reaction (I-2) and a very small KIE for reaction (I-1). Comparison of the BEBO and BEBO3 13-carbon KIEs shows that all the KIEs values become lower or more inverse as the value of $F_{\phi i}$ (i=1,2,3) is increased. This is the result of the effect of the F_{ϕ_i} (i=1,2,3) values on the frequencies most strongly associated with the C-H$_1$ bond in the transition state. Specifically, the carbon effect is the result of differences in the CH$_3$ asymmetric stretching, ν_5, and degenerate bending, ν_6, frequencies in the activated complex and their corresponding reactant state values. The ν_1 and ν_4 activated complex frequencies for the symmetric and asymmetric motion along the reaction coordinate, respectively, also contribute to the carbon effect.

However, the ν_7 and ν_8 linear bending frequencies are virtually unaffected by isotopic carbon substitution. It should be noted that the values labeled "Pimentel" in Table XXIV are calculated with all LMR-PES harmonic frequencies except the isotopic out-of-plane bending frequencies which are calculated using a harmonic force constant adjusted to produce a CH_3 out-of-plane bending frequency of 607 cm^{-1} which corresponds to the spectroscopic frequency reported by Tan, Winer and Pimentel (also, see discussion of this force constant in the secondary α-deuterium KIE section).[38] The 13-carbon KIE calculated using this frequency is normal but exhibits an inverse temperature dependence. The LMR-PES 13-carbon KIE using the Gaussian 70 out-of-plane bending frequency is normal with a very small normal temperature dependence. This difference is the result of the smaller isotopic change in the "Pimentel" calculated, 607 cm^{-1}, than the Gaussian 70 calculated, 847 cm^{-1}, CH_3 out-of-plane bending frequencies.[38]

Precise experimental determinations of carbon isotope effects for reaction (I-1) and/or (I-2) would allow some additional insight into which one if any of the LMR-PES, BEBO and BEBO3 theoretical models have any validity. Also, carbon effects could be intepreted and contrasted with the primary effects already discussed to give a more quantitative description of the bonding that occurs in the transition state for the abstraction reaction. This information could possible be used to construct a better theoretical model of the reaction hypersurface.

Theoretical Secondary α-Deuterium Effects

"Exact" calculations for model reactions within the framework of absolute rate theory show that secondary α-deuterium isotope effects are

TABLE XXV

COMPARISON OF SECONDARY α-DEUTERIUM $k(CH_4,H)/k(CD_3H,H)$ RESULTS[a]

Activated Complex Used	Transition State Theory Results					Arrhenius Results[b]		
	Temperature °K	MMI	EXC	ZPE	KIE	A_1/A_2	ΔE	Temperature Range °K
LMR-PES[c]	296	1.319	0.858	1.395	1.579			
	546	1.319	0.771	1.198	1.218	0.889 ± 0.002	332 ± 2	273-546
BEBO[d]	296	1.274	0.903	1.123	1.293			
	546	1.274	0.830	1.065	1.127	0.962 ± 0.003	175 ± 2	273-546
BEBO3[e]	296	1.275	0.645	1.832	1.507			
	546	1.275	0.642	1.389	1.136	0.807 ± 0.003	367 ± 2	273-546
BEBO3[f]	296	1.275	0.930	0.601	0.712			
	546	1.275	0.879	0.759	0.850	1.052 ± 0.002	-229 ± 1	273-546

[a] For purposes of comparison all results were calculated using the LMR-PES reactant data with the activated complex parameters from the specified source.

[b] Results obtained by linear least squares fit of $\ln(k_H/k_D)$ vs. T^{-1} for 12 values over the specified temperature range. ΔE is in calories per mole. Deviations are standard deviations.

[c] Calculated using the LMR-PES data.

[d] Calculated using the BEBO activated complex data from Reference 12.

[e] Calculated using the BEBO3 activated complex data with $F^{\ddagger}_{\phi_i}(i=1,2,3) = 0.0001$ mdyne-$\overset{\circ}{A}$ from Reference 14.

[f] Calculated using the BEBO3 activated complex data with $F^{\ddagger}_{\phi_i}(i=1,2,3) = 0.568$ mdyne-$\overset{\circ}{A}$ from Reference 14.

principally determined by the change in the α-hydrogen to carbon to leaving (entering) group bending force constants $[F_{\phi_i}^{\ddagger} \ (i=1,2,3)]$ in passing from the reactant state to the transition state.[3b-d] Since SW varied $F_{\phi_i}^{\ddagger} \ (i=1,2,3)$ in their BEBO3 activated-complex models, the smallest and largest values of these force constants were used with the other reported BEBO3 parameters in Table XVI to calculate secondary α-deuterium KIEs.[14] The BEBO parameters reported by KHT[12] were also used to calculate secondary α-deuterium KIEs since their reported $F_{\phi_i}^{\ddagger} \ (i=1,2,3)$ value is almost the same as the median value used by SW[14], see Table XVI. For purposes of comparison, the LMR-PES reactant-state frequencies and parameters were used in all the secondary α-deuterium KIE calculations. The secondary α-deuterium KIEs for reaction (I-1) are presented in Table XXV. Obviously, using the very large $F_{\phi_i}^{\ddagger} \ (i=1,2,3)$ value of 0.568 mdyne-$\overset{o}{A}$ in the BEBO3 model[14] has a dramatic effect on the secondary α-deuterium KIEs; it produces inverse KIEs while the LMR-PES[2], BEBO[12] and the BEBO3 with $F_{\phi_i}^{\ddagger} \ (i=1,2,3) = 0.0001$ mdyne-$\overset{o}{A}$ all predict normal KIEs. This change to an inverse KIE for large values of $F_{\phi_i}^{\ddagger} \ (i=1,2,3)$ occurs because the differences in the isotopic activated-complex frequencies exceeds the differences in the isotopic reactant frequencies as is evidenced by the ZPE values in Table XXV. The differences in the MMI terms are the result of the differences in the activated complex geometries which produce different moments of inertia about the cartesian coordinate axes. The method of calculating these moments of inertia about the cartesian coordinate axes is given in Appendix B. The Arrhenius activation-energy differences, ΔE, and preexponential factors (A_1/A_2) for the LMR-PES and BEBO3 $[F_{\phi_i}^{\ddagger} \ (i=1,2,3) = 0.0001$ mdyne-$\overset{o}{A}]$ appear to show the best agreement in both Table XXV and Table

XXVI. However, this agreement is apparently due to a fortuitous set of compensating factors. As seen in Table XXVI all secondary α-deuterium isotope effects for reaction (I-2) are inverse. The large $F_{\phi_i}^{\ddagger}$ (i=1,2,3) = 0.568 mdyne-$\overset{\circ}{A}$ for BEBO3 merely causes the secondary KIE to become more inverse. The more inverse KIEs for larger $F_{\phi_i}^{\ddagger}$ (i=1,2,3), as expected, show a larger negative ΔE compared to the other ΔE values in Table XXVI. It should be noted that the LMR-PES isotopic CH_3 normal-mode frequencies are used in all the secondary KIEs in Table XXVI and include the isotopic out-of-plane bending frequencies calculated using the Gaussian 70 out-of-plane bending force constant given in Chapter II, except for the KIEs labeled Pimentel. The α effects labeled as Pimentel are based on the use of the out-of-plane bending normal mode frequency calculated using the out-of-plane bending force constant of Tan, Winer and Pimentel (TWP).[38] These authors obtained this force constant from their spectroscopic frequencies.[38] It should be noted that their reported force constant could not be weighted or adjusted in such a way as to exactly reproduce the harmonic frequencies that TWP report having calculated.[38] However, the difference is negligible, both our calculation and TWP give 607.0 cm^{-1} for CH_3, but TWP gives 470.2 cm^{-1} for CD_3 compared to our 470.5 cm^{-1} for CD_3. The various isotopic CH_3 harmonic normal-mode frequencies that were calculated using this force constant are tabulated in Appendix C. Harmonic normal-mode frequencies were used instead of spectroscopic methyl radical frequencies for three reasons: First, TWP did not report spectroscopic frequencies for all the isotopic methyl radicals needed. Second, for the purpose of consistency, all other frequencies used to calculate the KIEs are harmonic normal-mode frequencies. Third, the use of spectroscopic frequencies for the

TABLE XXVI

COMPARISON OF SECONDARY α-DEUTERIUM $k(CH_3,H_2)/k(CD_3,H_2)$ RESULTS[a]

Activated Complex Used	Transition State Theory Results					Arrhenius Results[b]		
	Temperature °K	MMI	EXC	ZPE	KIE	A_1/A_2	ΔE	Temperature Range °K
LMR-PES[c]	296	1.669	0.871	0.577	0.838	1.138 ± 0.008	−179 ± 5	273-546
	546	1.669	0.773	0.742	0.958			
Pimentel[d]	296	1.669	0.895	0.506	0.756	1.190 ± 0.010	−266 ± 3	273-546
	546	1.669	0.800	0.691	0.923			
BEBO3[f]	296	1.613	0.917	0.464	0.686	1.217 ± 0.001	−336 ± 6	273-546
	546	1.613	0.833	0.660	0.886			
BEBO3[f]	296	1.613	0.655	0.757	0.800	1.021 ± 0.002	−144 ± 1	273-546
	546	1.613	0.644	0.860	0.894			

TABLE XXVI (Continued)

| Activated Complex Used | Transition State Theory Results | | | | | Arrhenius Results[b] | | |
	Temperature °K	MMI	EXC	ZPE	KIE	A_1/A_2	ΔE	Temperature Range °K
BEBO3[g]	296	1.613	0.943	0.248	0.377	1.331 ± 0.009	-739 ± 5	273–546
	546	1.613	0.882	0.470	0.668			

[a]For purposes of comparison all results were calculated using the LMR-PES reactant data with Gaussian-70 out-of-plane bending frequencies (unless specified otherwise) with the activated complex parameters from the specified source.

[b]Results obtained by linear least squares fit of $\ln(k_H/k_D)$ vs. T^{-1} for 12 values over the specified temperature range. See Appendix D. ΔE is calories per mole.

[c]Calculated using the LMR-PES data with Gaussian-70 out-of-plane bending frequencies.

[d]Calculated using the LMR-PES data with the methyl radical out-of-plane bending frequencies corresponding to the calculated harmonic values in Reference 38.

[e]Calculated using the BEBO activated complex data from Reference 12.

[f]Calculated using the BEBO3 activated complex data with $F^{\ddagger}_{\phi_i}(i=1,2,3) = 0.0001$ mdyne-Å from Reference 14.

[g]Calculated using the BEBO3 activated complex data with $F^{\ddagger}_{\phi_i}(i=1,2,3) = 0.568$ mdyne-Å from Reference 14.

out-of-plane bending mode in the transition-state-theory calculation would only raise the KIE by about 2-5 percent over the KIE calculated using harmonic frequencies. The Pimentel KIEs in Table XXVI have a slightly greater more inverse temperature dependence than the corresponding KIE calculated using the Gaussian 70 force constant. However, this difference is smaller than the differences in the transition-state theory KIEs obtained using the BEBO and BEBO3 models.

Careful experimental determination of the KIEs in Tables XXV and XXVI might help distinguish which model if any adequately describes the real reaction hypersurface. The experimental rate constants reported by Majury and Steacie (MS)[16] and Whittle and Steacie (WS)[15] can be used to calculate secondary α-deuterium isotope effects. The values for $k(CH_3,H_2)/k(CD_3,H_2)$ are 0.91, 0.80, and 0.72 for MS[16], and 0.85, 0.69, and 0.60 for WS[15] at the temperatures 403, 483 and 563 ^{o}K, respectively, using the method I rate constants for $k(CD_3,H_2)$. For the method II $k(CD_3,H_2)$ values, the experimental $k(CH_3,H_2)/k(CD_3,H_2)$ isotope effects are 0.89, 0.71, and 0.62 for MS,[16] and 1.23, 0.83, and 0.64 for WS[15] at 403, 483, and 563 ^{o}K, respectively. Obviously, these experimental secondary α-deuterium KIEs become more inverse with increasing temperature. This experimental result defies both logical and theoretical predictions, since isotopic substitution should become less important at higher temperatures, especially at temperatures well above room temperature, and the KIEs should approach unity (or $v_{1L}^{\ddagger}/v_{2L}^{\ddagger}$) as the temperature increases. Nevertheless, the individual experimental KIEs are all inverse, except for one WS value at 403 ^{o}K, as are all of the theoretical KIEs, and the magnitudes of the experimental and theoretical KIEs are not greatly different. Therefore, one can conclude that the

true secondary α-deuterium KIE for the reaction $CH_3(CD_3) + H_2$ is most likely inverse. However, the experimental temperature dependence for this reaction is questionable. The transition-state theory calculated KIEs in Table XXVI have more reasonable temperature dependences than experiment. Therefore, a more accurate determination of the experimental secondary α-deuterium KIE for this reaction would be very helpful in quantifying the theoretical results. Quantitative comparison of the present theoretical and experimental KIEs is virtually impossible or at best meaningless due to the opposing trends of their temperature dependences.

The fact that the transition-state theory secondary α-deuterium KIEs for reaction (I-1) of $CH_4(CD_3H) + H$ in Table XXV produces normal KIEs and for reaction (I-2) of $CH_3(CD_3) + H_2$ in Table XXVI produces inverse KIEs is explained by the change in bonding between reactants and activated complex. For reaction (I-1) the HCH_1 bending force constant, F_{ϕ_i} (i=1,2,3), is usually reduced to a smaller $F_{\phi_i}^{\ddagger}$ (i=1,2,3) in the activated complex. This means that α-deuterium substitution produces less change in the normal-mode frequencies in the activated complex than in reactants. This produces a normal KIE. However, if F_{ϕ_i} (i=1,2,3) $\leq F_{\phi_i}^{\ddagger}$ (i=1,2,3), as is the case with one BEBO3 value in Table XXV and all the KIEs in Table XXVI, then inverse KIEs are produced. The inverse BEBO3 KIE in Table XXV is the result of the unrealistic assumption that F_{ϕ_i} (i=1,2,3) $= F_{\phi_i}^{\ddagger}$ (i=1,2,3). However, the inverse KIEs in Table XXVI for reaction (I-2) are the result of more bonds being associated with the α-deuteriums in the activated complex than in the reactants (that is, there is no F_{ϕ_i} (i=1,2,3) value in the

reactants, since there is no $C-H_1$ bond). Therefore, the α-deuterium

substitution in reaction (I-2) causes a greater change in the normal

mode frequencies in the activated complex than in the reactants. Ob-

serving the form of the equations (I-3) and (I-4), it is then reasonable

that the secondary α-deuterium KIEs in Table XXVI should be inverse and

the corresponding KIEs for reaction (I-1) in Table XXV should be normal.

A comparison of the magnitude of the MMI terms in Tables XXIII and

XXIV show that the BEBO and BEBO3 models have somewhat larger MMI values

than the LMR-PES. However, in Tables XXV and XXVI for the secondary

α-deuterium KIEs the MMI terms using the BEBO and BEBO3 models are

smaller than the corresponding MMI values for the LMR-PES. The differ-

ence in these MMI relationships is directly related to the differences

in the activated complex geometries. The LMR-PES has longer non-react-

ing C-H bond lengths than does either the BEBO or BEBO3 models. There-

fore, the α-deuterium atom substitution causes a greater change in the

moments of inertia for the LMR-PES isotopic configurations than in the

BEBO and BEBO3 models. Similarly, differences in the C-H, reacting

bondlength create slightly greater differences in the 13-carbon MMI

terms for BEBO and BEBO3 models than for the LMR-PES.

The Effect of Transition-State Geometry on the
Isotope Effects

Shapiro and Weston (SW) report that a change in the geometry of

the CH_3 group relative to the C-H-H entity in the activated complex

from tetrahedral to planar produced significant changes in the activated-

complex normal-mode frequencies.[14] However, these authors found for

the reaction $CH_3 + H_2$ that this geometry change altered the primary

KIEs by less than one percent.[14] The effect of CH_3 geometry in the activated complex was extensively tested by calculating various KIEs based upon the LMR-PES. The results are presented in Tables XXVII and XXVIII. The frequencies used to calculate these KIEs are tabulated in Appendix C. It can be seen in Table XXVII that the primary deuterium and ^{14}C KIEs all show a maximum percentage deviation between the highest and lowest values for the three KIEs in each row of less than one percent. This is in agreement with the findings of SW for primary effects.[14] However, the secondary deuterium KIEs for reactions (I-1) and (I-2) at 296 °K differ by a maximum of 10 percent. This somewhat larger effect on the secondary deuterium KIEs is expected, since changing the CH_3 geometry affects the positions of the isotopic atoms in the activated complex. Wolfsberg and Stern have shown for a similar reaction involving elimination of χ from CH_3X or CD_3X that at 300 °K a change from tetrahedral CH_3 or CD_3 to planar CH_3 or CD_3 geometry produces a 5.3% change in the secondary α-deuterium isotope effect.[3c] They also state that this change is directly related to the MMI factor, but that information about the MMI factor and the corresponding geometry of the activated complex seem impossible to obtain directly from an experimental set of KIEs.[3c] However, Wolfsberg and Stern also state that the secondary α-deuterium isotope effects are primarily the result of force constant changes between reactants and activated complex.[3c] In summary, since secondary deuterium KIEs are more strongly affected by such geometry changes than primary KIEs, then more uncertainty can be expected in the force constants deduced from experimental secondary deuterium KIEs. The values in Table XXVIII are the Arrhenius parameters obtained by fitting the KIEs in Table XXVII over the specified

TABLE XXVII

THE EFFECT OF CH_3 GEOMETRY IN THE ACTIVATED COMPLEX

Rate Constant Ratios	Temperature °K	Calculated Isotope Effects[a]			Standard[e] Deviation	Maximum[f] Percent Deviation
		Tetrahedral[b]	LMR-PES[c]	Planar[d]		
$\dfrac{k(CH_4 + H)}{k(CD_3H + H)}$	296	1.549	1.579	1.704	± 0.082	10.0
	546	1.213	1.218	1.236	± 0.012	1.9
$\dfrac{k(CH_4 + H)}{k(^{14}CH_4 + H)}$	296	1.067	1.066	1.068	± 0.0009	0.2
	546	1.035	1.034	1.034	± 0.0004	0.1
$\dfrac{k(CH_4 + H)}{k(CH_4 + D)}$	296	0.251	0.251	0.252	± 0.0007	0.4
	546	0.554	0.554	0.555	± 0.0006	0.2
$\dfrac{k(CH_4 + H)}{k(CH_3D + H)}$	296	5.593	5.590	5.618	± 0.015	0.5
	546	2.422	2.421	2.426	± 0.003	0.2
$\dfrac{k(CH_3 + H_2)}{k(CD_3 + H_2)}$	296	0.822	0.838	0.904	± 0.044	10.0
	546	0.954	0.958	0.972	± 0.010	1.9
$\dfrac{k(CH_3 + H_2)}{k(^{14}CH_3 + H_2)}$	296	1.013	1.012	1.014	± 0.0009	0.2
	546	1.012	1.011	1.011	± 0.0004	0.1

TABLE XXVII (Continued)

Rate Constant Ratios	Temperature °K	Calculated Isotope Effects[a]			Standard[e] Deviation	Maximum[f] Percent Deviation
		Tetrahedral[b]	LMR-PES[c]	Planar[d]		
$\dfrac{k(CH_3 + H_2)}{k(CH_3 + HD)}$	296	0.929	0.930	0.934	± 0.003	0.5
	546	1.055	1.055	1.057	± 0.001	0.2
$\dfrac{k(CH_3 + H_2)}{k(CH_3 + DH)}$	296	1.875	1.874	1.883	± 0.005	0.5
	546	1.622	1.621	1.625	± 0.002	0.2

[a] Kinetic isotope effects calculated using the harmonic LMR-PES reactant frequencies.

[b] Calculated using tetrahedral CH_3 geometry in the activated complex.

[c] Calculated using the LMR-PES CH_3 geometry in the activated complex.

[d] Calculated using the planar CH_3 geometry in the activated complex.

[e] Standard deviation in the three KIEs in the row.

[f] Largest difference relative to the smallest KIE in the row.

TABLE XXVIII

THE EFFECT OF CH_3 GEOMETRY ON THE TEMPERATURE DEPENDENCES[a]

Rate Constant Ratios	A_1/A_2 [b]			Std.[g] Dev.
	Tetrahedral[d]	LMR-PES[e]	Planar[f]	
$\dfrac{k(CH_4 + H)}{k(CD_3\underset{\sim}{H} + H)}$	$0.901 \pm 6 \times 10^{-4}$	$0.889 \pm 3 \times 10^{-4}$	0.846 ± 0.002	$\pm.029$
$\dfrac{k(CH_4 + H)}{k(^{14}CH_4 + H)}$	$0.997 \pm 8 \times 10^{-5}$	$0.998 \pm 9 \times 10^{-5}$	$0.995 \pm 2 \times 10^{-4}$	$\pm.002$
$\dfrac{k(CH_4 + H)}{k(CH_4 + D)}$	1.407 ± 0.002	1.406 ± 0.002	1.404 ± 0.002	$\pm.002$
$\dfrac{k(CH_4 + H)}{k(CH_3\underset{\sim}{D} + H)}$	0.896 ± 0.001	0.895 ± 0.001	0.894 ± 0.001	$\pm.001$
$\dfrac{k(CH_3 + H_2)}{k(CD_3 + H_2)}$	1.115 ± 0.005	1.101 ± 0.005	1.047 ± 0.002	$\pm.036$
$\dfrac{k(CH_3 + H_2)}{k(^{14}CH_3 + H_2)}$	$1.010 \pm 5 \times 10^{-5}$	$1.010 \pm 4 \times 10^{-5}$	$1.008 \pm 7 \times 10^{-5}$	$\pm.001$
$\dfrac{k(CH_3 + H_2)}{k(CH_3 + \underset{\sim}{H}D)}$	1.219 ± 0.002	1.218 ± 0.002	1.216 ± 0.002	$\pm.002$
$\dfrac{k(CH_3 + H_2)}{k(CH_3 + \underset{\sim}{D}H)}$	1.341 ± 0.006	1.340 ± 0.006	1.338 ± 0.006	$\pm.002$

Rate Constant Ratios	ΔE [c] (calories/mole)			Std.[g] Dev.
	Tetrahedral[d]	LMR-PES[e]	Planar[f]	
$\dfrac{k(CH_4 + H)}{k(CD_3\underset{\sim}{H} + H)}$	323 ± 0.6	341 ± 0.3	410 ± 1.9	±46
$\dfrac{k(CH_4 + H}{k(^{14}CH_4 + H)}$	40 ± 0.1	39 ± 0.1	41 ± 0.2	±1

TABLE XXVIII (Continued)

Rate Constant Ratios	ΔE^c (calories/mole)			Std.[g] Dev.
	Tetrahedral[d]	LMR-PES[e]	Planar[f]	
$\dfrac{k(CH_4 + H)}{k(CH_4 + D)}$	-1011 ± 1	-1010 ± 1	-1006 ± 1	± 2
$\dfrac{k(CH_4 + H)}{k(CH_3D + H)}$	1079 ± 1	1079 ± 1	1083 ± 1	± 2
$\dfrac{k(CH_3 + H_2)}{k(CD_3 + H_2)}$	-166 ± 4	-149 ± 4	-79 ± 2	± 46
$\dfrac{k(CH_3 + H_2)}{k(^{14}CH_3 + H_2)}$	1.7 ± 0.05	1.0 ± 0.04	3.2 ± 0.05	± 1.1
$\dfrac{k(CH_3 + H_2)}{k(CH_3 + HD)}$	-156 ± 1	-155 ± 1	-151 ± 1	± 2
$\dfrac{k(CH_3 + H_2)}{k(CH_3 + DH)}$	209 ± 4	209 ± 4	213 ± 4	± 2

[a] All deviations are standard deviations in the Arrhenius equation parameters from a least squares fit to $\ln(k_1/k_2) = \ln(A_1/A_2) + (\Delta E/R)$ $(1/T)$ using LMR-PES reactant frequencies over the temperature range 371-546°K.

[b] Isotopic ratio of Arrhenius preexponential factors.

[c] Isotopic difference in Arrhenius activation energies in kcal/mole.

[d] Calculated using tetrahedral CH_3 geometry in the activated complex.

[e] Calculated using the LMR-PES CH_3 geometry in the activated complex.

[f] Calculated using the planar CH_3 geometry in the activated complex.

[g] Standard deviation in the preceding three values in the row.

range of temperatures to equation (III-13). As expected from Table XXVII the largest deviations in Table XXVIII are for the secondary deuterium KIEs. The geometry caused deviations in the primary carbon and deuterium effects are negligible.

Contributions of the Bending and Stretching
Frequencies to the Primary KIE

At reasonably low temperatures ($\leq 100^{\circ}$C), primary deuterium iso-tope effects primarily reflect the magnitude of ZPE. Therefore, an estimate of the degree to which the KIE is influenced by normal mode bending frequencies can be made by calculating the ZPE contributions to the KIE using stretching and bending normal-mode frequency values in separate calculations. The isotopic reactant and transition-state fre-quencies used for these calculations are given in Tables XXIX and XXX respectively, along with the summations over the separate sets of stretching and bending normal modes. The isotopic differences between these summations are used in equation (I-7) to obtain the contributions to the ZPE term tabulated in Table XXXI. For the CH_4+H reaction, ZPE values calculated using only the stretching normal-mode frequencies are in better agreement with the "total ZPE" values than those ZPE contri-butions calculated with either the bending normal mode frequencies alone or the stretching plus linear bending frequencies. However, for the reaction of CH_3 with H_2 and D_2 or HD, the addition of the isotopic linear bending frequency values to the corresponding isotopic stretch-ing frequency values produced two ZPE contributions within three per-cent of the corresponding "Total ZPE" values in Table XXXI. The ZPE contributions involving abstraction of D from HD differ considerably

TABLE XXIX

REACTANT ISOTOPIC FREQUENCIES[a]

Normal Modes	Methane		Methyl and Molecular Hydrogen			
	CH_4	CH_3D	CH_3	H_2	D_2	HD
ν_1	2917.0	2224.1	2914.2	4468.1	3160.6	3870.0
ν_{2a}	1526.6	1476.3	847.1			
ν_{2b}	1526.6	1476.3				
ν_{3a}	3080.1	3080.1	3099.6			
ν_{3b}	3080.1	3080.1	3099.6			
ν_{3c}	3080.1	2966.4				
ν_{4a}	1366.1	1356.7	1605.9			
ν_{4b}	1366.1	1197.9	1605.9			
ν_{4c}	1366.1	1197.9				

	CH_4	CH_3D	$CH_3 + H_2$	$CH_3 + D_2$	$CH_3 + HD$
$\sum_{i=1}^{3n-6} \nu_i$ [b]	19308.8	18055.8	17640.4	16332.9	17042.3
$Sum(\nu_2+\nu_4)$ [c]	7151.5	6705.1	4058.9	4058.9	4058.9
$Sum(\nu_1+\nu_3)$ [d]	12157.3	11350.7	13581.5	12274.0	12983.4

[a] All values in cm^{-1}. All values calculated using LMR-PES force constants and geometry except ν_2 under CH_3 determined from Gaussian-70 force constant and geometry.

[b] Sum of all isotopic frequencies for a particular reactant or reactants.

[c] Sum of all isotopic bending frequencies for a particular reactant or reactants.

[d] Sum of all isotopic stretching frequencies for a particular reactant or reactants.

TABLE XXX

TRANSITION-STATE ISOTOPIC FREQUENCIES[a]

Normal Modes	CH_3-H-H	CH_3-D-D	CH_3-D-H	CH_3-H-D
ν_1	3388.4	2405.0	3106.0	2720.9
ν_2	2937.7	2939.3	2937.0	2941.2
ν_3	964.7	953.6	959.3	956.9
ν_4	1479.3i	1115.0i	1181.7i	1350.4i
ν_5[b]	3085.6	3085.7	3085.7	3085.7
ν_6[b]	1502.9	1502.9	1502.9	1502.9
ν_7[b]	752.3	632.6	636.6	746.1
ν_8[b]	367.3	296.0	345.7	327.5
$\sum_{i=1}^{3n-7} \nu_i$[c]	18707.0	17332.3	18144.1	17943.4
$Sum(\nu_3+\nu_6)$	3970.5	3959.4	3965.1	3962.7
$Sum(\nu_7+\nu_8)$[d]	2239.2	1857.2	1964.6	2147.2
Bending sum ν[e]	6209.7	5816.6	5929.7	6109.9
Stretching sum ν[f]	12497.3	11515.7	12214.4	11833.5

[a]All values in cm^{-1}. Based upon the LMR-PES.

[b]Doubly degenerate normal mode frequencies.

[c]Sum of all real frequencies omitting ν_4 the imaginary frequency.

[d]Sum of the associated linear bending frequencies ν_7 and ν_8.

[e]Sum of all the bending frequencies ν_3, ν_6, ν_7 and ν_8.

[f]Sum of all the real stretching frequency values ν_1, ν_2 and ν_5.

TABLE XXXI

BENDING AND STRETCHING FREQUENCY CONTRIBUTIONS TO THE ZPE[a]

Isotopic Ratio of Reactants	Bending[b]		Stretching[c]		Linear Bending + Stretching[d]		Total[e]
	ZPE	% Dev.[f]	ZPE	% Dev.[f]	ZPE	% Dev.[f]	ZPE
$\dfrac{CH_4 + H}{CH_3D + D}$	1.138	53.0	0.654	−12.1	0.258	−65.3	0.744
$\dfrac{CH_4 + H}{CH_3D + H}$	1.499	−72.0	3.571	−33.2	1.832	−65.8	5.349
$\dfrac{CH_4 + H}{CH_4 + D}$	0.785	403.2	0.199	27.6	0.249	59.6	0.156
$\dfrac{CH_3 + H_2}{CH_3 + D_2}$	0.385	−54.6	2.206	160.1	0.872	2.7	0.849
$\dfrac{CH_3 + H_2}{CH_3 + DH}$	0.506	−53.5	2.151	97.5	1.558	43.1	1.089
$\dfrac{CH_3 + H_2}{CH_3 + HD}$	0.785	17.3	0.852	27.4	0.681	1.8	0.669

[a]Frequency contributions to the vibrational zero point energy term (ZPE) calculated at 296°K, see (I-7).

[b]Calculated using only the bending frequencies from the LMR-PES reactant and transition-state species.

[c]Calculated using only the stretching frequencies from the LMR-PES reactant and transition-state species.

[d]Calculated using only the linear bending and stretching frequencies from the isotopic LMR-PES reactant and transition-state species.

[e]Calculated using all the isotopic LMR-PES frequencies.

[f]Percent deviation from the total ZPE.

from the "Total ZPE" value, but the linear bending plus stretching frequencies still produce a ZPE contribution in better agreement with the "Total ZPE" value than either the bending or stretching ZPE contribution alone. Clearly, the addition of linear bending frequency values to the stretching frequencies improves the agreement of the calculated ZPE contributions with the "Total ZPE" values for reaction (I-2) [that is, CH_3 + isotopic H_2]. However, combination of linear bending and stretching frequencies produces ZPE contributions in worse agreement with the "Total ZPE" values for reaction (I-1) [that is, isotopic CH_4 + H(D)] than obtained from use of stretching frequencies alone. The origin of this difference between the ZPE contributions for reactions (I-1) and (I-2) is the relative magnitude of the differences between the reactant and transition-state bending frequencies. For reaction (I-2), the transition-state linear bending frequencies have a dominate effect on the ZPE contributions. However, for reaction (I-1) the reactant bending frequencies contribute approximately as much as the transition-state linear-bending frequencies to the ZPE value. Therefore, the addition of only the transition-state linear-bending frequencies to the stretching frequencies in reaction (I-1) without the compensating effect of the reactant bending frequencies actually decreases the agreement of the calculated ZPE contributions with the "Total ZPE" values in Table XXXI.

The separate bending, stretching and linear-bending plus stretching frequency contributions to the EXC values are given in Table XXXII. Due to the function form of the equation for calculating the EXC values, (that is, $1-e^{-u_i}$), see (I-6), the largest frequency values have the least effect on the calculated

TABLE XXXII

BENDING AND STRETCHING FREQUENCY CONTRIBUTIONS TO THE EXC[a]

Isotopic Ratio of Reactants	Bending[b]		Stretching[c]		Linear Bending + Stretching[d]		Total[e]
	EXC	% Dev.[f]	EXC	% Dev.[f]	EXC	% Dev.[f]	EXC
$\dfrac{CH_4 + H}{CH_3D + D}$	0.808	0	1.000	23.8	0.805	-0.4	0.808
$\dfrac{CH_4 + H}{CH_3D + H}$	0.921	0	1.000	8.6	0.918	-0.3	0.921
$\dfrac{CH_4 + H}{CH_4 + D}$	0.914	0	1.000	9.4	0.914	0	0.914
$\dfrac{CH_3 + H_2}{CH_3 + D_2}$	0.805	0	1.000	24.2	0.805	0	0.805
$\dfrac{CH_3 + H_2}{CH_3 + DH}$	0.918	0	1.000	8.9	0.918	0	0.918
$\dfrac{CH_3 + H_2}{CH_3 + HD}$	0.914	0	1.000	9.4	0.914	0	0.914

[a]Frequency contributions to the vibrational excitation factor (EXC), see (I-6). All values calculated at 296°K.

[b]Calculated using only the bending frequencies from the isotopic LMR-PES reactant and transition-state species.

[c]Calculated using only the stretching frequencies from the isotopic LMR-PES reactant and transition-state species.

[d]Calculated using only the linear bending and stretching frequencies from the isotopic LMR-PES reactant and transition-state species.

[e]Calculated using all the isotopic LMR-PES frequencies.

[f]Percent deviation from the total EXC.

EXC values. For this reason, the relatively large stretching frequencies produce negligibly small EXC contributions. Since the transition-state linear-bending frequencies are the smallest in magnitude, then the combinations of the stretching and linear-bending frequencies produce EXC contributions almost identical to the "Total EXC" values in Table XXXII. The bending frequencies alone produce EXC contributions identical to the "Total EXC" values to the accuracy expressed in Table XXXII.

The separate frequency contributions to the VP values are given in Table XXXIII. The stretching frequencies alone do not produce VP contributions in good agreement with the "Total VP" values. Use of the linear-bending frequencies plus the stretching frequencies produces VP contributions in excellent agreement with the "Total VP" values except for the first two cases in Table XXXIII. For these two cases the reactant $H_i CH_1$ (i=2,3,4) bending frequencies exert a considerable influence on the magnitude of VP. The bending frequencies alone produce VP values that are very close to the total VP values in the first and fourth rows in Table XXXIII. This excellent agreement can be interpreted as the complimentary effect of the isotopic reactant HCH bending and activated complex linear bending frequencies on the former VP, and the dominate influence of the isotopic activated complex linear bending frequencies over the latter VP in row four. The VP values involving the CH_3-H-D and CH_3-D-H frequencies require more compensating effects between the bending and stretching isotopic frequencies to obtain the total VP value.

The contributions of the bending, stretching and linear-bending plus stretching frequencies to the ZPE, EXC and VP values tabulated in Tables XXXI through XXXIII are combined in Table XXXIV with the $v_{1L}^{\ddagger}/v_{2L}^{\ddagger}$

TABLE XXXIII

BENDING AND STRETCHING FREQUENCY CONTRIBUTIONS TO THE VP[a]

Isotopic Ratio of Reactants	Bending[b]		Stretching[c]		Linear Bending[d] + Stretching		Total[e]
	VP	% Dev.[f]	VP	% Dev.[f]	VP	% Dev.[f]	VP
$\dfrac{CH_4 + H}{CH_3D + D}$	1.573	-3.3	1.034	-36.4	2.252	38.4	1.627
$\dfrac{CH_4 + H}{CH_3D + H}$	1.132	24.8	0.801	-11.7	1.263	39.3	0.907
$\dfrac{CH_4 + H}{CH_4 + D}$	1.289	-19.6	1.244	-22.4	1.591	-0.8	1.604
$\dfrac{CH_3 + H_2}{CH_3 + D_2}$	2.203	-0.4	0.996	-54.6	2.169	-1.1	2.194
$\dfrac{CH_3 + H_2}{CH_3 + DH}$	1.585	-5.7	0.945	-37.0	1.490	-0.6	1.499
$\dfrac{CH_3 + H_2}{CH_3 + HD}$	1.289	-7.2	1.077	-22.5	1.378	-0.8	1.389

[a]Frequency contributions to the vibrational product (VP) factor, see (I-8). All values calculated at 296°K.

[b]Calculated using only the bending frequencies from the isotopic LMR-PES reactant and transition-state species.

[c]Calculated using only the stretching frequencies from the isotopic LMR-PES reactant and transition-state species.

[d]Calculated using only the stretching and linear bending frequencies from the LMR-PES reactant and transition-state species.

[e]Calculated using all the isotopic LMR-PES frequencies.

[f]Percent deviation from the total VP.

TABLE XXXIV

BENDING AND STRETCHING FREQUENCY CONTRIBUTIONS TO THE KIE[a]

Isotopic Ratio of Reactants	Bending[b]		Stretching[c]		Linear Bending + Stretching[d]		$\nu_{1L}^{\ddagger}/\nu_{2L}^{\ddagger}$	Total[e]
	KIE	% Dev.[f]	KIE	% Dev.[f]	KIE	% Dev.[f]		KIE
$\dfrac{CH_4 + H}{CH_3D + D}$	1.919	48.1	0.897	-30.8	0.621	-52.1	1.3267	1.296
$\dfrac{CH_4 + H}{CH_3D + H}$	1.956	-65.0	3.581	-35.9	2.659	-52.4	1.2518	5.590
$\dfrac{CH_4 + H}{CH_4 + D}$	1.013	304.6	0.271	8.0	0.397	58.2	1.0955	0.251
$\dfrac{CH_3 + H_2}{CH_3 + D_2}$	0.906	-54.4	2.915	46.6	2.020	1.6	1.3267	1.988
$\dfrac{CH_3 + H_2}{CH_3 + DH}$	0.922	-50.8	2.545	35.8	2.668	42.4	1.2518	1.874
$\dfrac{CH_3 + H_2}{CH_3 + HD}$	1.013	-8.9	1.005	8.1	0.940	1.1	1.0955	0.930

[a] Bending and stretching KIE values calculated using the VP, EXC, and ZPE quantities in the accompanying tables, see (I-4). All values calculated at 296°K.

[b] Calculated using only the bending frequencies from the isotopic LMR-PES reactant and transition-state species times $\nu_{1L}^{\ddagger}/\nu_{2L}^{\ddagger}$.

[c] Calculated using only the stretching frequencies from the isotopic LMR-PES reactant and transition-state species times $\nu_{1L}^{\ddagger}/\nu_{2L}^{\ddagger}$.

[d] Calculated using only the linear bending plus the stretching frequencies from the isotopic LMR-PES reactant and transition-state species times $\nu_{1L}^{\ddagger}/\nu_{2L}^{\ddagger}$.

[e] Calculated using all the isotopic LMR-PES frequencies.

[f] Percent deviation from the total KIE.

values to give the corresponding comparisons for the calculated KIE values. It can be seen that few of the individual contributions to the total KIE come close to agreeing with the total KIE values. Two notable exceptions are the contributions due to the linear bending plus stretching frequencies in rows four and six of Table XXXIV. These differ from the total KIE value by 1.6% and 1.1%, respectively. The other values differ by about 8 percent to as much as 304.6 percent. The data in Table XXXIV show that the stretching frequencies alone tend to reproduce the KIE values as well or better than all the other bending or linear-bending plus stretching frequency sets, except for the two cases previously mentioned. However, except for these two exceptions, the error due to using an incomplete vibrational frequency data set, as discussed in Chapter I, can lead to very large errors in the calculated KIEs.

Relating Primary Deuterium and Tritium Isotope Effects

The relationship between tritium and deuterium primary KIEs is commonly referred to as the Swain-Schaad relation.[23] This relationship was tested for its applicability to the CH_4+H and CH_3+H_2 reactions by using the LMR-PES isotopic frequencies to obtain transition-state theory calculated KIEs which are compared using Bigeleisen's definition of r (see footnote a in Table XXXV).[24] The results are given in Table XXXV. The isotopic reactions compared in Table XXXV were chosen based upon the feasibility of their experimental determination rather than their being pure primary isotope effects. As discussed in Chapter I, the Swain-Schaad relation is only supposed to be applicable to reac-

TABLE XXXV

RELATIONSHIPS OF TRITIUM AND DEUTERIUM ISOTOPE EFFECTS

Ratio of Rate Constants	k_H/k_D	k_H/k_T	r^a	Δr_{ss}^b	Temperature °K
$\dfrac{k(CH_4,\underline{H})^c}{k(CH_3\underset{\sim}{X},H}$	2.311×10^4	1.640×10^6	1.424	$-.018$	50
	1.614×10^2	1.407×10^3	1.426	$-.016$	100
	5.4573	11.230	1.425	$-.017$	300
	2.4207	3.5396	1.430	$-.012$	546
	1.2518	1.4324	1.600	0.158	∞
$\dfrac{k(CH_4,\underline{H})^c}{k(CH_4,X)}$	2.970×10^{-5}	4.103×10^{-7}	1.411	$-.031$	50
	7.165×10^{-3}	9.610×10^{-4}	1.407	$-.035$	100
	0.2569	0.1517	1.388	$-.054$	300
	0.5539	0.4501	1.351	-0.091	546
	1.0955	1.1641	1.666	0.224	∞
$\dfrac{k(CH_3,\underline{H}X)^c}{k(CH_3,\underline{X}H}$	22.085	96.327	1.476	0.034	50
	5.2396	11.607	1.480	0.038	100
	2.0011	2.7751	1.471	0.029	300
	1.5370	1.8741	1.461	0.019	546
	1.1428	1.2306	1.554	0.112	∞
$\dfrac{k(CH_3,\underline{H}_2)^c}{k(CH_3,X_2)}$	1.0995	1.4199	3.696	2.254	50
	1.7567	2.6103	1.703	0.261	100
	1.9847	2.8476	1.527	0.085	300
	1.7908	2.3950	1.499	0.057	546
	1.3267	1.5394	1.526	0.084	∞

$^a r = \ln(k_H/k_T)/\ln(k_H/k_D)$, see Reference 24.

$^b \Delta r_{ss} = r - r_{ss}$, where $r_{ss} = \dfrac{(1/m_H)^{.5} - (1/m_T)^{.5}}{(1/m_H)^{.5} - (1/m_D)^{.5}} = 1.442$.

^{c}X = D or T. The underlined element represents the atom being abstracted if there is more than one possibility.

tions involving transfer of the isotopic hydrogen at rather low temperatures ($< 100^{\circ}$C). It can be seen that the only pure primary isotope effect in Table XXXV is $k(CH_4,H)/k(CH_3\underset{\sim}{X},H)$. Over the temperature range considered, the calculated value of $k(CH_4,H)/k(CH_3\underset{\sim}{X},H)$ agrees quite well with the theoretical $r_{ss} = 1.442$ determined only from the H, D, and T atomic weights (as shown in footnote b of Table XXXV). The KIEs and r values reported for infinite temperature are obtained from the high temperature limits to the KIEs (that is, $v_{1L}^{\ddagger}/v_{2L}^{\ddagger}$). The other extreme is represented by the $k(CH_4,H)/k(CH_4,X)$ values which are pure end atom effects. It can be seen that these KIE values are inverse (that is, the heavier isotopic reactants react faster) and that the KIE values go past (or crossover) unity at some temperature above 546°K (approximately 1500 to 2000°K). It has been noted by Stern and Vogel that when the KIEs are very near unity, the r values become anomalous and useless as a method of approximately tritium KIEs from deuterium KIEs or vice versa.[25] The other two KIEs for which r values were determined in Table XXXV are combined end atom plus normal primary KIEs. Their calculated r values decrease toward $r_{ss} = 1.442$ until between 600 and 1000°K, and then increase until the infinite temperature value is reached. The $k(CH_3,\underset{\sim}{H}X)/k(CH_3,\underset{\sim}{X}H)$ values show better overall agreement with the $r_{ss} = 1.442$ since each individual D or T KIE increases monotonically with lowering temperature. The $k(CH_3,H_2)/k(CH_3,X_2)$ values have an inflection point at approximately 200°K and decrease in value at lower temperature. Since the D and T inflection points do not occur at exactly the same temperature the calculated r values decrease in their agreement with r_{ss} at lower temperatures. These results in Table XXXV seem to indicate that this simple Swain-Schaad relationship can

be used to give a reasonable estimate of the expected k_H/k_T value given

an accurate value for k_H/k_D and raising it to the r_{ss} = 1.442 power.

The values for the first three KIEs in Table XXXV indicate that such a

relationship would be reasonably correct over a very broad range of

temperature. However, the $k(CH_3,H_2)/k(CH_3,X_2)$ values show that the

Swain-Schaad relationship will yield only fair results at the supposedly

most optimum temperature and worse results at lower temperatures.

Relating ^{13}C and ^{14}C Isotope Effects

Since the Swain-Schaad relationship in its most abbreviated form

appears to work for the $CH_4 + H \rightleftarrows CH_3 + H_2$ reaction system even at

higher temperatures (> 100°C) than it is supposed to be valid, and since

reasonable values were obtained for isotopic configurations other than

the strictly primary D(or T) effects, it was reasoned that possibly a

similar relation might be applicable to 13-carbon and 14-carbon KIEs.

The results obtained from the extension to carbon isotope effects using

the LMR-PES predicted 13-carbon and 14-carbon effects are shown in

Table XXXVI. To estimate the magnitude of a 14-carbon KIE at a particu-

lar temperature, the 13-carbon KIE at that temperature is raised to

the r = 1.888 power (see footnote b in Table XXXVI). The estimated

accuracy of this relation is given by calculating the r_c values (see

footnote (a) in Table XXXVI) and determining the differences between

these r_c values and the theoretical r = 1.888. It can be seen in Table

XXXVI that the CH_4+H carbon effects fit the theoretical r = 1.888 very

well over the entire temperature range. However, the CH_3+H_2 carbon

effects tend to fall off rather rapidly at low temperature and the re-

lationship is not very accurate below room temperature ($\sim 300^\circ$K). This

TABLE XXXVI

RELATIONSHIPS OF ^{13}C and ^{14}C ISOTOPE EFFECTS

Ratio of Rate Constants	k_{12}/k_{13}	k_{12}/k_{14}	r_c [a]	Δr_c [b]	Temperature °K
$\dfrac{k(CH_4,H)}{k(*CH_4,H)}$	1.2241	1.4566	1.860	-.028	50
	1.1074	1.2089	1.860	-.028	100
	1.03513	1.06633	1.860	-.028	296
	1.01825	1.03422	1.860	-.028	546
	1.00544	1.01024	1.878	-0.10	∞
$\dfrac{k(CH_3,H_2)}{k(*CH_3,H_2}$	1.00396	1.00639	1.614	-.274	50
	1.00584	1.01048	1.792	-.096	100
	1.00637	1.01186	1.857	-.031	296
	1.00601	1.01123	1.864	-.024	546
	1.00544	1.01024	1.878	-.010	∞

[a] $r_c = \ln(k_{12}/k_{14})/\ln(k_{12}/k_{13})$.

[b] $\Delta r_c = r_c - r$, where $r = \dfrac{(1/m_{12})^{.5} - (1/m_{14})^{.5}}{(1/m_{12})^{.5} - (1/m_{13})^{.5}} = 1.888$.

relationship was also tested with some fractionation factor equilibria values reported by Hartshorn and Shiner that were calculated at $298^{\circ}K$.[45] The reactions used are given by equations (III-14) and (III-15).

$$^{13}CO_2 + CO_3^= \rightarrow CO_2 + {}^{13}CO_3^= \qquad \text{(III-14)}$$

$$^{13}CO_2 + CH_4 \rightarrow CO_2 + {}^{13}CH_4 \qquad \text{(III-15)}$$
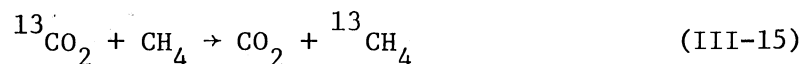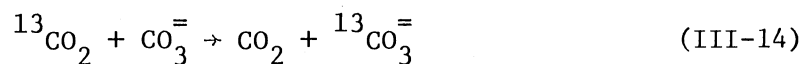
Hartshorn and Shiner (HS) report a value of 1.0066 for the 13-carbon effect in (III-14). By raising this value to the 1.888 power, a value of 1.0125 was obtained which compares favorably with 14-carbon effect value of 1.0122 reported by HS.[45] Similarly, the relation for the 14-carbon effect in (III-15) is given by

$$(0.9429)^{1.888} = 0.8949 \qquad \text{(III-16)}$$

The 14-carbon effect value reported by HS is 0.8948.[45] The fact that these calculated values agree within 0.03% of the absolute rate theory calculated values reported by HS supports the validity of the relationship expressed in Table XXXVI.

Rule of the Geometric Mean Relationships

As discussed in Chapter I, the rule of the geometric mean is based on the applicability of vibrational frequency sum rules to the calculation of transition-state theory isotope effects. Table XXXVII shows the relationship between the various secondary α-deuterium KIEs for both the CH_4 + H and the CH_3 + H_2 reactions. It can be seen that the k(H/D) and F(H/D) (see footnote a in Table XXXVII) values for one

TABLE XXXVII

RULE OF THE GEOMETRIC MEAN RELATIONSHIPS FOR SECONDARY ISOTOPE EFFECTS

Isotope Effect Relationship[a,b]	Temperature of Isotope Effect					
	50°K	273°K	546°K	746°K	1046°K	2246°K
$k(CH_4,H/CD_3\underline{H},H)$	9.4826	1.6502	1.2182	1.1251	1.06675	1.01563
$F(CH_4,H/CD_3\underline{H},H)$	9.4755	1.6490	1.2173	1.1243	1.06595	1.01487
$[k(CH_4,H/CH_2D\underline{H},H)]^3$	8.6101	1.6430	1.2176	1.1249	1.06668	1.01559
$[F(CH_4,H/CH_2D\underline{H},H)]^3$	8.6038	1.6418	1.2167	1.1241	1.06590	1.01486
$k(CH_4,H/CHD_2\underline{H},H)$	4.3250	1.3942	1.1404	1.08171	1.04399	1.01038
$F(CH_4,H/CHD_2\underline{H},H)$	4.3229	1.3935	1.1399	1.08117	1.04348	1.00989
$[k(CH_4,H/CH_2D\underline{H},H)]^2$	4.2009	1.3924	1.1403	1.08164	1.04397	1.01037
$[F(CH_4,H/CH_2D\underline{H},H)]^2$	4.1988	1.3917	1.1397	1.08112	1.04346	1.00988
$k(CH_4,H/CH_2D\underline{H},H)$	2.0496	1.1800	1.06783	1.04002	1.02175	1.00517
$F(CH_4,H/CH_2D\underline{H},H)$	2.0491	1.1797	1.06757	1.03977	1.02150	1.00493
$k(CH_3,H_2/CD_3,H_2)$	.06413	.8115	.9579	.9804	.9915	.99902
$F(CH_3,H_2/CD_3,H_2)$	.06408	.8109	.9572	.9796	.9908	.99827
$[k(CH_3,H_2/CH_2D,H_2)]^3$	.05756	.8093	.9574	.9800	.9913	.99898
$[F(CH_3,H_2/CH_2D,H_2)]^3$	.05751	.8088	.9568	.9794	.9907	.99826
$k(CH_3,H_2/CHD_2,H_2)$	.1548	.8697	.9717	.9868	.9943	.99934
$F(CH_3,H_2/CHD_2,H_2)$	.1547	.8692	.9712	.9863	.9938	.99884
$[k(CH_3,H_2/CH_2D,H_2)]^2$	.1491	.8684	.9714	.9866	.9942	.99932
$[F(CH_3,H_2/CH_2D,H_2)]^2$	.1490	.8681	.9710	.9862	.9938	.99884
$k(CH_3,H_2/CH_2D,H_2)$	.3861	.9319	.9856	.9933	.9971	.99966
$F(CH_3,H_2/CH_2D,H_2)$	.3860	.9317	.9854	.9931	.9969	.99942

[a] $k(1/2) = (\nu_{1L}^{\ddagger}/\nu_{2L}^{\ddagger})F(1/2)$, where 1 and 2 represent the light and heavy isotope species respectively and $F(1/2) = \dfrac{s_2/s_1 f(2/1)}{s_2^{\ddagger}/s_1^{\ddagger} f^{\ddagger}(2/1)} = VP \cdot EXC \cdot ZPE$, see (I-29).

[b] Where applicable the atom being abstracted is underlined.

α-deuterium when squared and cubed give reasonable approximations to the transition-state theory calculated k(H/D) and F(H/D) values having two and three α-deuteriums, respectively. This relationship produces better results at higher temperature, since the sum rules upon which this relationship is based apply to the high temperature approximation to the transition-state theory calculated KIEs which is only valid at elevated temperatures, see (I-23) and (III-17).[46]

$$\ln(k_H/k_D) = \ln(\nu_{1L}^{\ddagger}/\nu_{2L}^{\ddagger}) + \frac{1}{24}[\sum_{i=1}^{3n-6}(u_{i1}^2 - u_{i2}^2) - \sum_{i=1}^{3n-7}(u_{i1}^{\ddagger 2} - u_{i2}^{\ddagger 2})] \quad \text{(III-17)}$$

An indepth study of the deviations from the rule of the mean as it is related to the method of finite orthogonal polynomial expansions has been recently given by Ishida and Bigeleisen, see (I-25).[27,47] However, the simple relationships expressed in Chapter I satisfy the comparisons made in Table XXXVII.

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APPENDIX A

LMR-PES COORDINATE RELATIONSHIPS

The relationship between cartesian coordinates and the LMR-PES internal coordinates is controlled by three sets of equations in the computer code. The first set, shown in Equation (A-1) initializes the cartesian coordinates for each numbered atom in Figure 1 given values for Z_1 and Z_6 equal to r_1 and $(r_1 + r_6)$, respectively, in Table III or Table V,

$$y_2 = r_e \sin\theta$$

$$z_2 = r_e \cos\theta$$

$$x_3 = r_e \sin\theta \, \cos(11\pi/6)$$

$$y_3 = r_e \sin\theta \, \sin(11\pi/6)$$

$$z_3 = r_e \cos\theta$$

$$x_4 = r_e \sin\theta \, \cos(7\pi/6)$$

$$y_4 = r_e \sin\theta \, \sin(7\pi/6)$$

$$z_4 = r_e \cos\theta \tag{A-1}$$

with θ defined by

$$\theta = 90°, \ (r_1 > 6.274)$$

$$\theta = \tau \quad , \ (r_1 \le r_e)$$

$$\theta = \tau - a_5(r_1 - r_e), \ (r_e < r_1 \le 6.274) \tag{A-2}$$

where r_e has the value 2.0673 atomic units, a_5 is defined in Table IV,

τ is the tetrahedral angle and x_1, y_1, x_2, x_5, y_5, z_5, x_6, and y_6 are set equal to zero. These cartesian coordinates are converted to the 15 possible interatomic distances by the DIST routine defined by (A-3),

$$D_{ij} = [(x_i-x_j)^2 + (y_i-y_j)^2 + (z_i-z_j)^2]^{1/2} \qquad \text{(A-3)}$$

where i and j are the atom numbers 1 through 6 with i$\neq$j. The corresponding interatomic distances defined in Tables III and V are given by (A-4).

$$r_1 = D_{1,5}$$
$$r_2 = D_{2,5}$$
$$r_3 = D_{3,5}$$
$$r_4 = D_{4,5}$$
$$r_5 = D_{6,5}$$
$$r_6 = D_{1,6}$$
$$r_7 = D_{2,6}$$
$$r_8 = D_{3,6}$$
$$r_9 = D_{4,6}$$
$$r_{10} = D_{1,2}$$
$$r_{11} = D_{1,3}$$
$$r_{12} = D_{1,4}$$
$$r_{13} = D_{2,3}$$
$$r_{14} = D_{2,4}$$
$$r_{15} = D_{3,4} \qquad \text{(A-4)}$$

The last six interatomic distances (r_{10} through r_{15}) are used to calculate the six angles θ_1 through θ_6. The ANGLE routine uses the

law of cosines and the interatomic distances in (A-4) to calculate θ_i (i=1,2,3,4,5,6), see (A-5).

$$\theta_i = \arccos[(r_1^2 + r_{i+1}^2 - r_{i+9}^2)/(2r_1 r_{i+1})], \quad (i=1,2,3)$$

$$\theta_{j+3} = \arccos[(r_2^2 + r_{j+2}^2 - r_{j+12}^2)/(2r_2 r_{j+2})], \quad (i=1,2)$$

$$\theta_6 = \arccos[(r_3^2 + r_4^2 - r_{15}^2)/(2r_3 r_4)] \tag{A-5}$$

Therefore, when a cartesian coordinate is incremented the DIST and ANGLE routines convert that change to LMR-PES coordinates before the energy is calculated.

The relationships between the internal valence coordinates designations (given in Table V) and the corresponding LMR-PES coordinates was established by equations relating the valence coordinates designations to the proper cartesian coordinate representations. The cartesian coordinate values calculated using these equations were then used in subroutine DIST to obtain the proper values for the LMR-PES coordinates designations. Each valence coordinate in the last column of Table V has a discrete functional cartesian coordinate representation programmed into the routine QRESET or ALBEND. For example, when R_1 is incremented by h the QRESET function is given by (A-6),

$$r_1 = r_{C1} + h$$
$$Z_6 = (r_1 - Z_{C1}) + Z_{C6}$$
$$Z_1 = r_1 \tag{A-6}$$

where r_{C1} and Z_{C1} and Z_{C6} are the equilibrium LMR-PES and cartesian coordinate values, respectively, for the molecular configuration for

which force constants are being determined. The Z_1 and Z_6 values are then used in the DIST routine to obtain the corresponding LMR-PES coordinates changes relative to $R_1 = f(r_1,r_5,r_7,r_8,r_9)$. The same notation is used for each of the following valence coordinate relationships. The non-reacting C-H bond stretching relationships from incrementation of R_i (i=2,3,4) by h is given by (A-7),

$$r_i = r_{Ci} + h$$
$$A = \phi_{i-1} - \left(\frac{\pi}{2}\right)$$
$$r_{pi} = r_i \cos(A)$$
$$T = \arctan(x_{Ci}/y_{Ci})$$
$$x_i = r_{pi} \sin(T)$$
$$y_i = r_{pi} \cos(T)$$
$$z_i = -r_i \sin(A) \qquad\qquad\qquad \text{(A-7)}$$

where i=2,3,4, r_{pi} is r_i projected into the xy plane, see Figure 1, and A is the angle of r_i out of the xy plane. DIST then converts x_i, y_i and z_i, (i=2,3,4) to the corresponding LMR-PES coordinates.

The H-H bond stretching relationship for incrementation of R_5 by h is geometrically related to the linear-bending valence coordinates α_x and α_y. Therefore, R_5, α_x and α_y relationships are all handled by the same set of equations programmed in the ALBEND routine. These equations relating the incremented coordinates $r_6 = r_{C6} + h$, $\alpha_x = \alpha_x + h$, or $\alpha_y = \alpha_y + h$ to the LMR-PES coordinates are given in (A-8),

$$\Delta\alpha_x = \pi - \alpha_x$$
$$\Delta\alpha_y = \pi - \alpha_y$$
$$S = 1 - \sin^2(\Delta\alpha_x)\sin^2(\Delta\alpha_y)$$

$$R_{x_6} = r_6\cos^2(\Delta\alpha_y)/S$$

$$R_{y_6} = r_6\cos^2(\Delta\alpha_x)/S$$

$$x_6 = R_{x_6}\sin(\Delta\alpha_x)$$

$$y_6 = R_{x_6}\sin(\Delta\alpha_y)$$

$$z_6 = [R_{x_6}\cos(\Delta\alpha_x)] + r_1 \qquad\qquad (A-8)$$

where R_5 and r_6 correspond to the same interatomic distance, but R_5 is also a function of the LMR-PES coordinates r_5, r_7, r_8 and r_9 as are the α_x and α_y valence coordinates from Table V. Application of the DIST equations complete the transformation of the incremented R_5, α_x or α_y coordinates to the corresponding set of LMR-PES coordinates.

The incremented ϕ_i (i=1,2,3) valence angle coordinates are transformed into LMR-PES coordinates by (A-9),

$$\theta_i = \phi_i + h$$

$$A = \theta_i - (\pi/2)$$

$$r_{pi+1} = r_{i+1}\cos A$$

$$T = \arctan(x_{i+1}/y_{i+1})$$

$$x_{i+1} = r_{pi+1}\sin(T)$$

$$y_{i+1} = r_{pi+1}\cos(T)$$

$$z_{i+1} = r_{i+1}\sin(A) \qquad\qquad (A-9)$$

where x_{i+1}, y_{i+1} and z_{i+1} (i=1,2,3) correspond to the cartesian coordinates of the non-reacting hydrogens in Figure 1. The corresponding change in the r_{i+6} (i=1,2,3) values during incrementation of

$\phi_i = f(\theta_i, r_{i+6})$, (i=1,2,3) is calculated by application of the DIST equations.

Equation (A-10) interrelates valence angle coordinates ϕ_i (i=4,5,6) and the LMR-PES coordinates for the HCH angles associated with the non-reacting C-H bonds.

$$\theta_i = \phi_i + h$$

$$A_1 = \phi_1 - (\pi/2)$$

$$A_2 = \phi_{i-2} - (\pi/2)$$

$$r_{p1} = r_2 \cos(A_1)$$

$$r_{p2} = r_{i-1} \cos(A_2)$$

$$r_{\theta_i} = [r_2^2 + r_{i-1}^2 - 2r_2 r_{i-1} \cos\theta_i]^{1/2}$$

$$pr_{\theta_i} = r_{\theta_i} \cos[\arcsin(\frac{|z_2 - z_{i-1}|}{r_{\theta_i}})]$$

$$P_{\theta_i} = \text{arcos}[(r_{p1}^2 + r_{p2}^2 - pr_{\theta_i}^2)/(2r_{p1} r_{p2})]$$

$$D_{\theta_i} = 1/2[(2\pi/3) - P_{\theta_i}]$$

$$\theta_{x_2} = D_{\theta_i} + \arcsin(x_2/r_{p1})$$

$$x_2 = r_{p1} \sin(\theta_{x_2})$$

$$y_2 = r_{p1} \cos(\theta_{x_2})$$

$$z_2 = -r_2 \sin(A_1)$$

$$\theta_{y_i} = D_{\theta_i} - (\pi/6) + \arcsin(x_2/r_{p1})$$

$$x_{i-1} = r_{p2}\cos(\theta_{y_i})$$

$$y_{i-1} = r_{p2}\sin(\theta_{y_i})$$

$$z_{i-1} = -r_{i-1}\sin(A_2) \qquad \text{(A-10)}$$

For $i=4$ or 5 in equation (II-35) r_{p1} and r_{p2} are the r_2 and r_{i-1} bond-lengths projected into the xy plane, respectively, and the cartesian coordinates x_2, y_2, z_2, x_{i-1}, y_{i-1}, and z_{i-1} convert the incremented ϕ_4 and ϕ_5 coordinates into the properly changed LMR-PES coordinate values through application of (A-3) and (A-4). The valence coordinate transformation for incrementation of ϕ_6 by h is given by (A-11),

$$\theta_6 = \phi_6 + h$$

$$A_3 = \phi_2 - (\pi/2)$$

$$A_4 = \phi_3 - (\pi/2)$$

$$r_{p3} = r_3\cos(A_3)$$

$$r_{p4} = r_4\cos(A_4)$$

$$r_{\theta_6} = [r_3^2 + r_4^2 - 2r_3r_4\cos\theta]^{1/2}$$

$$pr_{\theta_6} = r_{\theta_6}\cos[\arcsin(\frac{z_2 - z_3}{r_{\theta_6}})]$$

$$P_{\theta_6} = \text{arcos}[(r_{p3}^2 + r_{p4}^2 - pr_{\theta_6}^2)/(2r_{p3}r_{p4})]$$

$$D_{\theta_6} = 1/2[(2\pi/3) - P_{\theta_6}]$$

$$\theta_{y_3} = -\frac{\pi}{6} - D_{\theta_6}$$

$$\theta_{y_4} = \theta_{y_3}$$

$$x_3 = r_{p3}\cos(\theta_{y_3})$$

$$y_3 = r_{p3}\sin(\theta_{y_3})$$

$$z_3 = -r_3\sin(A_3)$$

$$x_4 = -r_{p4}\cos(\theta_{y_4})$$

$$y_4 = r_{p4}\sin(\theta_{y_4})$$

$$z_4 = -r_4\sin(A_4) \tag{A-11}$$

where r_{p3} and r_{p4} are the r_3 and r_4 bondlengths projected into the xy plane, respectively, and the cartesian coordinates x_3, y_3, z_3, x_4, y_4 and z_4 transform the incremented ϕ_6 coordinate into the proportionally changed LMR-PES coordinates through application of (A-3) and (A-4). It should be noted that the ANGLE transformation routine was not used in incrementing a valence angle coordinate(s) since the internal valence coordinates not being used to obtain a particular derivative must be held constant while the energy values are computed as a function of a particular coordinate's values. Use of the ANGLE routine equations would not allow this to be done.

APPENDIX B

CALCULATION OF NORMAL MODE FREQUENCIES

AND ASSOCIATED PARAMETERS

Calculation of Normal Mode Frequencies

The normal mode frequencies for the various isotopic configurations were calculated using the Wilson FG matrix method which has been programmed in the Wolfsberg modification of the Schachtschneider program (WMS).[9] The purpose of this appendix is to describe the relationship between the cartesian coordinate force constant matrices and the internal coordinate force constant matrices used in the FXGEN ROUTINE in addition to describing the calculational methods generally associated with the Wilson FG matrix calculations used in the Schachtschneider program.[9]

The usual input procedures requires the masses and cartesian coordinates associated with each atom and an internal coordinate code for each internal coordinate in the molecule.[9,48] The LMR-PES cartesian coordinates are easily obtained from Tables III and V and the equations (A-1) and (A-2) in Appendix A. The internal coordinate specifications are also obtained from Tables III and V. These specifications are combined with the cartesian coordinates of each atom to generate the transformation matrix, B, having I rows and 3N columns where I is the number of internal coordinates and N is the

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number of atoms.[49] The B matrix transforms the cartesian coordinate column vector X, where $X^t = [x_1, y_1, z_1, x_2 \ldots Z_N]$, into the column vector of internal coordinates R, where $R^t = [R_1, R_2, \ldots R_I]$, by (B-1),

$$R = Bx \qquad (B-1)$$

where the superscript t indicates transposition of the column vector to the corresponding row vector.[9,48] The inverse kinetic energy matrix, G, is calculated by (B-2),

$$G = BM^{-1}B^t \qquad (B-2)$$

where M^{-1} is the diagonal inverse mass matrix in which m_{ix}, m_{iy}, and m_{iz} are the masses associated with each atom i from one to N for each cartesian coordinate in (B-3).[49]

$$M = \begin{bmatrix} 1/m_{1x} & 0 & 0 & \ldots \ldots \ldots .0 \\ 0 & 1/m_{1y} & & & \\ 0 & & 1/m_{1z} & & \\ & & & \ddots & \\ & & & & \ddots \\ 0 & \ldots \ldots \ldots \ldots \ldots & .1/m_{NZ} \end{bmatrix} \qquad (B-3)$$

The resultant G matrix is an I by I square matrix. Frequencies are obtained by solution of the corresponding GF product matrix secular equation, (B-4),

$$GFL = L\Lambda \qquad (B-4)$$

where F is the I by I internal coordinate force constant matrix, L is the transformation matrix which must be normalized to properly remove any redundant internal coordinates from the diagonal eigenvalue matrix Λ.[50] The Λ matrix values are related to the vibrational frequency values ν_i (cm^{-1}) by (B-5),

$$\Lambda_{ii} = \frac{4\pi^2 c^2 \nu_i^2}{N} = (5.88852 \times 10^{-7})\nu_i^2 \qquad (B-5)$$

The numerical constant in (B-5) is that used in the Schachtschneider program.[9]

The vibrational potential energy, V, is defined by (B-6).[9,50]

$$2V = R^t FR \qquad (B-6)$$

Substitution of (B-1) into (B-6) gives (B-7).

$$2V = (Bx)^t F(Bx) = x^t B^t FBx \qquad (B-7)$$

Since the vibrational potential energy is defined as the scalar product of a force constant matrix and its associated coordinate vectors as in (B-6) then the 3N by 3N cartesian coordinate force constant matrix F_x in equation (B-8) is equivalent to $B^t FB$ in equation (B-7).[51]

$$2V = x^t F_x x \qquad (B-8)$$

Combining (B-7) and (B-8) produces a method of transforming internal coordinate force constant matrices into their corresponding cartesian coordinate force constant matrices.[51,52]

$$F_x = B^t F B \qquad (B-9)$$

If a cartesian coordinate force constant matrix is used in the frequency calculation then the G matrix equals M^{-1} and the secular equation reduces from (B-4) to (B-10).[51]

$$M^{-1} F_x L = L \Lambda \qquad (B-10)$$

The functional form of the secular equation (B-10) with the symmetric $M^{-1} F_x$ product matrix allows it to be solved more easily than the unsymmetric GF product matrix. Also, if F_x is obtained from (B-9) it is properly normalized and all eigenvalues except the normal mode frequencies will be zero upon solution of (B-10).[9,51] If F_x is calculated directly from a potential energy surface the eigenvalue solution to (B-10) may exhibit some small residual rotational-translational character unless special care is taken in the calculation of F_x.

The more involved solution of the internal coordinate GF secular equation used in the WMS program as described by Schachtschneider follows.[9] The solution of an unsymmetric GF matrix is avoided by solving two symmetric secular equations. The G matrix is factored into conjugate W matrices by an eigenvalue-eigenvector diagonalization procedure to solve (B-11),

$$GD = D\Gamma \qquad (B-11)$$

where D is the eigenvector matrix of G and Γ is the diagonal eigenvalue matrix of G. Since G is a symmetric matrix of real values, D must be orthogonal and the Γ_i roots must be real. Therefore, (B-12) is

correct and the W matrix is defined by (B-13),

$$G = D\Gamma D^t = (D\Gamma^{\frac{1}{2}})(\Gamma^{\frac{1}{2}}D^t) \qquad \text{(B-12)}$$

$$W = D\Gamma^{\frac{1}{2}} \qquad \text{(B-13)}$$

where $\Gamma^{\frac{1}{2}}$ is the diagonal matrix of square roots of the Γ_i eigenvalues.[9] The G matrix is then defined by (B-14).

$$G = WW^t \qquad \text{(B-14)}$$

A real symmetric H matrix which is equivalent to the corresponding GF product matrix is defined by (B-15).

$$H = W^t FW \qquad \text{(B-15)}$$

The solution of the secular equation (B-16) by diagonalization of H

$$HC = C\Lambda \qquad \text{(B-16)}$$

produces the eigenvector matrix C and the diagonal eigenvalue matrix Λ which is the same as the Λ in (B-4) and (B-5). The major difference between (B-4) and (B-16) is that in (B-4) L must be properly normalized to remove the redundant normal coordinate representations in the GF matrix (that is those over the 3N-6 limit). However, the symmetric form of H causes these redundancies to be automatically removed during the solution of (B-16).[9]

Calculation of Moments of Inertia

The first step in the calculation of the mass moments of inertia, I_x, I_y, and I_z for a particular molecular species is the calculation

of the cartesian coordinates of the center of mass, C_x, C_y, and C_z, for that molecular species using equation (B-17),

$$C_x = -\frac{1}{M} \sum_{i=1}^{N} m_i x_i$$

$$C_y = -\frac{1}{M} \sum_{i=1}^{N} m_i y_i$$

$$C_z = -\frac{1}{M} \sum_{i=1}^{N} m_i z_i \qquad \text{(B-17)}$$

where M is the molecular weight, N is the number of atoms, m_i is the atomic weight of atom i (H = 1.007825 amu, D = 2.0141 amu, T = 3.01605 amu, ^{12}C = 12.000 amu, ^{13}C = 13.00335 amu, and ^{14}C = 14.0032 amu), and x_i, y_i, and z_i are the cartesian coordinates of atom i. The next step involves the calculation of the elements of the moment of inertia tensor matrix. The diagonal elements of the moment of inertia tensor matrix require the distance, r_i, of each atom i from the center of mass.

$$r_i = [(x_i + C_x)^2 + (y_i + C_y)^2 + (z_i + C_z)^2]^{\frac{1}{2}} \qquad \text{(B-18)}$$

The individual elements of the moment of inertia tensor matrix are given by (B-19)

$$I_{xx} = \sum_{i=1}^{N} m_i [r_i^2 - (x_i + C_x)^2]$$

$$I_{yy} = \sum_{i=1}^{N} m_i [r_i^2 - (y_i + C_y)^2]$$

$$I_{zz} = \sum_{i=1}^{N} m_i [r_i^2 - (z_i + C_z)^2]$$

$$I_{xy} = I_{yx} = \sum_{i=1}^{N} m_i (x_i + C_x)(y_i + C_y)$$

$$I_{xz} = I_{zx} = \sum_{i=1}^{N} m_i (x_i + C_x)(Z_i + C_z)$$

$$I_{yz} = I_{zy} = \sum_{i=1}^{N} m_i (y_i + C_y)(z_i + C_z) \qquad \text{(B-19)}$$

The moment of inertia tensor T in (B-20) is

$$T = \begin{bmatrix} I_{xx} & I_{xy} & I_{xz} \\ I_{yx} & I_{yy} & I_{yz} \\ I_{zx} & I_{zy} & I_{zz} \end{bmatrix} \qquad \text{(B-20)}$$

then diagonalized to obtain the eigenvalues I_x, I_y, and I_z which are the principal moments of inertia for a particular molecular species about each of the center of mass cartesian coordinate axes.[53]

APPENDIX C

TABULATION OF ISOTOPIC NORMAL MODE FREQUENCIES

AND PARAMETERS USED IN TRANSITION-STATE

THEORY ISOTOPE EFFECT CALCULATIONS

All normal mode frequencies, that are tabulated in this Appendix and are specified as being calculated using data from the LMR-PES, were calculated using internal coordinate force constants determined from the LMR-PES by the three-point difference method with an increment size of 1×10^{-4}. The other tabulated frequencies and parameters were calculated using the internal coordinate force constants and geometry from the specified source. The symbol $F_{\beta}^{\ddagger}$ used in the latter tables refers to the HCH valence angle bending force constant $F_{\phi_{1-3}}^{\ddagger}$, see Table V.

TABLE XXXVIII

LMR-PES DATA FOR ISOTOPIC HYDROGEN

	Molecular Hydrogen Isotopic Configurations Data					
	H_2	HD	D_2	T_2	HT	DT
ν_1[a]	4468.1	3870.0	3160.6	2582.8	3649.3	2886.2
I_x[b]	0.0	0.0	0.0	0.0	0.0	0.0
I_y[b]	0.27736	0.36972	0.54429	0.83004	0.41578	0.66470
I_z[b]	0.27736	0.36972	0.55429	0.83004	0.41578	0.66470
Molecular Weight[c]	2.01565	3.02193	4.02820	6.03210	4.02388	5.03015

[a]Frequencies are in cm^{-1}. Date from LMR-PES.

[b]The principal moment of inertia about the respective cartesian coordinate axis in units of amu Å^2.

[c]Molecular weight in amu.

TABLE XXXIX

LMR-PES DATA FOR ISOTOPIC METHYL RADICAL

	Methyl Radical Isotopic Configurations[a]					
	CH_3	CD_3	CHD_2	CH_2D	$^{13}CH_3$	$^{14}CH_3$
$\nu_1{}^{b}$	2914.2	2061.5	2138.9	2229.4	2914.2	2914.2
$\nu_2{}^{b,c}$	847.1	656.7	725.7	788.8	840.5	834.8
$\nu_2{}^{b,d}$	607.0	470.5	520.0	565.2	602.3	598.2
$\nu_3{}^{e}$	3099.6	2323.6	2327.7	2989.4	3085.2	3073.0
	3099.6	2323.6	3048.2	3098.9	3085.2	3073.0
$\nu_4{}^{e}$	1605.9	1174.7	1461.9	1344.4	1600.8	1596.4
	1605.9	1174.7	1185.6	1590.4	1600.8	1596.4
$I_x{}^{f}$	1.8092	3.6155	3.6155	2.9378	1.8092	1.8092
$I_y{}^{f}$	1.8092	3.6155	2.3402	1.8092	1.8092	1.8092
$I_z{}^{f}$	3.6183	7.2311	5.9557	4.7470	3.6183	3.6183
Molecular Weight[g]	15.0235	18.0423	17.0360	16.0298	16.0268	17.0267

[a]Frequencies are in cm^{-1}. Data calculated from the LMR-PES except as stated.

[b]Non-degenerate normal mode frequencies.

[c]Out-of-plane bending frequency calculated using Gaussian 70 force constant weighted by LMR-PES bond length.

[d]Out-of-plane bending frequencies calculated using the adjusted Tan, Winer and Pimental force constant weighted by the LMR-PES bond length. See Reference 38.

[e]Doubly degenerate frequencies for symmetric species.

[f]The principal moments of inertia about the respective cartesian coordinate axis in amu-$Å^2$.

[g]Molecular weight in amu.

TABLE XL

LMR-PES DATA FOR ISOTOPIC METHANE

	Methane Isotopic Configurations[a]								
	CH_4	CH_3D	CH_2D_2	CHD_3	CD_4	$^{13}CH_4$	$^{14}CH_4$	CH_3T	CD_3T
$\nu_1{}^b$	2917.0	2224.1	2166.4	2113.2	2063.4	2917.0	2917.0	1890.2	1850.5
$\nu_2{}^c$	1526.6	1476.3	1449.3	1303.5	1079.9	1526.6	1526.6	1470.5	1061.4
	1526.6	1476.3	1322.2	1303.5	1079.9	1526.6	1526.6	1470.5	1061.4
$\nu_3{}^d$	3080.1	2966.4	3080.1	3046.2	2287.8	3068.3	3058.3	2964.3	2160.7
	3080.1	3080.1	3008.7	2287.9	2287.8	3068.3	3058.3	3080.1	2287.7
	3080.1	3080.1	2288.1	2287.9	2287.8	3068.3	3058.3	3080.1	2287.7
$\nu_4{}^d$	1366.1	1356.7	1280.7	1040.0	1029.4	1358.0	1350.9	1343.3	1017.7
	1366.1	1197.9	1133.2	1052.6	1029.4	1358.0	1350.9	1121.8	951.7
	1366.1	1197.9	1052.9	1052.6	1029.4	1358.0	1350.9	1121.8	951.7

TABLE XL (Continued)

	Methane Isotopic Configurations[a]								
	CH_4	CH_3D	CH_2D_2	CHD_3	CD_4	$^{13}CH_4$	$^{14}CH_4$	CH_3T	CD_3T
I_x^e	3.2163	4.3494	5.5352	6.4276	6.4276	3.2163	3.2163	5.3520	7.5696
I_y^e	3.2163	4.3494	4.8219	5.1597	6.4276	3.2163	3.2163	5.3520	7.5696
I_z^e	3.2163	3.2163	3.9296	5.1597	6.4276	3.2163	3.2163	3.2163	6.4276
Molecular^f Weight	16.0313	17.0376	18.0438	19.0501	20.0564	17.0346	18.0345	18.0395	21.0584

[a] Frequencies are in cm^{-1}. Data calculated from the LMR-PES.

[b] Non-degenerate normal mode frequencies.

[c] Doubly degenerate normal mode frequencies for symmetric species.

[d] Triply degenerate normal mode frequencies for symmetric species.

[e] The principal moment of inertia about the respective cartesian coordinate axis in amu-$Å^2$.

[f] Molecular weight in amu.

TABLE XLI

LMR-PES ACTIVATED COMPLEX DATA

	Activated Complex Isotopic Configurations[a]					
	CH_3-H-H	CH_2D-H-H	CHD_2-H-H	CD_3-H-H	CD_3-H-D	CD_3-D-H
ν_1[b]	3388.4	3388.3	3388.1	3387.8	2724.7	3104.8
ν_2[b]	2937.7	2228.7	2158.0	2095.3	2093.7	2095.2
ν_3[b]	964.7	906.6	836.4	735.0	726.4	728.0
ν_4[b]	1479.3i	1478.9i	1478.6i	1478.2i	1349.1i	1180.5i
ν_5[c]	3085.6	3085.3	3043.1	2303.2	2303.2	2303.2
	3085.6	2995.4	2305.3	2303.2	2303.2	2303.2
ν_6[c]	1502.9	1478.9	1353.4	1093.8	1093.8	1093.8
	1502.9	1272.6	1130.2	1093.8	1093.8	1093.8
ν_7[c]	752.3	750.5	703.9	691.9	681.8	552.8
	752.3	696.4	692.0	691.9	681.8	552.8
ν_8[c]	367.3	365.9	344.2	313.6	274.3	308.7
	367.3	328.5	314.0	313.6	274.3	308.7
I_x[d]	9.6301	10.8995	11.7429	11.8790	16.7999	13.9858
I_y[d]	9.6301	9.8801	10.5286	11.8790	16.7999	13.9858
I_z[d]	3.3736	4.3931	5.5278	6.7427	6.7421	6.7421
Molecular[e] Weight	17.0391	18.0454	19.0517	20.0580	21.0642	21.0642

	Activated Complex Isotopic Configurations[a]					
	CH_3-H-D	CH_3-D-H	CH_3-D-D	CD_3-D-D	$^{13}CH_3$-H-H	$^{14}CH_3$-H-H
ν_1[b]	2720.9	3106.0	2405.0	2407.6	3387.3	3386.4
ν_2[b]	2941.2	2937.0	2939.3	2093.2	2936.0	2934.5
ν_3[b]	956.9	959.3	953.6	721.4	959.7	955.3
ν_4[b]	1350.4i	1181.7i	1115.0i	1113.5i	1471.3i	1464.3i

TABLE XLI (Continued)

	Activated Complex Isotopic Configurations[a]					
	CH_3-H-D	CH_3-D-H	CH_3-D-D	CD_3-D-D	$^{13}CH_3$-H-H	$^{14}CH_3$-H-H
$\nu_5{}^c$	3085.7	3085.7	3085.7	2303.2	3072.4	3061.1
$\nu_6{}^c$	1502.9	1502.9	1502.9	1093.8	1499.0	1495.7
$\nu_7{}^c$	746.1	636.6	632.6	543.2	750.8	749.5
$\nu_8{}^c$	327.5	345.7	296.0	262.4	367.0	366.6
$I_x{}^d$	14.2103	11.5250	15.7957	18.6144	9.6625	9.6913
$I_y{}^d$	14.2103	11.5250	15.7957	18.6144	9.6625	9.6913
$I_z{}^d$	3.3736	3.3736	3.3736	6.7421	3.3736	3.3736
Molecular Weight[e]	18.0454	18.0454	19.0517	22.0705	18.0425	19.0423

	Activated Complex Isotopic Configurations[a]					
	CH_3-H-T	CD_3-H-T	CH_3-T-H	CD_3-T-H	CH_3-T-T	CD_3-T-T
$\nu_1{}^b$	2445.6	2449.9	2997.5	2994.2	1973.3	1967.1
$\nu_2{}^b$	2939.9	2091.2	2934.9	2095.2	2938.9	2101.2
$\nu_3{}^b$	950.2	719.0	955.6	722.8	946.8	712.5
$\nu_4{}^b$	1270.8i	1269.3i	1032.7i	1031.1i	961.0i	958.7i
$\nu_5{}^c$	3085.7	2303.2	3085.7	2303.2	3085.7	2303.2
$\nu_6{}^c$	1502.9	1093.8	1502.8	1093.8	1502.9	1093.8
$\nu_7{}^c$	744.1	678.7	596.9	499.5	593.5	489.1
$\nu_8{}^c$	312.8	259.3	331.4	304.6	254.3	232.1
$I_x{}^d$	18.2899	21.2536	13.2127	15.8926	20.8221	25.2528
$I_y{}^d$	18.2899	21.2536	13.2127	15.8926	20.8221	25.2528

TABLE XLI (Continued)

	Activated Complex Isotopic Configurations[a]					
	CH_3-H-T	CD_3-H-T	CH_3-T-H	CD_3-T-H	CH_3-T-T	CD_3-T-T
I_z^d	3.3736	6.7421	3.3736	6.7421	3.3736	6.7421
Molecular[e] Weight	19.0474	22.0662	19.0474	22.0662	21.0556	24.0744

	Activated Complex Isotopic Configurations[a]			
	CH_3-D-T	CH_3-T-D	CD_3-D-T	CD_3-T-D
ν_1^b	2112.7	2275.3	2135.7	2278.5
ν_2^b	2939.1	2939.0	2071.9	2092.4
ν_3^b	948.3	951.1	715.4	717.5
ν_4^b	1070.2i	990.8i	1068.4i	988.8i
ν_5^c	3085.7	3085.7	2303.2	2303.2
ν_6^c	1502.9	1502.8	1093.8	1093.8
ν_7^c	631.4	594.2	540.5	491.3
ν_8^c	277.1	275.8	244.0	253.0
I_x^d	19.6223	17.2163	22.8219	20.2638

TABLE XLI (Continued)

	Activated Complex Isotopic Configurations[a]			
	CH_3-D-T	CH_3-T-D	CD_3-D-T	CD_3-T-D
I_y[d]	19.6223	17.2163	22.8219	20.2638
I_z[d]	3.3736	3.3736	6.7421	6.7421
Molecular Weight[e]	20.0536	20.0536	23.0724	23.0724

[a] Frequencies in cm^{-1}. Data calculated using the LMR-PES force constants and geometry.

[b] Non-degenerate normal mode frequencies.

[c] Doubly degenerate normal mode frequencies.

[d] The principal moment of inertia about the respective cartesian coordinate axis in amu-$Å^2$.

[e] Molecular weight in amu.

TABLE XLII

LMR-PES ACTIVATED COMPLEX DATA ϕ_i (i=1,2,3) = 90° AND ϕ_i (i=4,5,6) = 120°

	Planar CH_3 Activated Complex Isotopic Configurations[a]						
	CH_3-H-H	CH_3-D-D	CD_3-H-H	CH_3-D-H	CH_3-H-D	$^{13}CH_3$-H-H	$^{14}CH_3$-H-H
ν_1[b]	3386.3	2403.8	3386.3	3103.8	2720.6	3385.4	3384.6
ν_2[b]	2914.0	2914.0	2061.3	2914.0	2914.0	2914.0	2914.0
ν_3[b]	555.2	548.9	426.1	551.9	551.5	552.0	549.2
ν_4[b]	1469.5i	1108.1i	1469.5i	1174.1i	1340.7i	1461.6i	1454.7i
ν_5[c]	3099.8	3099.8	2324.4	3099.7	3099.8	3085.3	3073.0
ν_6[c]	1606.7	1606.6	1176.2	1606.6	1606.7	1601.5	1597.0
ν_7[c]	746.8	625.9	683.7	629.9	740.5	746.3	745.9
ν_8[c]	368.3	297.7	310.0	347.1	328.7	368.2	368.2

TABLE XLII (Continued)

		Planar CH_3 Activated Complex Isotopic Configurations[a]					
	CH_3-H-H	CH_3-D-D	CD_3-H-H	CH_3-D-H	CH_3-H-D	$^{13}CH_3$-H-H	$^{14}CH_3$-H-H
I_x^d	9.1465	14.9889	11.0948	10.9083	13.5185	9.1990	9.2457
I_y^d	9.1465	14.9889	11.0948	10.9083	13.5185	9.1990	9.2457
I_z^d	3.6183	3.6183	7.2311	3.6183	3.6183	3.6183	3.6183
Molecular Weight[e]	17.0391	19.0517	20.0580	18.0454	18.0454	18.0425	19.0423

[a] Frequencies in cm^{-1}. Data calculated using the LMR-PES force constants with the isotopic CH_3 group planar and perpendicular to r_1.

[b] Non-degenerate normal mode frequencies.

[c] Doubly degenerate normal mode frequencies.

[d] The principal moment of inertia about the respective cartesian coordinate axis in amu-$\overset{\circ}{A}^2$.

[e] Molecular weight in amu.

TABLE XLIII

LMR-PES ACTIVATED COMPLEX DATA FOR ϕ_i (i=1-6) = 109°28'

	Tetrahedral CH_3 Activated Complex Isotopic Configurations[a]						
	CH_3-H-H	CH_3-D-D	CD_3-H-H	CH_3-D-H	CH_3-H-D	$^{13}CH_3$-H-H	$^{14}CH_3$-H-H
$\nu_1{}^b$	3389.3	2405.2	3388.3	3107.4	2720.1	3388.1	3387.1
$\nu_2{}^b$	2952.9	2955.5	2117.4	2951.6	2958.6	2950.1	2947.6
$\nu_3{}^b$	1104.6	1093.2	837.5	1099.4	1096.0	1099.2	1094.5
$\nu_4{}^b$	1478.9i	1113.2i	1477.3i	1180.4i	1349.4i	1471.1i	1464.3i
$\nu_5{}^c$	3077.1	3077.1	2290.6	3077.1	3077.1	3064.5	3053.8
$\nu_6{}^c$	1451.9	1451.8	1053.1	1451.7	1451.9	1448.7	1440.9
$\nu_7{}^c$	751.1	631.1	693.2	635.2	744.8	749.3	747.6
$\nu_8{}^c$	365.8	295.0	313.8	344.6	326.0	365.3	364.9

TABLE XLIII (Continued)

	Tetrahedral CH_3 Activated Complex Isotopic Configurations[a]						
	CH_3-H-H	CH_3-D-D	CD_3-H-H	CH_3-D-H	CH_3-H-D	$^{13}CH_3$-H-H	$^{14}CH_3$-H-H
$I_x{}^d$	9.7949	16.0533	12.1351	11.7281	14.4346	9.8225	9.8471
$I_y{}^d$	9.7949	16.0533	12.1351	11.7281	14.4346	9.8225	9.8471
$I_z{}^d$	3.2163	3.2163	6.4276	3.2163	3.2163	3.2163	3.2163
Molecular Weight[e]	17.0391	19.0517	20.0580	18.0454	18.0454	18.0425	19.0423

[a]Frequencies in cm^{-1}. Date calculated using the LMR-PES force constants with the isotopic CH_3 group tetrahedral relative to r_1.

[b]Non-degenerate normal mode frequencies.

[c]Doubly degenerate normal mode frequencies.

[d]The principal moment of inertia about the respective cartesian coordinate axis in amu-$\mathring{A}^2$.

[e]Molecular weight in amu.

TABLE XLIV

BEBO ACTIVATED COMPLEX DATA[a]

	BEBO Activated Complex Isotopic Configurations									
	CH_3-H-H	CH_3-D-D	CD_3-H-H	CD_3-D-D	CH_3-H-D	CH_3-D-H	CD_3-H-D	CD_3-D-H	$^{13}CH_3$-H-H	$^{14}CH_3$-H-H
$\nu_1{}^b$	1610.3	1297.8	1596.6	1218.5	1300.2	1591.5	1226.4	1576.1	1601.7	1594.3
$\nu_2{}^b$	2980.3	2980.0	2139.6	2136.8	2980.0	2980.3	2136.8	2139.6	2977.4	2974.9
$\nu_3{}^b$	1178.9	1077.7	899.5	863.1	1089.0	1173.1	870.7	893.3	1174.3	1170.2
$\nu_4{}^b$	1688.9i	1213.1i	1688.3i	1211.8i	1648.7i	1250.2i	1648.2i	1248.4i	1686.8i	1685.0i
$\nu_5{}^c$	3046.9	3046.8	2249.1	2248.8	3046.9	3046.8	2249.1	2248.8	3036.7	3028.1
$\nu_6{}^c$	1459.0	1457.7	1065.9	1065.4	1459.0	1457.7	1065.9	1065.4	1455.1	1451.8
$\nu_7{}^c$	1046.1	858.3	980.2	761.8	1040.2	862.6	971.6	770.2	1043.1	1040.4
$\nu_8{}^c$	446.4	365.9	383.3	320.5	399.1	422.9	333.7	376.8	445.7	445.1

TABLE XLIV (Continued)

| | BEBO Activated Complex Isotopic Configurations | | | | | | | | | |
	CH_3-H-H	CH_3-D-D	CD_3-H-H	CD_3-D-D	CH_3-H-D	CH_3-D-H	CD_3-H-D	CD_3-D-H	$^{13}CH_3$-H-H	$^{14}CH_3$-H-H
I_x^d	8.1239	13.0996	10.3718	15.8724	12.1165	9.3369	14.7016	11.7648	8.1425	8.1591
I_y^d	8.1239	13.0996	10.3718	15.8724	12.1165	9.3369	14.7016	11.7648	8.1425	8.1591
I_z^d	3.1989	3.1989	6.3929	6.3929	3.1989	3.1989	6.3929	6.3929	3.1989	3.1989
Molecular Weight^e	17.0391	19.0517	20.0580	22.0705	18.0454	18.0454	21.0642	21.0642	18.0425	19.0423

[a]Frequencies in cm^{-1}. Data calculated using the BEBO force constants and geometry from Reference 12.

[b]Non-degenerate normal mode frequencies.

[c]Doubly degenerate normal mode frequencies.

[d]The principal moment of inertia about the respective cartesian coordinate axis in amu-$Å^2$.

[e]Molecular weight in amu.

TABLE XLV

LEPS ACTIVATED COMPLEX DATA[a]

	LEPS Activated Complex Isotopic Configurations							
	CH_3-H-H	CH_3-D-D	CD_3-H-H	CD_3-D-D	CH_3-H-D	CH_3-D-H	CD_3-H-D	CD_3-D-H
ν_1^{b}	1396.6	1234.3	1372.8	1080.7	1235.1	1368.6	1090.4	1336.2
ν_2^{b}	2979.9	2979.7	2136.8	2135.6	2979.7	2979.9	2135.6	2136.8
ν_3^{b}	1146.6	959.7	883.3	824.2	980.9	1130.1	838.2	873.2
ν_4^{b}	2024.4i	1448.1i	2024.0i	1447.2i	1948.1i	1525.8i	1947.8i	1524.8i
ν_5^{c}	3046.8	3046.7	2248.9	2248.6	3046.8	3046.7	2248.9	2248.6
ν_6^{c}	1458.1	1457.1	1065.6	1065.4	1458.1	1457.2	1065.6	1065.4
ν_7^{c}	1076.7	856.1	1029.9	779.7	1063.5	867.4	1012.7	799.2
ν_8^{c}	501.8	425.3	420.6	362.0	453.0	486.2	370.5	418.6

TABLE XLV (Continued)

		LEPS Activated Complex Isotopic Configurations						
	CH_3-H-H	CH_3-D-D	CD_3-H-H	CD_3-D-D	CH_3-H-D	CH_3-D-H	CD_3-H-D	CD_3-D-H
$I_x{}^d$	8.4210	13.6386	10.6812	16.4413	12.6318	9.6671	15.2420	12.1113
$I_y{}^d$	8.4210	13.6386	10.6812	16.4413	12.6318	9.6671	15.2420	12.1113
$I_z{}^d$	3.1989	3.1989	6.3929	6.3929	3.1989	3.1989	6.3929	6.3929
Molecular[e] Weight	17.0391	19.0517	20.0580	22.0705	18.0454	18.0454	21.0642	21.0642

[a]Frequencies in cm^{-1}. Data calculated using the LEPS force constants from Reference 12.

[b]Non-degenerate normal mode frequencies.

[c]Doubly degenerate normal mode frequencies.

[d]The principal moment of inertia about the respective cartesian coordinate axis in amu-$Å^2$.

[e]Molecular weight in amu.

TABLE XLVI

BEBO3 ACTIVATED COMPLEX DATA FOR $F_\beta^{\ddagger} = 0.0001$ mdyne-Å[a]

	BEBO3 Activated Complex Isotopic Configurations									
	CH_3-H-H	CH_3-D-D	CD_3-H-H	CD_3-D-D	CH_3-H-D	CH_3-D-H	CD_3-H-D	CD_3-D-H	$^{13}CH_3$-H-H	$^{14}CH_3$-H-H
ν_1[b]	1567.6	1195.9	1561.1	1175.7	1203.6	1546.7	1185.4	1539.5	1560.2	1553.9
ν_2[b]	3148.7	3148.5	2253.2	2251.7	3148.5	3148.7	2251.7	2253.2	3146.1	3144.0
ν_3[b]	938.4	925.3	730.3	709.4	931.5	954.1	715.1	724.9	953.8	949.8
ν_4[b]	1691.0i	1214.8i	1690.6i	1213.8i	1649.7i	1253.2i	1649.3i	1252.0i	1688.8i	1687.0i
ν_5[c]	3165.2	3165.2	2345.4	2345.4	3165.2	3165.2	2345.4	2345.4	3153.5	3143.5
ν_6[c]	1472.8	1472.7	1074.9	1074.8	1472.8	1472.7	1074.9	1074.8	1468.6	1465.0
ν_7[c]	622.9	442.7	622.4	442.0	582.9	494.2	582.3	493.6	622.8	622.6
ν_8[c]	13.7	13.0	11.0	10.1	13.0	13.5	10.2	10.7	13.7	13.6

TABLE XLVI (Continued)

| | BEBO3 Activated Complex Isotopic Configurations | | | | | | | | | |
	CH_3-H-H	CH_3-D-D	CD_3-H-H	CD_3-D-D	CH_3-H-D	CH_3-D-H	CD_3-H-D	CD_3-D-H	$^{13}CH_3$-H-H	$^{14}CH_3$-H-H
$I_x{}^d$	8.1200	13.0953	10.3642	15.8642	12.1123	9.3329	14.6936	11.7659	8.1386	8.1552
$I_y{}^d$	8.1200	13.0953	10.3642	15.8642	12.1123	9.3329	14.6936	11.7569	8.1386	8.1552
$I_z{}^d$	3.1931	3.1931	6.3812	6.3812	3.1931	3.1931	6.3812	6.3812	3.1931	3.1931
Molecular^e Weight	17.0391	19.0517	20.0580	22.0705	18.0454	18.0454	21.0642	21.0642	18.0425	19.0423

[a] Frequencies in cm^{-1}. Data calculated using the BEBO3 force constants from Reference 14 with $F^{\ddagger}_{\phi 1-3}$ equal to 0.0001 mdyne-Å.

[b] None-degenerate normal mode frequencies.

[c] Doubly degenerate normal mode frequencies.

[d] The principal moment of inertia about the respective cartesian coordinate axis in amu-Å^2.

[e] Molecular weight in amu.

TABLE XLVII

LEPS2 ACTIVATED COMPLEX DATA FOR $F_\beta^\ddagger = 0.0001$ mdyne-$\overset{o}{A}$[a]

| | LEPS2 Activated Complex Isotopic Configurations | | | | | | | |
	CH_3-H-H	CH_3-D-D	CD_3-H-H	CD_3-D-D	CH_3-H-D	CH_3-D-H	CD_3-H-D	CD_3-D-H
ν_1[b]	1391.6	1096.9	1384.1	1055.7	1106.1	1356.2	1071.3	1346.8
ν_2[b]	3148.5	3148.4	2252.0	2251.2	3148.4	3148.5	2251.2	2252.0
ν_3[b]	954.2	895.2	728.3	701.0	908.2	947.3	709.1	721.4
ν_4[b]	1838.7i	1315.7i	1838.4i	1315.0i	1769.5i	1383.5i	1769.2i	1382.7i
ν_5[c]	3165.2	3165.2	2345.5	2345.5	3165.2	3165.2	2345.5	2345.5
ν_6[c]	1472.9	1472.8	1075.3	1075.0	1472.9	1472.8	1075.2	1075.1
ν_7[c]	779.5	554.0	778.5	553.1	730.2	617.6	729.2	616.7
ν_8[c]	13.6	12.9	10.9	10.0	13.0	13.4	10.1	10.7

TABLE XLVII (Continued)

	LEPS2 Activated Complex Isotopic Configurations							
	CH_3-H-H	CH_3-D-D	CD_3-H-H	CD_3-D-D	CH_3-H-D	CH_3-D-H	CD_3-H-D	CD_3-D-H
$I_x{}^d$	8.3096	13.4401	10.5615	16.2277	12.4475	9.5376	15.0449	11.9716
$I_y{}^d$	8.3096	13.4401	10.5615	16.2277	12.4475	9.5376	15.0449	11.9716
$I_z{}^d$	3.1931	3.1931	6.3812	6.3812	3.1931	3.1931	6.3812	6.3812
Molecular^e Weight	17.0391	19.0517	20.0580	22.0705	18.0454	18.0454	21.0642	21.0642

[a] Frequencies in cm^{-1}. Data calculated using the LEPS2 force constants and geometry from Reference 14 with $F^{\ddagger}_{\phi 1-3}$ equal to 0.0001 mdyne-Å.

[b] Non-degenerate normal mode frequencies.

[c] Doubly degenerate normal mode frequencies.

[d] The principal moment of inertia about the respective cartesian coordinate axis in amu-Å^2.

[e] Molecular weight in amu.

TABLE XLVIII

BEBO3 ACTIVATED COMPLEX DATA FOR $F_\beta^\ddagger = 0.26$ mdyne-$\overset{o}{A}$[a]

| | BEBO3 Activated Complex Isotopic Configurations | | | | | | | |
	CH_3-H-H	CH_3-D-D	CD_3-H-H	CD_3-D-D	CH_3-H-D	CH_3-D-H	CD_3-H-D	CD_3-D-H
ν_1[b]	1577.5	1273.8	1566.0	1196.3	1276.2	1558.3	1204.1	1545.2
ν_2[b]	3148.7	3148.5	2253.6	2252.1	3148.5	3148.7	2252.1	2253.6
ν_3[b]	1156.3	1055.0	883.8	846.8	1066.6	1150.3	854.6	877.4
ν_4[b]	1690.5i	1214.1i	1690.0i	1212.8i	1649.3i	1252.3i	1648.8i	1250.7i
ν_5[c]	3166.5	3166.4	2348.4	2348.2	3166.5	3166.4	2348.4	2348.2
ν_6[c]	1479.9	1478.9	1076.6	1076.0	1479.9	1478.9	1076.5	1076.0
ν_7[c]	1008.1	827.4	944.0	733.9	1002.5	831.4	935.8	741.9
ν_8[c]	429.6	351.9	368.9	308.3	384.1	406.8	321.2	362.6

TABLE XLVIII (Continued)

		BEBO3 Activated Complex Isotopic Configurations							
		CH_3-H-H	CH_3-D-D	CD_3-H-H	CD_3-D-D	CH_3-H-D	CH_3-D-H	CD_3-H-D	CD_3-D-H
$I_x{}^d$		8.1200	13.0953	10.3642	15.8642	12.1123	9.3329	14.6936	11.7569
$I_y{}^d$		8.1200	13.0953	10.3642	15.8642	12.1123	9.3329	14.6936	11.7569
$I_z{}^d$		3.1931	3.1931	6.3812	6.3812	3.1931	3.1931	6.3812	6.3812
Molecular^e Weight		17.0391	19.0517	20.0580	22.0705	18.0454	18.0454	21.0642	21.0642

[a]Frequencies in cm^{-1}. Data calculated using the BEBO3 force constants and geometry from Reference 14 with $F^{\ddagger}_{\phi 1-3}$ equal to 0.26 mdyne-$\overset{\circ}{A}$.

[b]Non-degenerate normal mode frequencies.

[c]Doubly degenerate normal mode frequencies.

[d]The principal moment of inertia about the respective cartesian coordinate axis in amu-$\overset{\circ}{A}{}^2$.

[e]Molecular weight in amu.

TABLE XLIX

LEPS2 ACTIVATED COMPLEX DATA FOR $F_\beta^\ddagger = 0.26$ mdyne $\overset{\text{o}}{\text{A}}$[a]

| | LEPS2 Activated Complex Isotopic Configurations | | | | | | | |
	CH_3-H-H	CH_3-D-D	CD_3-H-H	CD_3-D-D	CH_3-H-D	CH_3-D-H	CD_3-H-D	CD_3-D-H
ν_1[b]	1411.8	1231.6	1391.6	1091.4	1232.9	1383.4	1102.1	1356.5
ν_2[b]	3148.5	3148.5	2252.4	2251.6	3148.4	3148.5	2251.6	2252.4
ν_3[b]	1141.9	968.1	879.3	823.3	989.1	1127.7	836.6	869.8
ν_4[b]	1838.4i	1315.1i	1838.0i	1314.2i	1769.2i	1382.8i	1768.9i	1381.7i
ν_5[c]	3166.5	3166.5	2348.6	2348.3	3166.5	3166.5	2348.6	2348.3
ν_6[c]	1480.0	1479.0	1076.8	1076.1	1380.0	1479.0	1076.7	1076.1
ν_7[c]	1078.4	858.0	1030.8	781.2	1065.5	869.1	1014.0	800.2
ν_8[c]	500.4	423.5	420.0	360.9	451.3	484.7	369.5	417.9

TABLE XLIX (Continued)

	LEPS2 Activated Complex Isotopic Configurations							
	CH_3-H-H	CH_3-D-D	CD_3-H-H	CD_3-D-D	CD_3-H-D	CH_3-D-H	CD_3-H-D	CD_3-D-H
I_x^d	8.3096	13.4401	10.5615	16.2277	12.4475	9.5376	15.0449	11.9716
I_y^d	8.3096	13.4401	10.5615	16.2277	12.4475	9.5376	15.0449	11.9716
I_z^d	3.1931	3.1931	6.3812	6.3812	3.1931	3.1931	6.3812	6.3812
Molecular^e Weight	17.0391	10.0517	20.0580	22.0705	18.0454	18.0454	21.0642	21.0642

^{a}Frequencies in cm^{-1}. Data calculated using the LEPS2 force constants and geometry from Reference 14 with $F_{\phi 1-3}^{\ddagger}$ equal to 0.26 mdyne-Å.

^{b}Non-degenerate normal mode frequencies.

^{c}Doubly degenerate normal mode frequencies.

^{d}The principal moment of inertia about the respective cartesian coordinate axis in amu-Å^2.

^{e}Molecular weight in amu.

TABLE L

BEBO3 ACTIVATED COMPLEX DATA FOR $F_{\beta}^{\ddagger} = 0.568$ mdyne-$\overset{\circ}{A}$ [a]

	BEBO3 Activated Complex Isotopic Configurations									
	CH_3-H-H	CH_3-D-D	CD_3-H-H	CD_3-D-D	CH_3-H-D	CH_3-D-H	CD_3-H-D	CD_3-D-H	$^{13}CH_3$-H-H	$^{14}CH_3$-H-H
ν_1 [b]	1603.4	1432.8	1574.0	1239.7	1432.9	1589.1	1244.2	1554.4	1591.7	1581.8
ν_2 [b]	3148.7	3148.6	2254.3	2252.7	3148.6	3148.7	2252.7	2254.3	3146.2	3144.0
ν_3 [b]	1337.1	1102.7	1033.3	960.6	1116.4	1326.2	971.8	1025.5	1334.1	1331.3
ν_4 [b]	1690.1i	1213.5i	1689.4i	1211.9i	1469.0i	1251.5i	1648.4i	1249.5i	1688.1i	1686.3i
ν_5 [c]	3168.3	3168.1	2353.3	2352.4	3168.3	3168.1	2353.3	2352.4	3156.3	3146.0
ν_6 [c]	1526.9	1497.7	1276.1	1086.8	1526.6	1497.7	1273.4	1087.0	1526.4	1526.0
ν_7 [c]	1355.1	1168.9	1072.8	1011.1	1353.6	1170.0	1072.7	1013.3	1348.0	1341.8
ν_8 [c]	457.5	363.4	403.9	326.9	407.3	421.7	349.4	387.8	457.1	456.7

TABLE L (Continued)

		BEBO3 Activated Complex Isotopic Configurations								
		CH_3-H-H	CH_3-D-D	CD_3-H-H	CD_3-D-D	CH_3-H-D	CH_3-D-H	CD_3-H-D	CD_3-D-H	$^{13}CH_3$-H-H	$^{14}CH_3$-H-H
I_x^d		8.1200	13.0953	10.3642	15.8642	12.1123	9.3329	14.6936	11.7569	8.1386	8.1552
I_y^d		8.1200	13.0953	10.3642	15.8642	12.1123	9.3329	14.6936	11.7569	8.1386	8.1552
I_z^d		3.1931	3.1931	6.3812	6.3812	3.1931	3.1931	6.3812	6.3812	3.1931	3.1931
Molecular^e Weight		17.0391	19.0517	20.0580	22.0705	18.0454	18.0454	21.0642	21.0642	18.0425	19.0423

[a] Frequencies in cm^{-1}. Data calculated using the BEBO3 force constants and geometry from Reference 14 with $F_{\phi 1-3}^{\ddagger}$ equal to 0.568 mdyne-Å.

[b] Non-degenerate normal mode frequencies.

[c] Doubly degenerate normal mode frequencies.

[d] The principal moment of inertia about the respective cartesian coordinate axis in amu-Å^2.

[e] Molecular weight in amu.

TABLE LI

LEPS2 ACTIVATED COMPLEX DATA FOR $F_\beta^\ddagger = 0.568$ mdyne-$\overset{\circ}{A}$[a]

| | LEPS2 Activated Complex Isotopic Configurations | | | | | | | |
	CH_3-H-H	CH_3-D-D	CD_3-H-H	CD_3-D-D	CH_3-H-D	CH_3-D-H	CD_3-H-D	CD_3-D-H
ν_1[b]	1481.7	1417.8	1405.6	1167.0	1417.9	1471.1	1171.1	1374.7
ν_2[b]	3148.6	3148.4	2253.0	2252.1	3148.4	3148.6	2252.1	2253.0
ν_3[b]	1278.6	988.5	1022.9	905.0	1010.7	1246.7	925.0	1009.0
ν_4[b]	1838.1i	1314.6i	1837.6i	1313.5i	1768.9i	1382.2i	1768.6i	1380.7i
ν_5[c]	3168.4	3168.2	2353.6	2352.5	3168.4	3168.2	2353.6	2352.5
ν_6[c]	1535.4	1497.9	1325.9	1089.5	1534.3	1497.9	1319.4	1090.4
ν_7[c]	1384.1	1183.1	1074.8	1033.3	1380.7	1186.0	1074.5	1038.4
ν_8[c]	555.2	448.0	482.6	397.6	496.2	518.0	419.7	468.9

TABLE LI (Continued)

	LEPS2 Activated Isotopic Configurations							
	CH_3-H-H	CH_3-D-D	CD_3-H-H	CD_3-D-D	CH_3-H-D	CH_3-D-H	CD_3-H-D	CD_3-D-H
$I_x{}^d$	8.3096	13.4401	10.5615	16.2277	12.4475	9.5376	15.0449	11.9716
$I_y{}^d$	8.3096	13.4401	10.5615	16.2277	12.4475	9.5376	15.0449	11.9716
$I_z{}^d$	3.1931	3.1931	6.3812	6.3812	3.1931	3.1931	6.3812	6.3812
Molecular^e Weight	17.0391	19.0517	20.0580	22.0705	18.0454	18.0454	21.0642	21.0642

[a]Frequencies in cm^{-1}. Data calculated using the LEPS2 force constants and geometry from Reference 14 with $F\dagger_{\phi 1-3}$ equal to 0.568 mdyne-Å.

[b]Non-degenerate normal mode frequencies.

[c]Doubly degenerate normal mode frequencies.

[d]The principal moment of inertia about the respective cartesian coordinate axis in amu-Å^2.

[e]Molecular weight in amu.

APPENDIX D

TABULATION OF THE KIEs USED TO OBTAIN

TEMPERATURE DEPENDENCE PARAMETERS

This Appendix presents tables of kinetic isotope effects

calculated as a function of temperature. These data were used to

calculate the temperature dependence for each kinetic isotope effect.

TABLE LII

VALUES FOR $k(CH_4,H)/k(CH_4,D)$

			KHT[b]		SW[c]					
Temperature °K	LMR-PES	LMR-PES[a] + Bell Tunneling	BEBO	LEPS	BEBO3 F_β = 0.0001	BEBO3 F_β = 0.26	BEBO3 F_β = 0.568	LEPS2 F_β = 0.0001	LEPS2 F_β = 0.26	LEPS2 F_β = 0.568
396	0.390	0.618	0.597	0.691	0.634	0.634	0.634	0.687	0.686	0.685
421	0.421	0.592	0.625	0.719	0.663	0.663	0.663	0.715	0.714	0.714
446	0.450	0.590	0.650	0.744	0.690	0.690	0.689	0.740	0.739	0.739
471	0.478	0.598	0.674	0.766	0.713	0.713	0.713	0.762	0.762	0.762
496	0.505	0.610	0.695	0.786	0.735	0.735	0.735	0.783	0.782	0.782
521	0.530	0.624	0.714	0.805	0.755	0.755	0.744	0.801	0.801	0.800
546	0.554	0.639	0.732	0.821	0.773	0.773	0.773	0.818	0.818	0.818
571	0.576	0.654	0.748	0.836	0.789	0.789	0.789	0.388	0.833	0.833
596	0.598	0.669	0.763	0.850	0.804	0.804	0.804	0.846	0.846	0.846
621	0.618	0.684	0.776	0.862	0.818	0.818	0.818	0.859	0.859	0.859
646	0.638	0.699	0.789	0.873	0.830	0.830	0.830	0.870	0.870	0.870
696	0.674	0.727	0.811	0.893	0.853	0.853	0.853	0.890	0.890	0.890

[a] Values include a Bell tunneling correction, see (III-12).

[b] Values calculated using force constants and geometry from Reference 12.

[c] Values calculated using force constants and geometry from Reference 14. $F_\beta = F^\ddagger_{\phi_i}(i=1,2,3)$ in mdyne-Å.

TABLE LIII

VALUES FOR $k(CH_3,H_2)/k(CH_3,D_2)$

Temperature °K	LMR-PES[a]	LMR-PES[b] + Bell Tunneling	KHT[c,d]		SW[d,e]					
			BEBO	LEPS	BEBO3 $F_\beta = 0.0001$	BEBO3 $F_\beta = 0.26$	BEBO3 $F_\beta = 0.568$	LEPS2 $F_\beta = 0.0001$	LEPS2 $F_\beta = 0.26$	LEPS2 $F_\beta = 0.568$
396	1.904	5.171	4.068	4.098	4.894	4.092	3.460	4.814	4.065	3.463
421	1.883	4.097	3.868	3.890	4.558	3.877	3.321	4.502	3.861	3.331
446	1.863	3.512	3.692	3.707	4.273	3.689	3.198	4.234	3.681	3.211
471	1.844	3.140	3.536	3.544	4.028	3.523	3.087	4.002	3.522	3.102
496	1.825	2.882	3.396	3.399	3.815	3.375	2.986	3.799	3.379	3.003
521	1.808	2.691	3.271	3.268	3.630	3.243	2.895	3.620	3.250	2.913
546	1.791	2.543	3.157	3.150	3.466	3.125	2.811	3.461	3.134	2.829
571	1.775	2.426	3.054	3.043	3.320	3.017	2.734	3.320	3.038	2.752
596	1.759	2.329	2.960	2.945	3.190	2.920	2.662	3.193	2.932	2.681
621	1.745	2.248	2.874	2.856	3.073	2.831	2.597	3.078	2.844	2.615
646	1.731	2.179	2.796	2.774	2.968	2.750	2.536	2.975	2.763	2.554
696	1.704	2.068	2.656	2.629	2.786	2.606	2.426	2.795	2.620	2.444

[a] Values calculated using the LMR-PES H_2 and D_2 frequencies.

[b] LMR-PES values corrected for Bell tunneling, see (III-12).

[c] Values calculated using the force constants and geometry in Reference 12.

[d] Values adjusted to the rotationally corrected reactant H_2 and D_2 frequencies of Persky and Klein, see Chapter III and Reference 43.

[e] Values calculated using the force constants and geometry in Reference 14. $F_\beta = F^{\ddagger}_{\phi_i} (i=1,2,3)$ in mdyne Å.

TABLE LIV

VALUES FOR $k(CD_3,H_2)/k(CD_3,D_2)$

Temperature °K	LMR-PES[a]	LMR-PES[b] + Bell Tunneling	KHT[c,d]		SW[d,e]					
			BEBO	LEPS	BEBO3 $F\beta = 0.0001$	BEBO3 $F\beta = 0.26$	BEBO3 $F\beta = 0.568$	LEPS2 $F\beta = 0.0001$	LEPS2 $F\beta = 0.26$	LEPS2 $F\beta = 0.568$
396	1.900	5.149	3.900	4.076	4.893	4.068	3.394	3.813	4.043	3.401
421	1.880	4.085	3.713	3.873	4.558	3.859	3.268	4.501	3.844	3.280
446	1.861	3.505	3.547	3.693	4.273	3.675	3.155	4.234	3.668	3.169
471	1.842	3.136	3.400	3.533	4.028	3.512	3.052	4.002	3.511	3.068
496	1.824	2.879	3.268	3.390	3.816	3.367	2.958	3.799	3.370	2.975
521	1.807	2.689	3.148	3.261	3.630	3.237	2.871	3.620	3.243	2.889
546	1.790	2.542	3.041	3.144	3.467	3.120	2.791	3.462	3.128	2.810
571	1.775	2.425	2.942	3.038	3.321	3.014	2.717	3.320	3.024	2.736
596	1.759	2.329	2.853	2.944	3.191	2.917	2.649	3.193	2.928	2.668
621	1.745	2.248	2.771	2.853	3.074	2.829	2.585	3.079	2.841	2.604
646	1.731	2.179	2.695	2.772	2.969	2.748	2.526	2.975	2.761	2.545
696	1.705	2.068	2.561	2.628	2.787	2.605	2.420	2.795	2.619	2.437

[a] Values calculated using the LMR-PES H_2 and D_2 frequencies.

[b] LMR-PES values corrected for Bell tunneling, see (III-12).

[c] Values calculated using the force constants and geometry in Reference 12.

[d] Values adjusted to the rotationally corrected H_2 and D_2 frequencies of Persky and Klein, see Chapter III and Reference 43.

[e] Values calculated using the force constants and geometry in Reference 14. $F_\beta = F^{\ddagger}_{\phi_i} (i=1,2,3)$ in mdyne Å.

TABLE LV

VALUES FOR $k(CH_3,\underset{\sim}{HD})/k(CH_3,\underset{\sim}{DH})$

			KHT[b]		SW[c]					
Temperature °K	LMR-PES	LMR-PES[a] + Bell Tunneling	BEBO	LEPS	BEBO3 F_β = 0.0001	BEBO3 F_β = 0.26	BEBO3 F_β = 0.568	LEPS2 F_β = 0.0001	LEPS2 F_β = 0.26	LEPS2 F_β = 0.568
396	1.748	2.637	1.488	1.235	1.782	1.491	1.261	1.476	1.247	1.063
421	1.702	2.366	1.476	1.240	1.737	1.477	1.266	1.459	1.252	1.080
446	1.661	2.183	1.464	1.245	1.697	1.466	1.271	1.443	1.256	1.095
471	1.625	2.049	1.454	1.249	1.663	1.455	1.275	1.430	1.259	1.109
496	1.593	1.946	1.445	1.252	1.633	1.445	1.278	1.418	1.261	1.121
521	1.563	1.863	1.436	1.255	1.607	1.436	1.282	1.407	1.264	1.133
546	1.537	1.795	1.428	1.257	1.584	1.428	1.285	1.398	1.265	1.143
571	1.573	1.738	1.421	1.259	1.563	1.421	1.287	1.389	1.267	1.152
596	1.491	1.689	1.415	1.261	1.545	1.414	1.289	1.381	1.268	1.160
621	1.471	1.647	1.409	1.262	1.528	1.408	1.292	1.374	1.270	1.168
646	1.453	1.610	1.403	1.263	1.514	1.402	1.293	1.368	1.271	1.175
696	1.421	1.549	1.394	1.266	1.488	1.393	1.297	1.357	1.272	1.187

[a]Values corrected for Bell tunneling, see (III-12).

[b]Values calculated using force constants and geometries in Reference 12.

[c]Values calculated using force constants and geometry in Reference 14. $F_\beta = F^{\ddagger}_{\phi_i}(i=1,2,3)$ in mdyne-Å.

TABLE LVI

VALUES FOR $k(CD_3, \underset{\sim}{H}D)/k(CD_3, \underset{\sim}{D}H)$

Temperature °K	LMR-PES	LMR-PES[a] + Bell Tunneling	KHT[b]		SW[c]					
			BEBO	LEPS	BEBO3 $F_\beta = 0.0001$	BEBO3 $F_\beta = 0.26$	BEBO3 $F_\beta = 0.568$	LEPS2 $F_\beta = 0.0001$	LEPS2 $F_\beta = 0.26$	LEPS2 $F_\beta = 0.568$
396	1.744	2.628	1.478	1.228	1.782	1.482	1.237	1.475	1.240	1.044
421	1.699	2.360	1.468	1.234	1.736	1.470	1.246	1.458	1.246	1.063
446	1.659	2.179	1.458	1.240	1.697	1.460	1.254	1.443	1.251	1.081
471	1.623	2.046	1.449	1.245	1.663	1.450	1.260	1.430	1.255	1.097
496	1.591	1.943	1.440	1.248	1.633	1.441	1.266	1.418	1.258	1.111
521	1.562	1.861	1.433	1.252	1.607	1.433	1.271	1.407	1.261	1.123
546	1.536	1.794	1.426	1.254	1.584	1.426	1.276	1.398	1.263	1.135
571	1.512	1.737	1.419	1.257	1.564	1.419	1.28-	1.389	1.265	1.145
596	1.491	1.688	1.413	1.259	1.545	1.413	1.283	1.381	1.267	1.154
621	1.471	1.646	1.407	1.261	1.529	1.407	1.286	1.374	1.268	1.163
646	1.453	1.610	1.402	1.262	1.514	1.402	1.289	1.368	1.270	1.170
696	1.420	1.549	1.393	1.265	1.489	1.392	1.293	1.357	1.272	1.183

[a]Values corrected for Bell tunneling, see (III-12).

[b]Values calculated using force constants and geometry in Reference 12.

[c]Values calculated using force constants and geometry in Reference 14. $F_\beta = F^{\ddagger}_{\phi_i} (i=1,2,3)$ in mdyne-Å.

TABLE LVII

VALUES FOR $k(CH_4,H)/k(^{13}CH_4,H)$

Temperature °K	LMR–PES	BEBO[a]	BEBO3[b] $F_\beta = 0.0001$	BEBO3[b] $F_\beta = 0.568$
273	1.038	1.024	1.031	1.0086
296	1.035	1.022	1.028	1.0080
321	1.032	1.020	1.025	1.0075
346	1.030	1.019	1.023	1.0071
371	1.028	1.017	1.021	1.0067
396	1.026	1.016	1.020	1.0064
421	1.024	1.015	1.018	1.0061
446	1.023	1.014	1.017	1.0058
471	1.021	1.013	1.016	1.0056
496	1.020	1.013	1.015	1.0053
521	1.019	1.012	1.014	1.0051
546	1.018	1.011	1.013	1.0049

[a]Values calculated using the force constants and geometry in Reference 12.

[b]Values calculated using the force constants and geometry in Reference 14.

TABLE LVIII

VALUE FOR $k(CH_3,H_2)/k(^{13}CH_3,H_2)$

Temperature °K	LMR-PES[a]	LMR-PES[b] + Pimentel	BEBO[c]	BEBO3[d] $F_\beta = 0.0001$	BEBO3[d] $F_\beta = 0.586$
273	1.0064	1.0021	0.9923	0.9993	0.978
296	1.0064	1.0026	0.9935	0.9995	0.980
321	1.0063	1.0030	0.9945	0.9997	0.982
346	1.0063	1.0033	0.9954	0.9999	0.984
371	1.0063	1.0036	0.9962	1.0001	0.986
396	1.0062	1.0038	0.9969	1.0003	0.987
421	1.0062	1.0040	0.9974	1.0004	0.988
446	1.0061	1.0041	0.9979	1.0005	0.990
471	1.0061	1.0043	0.9984	1.0006	0.991
496	1.0061	1.0044	0.9987	1.0007	0.991
521	1.0060	1.0045	0.9990	1.0008	0.992
546	1.0060	1.0046	0.9993	1.0009	0.993

[a] Values calculated using the LMR-PES force constants and geometry plus the Gaussian 70 CH_3 out-of-plane bending force constant, see Chapter II.

[b] Values calculated using the LMR-PES force constants and geometry plus the Tan, Winer, and Pimentel harmonic CH_3 out-of-plane bending frequency, see Appendix C.

[c] Values calculated using the BEBO data in Reference 12.

[d] Values calculated using the BEBO3 data in Reference 14. $F_\beta = F^\dagger_{\phi_i} (i=1,2,3)$ in mdyne-Å.

TABLE LIX

VALUES FOR $k(CH_4,H)/k(CD_3H,H)$

Temperature °K	LMR–PES	BEBO[a]	BEBO3[b] $F_\beta = 0.0001$	BEBO3[b] $F_\beta = 0.568$
273	1.650	1.321	1.591	0.687
296	1.579	1.293	1.507	0.712
321	1.514	1.266	1.434	0.735
346	1.460	1.242	1.374	0.755
371	1.413	1.222	1.324	0.772
396	1.372	1.203	1.283	0.787
421	1.338	1.186	1.248	0.800
446	1.307	1.172	1.219	0.812
471	1.281	1.159	1.193	0.823
496	1.257	1.147	1.172	0.833
521	1.237	1.136	1.153	0.842
546	1.218	1.127	1.136	0.850

[a]Values calculated using the BEBO data in Reference 12.

[b]Values calculated using the BEBO3 data in Reference 14. $F_\beta = F^{\ddagger}_{\phi_i}$ (i=1,2,3) in mdyne-Å.

TABLE LX

VALUES FOR $k(CH_3,H_2)/k(CD_3,H_2)$

Temperature °K	LMR-PES[a]	LMR-PES[b] + Pimentel	BEBO[c]	BEBO3[d] $F_\beta = 0.0001$	BEBO3[d] $F_\beta = 0.568$
273	0.811	0.722	0.650	0.782	0.338
296	0.838	0.756	0.686	0.800	0.378
321	0.862	0.787	0.721	0.816	0.418
346	0.882	0.813	0.751	0.830	0.456
371	0.898	0.835	0.776	0.842	0.491
396	0.911	0.854	0.799	0.852	0.523
421	0.923	0.871	0.819	0.861	0.552
446	0.932	0.884	0.836	0.869	0.579
471	0.940	0.896	0.851	0.876	0.604
496	0.947	0.907	0.864	0.883	0.627
521	0.953	0.916	0.876	0.888	0.649
546	0.958	0.923	0.886	0.894	0.668

[a] Values calculated using the LMR-PES force constants and geometry plus the Gaussian 70 CH_3 out-of-plane bending force constant, see Chapter II, and Appendix C.

[b] Values calculated using the LMR-PES force constants and geometry plus the Tan, Winer, and Pimentel harmonic CH_3 out-of-plane bending frequency, see Appendix C.

[c] Values calculated using the BEBO data in Reference 12.

[d] Values calculated using the BEBO3 data in Reference 14. $F_\beta = F^{\ddagger}_{\phi_i} (i=1,2,3)$ in mdyne-Å.

TABLE LXI

LMR-PES KIEs USING DIFFERENT TRANSITION-STATE GEOMETRIES

Temperature °K	$k(CH_4,H)/k(^{14}CH_4,H)$			$k(CH_3,H_2)/k(^{14}CH_3,H_2)$		
	Tetrahedral[a] CH$_3$	LMR-PES	Planar[b] CH$_3$	Tetrahedral[a] CH$_3$	LMR-PES	Planar[b] CH$_3$
371	1.0527	1.0520	1.0526	1.0124	1.0117	1.0123
396	1.0491	1.0484	1.0488	1.0123	1.0116	1.0120
421	1.0459	1.0453	1.0455	1.0122	1.0115	1.0117
446	1.0431	1.0425	1.0426	1.0121	1.0115	1.0115
471	1.0407	1.0401	1.0400	1.0119	1.0114	1.0113
496	1.0384	0.0379	0.0377	1.0118	1.0113	1.0112
521	1.0365	1.0360	1.0357	1.0117	1.0113	1.0110
546	1.0347	1.0342	1.0339	1.0117	1.0112	1.0109

[a]ϕ_i(i=1-6) = 109°28'16".

[b]ϕ_i(i=1,2,3) = 90°, ϕ_i(i=4,5,6) = 120°.

TABLE LXII

LMR-PES KIEs USING DIFFERENT TRANSITION-STATE GEOMETRIES

Temperature °K	$k(CH_4,H)/k(CH_4,D)$			$k(CH_3,H_2)/k(CH_3,\underset{\sim}{H}D)$		
	Tetrahedral[a] CH_3	LMR-PES	Planar[b] CH_3	Tetrahedral[a] CH_3	LMR-PES	Planar[b] CH_3
371	0.357	0.357	0.358	0.986	0.986	0.989
396	0.389	0.390	0.391	1.000	1.000	1.003
421	0.420	0.421	0.422	1.012	1.012	1.014
446	0.450	0.450	0.451	1.023	1.023	1.025
471	0.478	0.478	0.479	1.032	1.032	1.035
496	0.505	0.505	0.506	1.041	1.041	1.043
521	0.530	0.530	0.531	1.048	1.048	1.050
546	0.554	0.554	0.555	1.055	1.055	1.057

[a] ϕ_i (i=1-6) = 109°28'16".

[b] ϕ_i (i=1,2,3) = 90°, ϕ_i (i=4,5,6) = 120°.

TABLE LXIII

LMR-PES KIEs USING DIFFERENT TRANSITION-STATE GEOMETRIES

Temperature °K	$k(CH_4,H)/k(CH_3D,H)$			$k(CH_3,H_2)/k(CH_3,\underset{\sim}{D}H)$		
	Tetrahedral[a] CH_3	LMR-PES	Planar[b] CH_3	Tetrahedral[a] CH_3	LMR-PES	Planar[b] CH_3
371	3.871	3.869	3.883	1.777	1.776	1.782
396	3.529	3.527	3.539	1.749	1.748	1.754
421	3.252	3.250	3.260	1.724	1.723	1.728
446	3.024	3.023	3.031	1.700	1.699	1.704
471	2.835	2.834	2.841	1.679	1.678	1.682
496	2.676	2.674	2.680	1.658	1.658	1.661
521	2.540	2.538	2.544	1.640	1.639	1.642
546	2.423	2.421	2.426	1.622	1.621	1.625

[a] ϕ_i (i=1-6) = 109°28'16".

[b] ϕ_i (i=1,2,3) = 90°, ϕ_i (i=4,5,6) = 120°.

TABLE LXIV

LMR-PES KIEs USING DIFFERENT TRANSITION-STATE GEOMETRIES

Temperature °K	$k(CH_4,H)/k(CD_3H,H)$			$k(CH_3,H_2)/k(CD_3,H_2)$		
	Tetrahedral[a] CH_3	LMR-PES	Planar[b] CH_3	Tetrahedral[a] CH_3	LMR-PES	Planar[b] CH_3
371	1.396	1.413	1.478	0.887	0.898	0.939
396	1.359	1.372	1.426	0.902	0.911	0.947
421	1.326	1.338	1.381	0.915	0.923	0.953
446	1.298	1.307	1.344	0.925	0.932	0.958
471	1.273	1.281	1.311	0.934	0.940	0.963
496	1.250	1.257	1.283	0.942	0.947	0.966
521	1.231	1.237	1.258	0.948	0.953	0.970
546	1.213	1.218	1.237	0.954	0.958	0.972

[a] ϕ_i (i=1-6) = 109°28'16".

[b] ϕ_i (i=1,2,3) = 90°, ϕ_i (i=4,5,6) = 120°.

APPENDIX E

LISTING OF COMPUTER PROGRAMS

The following computer programs are arranged in the relative

order of usage to calculate transition-state theory kinetic isotope

effects. The first program is the SCANNING ROUTINE used to search

out and define the LMR-PES activated complex geometric configuration,

CH_3-H-H, for the axial hydrogen abstraction reaction. This is

followed by the subroutines describing the LMR-PES, that is, POT6,

TRI, PLACE, DIST, ANGLE and READ.[2] Subroutine TETRAH contains

equations describing a geometric derivation of the tetrahedral angle

and is called no more than once in any one program. The next program

is the INTERNAL COORDINATE FORCE CONSTANT ROUTINE which uses the

subroutines describing the LMR-PES[2] in addition to CPUNCH for punching

the force constants in the proper form for use with the Schacht-

schneider normal mode frequency program,[9] and ALBEND and QRESET whose

functional forms are described in Appendix A. The third program,

FXGEN ROUTINE, was used to convert internal coordinate force constants

to cartesian coordinate force constants by the matrix methods

described in Appendix B. The fourth program is the CARTESIAN

COORDINATE FORCE CONSTANT ROUTINE which uses the subroutine describing

the LMR-PES[2] in addition to the polynomial least squares subroutine

LESQ.[32] The fifth program is the ABSOLUTE RATE THEORY ROUTINE which

controls the input to the subroutine THERMO. Then THERMO calculates

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the transition-state theory kinetic isotope effect ratios and their
temperature dependence using subroutine LESQ.[32] THERMO has also been
modified to use a temperature dependent exponential factor like those
in (III-10) and (III-11).

```
      C##############################################################
      C                  LMR-PES SCANNING ROUTINE
      C     THE LMR-PES OR L. M. RAFF POTENTIAL ENERGY SURFACE IS PROGRAMMED IN THE
      C     SUBROUTINES PUT6, TRI, PLACE, DIST AND ANGLE.
      C##############################################################
0001        IMPLICIT REAL*8 (A-H,O-Z)
0002        DIMENSION P(61,100),XMAX(6),YMAX(6),ZMAX(6),RMAX(15),AMAX(6)
0003        DIMENSION X(6),Y(6),Z(6),R(15),DER(15),AG(6),R2(15),DI(3),D3(3),
           1 ALPH(3),RE(3),BETA(3),CC(3),AA(3),SIG(3),RSTR(3),ACS(6),DK(6),
           2 Y1(6),Y2(6),ASS(6),F(4),GF(4),RX(6),PX(6),PY(6),PZ(6),DX(6),
           3 DY(6),DZ(6),DPX(6),DPY(6),DPZ(6),DF(15,3)
0004        DIMENSION APARM(5)
0005        COMMON X,Y,Z,R,DER,AG,R2,DI,ALPH,RE,D3,BETA,CC,AA,SIG,RSTR,TAU,
           1 RV,DIJ,CP,EE,ACS,ASS,RX,XII,              V1,V2,V3,V4,BMAX,
           2 RSS,VR,PER,H,PX,PY,PZ,WH,WC,WBR,W,DT,DX,DY,DZ,DPX,DPY,DPZ,T,DF,
           3 TEMP,RRT,START,APARM,PI,T3PI,EL6PI,S6PI,
           4 III,JJJ,KKK,LLL,NV1,NV2,NV3,NV4,JJ,NI,KEE
0006        REAL*4  P,PPP
      C&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&
      C     THIS ROUTINE SCANS A REGION OF THE POTENTIAL ENERGY SURFACE DESCRIBED BY
      C     THE LMR-PES IN SEARCH OF THE ENERGY AND CH5 STRUCTURE FOR THE AXIAL
      C     HYDROGEN ABSTRACTION  REACTION AT THE TOP OF THE BARRIER ALONG THE
      C     REACTION COORDINATE BY INCREMENTING THE C-H DISTANCE VERSUS THE H-H
      C     DISTANCE SYSTEMATICALLY.
      C&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&
0007        ABS(X)=DABS(X)
0008        READ(5,100) A,B,C,D,E
0009   100  FORMAT(5A1)
0010   300  DO 5 I=1,61
0011        DO 5 J=1,100
0012   5    P(I,J)=E
0013        DO 1 I=1,100
0014        P(1,I)=A
0015   1    P(61,I)=A
0016        DO 2 I=2,61
0017        P(I,1)=B
0018   2    P(I,100)=B
0019        DO 3 I=6,56,5
0020        DO 4 J=1,100
0021   4    P(I,J)=B
0022   3    CONTINUE
0023        WRITE(6,101)
0024   101  FORMAT(1H1)
0025        CALL READ
0026        TMAX=0.0D0
0027        XX=2.842500
      C ////////////////////////////////////////////////////////////
      C     CALCULATE PI AND FRACTIONS OF PI
0028        PI=2.0D0*DARSIN(1.0D0)
0029        T3PI=(2.0D0*PI)/3.0D0
0030        EL6PI=(11.0D0*PI)/6.0D0
0031        S6PI=(7.0D0*PI)/6.0D0
0032        CALL TETRAH(TAU,PI)
0033        PPP=2.40
0034        K=1
0035        Z(1)=3.2D0
      C ////////////////////////////////////////////////////////////
      C     START INCREMENTATION.
```

```
FORTRAN IV G1  RELEASE 2.0        MAIN        DATE = 76302        10/03/46

0036              DO 50 I=1,132
0037              I=1.006
0038              Z0=XX
0039              DO 51 J=1,100
0040              Z(6)=Z(1)+Z0
      C ////////////////////////////////////////////////////////////////////////////////
      C    CALCULATE ENERGY AFTER SETTING GEOMETRY AS A FUNCTION OF BOND LENGTH OF
      C    REACTING C-H BOND.
0041              CALL PLACE(Z(1))
0042              CALL DIST
0043              CALL ANGLE
0044              CALL FCTG
0045              E=E+12.723200
      C ////////////////////////////////////////////////////////////////////////////////
      C    TEST FOR MINIMUM ENERGY  (REACTION COORDINATE POSITION) ALONG THE H-H INCRE
      C    MENTATION SCAN.
0046       1777   IF(T-EE) 20,21,21
0047         21   T=EE
0048              GO TO 22
0049         20   I=ABS(T/3.0+DD-60.0001)
0050              IF(L-EE) 70,70,71
0051         71   L=EE
0052         70   CONTINUE
0053              P(L,N)=0
0054              N=N+1
0055              IF(E-TMAX) 400,400,401
      C &&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&
      C    STORE GEOMETRY OF MAXIMUM ENERGY CONFIGURATION.
0056        401   TMAX=EE
0057              DO 402 IK=1,6
0058              XMAX(IK)=X(IK)
0059              YMAX(IK)=Y(IK)
0060              ZMAX(IK)=Z(IK)
0061        402   AMAX(IK)=AO(IK)*180.000/PI
0062              DO 403 IK=1,15
0063        403   RMAX(IK)=R(IK)
0064        400   CONTINUE
0065              GO TO 50
      C &&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&
      C    INCREMENT H-H DISTANCE.
0066         22   Z6=Z6+3.0D-4
0067         51   CONTINUE
      C &&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&&
      C    INCREMENT C-H DISTANCE
0068         50   Z(1)=Z(1)-3.0D-4
0069              DO 60 I=1,12
0070              M=5*(I-1)+1
0071              WRITE(6,102) PPP,(P(M,N),N=1,100)
0072              PPP=PPP-0.20
0073        102   FORMAT(1X,F5.2,2X,100A1)
0074        103   FORMAT(8X,100A1)
0075              DO 61 J=1,4
0076              M=5*(I-1)+J+1
0077         61   WRITE(6,103) (P(M,N),N=1,100)
0078         60   CONTINUE
0079              PPP=0.0
0080              WRITE(6,102) PPP,(P(61,N),N=1,100)
0081              WRITE(6,105)
```

```
FORTRAN IV G1  RELEASE 2.0            MAIN            DATE = 76302          10/03/48

0082              135   FORMAT(40X,19HREACTION COORDINATE)
0083              777 CONTINUE
0084                  WRITE(6,101)
0085                  WRITE(6,404)
0086              404   FORMAT(20X,39HENERGY AND GEOMETRY OF THE SADDLE-POINT//
                 1  10X,6HATOM 1,15X,6HATOM 2,15X,6HATOM 3,15X,6HATOM 4,15X,6HATOM 5,
                 2  15X,6HATOM 6//)
0087                  WRITE(6,405) XMAX,YMAX,ZMAX
0088              405 FORMAT(1X,1HX,2X,6(1PD21.14)/1X,1HY,2X,6(1PD21.14)/1X,1HZ,2X,6(1PD
                 1 21.14)/)
0089                  DO 406 I=1,15
0090              406   WRITE(6,407) I,RMAX(I)
0091              407 FORMAT(15X,1HR,I2,1H=,1X,1PD22.15)
0092                  WRITE(6,408) AMAX
0093              408 FORMAT(//20X,6HANGLES//10X,3HT1=,3PD15.6,2X,3HT2=,3PD15.6,2X,
                 1  3HT3=,3PD15.6,2X,3HT4=,3PD15.6,2X,3HT5=,3PD15.6,2X,3HT6=,3PD15.6,
                 2 //)
0094                  TMAX=(TMAX-0.4000)*23.060500
0095                  WRITE(6,409) TMAX
0096              409 FORMAT(10X,28HBARRIER HEIGHT IN KCAL/MOLE=,2PD25.15)
0097                  GO TO 300
0098                  END
```

```
FORTRAN IV G LEVEL  21              POT6            DATE = 76044          14/04/41

      0001            SUBROUTINE POT6
            C***************************************************************************
            ·C    SEE REFERENCE:  L. M. RAFF, J. CHEM. PHYS., VOL. 60, 2220(1974)
            C SUBROUTINE TO CALCULATE THE CH4-H SURFACE
            C REQUIRES SUBROUTINES DIST,ANLGE,AND TRI
            C ALSO COMPUTES DE/DR FOR ALL R AND STORES RESULTS IN ARRAY DER
            C***************************************************************************
      0002            IMPLICIT REAL*8 (A-H,O-Z)
      0003            DIMENSION FR(4),DFR(4)
      0004            DIMENSION X(6),Y(6),Z(6),R(15),DER(15),AG(6),R2(15),D1(3),D3(3),
                     1 ALPH(3),RE(3),BETA(3),CC(3),AA(3),SIG(3),RSTR(3),ACS(6),DK(6),
                     2 Y1(6),Y2(6),ASS(6),F(4),DF(4),RX(6),PX(6),PY(6),PZ(6),DX(6),
                     3 DY(6),DZ(6),DPX(6),DPY(6),DPZ(6),GF(15,3)
      0005            DIMENSION APAPM(5)
      0006            COMMON X,Y,Z,R,DEP,AG,R2,D1,ALPH,RE,D3,BETA,CC,AA,SIG,RSTR,TAU,
                     1 RV,DIJ,CP,EE,ACS,ASS,RX,XII,                V1,V2,V3,V4,BMAX,
                     2RSS,VR,PEE,HH,PX,PY,PZ,WH,WC,WBR,WW,DT,DX,DY,DZ,DPX,DPY,DPZ,T,GF,
                     3TEMP,RRT,START,APARM,PI,T3PI,FL6PI,S6PI,
                     4III,JJJ,KKK,LLL,NV1,NV2,NV3,NV4,JJ,NI,KEE
      0007            EXP(X)=DEXP(X)
      0008            SQRT(X)=DSQRT(X)
      0009            COS(X)=DCOS(X)
      0010            SIN(X)=DSIN(X)
      0011            ARCOS(X)=DARCOS(X)
      0012            ARSIN(X)=DARSIN(X)
            C //////////////////////////////////////////////////////////////////////////
            C COMPUTE THE INTERPARTICLE DISTANCES R
            C     CALL DIST
            C***************************************************************************
            C CHECK FOR THE FIFTH ATOM--I.E.--CH4---(H)
            C  BY DEFINITION THE FIFTH H ATOM IS THE ONE WHOSE C-H DISTANCE IS MAXIMUM
            C //////////////////////////////////////////////////////////////////////////
      0013            RHMAX=R(1)
      0014            KMAX=1
      0015            IF(R(2).LT.RHMAX) GO TO 1100
      0016            RHMAX=R(2)
      0017            KMAX=2
      0018     1100   IF(R(3).LT.RHMAX) GO TO 1101
      0019            RHMAX=R(3)
      0020            KMAX=3
      0021     1101   IF(R(4).LT.RHMAX) GO TO 1102
      0022            RHMAX=R(4)
      0023            KMAX=4
      0024     1102   IF(R(5).LT.RHMAX) GO TO 1103
      0025            RHMAX=R(5)
      0026            KMAX=5
      0027     1103 CONTINUE
            C     CALL SWITCH(KMAX,1)
            C ***************************************************************************
            C COMPUTE THE HCH ANGLES AND STORE RESULTS IN ARRAY AG
            C     CALL ANGLE
            C***************************************************************************
      0028            DO 50 I=1,15
      0029     50 DER(I)=0.0D0
            C COMPUTE THE FOUR TRIATOMIC TERMS
      0030            CALL TRI(R(1),R(5),R(6),DER(1),DER(5),DER(6),1,3,2,EE)
      0031            CALL TRI(R(2),R(5),R(7),DER(2),CR2,DER(7),1,3,2,E)
      0032            EE=EE+E
```

```
0033          DER(5)=DER(5)+DR2
0034          CALL TRI(R(3),R(5),R(8),DER(3),DR2,DER(8),1,3,2,E)
0035          EE=EE+E
0036          DER(5)=DER(5)+DR2
0037          CALL TRI(R(4),R(5),R(9),DER(4),DR2,DER(9),1,3,2,E)
0038          EE=EE+E
0039          DER(5)=DER(5)+DR2
C*********************************************************************************
C COMPUTE FORCE CONSTANTS
C COMPUTE ATTENUATION TERMS
0040          XA=R(1)-RE(1)
0041          XB=R(2)-RE(1)
0042          XC=R(3)-RE(1)
0043          XD=R(4)-RE(1)
0044          XA2=XA*XA
0045          XB2=XB*XB
0046          XC2=XC*XC
0047          XD2=XD*XD
0048          XXA=R(6)-RE(2)
0049          XXB=R(7)-RE(2)
0050          XXC=R(8)-RE(2)
0051          XXD=R(9)-RE(2)
0052          EXA11=EXP(-APARM(2)*R2(6))
0053          EXA12=EXP(-APARM(2)*R2(7))
0054          EXA13=EXP(-APARM(2)*R2(8))
0055          EXA14=EXP(-APARM(2)*R2(9))
0056          EXA21=EXP(-APARM(5)*XXA*XXA)
0057          EXA22=EXP(-APARM(5)*XXB*XXB)
0058          EXA23=EXP(-APARM(5)*XXC*XXC)
0059          EXA24=EXP(-APARM(5)*XXC*XXC)
0060          A11=1.0D0-EXA11
0061          A12=1.0D0-EXA12
0062          A13=1.0D0-EXA13
0063          A14=1.0D0-EXA14
0064          A21=APARM(3)+APARM(4)*EXA21
0065          A22=APARM(3)+APARM(4)*EXA22
0066          A23=APARM(3)+APARM(4)*EXA23
0067          A24=APARM(3)+APARM(4)*EXA24
0068          EXF1=EXP(-A21*XA2)
0069          EXF2=EXP(-A22*XB2)
0070          EXF3=EXP(-A23*XC2)
0071          EXF4=EXP(-A24*XD2)
0072          F(1)=A11*EXF1
0073          F(2)=A12*EXF2
0074          F(3)=A13*EXF3
0075          F(4)=A14*EXF4
C DK'S ARE THE FORCE CONSTANTS
0076          DK(1)=APARM(1)*F(1)*F(2)
0077          DK(2)=APARM(1)*F(1)*F(3)
0078          DK(3)=APARM(1)*F(1)*F(4)
0079          DK(4)=APARM(1)*F(2)*F(3)
0080          DK(5)=APARM(1)*F(2)*F(4)
0081          DK(6)=APARM(1)*F(3)*F(4)
C*********************************************************************************
C COMPUTE THE EQUILIBRIUM ANGLES
C FIND THE LARGEST C-H DISTANCE
0082          RGR=R(1)
0083          KLM=1
```

```
FORTRAN IV G LEVEL  21                    POT6              DATE = 76044          14/04/41

C084              IF(R(2).LT.RGR) GO TO 800
0085              RGR=R(2)
0086              KLM=2
C087        800   IF(R(3).LT.RGR) GO TO 801
0088              RGR=R(3)
0089              KLM=3
C090        801   IF(R(4).LT.RGR) GO TO 802
0091              KLM=4
0092              RGR=R(4)
0093        802   RCH=SQRT(R2(KLM)+R2(5)-2.0D0*R(KLM)*R(5)*COS(TAU))
0094              IF(R(KLM+5).GT.RCH) GO TO 4000
0095              DIJF=DIJ
0096              CPF=CP
0097              DAA=0.0D0
0098              GO TO 4001
C099        4000  IF(R(5).GT.DIJ) GO TO 4002
0100              CPF=0.339757D0/(R(5)-RE(1))
0101              DIJF=R(5)
0102              DAA=-CPF/(R(5)-RE(1))
0103              DAA=-DAA*(RGR-RE(1))
0104              GO TO 4001
0105        4002  CPF=CP
0106              DAA=0.0D0
0107              DIJF=DIJ
C108        4001  IF(RGR.GT.DIJF) GO TO 803
0109              IF(RGR.LT.RE(1)) GO TO 804
C COMPUTE EQUILIBRIUM FRONTSIDE ANGLE
0110              ASF=TAU-CPF*(RGR-RE(1))
C COMPUTE BACKSIDE EQUILIBRIUM ANGLE
C111              XYZ=SIN(ASF)
0112              ASB=ARCOS(1.0D0-1.5D0*XYZ*XYZ)
C COMPUTE DERIVATIVES OF EQUILIBRIUM ANGLE WITH RESPECT TO RGR
0113              DASF=-CPF
0114              DASB=-3.0D0*CPF*XYZ*COS(ASF)/SIN(ASB)
0115              GO TO 805
C116        803   ASF=PI/2.0D0
0117              ASB=T3PI
0118              DASF=0.0D0
0119              DASB=0.0D0
0120              GO TO 805
0121        804   ASF=TAU
C122              ASB=TAU
0123              DASF=0.0D0
0124              DASB=0.0D0
C*********************************************************************************
C COMPUTE CONTRIBUTION TO THE TOTAL ENERGY FROM THE ANGLE TERMS
0125        805   GO TO (806,807,808,809),KLM
0126        806   SUM=0.0D0
0127              IF1=1
0128              IF2=2
0129              IF3=3
0130              IB1=4
0131              IB2=5
0132              IB3=6
0133              DO 810 I=1,3
0134              Q=AG(I)-ASF
0135              Y1(I)=Q
0136              Y2(I)=Q*Q
```

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0137          810   SUM=SUM+DK(I)*Y2(I)
0138                DO 330 I=4,6
0139                Y1(I)=AG(I)-ASB
0140                Y2(I)=Y1(I)*Y1(I)
0141          830   SUM=SUM+DK(I)*Y2(I)
0142                EE=EE+0.5D0*SUM
      C#############################################################################
0143                IF(KEE.EQ.-1)RETURN
      C#############################################################################
0144                GO TO 820
0145          807   SUM=0.0D0
0146                IF1=1
0147                IF2=4
0148                IF3=5
0149                IB1=2
0150                IB2=3
0151                IB3=6
0152                O=AG(1)-ASF
0153                Y1(1)=O
0154                Y2(1)=O*O
0155                SUM=SUM+DK(1)*Y2(1)
0156                DO 811 I=4,5
0157                O=AG(I)-ASF
0158                Y1(I)=O
0159                Y2(I)=C*C
0160          811   SUM=SUM+DK(I)*Y2(I)
0161                DO 831 I=2,3
0162                Y1(I)=AG(I)-ASB
0163                Y2(I)=Y1(I)*Y1(I)
0164          831   SUM=SUM+DK(I)*Y2(I)
0165                Y1(6)=AG(o)-ASB
0166                Y2(6)=Y1(6)*Y1(6)
0167                SUM=SUM+DK(6)*Y2(6)
0168                EE=EE+0.5D0*SUM
      C#############################################################################
0169                IF(KEE.EQ.-1)RETURN
      C#############################################################################
0170                GO TO 820
0171          808   SUM=0.0D0
0172                IF1=2
0173                IF2=4
0174                IF3=6
0175                IB1=1
0176                IB2=3
0177                IB3=4
0178                DO 812 I=2,6,2
0179                Y1(I)=AG(I)-ASF
0180                Y2(I)=Y1(I)*Y1(I)
0181          812   SUM=SUM+DK(I)*Y2(I)
0182                DO 832 I=1,5,2
0183                Y1(I)=AG(I)-ASB
0184                Y2(I)=Y1(I)*Y1(I)
0185          832   SUM=SUM+DK(I)*Y2(I)
0186                EE=EE+0.5D0*SUM
      C#############################################################################
0187                IF(KEE.EQ.-1)RETURN
      C#############################################################################
0188                GO TO 820
```

```
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  0189          809 SUM=0.0D0
  0190              IF1=3
  0191              IF2=5
  0192              IF3=6
  0193              IB1=1
  0194              IB2=2
  0195              IB3=4
  0196              Y1(3)=AG(3)-ASF
  0197              Y2(3)=Y1(3)*Y1(3)
  0198              SUM=DK(3)*Y2(3)
  0199              DO 813 I=5,6
  0200              Y1(I)=AG(I)-ASF
  0201              Y2(I)=Y1(I)*Y1(I)
  0202          813 SUM=SUM+DK(I)*Y2(I)
  0203              DO 833 I=1,2
  0204              Y1(I)=AG(I)-ASB
  0205              Y2(I)=Y1(I)*Y1(I)
  0206          833 SUM=SUM+DK(I)*Y2(I)
  0207              Y1(4)=AG(4)-ASB
  0208              Y2(4)=Y1(4)*Y1(4)
  0209              SUM=SUM+DK(4)*Y2(4)
  0210              EE=EE+0.5D0*SUM
      C###############################################################################
  0211              IF(KEE.EQ.-1)RETURN
      C###############################################################################
      C*******************************************************************************
      C COMPUTE DERIVATIVES OF THE ANGLE ATTENUATION TERMS WITH RESPECT TO R6,R7,R8,
      C                        AND R9
  0212          820 DFR(1)=2.0D0*APARM(2)*R(6)*EXA11*EXF1+A11*EXF1*XA2*2.0D0*APARM(4)*
                   1 APARM(5)*XXA*EXA21
  0213              DFR(2)=2.0D0*APARM(2)*R(7)*EXA12*EXF2+A12*EXF2*XB2*2.0D0*APARM(4)*
                   1 APARM(5)*XXB*EXA22
  0214              DFR(3)=2.0D0*APARM(2)*R(8)*EXA13*EXF3+A13*EXF3*XC2*2.0D0*APARM(4)*
                   1 APARM(5)*XXC*EXA23
  0215              DFR(4)=2.0D0*APARM(2)*R(9)*EXA14*EXF4+A14*EXF4*XD2*2.0D0*APARM(4)*
                   1 APARM(5)*XXD*EXA24
      C COMPUTE DERIVATIVES OF ATTENUATION TERMS WITH RESPECT TO R1,R2,R3, AND R4
  0216              DF(1)=-2.0D0*A21*XA*F(1)
  0217              DF(2)=-2.0D0*A22*XB*F(2)
  0218              DF(3)=-2.0D0*A23*XC*F(3)
  0219              DF(4)=-2.0D0*A24*XD*F(4)
      C*******************************************************************************
      C ADD IN CONTRIBUTION TO DER FROM DK/DR ANGLE TERMS AND D(THETA)/DR TERMS
      C FIRST THREE ANGLE TERMS
  0220              DO 900 I=1,3
  0221              STP=0.5D0*DK(I)*Y2(I)
  0222              W=DK(I)*Y1(I)
  0223              DER(1)=DER(1)+STP*DF(1)/F(1)+W*(-1.0D0/(R(I+1)*ASS(I))+ACS(I)/
                   1 (R(1)*ASS(I)))
  0224              DER(I+1)=DER(I+1)+STP*DF(I+1)/F(I+1)+W*(-1.0D0/(R(1)*ASS(I))+
                   1 ACS(I)/(ASS(I)*R(I+1)))
  0225              DER(6)=DER(6)+STP*DFR(1)/F(1)
  0226              DER(I+6)=DER(I+6)+STP*DFR(I+1)/F(I+1)
  0227          900 DER(I+9)=DER(I+9)+W*R(I+9)/(R(1)*R(I+1)*ASS(I))
      C*******************************************************************************
      C FOURTH AND FIFTH ANGLE TERMS
  0228              DO 901 I=4,5
  0229              STP=0.5D0*DK(I)*Y2(I)
```

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0230              W=DK(I)*Y1(I)
0231              DER(2)=DER(2)+STP*DF(1)/F(2)+W*(-1.0D0/(ASS(I)*F(I-1))+
                 1 ACS(I)/(ASS(I)*R(2)))
0232              DER(7)=DER(7)+STP*DER(2)/F(2)
0233              DER(I-1)=DER(I-1)+STP*DF(I-1)/F(I-1)+W*(-1.0D0/(ASS(I)*F(2))+
                 1 ACS(I)/(ASS(I)*R(I-1)))
0234              DER(I+4)=DER(I+4)+STP*DER(I-1)/F(I-1)
0235       901    DER(I+9)=DER(I+9)+W*R(I+9)/(R(2)*R(I-1)*ASS(I))
          C CONTRIBUTION FROM SIXTH ANGLE TERM
0236              STP=0.500*DK(6)*Y2(6)
0237              W=DK(6)*Y1(6)
0238              DER(3)=DER(3)+STP*DF(3)/F(3)+W*(-1.0D0/(ASS(6)*R(4))+
                 1 ACS(6)/(ASS(6)*R(3)))
0239              DER(8)=DER(8)+STP*DER(3)/F(3)
0240              DER(4)=DER(4)+STP*DF(4)/F(4)+W*(-1.0D0/(ASS(6)*R(3))+
                 1 ACS(6)/(ASS(6)*R(4)))
0241              DER(9)=DER(9)+STP*DER(4)/F(4)
0242              DER(15)=DER(15)+W*R(15)/(ASS(6)*R(3)*R(4))
          C ************************************************************************
          C CONTRIBUTION FROM EQ. ANGLE VARIATION TO D(ANGLE)/DR ******
0243              DER(KLM)=DER(KLM)-(DK(IF1)*Y1(IF1)+DK(IF2)*Y1(IF2)+DK(IF3)*Y1(IF3)
                 1  )*DASF -(DK(IB1)*Y1(IB1)+DK(IB2)*Y1(IB2)+
                 2  DK(IB3)*Y1(IB3))*DASB
0244              DER(5)=DER(5)-(DK(IF1)*Y1(IF1)+DK(IF2)*Y1(IF2)+DK(IF3)*Y1(IF3))*
                 1 DAA -(DK(IB1)*Y1(IB1)+DK(IB2)*Y1(IB2)+DK(IB3)*Y1(IB3))*
                 2 *2.0D0*SIN(ASF)*COS(ASF)*DAA/SIN(ASB)
          C ************************************************************************
          C     CALL SWITCH (KMAX,2)
0245              RETURN
0246              END
```

```
0001          SUBROUTINE TRI(RR1,RR2,RR3,DR1,DR2,DR3,I,J,K,E)
      C*********************************************************************************
      C     SEE REFERENCE:  L. M. RAFF, J. CHEM. PHYS., VOL. 60, 2220(1974)
      C ROUTINE TO CALCULATE THREE-BODY ENERGY FOR ABC SYSTEM
      C RR1,RR2,RR3 ARE THE THREE INTERPARTICLE DISTANCES
      C DR1,DR2,DR3 ARE THE THREE DERIVATIVES WITH RESPECT TO RR1,RR2, AND RR3
      C I,J, AND K GIVE THE ARRAY NUMBER FOR THE APPROPRIATE POTENTIAL PARAMETERS
      C E IS THE FINAL THREE-BODY ENERGY
      C*********************************************************************************
0002          IMPLICIT REAL*8 (A-H,O-Z)
0003          DIMENSION APARM(5)
0004          DIMENSION X(6),Y(6),Z(6),R(15),DER(15),AG(6),P2(15),D1(3),D3(3),
             1 ALPH(3),RE(3),BETA(3),CC(3),AA(3),SIG(3),RSTR(3),ACS(6),DK(6),
             2 Y1(6),Y2(6),ASS(6),F(4),GF(4),RX(6),PX(6),PY(6),PZ(6),DX(6),
             3 DY(6),DZ(6),DPX(6),DPY(6),DPZ(6),DF(15,3)
0005          COMMON X,Y,Z,R,DER,AG,P2,D1,ALPH,RE,D3,BETA,CC,AA,SIG,RSTR,TAU,
             1 PV,DIJ,CP,EE,ACS,ASS,PX,XII,                 V1,V2,V3,V4,BMAX,
             2 RSS,VP,PER,H,PX,PY,PZ,WH,WC,WBK,W,DT,DX,DY,DZ,DPX,DPY,DPZ,T,DF,
             3 TEMP,RET,START,APARM,PI,T3PI,EL6PI,S6PI,
             4 III,JJJ,KKK,LLL,NV1,NV2,NV3,NV4,JJ,NI,KEE
0006          SQRT(X)=DSQRT(X)
0007          EXP(X)=DEXP(X)
0008          A=RR1-RE(I)
0009          B=RR2-RE(J)
0010          C=RR3-RE(K)
0011          A1= EXP(-ALPH(I)*A)
0012          B1= EXP(-ALPH(J)*B)
0013          C1= EXP(-ALPH(K)*C)
0014          A2=A1*A1
0015          B2=B1*B1
0016          C2=C1*C1
0017          E1AB=D1(I)*(A2-2.0D0*A1)
0018          E1AC=D1(J)*(B2-2.0D0*B1)
0019          E1BC=D1(K)*(C2-2.0D0*C1)
0020          DF1AB=2.0D0*ALPH(I)*D1(I)*(A1-A2)
0021          DF1AC=2.0D0*ALPH(J)*D1(J)*(B1-B2)
0022          DF1BC=2.0D0*ALPH(K)*D1(K)*(C1-C2)
0023          IF(RR1-RSTR(I))1,2,2
0024       1  AA1= EXP(-BETA(I)*A)
0025          AA2=AA1*AA1
0026          E3AB=D3(I)*(AA2+2.0D0*AA1)
0027          DE3AB=-2.0D0*BETA(I)*D3(I)*(AA1+AA2)
0028          GO TO 3
0029       2  AA1= EXP(-SIG(I)*RR1)
0030          E3AB=CC(I)*(RR1+AA(I))*AA1
0031          DF3AB=CC(I)*AA1*(1.0D0-SIG(I)*RR1-SIG(I)*AA(I))
0032       3  IF(RR2-RSTR(J))4,5,5
0033       4  BB1= EXP(-BETA(J)*B)
0034          BB2=BB1*BB1
0035          E3AC=D3(J)*(BB2+2.0D0*BB1)
0036          DE3AC=-2.0D0*BETA(J)*D3(J)*(BB1+BB2)
0037          GO TO 6
0038       5  BB1= EXP(-SIG(J)*RR2)
0039          F3AC=CC(J)*(RR2+AA(J))*BB1
0040          DE3AC=CC(J)*BB1*(1.0D0-SIG(J)*RR2-SIG(J)*AA(J))
0041       6  IF(RR3-RSTR(K)) 7,8,8
0042       7  CC1= EXP(-BETA(K)*C)
0043          CC2=CC1*CC1
```

```
0044            E3BC=D3(K)*(CC2+2.0D0*CC1)
0045            DE3BC=-2.0D0*BETA(K)*D3(K)*(CC1+CC2)
0046            GO TO 9
0047      8     CC1 = EXP(-SIG(K)*RR3)
0048            E3BC=CC(K)*(RP3+AA(K))*CC1
0049            DE3BC=CC(K)*CC1*(1.0D0-SIG(K)*RR3-SIG(K)*AA(K))
0050      9 QAB=(E1AB+E3AB)/2.0D0
0051            QAC=(E1AC+E3AC)/2.0D0
0052            QBC=(E1BC+E3BC)/2.0D0
0053            ALAB=(E1AB-E3AB)/2.0D0
0054            ALAC=(E1AC-E3AC)/2.0D0
0055            ALBC=(E1BC-E3BC)/2.0D0
0056            XX=ALAB-ALBC
0057            YY=ALBC-ALAC
0058            ZZ=ALAC-ALAB
0059            U=(XX*XX+YY*YY+ZZ*ZZ)/2.0D0
0060            U=SQRT(U)
0061            E=QAB+QBC+QAC-U
0062            BB=4.0D0*U
0063            DR1=(DE1AB+DE3AB)/2.0D0-(2.0D0*ALAB-ALBC-ALAC)*(DE1AB-DE3AB)/BB
0064            DR2=(DE1AC+DE3AC)/2.0D0-(2.0D0*ALAC-ALAB-ALBC)*(DE1AC-DE3AC)/BB
0065            DR3=(DE1BC+DE3BC)/2.0D0-(2.0D0*ALBC-ALAC-ALAB)*(DE1BC-DE3BC)/BB
0066            RETURN
0067            END
```

```
0001          SUBROUTINE PLACE(R1)
C*********************************************************************************
C    SEE REFERENCE:  L. M. RAFF, J. CHEM. PHYS., VOL. 60, 2220(1974)
C ROUTINE TO PLACE H2,H3,AND H4 IN EQUILIBRIUM POSITIONS FOR A GIVEN
C H1 DISTANCE EQUAL TO R1
C*********************************************************************************
0002          IMPLICIT REAL*8 (A-H,O-Z)
0003          DIMENSION APARM(5)
0004          DIMENSION X(6),Y(6),Z(6),R(15),DER(15),AG(6),R2(15),D1(3),D3(3),
     1 ALPH(3),RE(3),BETA(3),CC(3),AA(3),SIG(3),RSTR(3),ACS(6),DK(6),
     2 Y1(6),Y2(6),ASS(6),F(4),GF(4),RX(6),PX(6),PY(6),PZ(6),DX(6),
     3 DY(6),DZ(6),DPX(6),DPY(6),DPZ(6),DF(15,3)
0005          COMMON X,Y,Z,R,DER,AG,R2,D1,ALPH,RE,D3,BETA,CC,AA,SIG,RSTR,TAU,
     1 RV,DIJ,CP,EE,ACS,ASS,RX,XII,                    V1,V2,V3,V4,BMAX,
     2 RSS,VR,PFP,H,PX,PY,PZ,WH,WC,WBR,W,DT,DX,DY,DZ,DPX,DPY,DPZ,T,DF,
     3TEMP,PPT,START,APARM,PI,T3PI,EL6PI,S6PI,
     4III,JJJ,KKK,LLL,NV1,NV2,NV3,NV4,JJ,NI,KEE
0006          SIN(X)=DSIN(X)
0007          ARCOS(X)=DARCOS(X)
0008          COS(X)=DCOS(X)
0009          SQRT(X)=DSQRT(X)
C////////////////////////////////////////////////////////////////////////////////
C    SET ANGLE CUT OF THE XY PLANE DESCRIBED BY THE C-H BONDS IN THE CH3 GROUP.
C    BASED ON THE R1 DISTANCE FED TO THIS ROUTINE.
0010          IF(R1.LE.DIJ)GO TO 9
0011        8 TS=PI/2.0D0
0012          GO TO 10
0013        9 IF(R1.LT.RE(1))GO TO 11
0014          TS=TAU-CP*(R1-RE(1))
0015       10 CONTINUE
0016          GO TO 12
0017       11 TS=TAU
0018       12 CONTINUE
C////////////////////////////////////////////////////////////////////////////////
C    CALCULATE ALL CARTESIAN COORDINATE ATOM POSITIONS EXCEPT Z(1) AND Z(6)
C    WHICH ARE SET IN THE MAIN PROGRAM.
0019          S=SIN(TS)
0020          C=COS(TS)
0021          X(1)=0.0D0
0022          Y(1)=0.0D0
0023          X(2)=0.0D0
0024          Y(2)=RE(1)*S
0025          Z(2)=RE(1)*C
0026          X(3)=RE(1)*S*COS(EL6PI)
0027          Y(3)=RE(1)*S*SIN(EL6PI)
0028          Z(3)=RE(1)*C
0029          X(4)=RE(1)*S*COS(S6PI)
0030          Y(4)=RE(1)*S*SIN(S6PI)
0031          Z(4)=RE(1)*C
0032          X(5)=0.0D0
0033          Y(5)=0.0D0
0034          Z(5)=0.0D0
0035          X(6)=0.0D0
0036          Y(6)=0.0D0
0037          RETURN
0038          END
```

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```
0001            SUBROUTINE DIST
        C*********************************************************************************
        C     SEE REFERENCE:  L. M. RAFF, J. CHEM. PHYS., VOL. 60, 2220(1974)
        C     ROUTINE TO COMPUTE THE INTERPARTICLE DISTANCES FROM THE CARTESIAN
        C         COORDINATES OF THE ATOMS
        C*********************************************************************************
0002            IMPLICIT REAL*8 (A-H,O-Z)
0003            DIMENSION APARM(5)
0004            DIMENSION X(6),Y(6),Z(6),R(15),DER(15),AG(6),R2(15),D1(3),D3(3),
       1 ALPH(3),RE(3),BETA(3),CC(3),AA(3),SIG(3),RSTR(3),ACS(6),DK(6),
       2 Y1(6),Y2(6),ASS(6),F(4),GF(4),RX(6),PX(6),PY(6),PZ(6),DX(6),
       3 DY(6),DZ(6),DPX(6),DPY(6),DPZ(6),DF(15,3)
0005            COMMON X,Y,Z,R,DER,AG,R2,D1,ALPH,RE,D3,BETA,CC,AA,SIG,RSTR,TAU,
       1 RV,DIJ,CP,EE,ACS,ASS,RX,XII,                      V1,V2,V3,V4,BMAX,
       2 RSS,VP,PER,H,PX,PY,PZ,WH,WC,WBR,W,DT,DX,DY,DZ,DPX,DPY,DPZ,T,DF,
       3 TEMP,RCT,START,APARM,PI,T3PI,EL6PI,S6PI,
       4 III,JJJ,KKK,LLL,NV1,NV2,NV3,NV4,JJ,NI,KEE
0006            SQRT(X)=DSQRT(X)
0007            DO 1 I=1,4
0008            DF(I,1)=X(I)-X(5)
0009            DF(I,2)=Y(I)-Y(5)
0010            DF(I,3)=Z(I)-Z(5)
0011            R2(I)=DF(I,1)*DF(I,1)+DF(I,2)*DF(I,2)+DF(I,3)*DF(I,3)
0012    1       R(I) = SQRT(R2(I))
0013            DF(5,1)=X(5)-X(6)
0014            DF(5,2)=Y(5)-Y(6)
0015            DF(5,3)=Z(5)-Z(6)
0016            R2(5)=DF(5,1)*DF(5,1)+DF(5,2)*DF(5,2)+DF(5,3)*DF(5,3)
0017            R(5) = SQRT(R2(5))
0018            DO 2 I=1,4
0019            J=I+5
0020            DF(J,1)=X(I)-X(6)
0021            DF(J,2)=Y(I)-Y(6)
0022            DF(J,3)=Z(I)-Z(6)
0023            R2(J)=DF(J,1)*DF(J,1)+DF(J,2)*DF(J,2)+DF(J,3)*DF(J,3)
0024    2       R(J)= SQRT(R2(J))
0025            DO 3 I=1,3
0026            J=I+1
0027            K=I+9
0028            DF(K,1)=X(1)-X(J)
0029            DF(K,2)=Y(1)-Y(J)
0030            DF(K,3)=Z(1)-Z(J)
0031            R2(K)=DF(K,1)*DF(K,1)+DF(K,2)*DF(K,2)+DF(K,3)*DF(K,3)
0032    3       R(K)= SQRT(R2(K))
0033            DO 4 I=1,2
0034            J=I+2
0035            K=I+12
0036            DF(K,1)=X(2)-X(J)
0037            DF(K,2)=Y(2)-Y(J)
0038            DF(K,3)=Z(2)-Z(J)
0039            R2(K)=DF(K,1)*DF(K,1)+DF(K,2)*DF(K,2)+DF(K,3)*DF(K,3)
0040    4       R(K) = SQRT(R2(K))
0041            DF(15,1)=X(3)-X(4)
0042            DF(15,2)=Y(3)-Y(4)
0043            DF(15,3)=Z(3)-Z(4)
0044            R2(15)=DF(15,1)*DF(15,1)+DF(15,2)*DF(15,2)+DF(15,3)*DF(15,3)
0045            R(15)= SQRT(R2(15))
0046            RETURN
0047            END
```

```
FORTRAN IV G LEVEL  21              ANGLE            DATE = 76044          14/04/41

0001            SUBROUTINE ANGLE
        C*******************************************************************************
        C    SEE REFERENCE:  L. M. RAFF, J. CHEM. PHYS., VCL. 60, 2220(1974)
        C ROUTINE TO COMPUTE CH4 ANGLES FROM THE INTERPARTICLE DISTANCES
        C*******************************************************************************
0002            IMPLICIT REAL*8 (A-H,O-Z)
0003            DIMENSICN APARM(5)
0004            DIMENSIONXX(6),Y(6),Z(6),R(15),DER(15),AG(6),R2(15),D1(3),D3(3),
                1 ALPH(3),PE(3),BETA(3),CC(3),AA(3),SIG(3),RSTR(3),ACS(6),DK(6),
                2 Y1(6),Y2(6),ASS(6),F(4),GF(4),RX(6),PX(6),PY(6),PZ(6),DX(6),
                3 DY(6),DZ(6),DPX(6),DPY(6),DPZ(6),DF(15,3)
0005            COMMONXX,Y,Z,R,DER,AG,R2,DI,ALPH,PE,D3,BETA,CC,AA,SIG,RSTR,TAU,
                1 RV,DIJ,CP,EE,ACS,ASS,RX,XII,                    V1,V2,V3,V4,BMAX,
                2 RSS,VR,PER,H,PX,PY,PZ,WH,WC,WBR,W,DT,DX,DY,DZ,DPX,DPY,DPZ,T,CF,
                3TEMP,RRT,START,APARM,PI,T3PI,EL6PI,S6PI,
                4III,JJJ,KKK,LLL,NV1,NV2,NV3,NV4,JJ,NI,KEE
0006            SQRT(X)=DSQRT(X)
0007            ARCOS(X)=DARCOS(X)
0008            DO 2 I=1,3
0009            X=(R2(1)+R2(I+1)-R2(I+9))/(2.0D0*R(1)*R(I+1))
0010            ACS(I)=X
0011            ASS(I)=SQRT(1.0D0-X*X)
0012    2       AG(I)= ARCOS(X)
0013            DO 3 I=1,2
0014            X=(R2(2)+R2(I+2)-R2(I+12))/(2.0D0*R(2)*R(I+2))
0015            ACS(I+3) =X
0016            ASS(I+3)=SQRT(1.0D0-X*X)
0017    3       AG(I+3)= ARCOS(X)
0018            X=(R2(3)+R2(4)-R2(15))/(2.0D0*R(3)*R(4))
0019            ACS(6)=X
0020            ASS(6)=SQRT(1.0D0-X*X)
0021            AG(6)= ARCOS(X)
0022            RETURN
0023            END
```

```
0001          SUBROUTINE READ
       C     SEE REFERENCE:  L. M. RAFF, J. CHEM. PHYS., VOL. 60, 2220(1974)
       C ROUTINE TO READ IN INITIAL POTENTIAL SURFACE PARAMETERS
       C ROUTINE ALSO READS IN  INITIAL DYNAMIC VARIABLES
0002          IMPLICIT REAL*8 (A-H,O-Z)
0003          DIMENSION X(6),Y(6),Z(6),R(15),DER(15),AG(6),R2(15),D1(3),D3(3),
             1 ALPH(3),RE(3),BETA(3),CC(3),AA(3),SIG(3),RSTR(3),ACS(6),DK(6),
             2 Y1(6),Y2(6),ASS(6),F(4),GF(4),RX(6),PX(6),PY(6),PZ(6),DX(6),
             3 DY(6),DZ(6),DPX(6),DPY(6),DPZ(6),DF(15,3)
0004          DIMENSION APARM(5)
0005          COMMON X,Y,Z,R,DER,AG,R2,D1,ALPH,RE,D3,BETA,CC,AA,SIG,RSTR,TAU,
             1 RV,DIJ,CP,EE,ACS,ASS,RX,XII,                V1,V2,V3,V4,BMAX,
             2 RSS,VP,PER,H,PX,PY,PZ,WH,WC,WBR,W,DT,DX,DY,DZ,DPX,DPY,DPZ,T,DF,
             3TEMP,RRT,START,APARM,PI,T3PI,EL6PI,S6PI,
             4III,JJJ,KKK,LLL,NV1,NV2,NV3,NV4,JJ,NI,KFE
0006          READ(5,100) D1,D3,ALPH,RE,BETA,CC,AA,SIG,RSTR
0007      100 FORMAT(3D15.8)
0008          READ(5,101) TAU,RV
0009          READ(5,101) DIJ,CP
0010      101 FORMAT(2D15.8)
0011      102 FORMAT('H')
0012          WRITE(6,102)
0013          WRITE(6,103)
0014      103 FORMAT(38X,'SURFACE PARAMETERS',///)
0015          WRITE(6,104)
0016      104 FORMAT(19X,'C-H',23X,'H-X',23X,'C-X',/,33X,'SINGLET-STATE PARAMETERS',//)
             1RS',//)
0017          WRITE(6,105) D1,ALPH,RE
0018      105 FORMAT(5X,2HD1,3X,3(1PD20.8),/,3X,4HALPH,3X,3(1PD20.8),/,
             1 5X,2HRE,3X,3(1PD20.8),//)
0019          WRITE(6,106)
0020      106 FORMAT(33X,'TRIPLET-STATE PARAMETERS',//)
0021          WRITE(6,107) D3,BETA,CC,AA,SIG,RSTR
0022      107 FORMAT(5X,2HD3,3X,3(1PD20.8),/,3X,4HBETA,3X,3(1PD20.8),/,
             1 6X,1HC,3X,3(1PD20.8),/,6X,1HA,3X,3(1PD20.8),/,
             2 4X,3HSIG,3X,3(1PD20.8),/,3X,4HRSTR,3X,3(1PD20.8),///)
0023          WRITE(6,108) TAU,RV
0024      108 FORMAT(25X,28HEQUILIBRIUM ANGLE PARAMETERS,/,15X,4HTAU=,1PD20.12,
             1 5X,3HRV=,1PD20.12,///)
0025          WRITE(6,109) DIJ,CP
0026      109 FORMAT(25X,28HEQUILIBRIUM ANGLE PARAMETERS,/,15X,
             1 38HUPPER LIMIT PARAMETER-FRONTSIDE ANGLE=,1PD20.12,/,15X,
             2 32HSLOPE PARAMETER-FRONTSIDE ANGLE=,1PD20.12,/)
       C READ IN INITIAL RANDOM NUMBER--7 DECIMAL DIGITS.0
0027          READ(5,101) RX(1)
       C READ CH4 FUNDAMENTAL FREQUENCIES
0028          READ(5,110) V1,V2,V3,V4
0029      110 FORMAT(4D15.8)
       C READ IN MASSES
0030          READ(5,110) WH,WC,WBR
       C  READ IN BMAX AND RSS
0031          READ(5,101) BMAX,RSS
       C READ IN INITIAL VIBRATIONAL QUANTUM NUMBERS
0032          READ(5,111) NV1,NV2,NV3,NV4
0033      111 FORMAT(4I12)
       C READ INTEGRATION STEP SIZE
0034          READ(5,101) DT
       C READ INITIAL RELATIVE VELOCITY
```

```
0035              READ(5,101) VR
          C READ TEMPERATURE FOR ROTATIONAL AVERAGING
0036              READ(5,101) TEMP
0037              WRITE(6,112) PX(1)
0038          112 FORMAT(15X,22HINITIAL RANDOM NUMBER=,1PD20.12,/)
0039        * WRITE(6,113) V1,V2,V3,V4
0040          113 FORMAT(15X,'METHANE FUNDAMENTAL FREQUENCIES (IN EV.):',/,20X,3HV1=,
             1 ,D20.10,5X,3HV2=,D20.10,5X,3HV3=,D20.10,5X,3HV4=,D20.10,/)
0041              WRITE(6,114) WH,WC,WB9
0042          114 FORMAT(15X,6HMASSES,5X,2HH=,1PD20.10,5X,2HC=,2PD20.10,5X,2HX=,1PD2
             10.10,/)
0043              WRITE(6,115) BMAX,RSS
0044          115 FORMAT(15X,25HMAXIMUM IMPACT PARAMETER=,1PD20.8,5X,4HRSS=,1PD20.8,/)
             1 /)
0045              WRITE(6,116) NV1,NV2,NV3,NV4
0046          116 FORMAT(15X,32HINITIAL VIBRATION STATES OF CH4:,5X,4HNV1=,I3,5X,
             1 4HNV2=,I3,5X,4HNV3=,I3,5X,4HNV4=,I3,/)
0047              WRITE(6,117) VR,DT,TEMP
0048          117 FORMAT(15X,'9HRELATIVE VELOCITY=,1PD20.8,5X,'INTEGRATION STEP SIZE=
             1 =',1PD20.8,/,15X,'ROTATIONAL TEMPERATURE=',1PD20.8,/)
          C READ CONTROL PARAMETERS
0049              READ(5,111) III,JJJ,KKK,LLL
0050              READ(5,101) RPT,START
          C READ IN ANGULAR PARAMETERS
0051              READ(5,120) APARM
0052          120 FORMAT(5D15.8)
0053              WRITE(6,121)(I,APARM(I),I=1,5)
0054          121 FORMAT(15X,'ANGULAR ATTENUATION PARAMETERS:',/,10X,
             1 3(5X,'APARM(',I2,')=',1PD18.10),/,10X,2(5X,'APARM(',I2,')=',1PD18
             *.10),/)
0055              WRITE(6,122) RRT,START
0056          122 FORMAT(15X,'DISTANCE PARAMETERS',/,20X,'FINAL TEST DISTANCE=',
             1 1PD20.10,5X,'TWO-BODY DISTANCE=',1PD20.10,/)
0057              WRITE(6,102)
0058              RETURN
0059              END
```

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```
0001            SUBROUTINE TETRAH(TAU,PI)
        C      A DOUBLE PRECISION VALUE FOR PI MUST BE SUPPLIED
        C      THIS ROUTINE CALCULATES THE TETRAHEDRAL ANGLE TO DOUBLE PRECISION ACCURACY.
        C##############################################################################
        C      X=HEIGHT OF EQUILATERAL TRIANGLE FACE OF REGULAR TETRAHEDRON (EDGE=1).
        C      THETA=INTERNAL ANGLE BETWEEN FACES.
        C      PHI=INTERNAL ANGLE BETWEEN FACE AND AN EDGE OF TETRAHEDRAN.
        C      H=HEIGHT OF PYRAMID  (REGULAR TETRAHEDRON).
        C      Y=LENGTH BETWEEN ANY CORNER AND CENTER OF ANY FACE.
        C      GAMMA=ANGLE BETWEEN LINE H AND CORRESPONDING EDGE.
        C      TAU=TETRAHEDRAL ANGLE.
        C##############################################################################
0002            IMPLICIT REAL*8(A-H,O-Z)
0003            X=DSIN(PI/3.0D0)
0004            C=(2.0D0*(X*X)-1.0D0)/(2.0D0*(X*X))
0005            THETA = DARCOS(C)
0006            PHI=(PI-THETA)/2.0D0
0007            Y=0.5D0/X
0008            D=(Y*Y)+1.0D0-(2.0D0*Y*DCOS(PHI))
0009            H=DSQRT(D)
0010            F=((H*H)+1.0D0-(Y*Y))/(2.0D0*H)
0011            GAMMA=DARCOS(F)
0012            TAU=PI-(2.0D0*GAMMA)
0013            TAUD=(TAU/PI)*180.0D0
0014            WRITE(6,1)TAU,TAUD
0015          1 FORMAT(/,1X,'TETRAHEDRAL ANGLE =',1PD24.16,' RADIANS OR ',
               '3PD24.14,' DEGREES',//)
0016            RETURN
0017            END
```

```
C ***********************************************************************
C      INTERNAL COORDINATE FORCE CONSTANT ROUTINE
C ***********************************************************************
0001          IMPLICIT REAL*8 (A-H,O-Z)
C        SPECIFIC DIMENSION FOR MAIN PROGRAM
0002          DIMENSION E(15,15,7,7),D(15,15,7),DD(15,15),RK(15),AGK(6),XK(6),YK
     1(6),ZK(6),XKC(6),YKC(6),ZKC(6),AGKC(6)
     2 ,DD3(15,15)
C        THE VARIABLES E, D, & DD REQUIRE 102,600 BYTES OF CORE BY THEMSELVES
0003          REAL*8 DDLV(2,15,15),RKC(15)
0004          DIMENSION APARM(5)
0005          DIMENSION X(6),Y(6),Z(6),R(15),DER(15),AG(6),R2(15),D1(3),D3(3),
     1 ALPH(3),RE(3),BETA(3),CC(3),AA(3),SIG(3),RSTR(3),ACS(6),DK(6),
     2 Y1(6),Y2(6),ASS(6),F(4),GF(4),RX(6),PX(6),PY(6),PZ(6),DX(6),
     3 DY(6),DZ(6),DPX(6),DPY(6),DPZ(6),DF(15,3)
0006          COMMON X,Y,Z,R,DER,AG,R2,D1,ALPH,RE,D3,BETA,CC,AA,SIG,RSTR,TAU,
     1 RV,D1J,CP,EE,ACS,ASS,RX,XII,              V1,V2,V3,V4,BMAX,
     2 RSS,VR,PER,H,PX,PY,PZ,WH,WC,WBR,W,DT,DX,DY,DZ,DPX,DPY,DPZ,T,DF,
     3TEMP,RRT,START,APARM,PI,T3PI,EL6PI,S6PI,
     4III,JJJ,KKK,LLL,NV1,NV2,NV3,NV4,JJ,NI,KEE
C >>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>
C      THIS PROGRAM CALCULATES SECOND DERIVATIVES WITH RESPECT TO THE INTERNAL
C      COORDINATES OF THE CH5 H ATOM ABSTRACTION REACTION SYSTEM WHICH ARE
C      RELATED TO THE POT6 POTENTIAL ENERGY SURFACE COORDINATE SYSTEM..
C <<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<
C      READ IN SET OF POTENTIAL SURFACE PARAMETERS
0007          CALL READ
C >>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>
C      THE INTEGER "IRC" TELLS THE PROGRAM WHETHER IT IS TO READ IN  THE INTER-
C      ATOMIC DISTANCES (IF IRC IS GREATER THAN OR EQUAL TO ZERO)  OR
C      IF THE PROGRAM  IS TO READ IN THE CARTESIAN COORDINATES OF THE ATOMS,
C      (IF  IRC IS LESS THAN ZERO).
C >>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>
0008          READ(5,770)IRC,RINK
0009      770 FORMAT(I2,D10.3)
C####################################################################################
C
0010          KEE=-1
C    IF KEE EQUALS "-1" THEN POT6 WILL NOT COMPUTE ITS INTERNAL DERIVATIVES.
C
C####################################################################################
0011          DO 1 I=1,15
0012          R(I)=0.0D0
0013          RK(I)=0.0D0
0014          R2(I)=0.0D0
0015        1 CONTINUE
0016          DO 2 I=1,6
0017          X(I)=0.0D0
0018          Y(I)=0.0D0
0019          Z(I)=0.0D0
0020          XK(I)=0.0D0
0021          YK(I)=0.0D0
0022          ZK(I)=0.0D0
0023          AG(I)=0.0D0
0024          AGK(I)=0.0D0
0025        2 CONTINUE
0026          I=1
```

```
                      C    READ IN CONFIGURATION GEOMETRY
                      C4444444XZ4Z44444446445444A4444444444444444444444Z4444444Z4444444444444444
0027                         IF(IRC)4,3,3
                      C44444444444444444444444444444444444444444444444444444444444444444444444444
                      C    READ IN INITIAL INTERATOMIC DISTANCES
                      C    USING "4D20.13" FORMAT.
                      C4444444444444444444444444444444444444444444444444444444444444444444444444
C028                    3 READ(5,771)(R(I),I=1,15)
0029                  771 FORMAT(4D20.13)
C030                       OR1=R(1)
0031                       WRITE(6,772)(I,R(I),I=1,15)
0032                  772 FORMAT(//,5X,'INITIAL INTERATOMIC DISTANCES',/,15(7X,'R',I2,'=',1P
                     *D20.10,/))
C033                       GO TO 5
                      C4444444444444444444444444444444444444444444444444444444444444444444444444
                      C    READ IN CARTESIAN COORD. OF THE ATOMS IN ORDER OF THEIR ATOM NUMBER
                      C    ONE ATOM PER CARD USING "3D20.13" FORMAT.
                      C4444444444444444444444444444444444444444444444444444444444444444444444444
C034                    4 READ(5,773)(X(I),Y(I),Z(I),I=1,6)
0035                  773 FORMAT(3D20.13)
C036                       WRITE(6,774)(I,X(I),Y(I),Z(I),I=1,6)
C037                  774 FORMAT(//,1X,'ATOM',9X,'X',19X,'Y',19X,'Z',/,6(I4,2X,3D20.12,/))
                      C    CALCULATE INTERATOMIC DISTANCES IF CARTESIAN COORDINATES WERE READ IN.
C038                       CALL DIST
C039                       OR1=R(1)
0040                       WRITE(6,772)(I,R(I),I=1,15)
C041                    5 CONTINUE
0042                       WRITE(6,775)
0043                  775 FORMAT('1')
                      C ///////////////////////////////////////////////////////////////////////////
                      C    CALCULATE DOUBLE PRECISION PI AND FRACTIONS OF PI.
0044                       PI=2.0D0*DARSIN(1.0D0)
C045                       T3PI=(2.0D0*PI)/3.0D0
0046                       EL6PI=(11.0D0*PI)/6.0D0
0047                       S6PI=(7.0D0*PI)/6.0D0
                      C ///////////////////////////////////////////////////////////////////////////
                      C    CALCULATE DOUBLE PRECISION TETRAHEDRAL ANGLE NECESSARY FOR GEOMETRY CALCULA
                      C    -TIONS.
0048                       CALL TETRAH(TAU,PI)
0049                       IF(IRC)7,6,6
                      C ///////////////////////////////////////////////////////////////////////////
                      C    IF INTERATOMIC DISTANCES WERE READ IN , CALCULATE THE CH3 CARTESIAN COORDIN
                      C    -ATE ATOM POSITIONS BASED ON H1 ATOM ABSTRACTION DIATANCE R(1).
C050                    6 CALL PLACE(OR1)
0051                       Z(1)=OR1
0052                       Z(6)=R(5)
                      C ///////////////////////////////////////////////////////////////////////////
                      C    CALCULATE INTERATOMIC DISTANCES FROM CARTESIAN COORDINATES.
0053                       CALL DIST
C054                    7 CONTINUE
0055                       DO 8 I=1,15
0056                    8 RK(I)=R(I)
                      C ///////////////////////////////////////////////////////////////////////////
                      C    CALCULATE HCH ANGLES BASED ON INTERATOMIC DISTANCES.
0057                       CALL ANGLE
C058                       DO 9 I=1,6
0059                       XK(I)=X(I)
0060                       YK(I)=Y(I)
```

```
0061              ZK(I)=Z(I)
0062            9 AGK(I)=AG(I)
0063              WRITE(6,778)PI
0064          778 FORMAT(//,1X,'PI=',1PD24.15)
0065              WRITE(6,776)(I,R(I),I=1,15)
0066          776 FORMAT(//,6X,'INTERATOMIC DISTANCES',/,15(7X,'R',I2,'=',1PD20.12,/)
             1 ))
0067              WRITE(6,777)(I,AG(I),I=1,6)
0068          777 FORMAT(5X,'HCH ANGLES THETA',/,1X,6('T',I1,'=',1PD17.10,1X)/)
     C /////////////////////////////////////////////////////////////////////////////////
     C     CALCULATE EQUILIBRIUM GEOMETRY ENERGY.
0069              CALL PUT6
     C /////////////////////////////////////////////////////////////////////////////////
     C     CALCULATE FORCE CONSTANT CONVERSION FACTORS
     C     FACTOR TO CONVERT EV / (BOHR RADIUS)**2 TO MDYNE/ANGSTROM
0070              FACT=0.160210D0/(0.52916700*0.52916700)
     C     FACTOR TO CONVERT EV TERMS TO MDYNE-ANGSTROM (ANGLE TERMS)
0071              TFACT=0.160210D0
     C     FACTOR TO CONVERT EV / (RADIAN*BOHR RADIUS) TO MDYNE/RADIAN
     C     (ANGLE-STRETCH CROSS TERMS)
0072              CFACT=0.160210D0/0.52916700
0073              WRITE(6,774)(I,XK(I),YK(I),ZK(I),I=1,6)
0074              WRITE(6,775)
0075              I=1
0076              EEE=EL+18.323200
     C ********************************************************************************
     C     E = CALCULATED ENERGY MATRIX CAPABLE OF STORING 49 INCREMENTAL ENERGIES
     C         NEEDED FOR CALCULATING EACH INTERNAL COORDINATE FORCE CONSTANT IN THE
     C         13X13 MATRIX
     C     D = FIRST DERIVATIVE MATRIX BY SEVEN POINT METHOD
     C     DD = SECOND DERIVATIVE MATRIX BY SEVEN POINT METHOD
     C     DD3 = SECOND DERIVATIVE MATRIX BY 3 POINT METHOD
     C     XK, YK, ZK, XKC, YKC, AND ZKC = CARTESIAN COORDINATE CONSTANTS FOR RESETTIN
     C     G ATOM POSITIONS TO THE ORIGINAL OR AN INTERMEDIATE CONFIGURATION
     C     RK, AGK, AND AGKC = INTERATOMIC DISTANCE AND HCH ANGLE CONSTANTS FOR RESETT
     C                   ING INCREMENTED COORDINATES
     C     A, B, AND C = COEFFICIENTS OF THE SEVEN POINT DIFFERENTIATION METHOD
     C                   EQUATION
     C ********************************************************************************
0077              DO 10 I=1,15
0078              DO 10 IC=1,15
0079              DD(I,IC)=0.0D0
0080              DD3(I,IC)=0.0D0
0081              DO 10 IN=1,7
0082              D(I,IC,IN)=0.0D0
0083              DO 10 INC=1,7
0084              KE=IN+INC
0085              IF(KE.EQ.8)GO TO 12
0086              E(I,IC,IN,INC)=0.0D0
0087              GO TO 10
0088           12 E(I,IC,IN,INC)=EEE
0089           10 CONTINUE
     C     START INCREMENTING FOR ENERGY SETS
0090              A=0.75D0
0091              B=-0.15D0
0092              C=0.15D0/9.0D0
0093              KEY=1
0094              KD=1
```

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C095              DAX=0.0D0
C096              DAY=0.CD0
C097              DO 21 I=1,15
        C //////////////////////////////////////////////////////////////////////////////////
        C    NO INTERNAL COORDINATES CORRESPOND TO PUT6 COORDINATES 5, 7, 8, AND 9.
C098              IF(I.EQ.5.OR.I.EQ.9)GO TO 21
        C //////////////////////////////////////////////////////////////////////////////////
        C    INTERNAL COORDINATE LINEAR BENDS ARE KEYED BY LABELS FOR PUT6 COORDINATES
        C    7 & 8.
C099              IF(I.EQ.7.OR.I.EQ.8)KEY=I-6
0100              DO 20 IC=1,15
0101              IF(IC.EQ.5.OR.IC.EQ.9)GO TO 20
C102              IF(IC.EQ.7.OR.IC.EQ.8)KO=IC-6
0103              DO 19 IN=1,7
C104              IF(I.EC.IC)GO TO 80
0105              BH=RINK*(IN-4)
C106              GO TO 81
C107          80 IF(IN.GT.1.AND.IN.LT.7)GO TO 19
C108              GO TO 641
C109          81 CONTINUE
C110              R(I)=RK(I)+BH
0111              IF(I.GE.10)AG(I-9)=AGK(I-9)+BH
J112              IF(I.EQ.7.OR.I.EQ.8)GO TO 60
C113              GO TO 64
C114          60 CONTINUE
C115              GO TO (61,62),KEY
C116          61 ALPHAX=PI+BH
        C        DAX=PI-ALPHAX
0117              DAX=-1.0D0*BH
0118              WRITE(6,785)DAX,DAY
0119              GO TO 63
C120          62 ALPHAY=PI+BH
        C        DAY=PI-ALPHAY
0121              DAY=-1.0D0*BH
C122              WRITE(6,785)DAX,DAY
C123          63 CALL ALBEND(DAX,DAY)
0124              WRITE(6,784)KEY
0125         785 FORMAT(1X,'DAX=',1PD20.12,10X,'DAY=',1PD20.12)
0126         784 FORMAT(1X,'KEY=',I3)
0127          64 CONTINUE
        C //////////////////////////////////////////////////////////////////////////////////
        C    SET PUT6 COORDINATES 5,7,8, & 9 TO CORRESPOND TO THE INTERNAL COORDINATE INC
        C    REMENT FOR THE I TH  COORDINATE.
C128              IF(I.EQ.1)CALL Q1(DAX,DAY)
J129              IF(I.EQ.6)CALL J6(DAX,DAY)
C130              IF(I.GT.1.AND.I.LT.5)CALL QRESET(I,RK,XK,YK,ZK,AGK)
C131              IF(I.GT.9)CALL JANSET(I,RK,XK,YK,ZK,AGK)
0132         641 CONTINUE
C133              DO 16 KK=1,6
C134              XKC(KK)=X(KK)
C135              YKC(KK)=Y(KK)
C136              ZKC(KK)=Z(KK)
C137          16 AGKC(KK)=AG(KK)
C138              DO 161 KK=1,15
C139         161 RKC(KK)=R(KK)
C140              DO 18 INC=1,7
C141              IF(I.EC.IC)GO TO 85
0142              CH=RINK*(INC-4)
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0143              GO TO 86
0144          85 IF((IN+INC).EQ.8)GO TO 18
0145              CH=RINK*(IN+INC-8)
0146          86 CONTINUE
0147              R(IC)=RK(IC)+CH
0148              IF(IC.GE.10)AG(IC-9)=AGK(IC-9)+CH
      C        CROSS IC TERMS
0149              IF(IC.EQ.7.OR.IC.EQ.8)GO TO 65
0150              GO TO 69
0151          65 CONTINUE
0152              GO TO (66,67),KJ
0153          66 ALPHAX=PI+CH
      C        DAX=PI-ALPHAX
0154              DAX=-1.0D0*CH
0155              WRITE(6,785)DAX,DAY
0156              GO TO 68
0157          67 ALPHAY=PI+CH
      C        DAY=PI-ALPHAY
0158              DAY=-1.0D0*CH
0159              WRITE(6,785)DAX,DAY
0160          68 CALL ALBEND(DAX,DAY)
0161              WRITE(6,786)KU
0162         786 FORMAT(1X,'KU=',I3)
0163          69 CONTINUE
      C ///////////////////////////////////////////////////////////////////////////////
      C        SET POT6 COORDINATES 5,7,8, & 9 TO CORRESPOND TO THE INTERNAL COORDNATE INC
      C        REMENT FOR THE IC TH COORDINATE.
0164              IF(IC.EQ.1)CALL Q1(DAX,DAY)
0165              IF(IC.EQ.6)CALL Q6(DAX,DAY)
0166              IF(IC.GT.1.AND.IC.LT.5)CALL QRESET(IC,RKC,XKC,YKC,ZKC,AGKC)
0167              IF(IC.GT.9)CALL QANSET(IC,RKC,XKC,YKC,ZKC,AGKC)
0168         307 CONTINUE
      C ///////////////////////////////////////////////////////////////////////////////
      C        CALCULATE AND STORE INCREMENTED INTERNAL COORDINATE POT6 ENERGY
0169              CALL POT6
0170              E(1,IC,IN,INC)=EE+18.3232D0
0171              DO 17 KK=1,6
0172              X(KK)=XKC(KK)
0173              Y(KK)=YKC(KK)
0174              Z(KK)=ZKC(KK)
0175          17 AG(KK)=AGKC(KK)
0176              CALL DIST
0177          18 CONTINUE
      C ///////////////////////////////////////////////////////////////////////////////
      C        RESET ALL PARAMETERS TO ORIGINAL CONFIGURATION
0178              DO 131 KK=1,6
0179              X(KK)=XK(KK)
0180              Y(KK)=YK(KK)
0181         131 Z(KK)=ZK(KK)
0182              CALL DIST
0183              CALL ANGLE
0184              DAX=0.0D0
0185              DAY=0.0D0
0186          19 CONTINUE
0187              IF(1.NE.IC)GO TO 851
      C        STORE DUPLICATE ENERGY VALUES FOR DIAGONAL  MATRIX ELEMENT CALCULATION.
0188              DO 95 IN=1,7
0189              DO 95 INC=1,7
```

```
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C190           70 KD=IN+INC
C191              IF(KD.EQ.8)GO TO 95
C192              GO TO (71,72,73,74,75,76,77,78,79,90,91,92,93,94),KD
C193           71 CONTINUE
C194              GO TO 95
C195           72 E(I,IC,IN,INC)=E(I,IC,1,1)
C196              GO TO 95
C197           73 E(I,IC,IN,INC)=E(I,IC,1,2)
C198              GO TO 95
C199           74 E(I,IC,IN,INC)=E(I,IC,1,3)
C200              GO TO 95
C201           75 E(I,IC,IN,INC)=E(I,IC,1,4)
C202              GO TO 95
C203           76 E(I,IC,IN,INC)=E(I,IC,1,5)
C204              GO TO 95
C205           77 E(I,IC,IN,INC)=E(I,IC,1,6)
C206              GO TO 95
C207           78 E(I,IC,IN,INC)=E(I,IC,1,7)
C208              GO TO 95
C209           79 E(I,IC,IN,INC)=E(I,IC,7,2)
C210              GO TO 95
C211           90 E(I,IC,IN,INC)=E(I,IC,7,3)
C212              GO TO 95
C213           91 E(I,IC,IN,INC)=E(I,IC,7,4)
C214              GO TO 95
C215           92 E(I,IC,IN,INC)=E(I,IC,7,5)
C216              GO TO 95
C217           93 E(I,IC,IN,INC)=E(I,IC,7,6)
C218              GO TO 95
C219           94 E(I,IC,IN,INC)=E(I,IC,7,7)
C220           95 CONTINUE
C221          851 CONTINUE
     C //////////////////////////////////////////////////////////////////////////////////
     C     CALCULATE 7 POINT FIRST DERIVATIVES.
C222              DO 96 IN=1,7
C223              AD=E(I,IC,IN,5)-E(I,IC,IN,3)
C224              BD=E(I,IC,IN,6)-E(I,IC,IN,2)
C225              CD=E(I,IC,IN,7)-E(I,IC,IN,1)
C226              D(I,IC,IN)=((A*AD)+(B*BD)+(C*CD))/RINK
C227           96 CONTINUE
     C >>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>
     C     CALCULATE SEVEN POINT SECOND DERIVATIVES.
C228              ADD=D(I,IC,5)-D(I,IC,3)
C229              BDD=D(I,IC,6)-D(I,IC,2)
C230              CDD=D(I,IC,7)-D(I,IC,1)
C231              DD(I,IC)=((A*ADD)+(B*BDD)+(C*CDD))/RINK
C232              FAC=FACT
C233              IF(I.GE.7.OR.IC.GE.7)FAC=CFACT
C234              IF(I.GE.7.AND.IC.GE.7)FAC=TFACT
C235              IF(I.EQ.5.AND.IC.EQ.5)FAC=TFACT
C236              DD(I,IC)=DD(I,IC)*FAC
C237              WRITE(6,790)I,IC
C238          790 FORMAT('1',1X,'FOLLOWING ARE THE ENERGY SETS , ASSOCIATED FIRST DE
                1RIVATIVES AND THE RESULTANT SECOND DERIVATIVE FOR',/,1X,'I=',I3,' AND IC='
                1AND IC=',I3,/)
C239              WRITE(6,796)RINK
C240          796 FORMAT(5X,'RINK = ',1PD15.8,/)
C241              DO 87 IN=1,7
```

```
0242              IQD=IN-4
0243              WRITE(6,791)
0244          791 FORMAT(18X,'1*RINK',24X,'2*RINK ',24X,'3*RINK')
0245              WRITE(6,792)E(I,IC,IN,5),E(I,IC,IN,6),E(I,IC,IN,7)
0246          792 FORMAT(2X,'E+',2X,3(1PD30.15))
0247              WRITE(6,793)E(I,IC,IN,3),E(I,IC,IN,2),E(I,IC,IN,1)
0248          793 FORMAT(2X,'E-',2X,3(1PD30.15))
0249              WRITE(6,794)IQD,D(I,IC,IN)
0250          794 FORMAT(2X,'DV/D(Q',I2,')=',1PD25.15,/)
0251           87 CONTINUE
0252              WRITE(6,795)I,IC,DD(I,IC)
0253          795 FORMAT(2X,'SECOND DERIVATIVE FOR I=',I3,' IC=',I3,' DDV/(DQI)(DQIC)=',1PD2
             1)=',1PD25.15,///)
      C <<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<
      C     CALCULATE 3 POINT SECOND DERIVATIVES.
0254              EXY=E(I,IC,4,4)
0255              EPP=E(I,IC,5,5)
0256              EMM=E(I,IC,3,3)
0257              EPM=E(I,IC,5,3)
0258              EMP=E(I,IC,3,5)
0259              DHS=RINK*RINK
0260              EDD=(EPP+EMM-(2.0D0*EXY))/DHS
0261              EED=(EPM+EMP-(2.0D0*EXY))/DHS
0262              DD3(I,IC)=(EDD-EED)/4.0D0
0263              DD3(I,IC)=DD3(I,IC)*FAC
0264              WRITE(6,797)
0265          797 FORMAT(3X,'SECOND DERIVATIVE BY 3 POINT METHOD FOLLOWS')
0266              WRITE(6,795)I,IC,DD3(I,IC)
0267           20 CONTINUE
0268           21 CONTINUE
0269              WRITE(6,798)
0270          798 FORMAT('1',2X,'SECOND DERIVATIVES BY 3 POINT METHOD',/)
0271              DO 999 N=1,15
0272              WRITE(6,799)N
0273          799 FORMAT(//,'ROW',I3)
0274              WRITE(6,800)(DD3(N,L),L=1,15)
0275          800 FORMAT(7(1PD16.10))
0276          999 CONTINUE
0277              DO 1000 N=1,15
0278              DO 1000 L=1,15
0279              DDEV(1,N,L)=DD(N,L)
0280         1000 DDEV(2,N,L)=DD3(N,L)
      C //////////////////////////////////////////////////////////////////////////////
0281              CALL CPUNCH(DDEV)
0282         1111 STOP
0283              END
```

```
0001              SUBROUTINE CPUNCH(DDEV)
          C       SUBROUTINE CPUNCH
          C <<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<
          C       THIS ROUTINE PUNCHES THE INTERNAL COORDINATE FORCE CONSTANT SET IN A
          C       PROPER FORMAT FOR USE WITH THE SCHACHTSCHNEIDER NORMAL MODE FREQUENCY
          C       PROGRAM MODIFIED BY M. WOLFSBERG.
          C ///////////////////////////////////////////////////////////////////////////
0002              IMPLICIT REAL*8 (A-H,O-Z)
0003              DIMENSION NR2(91),NC2(91),NRV(91),NCV(91)
0004              REAL*8 DD2(91),DDV(91),FZ
0005              REAL*8 DDEV(2,15,15),DDE2(2,15,15)
0006              DO 1 N=1,15
C007              DO 1 L=1,15
0008              DO 1 J=1,2
0009              DDE2(J,N,L)=DDEV(J,N,L)
0010            1 CONTINUE
0011              WRITE(6,45)
0012           45 FORMAT('1',1X,'INTERNAL COORDINATE FORCE CONSTANT MATRIX GENERATED BY THE
                 ' BY THE SEVEN POINT DERIVATIVE APPROXIMATION METHOD',//)
0013              DO 35 N=1,15
0014              WRITE(6,47)N
0015              WRITE(6,46)(DDEV(1,N,L),L=1,15)
0016           35 CONTINUE
0017           47 FORMAT(/,1X,'ROW',I3)
0018           46 FORMAT(7(1PD18.10))
0019              DO 29 IZ=1,91
0020              DD2(IZ)=0.000
0021           29 DDV(IZ)=0.000
0022              FZ=1.000000000000
0023              L2=0
0024              LV=0
0025              DO 31 IZ=1,15
0026              IF(IZ.EQ.5.OR.IZ.EQ.9)GO TO 31
0027              LZ=IZ
0028              IF(IZ.GT.9)LZ=LZ-4
0029              IF(IZ.EQ.7.OR.IZ.EQ.8)LZ=LZ+5
0030              IF(IZ.EQ.8)LZ=LZ-1
0031              DO 30 IR=1,15
C032              IF(IR.EQ.5.OR.IR.EQ.9)GO TO 30
0033              LR=IR
0034              IF(IR.GT.9)LR=LR-4
0035              IF(IR.EQ.7.OR.IR.EQ.8)LR=LR+5
0036              IF(IR.EQ.8)LR=LR-1
0037              IF(LR.GT.LZ)GO TO 30
0038              IF(5.0D-7.GE.DABS(DDE2(2,IR,IZ)))GO TO 28
0039              L2=L2+1
C040              NR2(L2)=LR
0041              NC2(L2)=LZ
0042              DD2(L2)=DDE2(2,IR,IZ)
C043              WRITE(6,49)IR,LR,IZ,LZ,L2,DD2(L2),DDE2(2,IR,IZ)
0044           49 FORMAT(1X,5I4,F12.8,1PD20.12,' DD2')
0045           28 IF(5.0D-7.GE.DABS(DDEV(1,IR,IZ)))GO TO 30
C046              LV=LV+1
0047              NRV(LV)=LR
0048              NCV(LV)=LZ
C049              DDV(LV)=DDEV(1,IR,IZ)
0050              WRITE(6,50)IR,LR,IZ,LZ,LV,DDV(LV),DDEV(1,IR,IZ)
0051           50 FORMAT(50X,5I4,F12.8,1PD20.12,' DDV')
```

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```
0052            20 CONTINUE
C053            21 CONTINUE
0054               WRITE(6,772)
0055           772 FORMAT('1')
     C <<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<
     C      CONSTRUCT AND PUNCH LABELED INTERNAL COORDINATE FORCE CONSTANT MATRIX BY
     C      7 POINT METHOD.
0056               WRITE(6,42)LV
0057               WRITE(7,42)LV
0058            42 FORMAT(1X,'INTERNAL COORD. F.C. MATRIX BY 7 PT. METHOD CONTAINS ',
              1 I3,' ELEMENTS')
0059               WRITE(6,43)(NRV(M),NCV(M),M,FZ,M=1,LV)
0060               WRITE(6,51)(DDV(M),M=1,LV)
0061            51 FORMAT(6F12.9)
0062               WRITE(7,43)(NRV(M),NCV(M),M,FZ,M=1,LV)
0063               WRITE(7,51)(DDV(M),M=1,LV)
0064            43 FORMAT(4(3I3,F9.6))
     C <<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<
     C      CONSTRUCT AND PUNCH  LABELED INTERNAL COORDINATE FORCE CONSTANT MATRIX BY
     C      3 POINT METHOD.
0065               WRITE(6,772)
0066               WRITE(6,44)L2
0067               WRITE(7,44)L2
0068            44 FORMAT(1X,'INTERNAL COORD.F. C. MATRIX BY 3 PT. METHOD CONTAINS ',I3,' ELE
              *I3,' ELEMENTS')
0069               WRITE(6,43)(NR2(M),NC2(M),M,FZ,M=1,L2)
0070               WRITE(6,51)(DD2(M),M=1,L2)
0071               WRITE(7,43)(NR2(M),NC2(M),M,FZ,M=1,L2)
0072               WRITE(7,51)(DD2(M),M=1,L2)
C073               RETURN
0074               END
```

```
0001            SUBROUTINE ALBEND(DAX,DAY)
0002            IMPLICIT REAL*8 (A-H,O-Z)
0003            DIMENSION APARM(5)
0004            DIMENSION X(6),Y(6),Z(6),R(15),DER(15),AG(6),P2(15),D1(3),D3(3),
              1 ALPH(3),RF(3),BETA(3),CC(3),AA(3),SIG(3),RSTR(3),ACS(6),DK(6),
              2 Y1(6),Y2(6),ASS(6),F(4),GF(4),RX(6),PX(6),PY(6),PZ(6),DX(6),
              3 DY(6),DZ(6),DPX(6),DPY(6),DPZ(6),DF(15,3)
0005            COMMON X,Y,Z,R,DER,AG,R2,D1,ALPH,RE,D3,BETA,CC,AA,SIG,RSTR,TAU,
              1 RV,DIJ,CP,FF,ACS,ASS,RX,XII,                    V1,V2,V3,V4,BMAX,
              2 RSS,VF,PER,H,PX,PY,PZ,WH,WC,WBR,W,DT,DX,DY,DZ,DPX,DPY,DPZ,T,DF,
              3 TEMP,RET,START,APARM,PI,T3PI,EL6PI,SSPI,
              4 III,JJJ,KKK,LLL,NV1,NV2,NV3,NV4,JJ,NI,KFF
       C >>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>
       C    THIS ROUTINE HANDLES THE POT5 COORDINATES 5,7,8,& 9 RESET DUE TO INCREMENTS
       C OF C-H BOND R(1) AND H-H BOND R(6)
0006            ENTRY Q1(DAX,DAY)
0007            ENTRY Q6(DAX,DAY)
       C////////////////////////////////////////////////////////////////////////////////
       C    THIS SUBROUTINE CALCULATES THE LINEAR BEND POSITION OF ATOM 6 (BR OR H)
       C    HOLDING ATOM 1 (H1) AND ATOM 5 (C) ONTHE Z-AXIS.  THISPRODUCES IDENTICAL
       C    INTERNAL COORDINATE GEOMETRY CHANGES AS HOLDING ATOM 6 AND ATOM 5 ON THE Z-
       C    AXIS  (C AT THE ORIGIN) AND MOVING H1 OFF THE Z-AXIS WITH CORRESPONDING ROT
       C    ATION OF H2, H3, & H4 TO PRODUCE NO CHANGE IN THE HCH THETA ANGLES.
       C    DAX = ALPHAX -PI
       C    DAY = ALPHAY - PI
       C    ALPHAX AND ALPHAY ARE THE LINEAR BENDING ANGLES IN THE X-Z Y-Z PLANES
       C    RESPECTIVELY.
       C$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$$
0008            IF(DAX.EQ.0.0D0)GO TO 1
0009            DSX=DSIN(DAX)
0010            DCX=DCOS(DAX)
0011            GO TO 2
0012          1 DSX=0.0D0
0013            DCX=1.0D0
0014          2 IF(DAY.EQ.0.0D0)GO TO 3
0015            DSY=DSIN(DAY)
0016            DCY=DCOS(DAY)
0017            GO TO 4
0018          3 DSY=0.0D0
0019            DCY=1.0D0
0020          4 CONTINUE
0021            DCX2=DCX*DCX
0022            DCY2=DCY*DCY
0023            SSDD=1.0D0-(DSX*DSX*DSY*DSY)
0024            RX6=R(6)*DSQRT(DCY2/SSDD)
0025            RY6=R(6)*DSQRT(DCX2/SSDD)
0026            X(6)=RX6*DSX
0027            Y(6)=RY6*DSY
0028            Z(6)=(RX6*DCX)+R(1)
       C        Z(6)=(RY6*DCY)+R(1)    THIS WILL GIVE SAME RESULT AS EQTN. ABOVE
0029            Z(1)=P(1)
0030            CALL DIST
0031            RETURN
0032            END
```

```
FORTRAN IV G LEVEL  21              QRESET           DATE = 76044         14/06/51

0001            SUBROUTINE QRESET(I,RK,XK,YK,ZK,AGK)
      C#########################################################################
      C     THIS ROUTINE CALCULATES CHANGES IN THE POT& PARAMETERS P(5),P(7),P(8), AND
      C     P(9) THAT ARE NEEDED IN THE ENERGY CALCULATION BUT ARE NOT DIRECTLY RELATED
      C     TO THE SECOND DERIVATIVE INTERNAL COORDINATE FORCE CONSTANTS.
      C     OF THE 13 PARAMETERS USEFUL FOR FREQUENCY CALCULATION , ONLY THE
      C     INCREMENTED PARAMETER MUST VARY THE OTHER 12 (11 FOR OFF DIAGONAL TERMS)
      C     MUST REMAIN CONSTANT DURING THE DERIVATIVE APPROXIMATION PROCEDURE.
      C     THIS ROUTINES PERFORMANCE WAS VERIFIED BY PLACING GEOMETRY WRITE STATEMENTS
      C     IN THE MAIN ROUTINE AFTER EACH INCREMENTATION AND BEFORE EACH ENERGY CALCUL
      C     -ATION.
      C#########################################################################
0002            IMPLICIT REAL*8 (A-H,O-Z)
      C     SPECIFIC DIMENSION FOR QRESET
0003            DIMENSION RK(15),AGK(6),XK(6),YK(6),ZK(6)
      C######################################################################
0004            DIMENSION APARM(5)
0005            DIMENSION X(6),Y(6),Z(6),R(15),DER(15),AG(6),R2(15),D1(3),D3(3),
              1 ALPH(3),RE(3),BETA(3),CC(3),AA(3),SIG(3),RSTR(3),ACS(6),DK(6),
              2 Y1(6),Y2(6),ASS(6),F(4),GF(4),PX(6),PX(6),PY(6),PZ(6),DX(6),
              3 DY(6),DZ(6),DPX(6),DPY(6),DPZ(6),DF(15,3)
0006            COMMON X,Y,Z,P,DER,AG,P2,D1,ALPH,RE,D3,BETA,CC,AA,SIG,RSTR,TAU,
              1 RV,DIJ,CP,EE,ACS,ASS,FX,XII,                   V1,V2,V3,V4,BMAX,
              2 RSS,VK,PER,H,PX,PY,PZ,WH,WC,WBR,W,DT,DX,DY,DZ,DPX,DPY,DPZ,T,CF,
              3TEMP,RRT,START,APARM,PI,T3PI,EL6PI,S6PI,
              4III,JJJ,KKK,LLL,NV1,NV2,NV3,NV4,JJ,NI,KEE
      C######################################################################
0007            K=I
0008            GO TO 8
      C     ANGLE RESET ENTRY POINT
0009            ENTRY QANSET(I,RK,XK,YK,ZK,AGK)
0010            K=I-8
0011          8 CONTINUE
0012            SX=PI/3.0D0
0013            SY=PI/6.0D0
0014            GO TO (10,20,30,40,50,60,70),K
0015         10 Z(6)=(R(1)-ZK(1))+Z(6)
0016            Z(1)=R(1)
0017            GO TO 80
      C     P(2) RESET        <<<<<<<<<<<<<<<<<<<<<<<<<<<<<
0018         20 P2=AG(1)-(PI/2.0D0)
0019            IF(X(2).NE.0.0D0)GO TO 21
0020            Y(2)=R(2)*DCOS(P2)
0021            GO TO 23
0022         21 RP2=R(2)*DCOS(P2)
0023            T2=X(2)/Y(2)
0024            AT2=DATAN(T2)
0025            X(2)=RP2*DSIN(AT2)
0026            Y(2)=RP2*DCOS(AT2)
0027         23 CONTINUE
0028            Z(2)=-R(2)*DSIN(P2)
0029            GO TO 80
      C     P(3) RESET        <<<<<<<<<<<<<<<<<<<<<<<<<<<<<
0030         30 P3=AG(2)-(PI/2.0D0)
0031            RP3=R(3)*DCOS(P3)
0032            IF(XK(3).NE.X(2).OR.YK(3).NE.Y(3))GO TO 31
0033         34 X(3)=RP3*DSIN(SX)
0034            Y(3)=-RP3*DSIN(SY)
```

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FORTRAN IV G LEVEL  21              QRESET          DATE = 76044        14/06/51

0035                 GO TO 36
0035              31 IF(AGK(4).NE.AG(4))GO TO 32
0037                 IF(AGK(6).NE.AG(6))GO TO 33
0038                 IF(R(3).NE.RK(3))GO TO 34
0039                 IF(AGK(2).NE.AG(2))GO TO 34
0040                 GO TO 99
             C     ST. 99 IS AN ERROR ALERT WRITE ST.
0041              32 RP13=RK(13)
0042                 P2=AG(1)-(PI/2.0D0)
0043                 RP2=R(2)*DCOS(P2)
0044                 PK3=AGK(2)-(PI/2.0D0)
0045                 RKP3=RK(3)*DCOS(PK3)
0046                 CTP4=((RP2*RP2)+(RKP3*RKP3)-(RP13*RP13))/(2.0D0*RP2*RKP3)
0047                 TP4=DARCOS(CTP4)
0048                 DTP4=(T3PI-TP4)/2.0D0
0049                 SG3=(PI/6.0D0)-DTP4
0050                 X(3)=RP3*DCOS(SG3)
0051                 Y(3)=-RP3*DSIN(SG3)
0052                 GO TO 36
0053              33 RP15=RK(15)
0054                 PK3=AGK(2)-(PI/2.0D0)
0055                 RKP3=R K(3)*DCOS(PK3)
0056                 RP4=R(4)*DCOS(AG(3)-(PI/2.0D0))
0057                 CTP6=((RKP3*RKP3)+(RP4*RP4)-(RP15*RP15))/(2.0D0*RKP3*RP4)
0058                 TP6=DARCOS(CTP6)
0059                 DTP6=(T3PI-TP6)/2.0D0
0060                 SG3=(PI/6.0D0)+DTP6
0061                 X(3)=RP3*DCOS(SG3)
0062                 Y(3)=-RP3*DSIN(SG3)
0063              36 CONTINUE
0064                 Z(3)=-R(3)*DSIN(P3)
0065                 GO TO 80
             C     R(4) RESET          <<<<<<<<<<<<<<<<<<<<<<<<<<<<
0066              40 P4=AG(3)-(PI/2.0D0)
0067                 RP4=R(4)*DCOS(P4)
0068                 IF(XK(4).NE.X(4).OR.YK(4).NE.Y(4))GO TO 41
0069              44 X(4)=-RP4*DSIN(SX)
0070                 Y(4)=-RP4*DSIN(SY)
0071                 GO TO 46
0072              41 IF(AGK(5).NE.AG(5))GO TO 42
0073                 IF(AGK(6).NE.AG(6))GO TO 43
0074                 IF(RK(4).NE.R(4))GO TO 44
0075                 IF(AGK(3).NE.AG(3))GO TO 44
0076                 GO TO 99
0077              42 RP14=RK(14)
0078                 PK4=AGK(3)-(PI/2.0D0)
0079                 RKP4=RK(4)*DCOS(PK4)
0080                 RP2=R(2)*DCOS(AG(1)-(PI/2.0D0))
0081                 CTP5=((RP2*RP2)+(RKP4*RKP4)-(RP14*RP14))/(2.0D0*RP2*RKP4)
0082                 TP5=DARCOS(CTP5)
0083                 DTP5=(T3PI-TP5)/2.0D0
0084                 SG4=(PI/6.0D0)-DTP5
0085                 X(4)=-RP4*DCOS(SG4)
0086                 Y(4)=-RP4*DSIN(SG4)
0087                 GO TO 46
0088              43 RP15=RK(15)
0089                 PK4=AGK(3)-(PI/2.0D0)
0090                 RKP4=RK(4)*DCOS(PK4)
```

```
0091              RP3=R(3)*DCOS(AG(2)-(PI/2.0D0))
0092              CTP6=((RP3*RP3)+(RKP4*RKP4)-(RP15*RP15))/(2.0D0*RP3*RKP4)
0093              TP6=DARCOS(CTP6)
0094              DTP6=(T3PI-TP6)/2.0D0
0095              SG4=(PI/6.0D0)+DTP6
0096              X(4)=-RP4*DCOS(SG4)
0097              Y(4)=-RP4*DSIN(SG4)
0098           46 CONTINUE
0099              Z(4)=-R(4)*DSIN(P4)
0100              GO TO 80
        C      ROUTINE FOR THETA4 INCREMENT RESET
0101           50 P2=AG(1)-(PI/2.0D0)
0102              P3=AG(2)-(PI/2.0D0)
0103              RP2=R(2)*DCOS(P2)
0104              RP3=R(3)*DCOS(P3)
0105              R13=(R(2)*R(2))+(R(3)*R(3))-(2.0D0*R(2)*R(3)*DCOS(AG(4)))
0106              P(13)=DSQRT(R13)
0107              IF(Z(2).NE.Z(3))GO TO 51
0108              RP13=R(13)
0109              GO TO 52
0110           51 S13=DABS(Z(3)-Z(2))/R(13)
0111              RP13=R(13)*DCOS(DARSIN(S13))
0112           52 CONTINUE
0113              CTP4=((RP2*RP2)+(RP3*RP3)-(RP13*RP13))/(2.0D0*RP2*RP3)
0114              TP4=DARCOS(CTP4)
0115              DTP4=(T3PI-TP4)/2.0D0
0116              IF(X(2).EQ.0.0D0)GO TO 54
0117           53 S2=X(2)/RP2
0118              AX2=DARSIN(S2)
0119              TAX2=AX2+DTP4
0120              GO TO 55
0121           54 CONTINUE
0122              TAX2=DTP4
0123           55 CONTINUE
0124              X(2)=RP2*DSIN(TAX2)
0125              Y(2)=RP2*DCOS(TAX2)
0126              IF(XK(3).NE.X(3).OR.YK(3).NE.Y(3))GO TO 57
        C     THETA6 OR R3 MUST BE CROSSED WITH THETA4 IF TRANSFER TO ST. 57 OCCURS.
        C     THIS MEANS THAT TAX2=DTP4 ONLY IF NO TRANSFER OCCURS.
0127           56 TAX3=(PI/6.0D0)-DTP4
0128              X(3)=RP3*DCOS(TAX3)
0129              Y(3)=-RP3*DSIN(TAX3)
0130              GO TO 59
0131           57 IF(AGK(6).NE.AG(6))GO TO 58
0132              IF(RK(3).NE.R(3))GO TO 56
0133              IF(AGK(2).NE.AG(2))GO TO 56
0134              GO TO 99
0135           58 RP15=RK(15)
0136              RP4=R(4)*DCOS(AG(3)-(PI/2.0D0))
0137              CTP6=((RP3*RP3)+(RP4*RP4)-(RP15*RP15))/(2.0D0*RP3*RP4)
0138              TP6=DARCOS(CTP6)
0139              DTP6=(T3PI-TP6)/2.0D0
0140              SG3=(PI/6.0D0)+DTP6-DTP4
0141              X(3)=RP3*DCOS(SG3)
0142              Y(3)=-RP3*DSIN(SG3)
0143           59 CONTINUE
0144              Z(2)=-P(2)*DSIN(P2)
0145              Z(3)=-P(3)*DSIN(P3)
```

```
0146              GO TO 80
        C     ROUTINE FOR THETA5 INCREMENT RESET   (SHOULD RESEMBLE THETA4 RESET)
0147         60 P2=AG(1)-(PI/2.0D0)
0148            P4=AG(2)-(PI/2.0D0)
0149            RP2=R(2)*DCOS(P2)
0150            PP4=R(4)*DCOS(P4)
0151            R14=((R(2)*R(2))+(R(4)*R(4))-(2.0D0*R(2)*R(4)*DCOS(AG(5))))
0152            R(14)=DSQRT(R14)
0153            IF(Z(2).NE.Z(4))GO TO 61
0154            RP14=R(14)
0155            GO TO 62
0156         61 S14=DABS(Z(4)-Z(2))/R(14)
0157            RP14=R(14)*DCOS(DARSIN(S14))
0158         62 CONTINUE
0159            CTP5=((PP2*RP2)+(RP4*RP4)-(RP14*RP14))/(2.0D0*PP2*RP4)
0160            TP5=DARCOS(CTP5)
0161            DTP5=(T3PI-TP5)/2.0D0
0162            IF(X(2).EQ.0.0D0)GO TO 64
0163         63 S2=X(2)/RP2
0164            AX2=DARSIN(S2)
0165            TAX2=AX2-DTP5
0166            GO TO 65
0167         64 TAX2=-DTP5
0168         65 CONTINUE
0169            X(2)=RP2*DSIN(TAX2)
0170            Y(2)=RP2*DCOS(TAX2)
0171            IF(XK(4).NE.X(4).OR.YK(4).NE.Y(4))GO TO 67
0172         66 TAX4=(PI/6.0D0)-DTP5
0173            X(4)=-RP4*DCOS(TAX4)
0174            Y(4)=-RP4*DSIN(TAX4)
0175            GO TO 69
0176         67 IF(AGK(6).NE.AG(6))GO TO 68
0177            IF(RK(4).NE.R(4))GO TO 66
0178            IF(AGK(3).NE.AG(3))GO TO 66
0179            GO TO 99
0180         68 RP15=RK(15)
0181            RP3=R(3)*DCOS(AG(2)-(PI/2.0D0))
0182            CTP6=((RP3*RP3)+(RP4*RP4)-(RP15*RP15))/(2.0D0*RP3*RP4)
0183            TP6=DARCOS(CTP6)
0184            DTP6=(T3PI-TP6)/2.0D0
0185            SG4=(PI/6.0D0)+DTP6-DTP5
0186            X(4)=-RP4*DCOS(SG4)
0187            Y(4)=-RP4*DSIN(SG4)
0188         69 CONTINUE
0189            Z(2)=-R(2)*DSIN(P2)
0190            Z(4)=-R(4)*DSIN(P4)
0191            GO TO 80
        C     ROUTINE FOR THETA6 INCREMENT RESET
0192         70 P3=AG(2)-(PI/2.0D0)
0193            P4=AG(3)-(PI/2.0D0)
0194            RP3=R(3)*DCOS(P3)
0195            PP4=R(4)*DCOS(P4)
0196            R15=((R(3)*R(3))+(R(4)*R(4))-(2.0D0*R(3)*R(4)*DCOS(AG(6))))
0197            R(15)=DSQRT(R15)
0198            IF(Z(3).NE.Z(4))GO TO 71
0199            RP15=R(15)
0200            GO TO 72
0201         71 S15=DABS(Z(4)-Z(3))/R(15)
```

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0202              RP15=R(15)*DCOS(DARSIN(S15))
0203         72 CONTINUE
0204              CTP6=((RP3*RP2)+(RP4*RP4)-(RP15*RP15))/(2.0D0*RP3*RP4)
0205              TP6=DARCOS(CTP6)
0206              DTP6=(T3PI-TP6)/2.0D0
0207              IF(XK(3).NE.X(3).OR.YK(3).NE.Y(3))GO TO 75
0208              IF(XK(4).NE.X(4).OR.YK(4).NE.Y(4))GO TO 77
0209         73 TX34=(PI/6.0D0)+DTP6
0210              X(3)=RP3*DCOS(TX34)
0211              Y(3)=-RP3*DSIN(TX34)
0212              X(4)=-RP4*DCOS(TX34)
0213              Y(4)=-RP4*DSIN(TX34)
0214              GO TO 79
0215         75 IF(AGK(4).NE.AG(4))GO TO 76
0216              IF(RK(3).NE.R(3))GO TO 73
0217              GO TO 99
0218         76 RP13=RK(13)
0219              P2=AG(1)-(PI/2.0D0)
0220              RP2=R(2)*DCOS(P2)
0221              CTP4=((RP2*RP2)+(RP3*RP3)-(RP13*RP13))/(2.0D0*RP2*RP3)
0222              TP4=DARCOS(CTP4)
0223              DTP4=(T3PI-TP4)/2.0D0
0224              TX4=(PI/6.0D0)-DTP4+DTP6
0225              X(3)=RP3*DCOS(TX4)
0226              Y(3)=-RP3*DSIN(TX4)
0227              TX6=(PI/6.0D0)+DTP6
0228              X(4)=-RP4*DCOS(TX6)
0229              Y(4)=-RP4*DSIN(TX6)
0230              GO TO 79
0231         77 IF(AGK(5).NE.AG(5))GO TO 78
0232              IF(RK(4).NE.R(4))GO TO 73
0233              GO TO 99
0234         78 RP14=RK(14)
0235              P2=AG(1)-(PI/2.0D0)
0236              RP2=R(2)*DCOS(P2)
0237              CTP5=((RP2*RP2)+(RP4*RP4)-(RP14*RP14))/(2.0D0*RP2*RP4)
0238              TP5=DARCOS(CTP5)
0239              DTP5=(T3PI-TP5)/2.0D0
0240              TX5=(PI/6.0D0)-DTP5+DTP6
0241              X(4)=-RP4*DCOS(TX5)
0242              Y(4)=-RP4*DSIN(TX5)
0243              TX6=(PI/6.0D0)+DTP6
0244              X(3)=RP3*DCOS(TX6)
0245              Y(3)=-RP3*DSIN(TX6)
0246         79 CONTINUE
0247              Z(3)=-R(3)*DSIN(P3)
0248              Z(4)=-R(4)*DSIN(P4)
0249         80 CONTINUE
0250              CALL DIST
0251              RETURN
0252         99 WRITE(6,100)I
0253        100 FORMAT(1X,'SUBROUTINE QRESET INDICATES NO RESET POSSIBLE FOR I=',I3,/)
                   13,/)
0254              RETURN
0255              END
```

```
      C  ***************************************************************************
      C                        FXGEN ROUTINE
      C     INTERNAL COORDINATE TO CARTESIAN COORDINATE FORCE CONSTANT CONVERSION
      C  ***************************************************************************
0001          IMPLICIT REAL*8 (A-H,O-Z)
0002          DIMENSION F(18,18),B(13,18),NR(3),NC(3),DAT(3),WKAREA(400)
             1,NRO(91),NCO(91),NFO(91),Z(91),FO(91)
             2,KFR(4),KFC(4),DATINF(4),D(18,18),DD(18,18),A(18,18)
0003          REAL*8 SUMB,SUMA,BF(18,18),FX(18,18)
      C  ////////////////////////////////////////////////////////////////////////
      C     THIS PROGRAM READS IN SINGLE PRECISION F AND B-MATRIXES    AND MULTIPLIES
      C     THEM TOGETHER SUCH THAT     FX = B' F B
      C     FX(18X18) = B'(18X13) F(13X13) B(13X18)
      C     THE FX MATRIX GENERATED IS A CARTESIAN COORDINATE REPRESENTATION OF THE
      C     INTERNAL COORDINATE FORCE CONSTANT MATRIX F.
      C     THE B MATRIX USED IS OBTAINED FROM THE G-MATRIX FORMULATION PART OF THE
      C     SCHACHTSCHNEIDER PROGRAM FOR THE CALCULATION OF NORMAL MODE FREQUENCIES.
      C     THE FX MATRIX IS PUNCHED ON CARDS READY TO BE READ INTO THE SCHACHTSCHNEIDE
      C     R NORMAL MODE FREQUENCY CALCULATION PROGRAM.
      C  ////////////////////////////////////////////////////////////////////////
0004        1 READ(5,12)NF,NATOM,NZ,NFZ,NFX
0005       12 FORMAT(8I3)
      C  ////////////////////////////////////////////////////////////////////////
      C     NF = SIZE OF SQUARE F-MATRIX
      C     NATOM = # OF ATOMS
      C     NZ = # OF Z-MATRIX ENTRIES
      C     NFZ = # OF FORCE CONSTANTS USED IN F-MATRIX SET-UP
      C  ////////////////////////////////////////////////////////////////////////
0006          IF(NATOM+NF)2,1,2
0007        2 IF(NF+10)1111,1111,3
0008        3 NA=3*NATOM
0009          DO 8 I=1,NF
0010          DO 8 J=1,NA
0011          D(I,J)=0.0D0
0012          DD(I,J)=0.0D0
0013        7 F(I,J)=0.0D0
0014        8 B(I,J)=0.0D0
0015        9 READ(5,10)(NR(I),NC(I),DAT(I),I=1,3)
0016       10 FORMAT(2I3,E18.9,2I3,E18.9,2I3,E18.9)
0017          DO 20 I=1,3
0018          IF(5+NR(I))21,22,20
0019       20 B(NR(I),NC(I))=DAT(I)
0020          GO TO 9
0021       21 WRITE(6,11)
0022       11 FORMAT(//,1X,'ERROR IN B MATRIX CARD FOLLOWS',/)
0023          WRITE(6,10)(NR(I),NC(I),DAT(I),I=1,3)
0024       22 WRITE(6,16)
0025       16 FORMAT('1','BMATRIX')
0026          DO 23 I=1,NF
0027       23 WRITE(6,14)I,(B(I,J),J=1,NA)
0028       14 FORMAT(/,1X,'ROW # ',I3,/,8(1PE15.7))
0029          READ(5,13)(NRO(I),NCO(I),NFO(I),Z(I),I=1,NZ)
0030          WRITE(6,13)(NRO(I),NCO(I),NFO(I),Z(I),I=1,NZ)
0031          READ(5,15)(FO(I),I=1,NFZ)
0032          WRITE(6,15)(FO(I),I=1,NFZ)
0033       13 FORMAT(4(3I3,F9.6))
0034       15 FORMAT(6F12.8)
0035          DO 30 I=1,NZ
```

```
0036                 F(NRO(I),NCO(I))=Z(I)*FU(NFT(I))
0037             30  F(NCO(I),NPO(I))=F(NRO(I),NCO(I))
0038                 WRITE(6,17)
0039             17  FORMAT('1','F-MATRIX')
0040                 DO 24 I=1,NF
0041             24  WRITE(6,14)I,(F(I,J),J=1,NF)
0042                 DO 26 I=1,NA
0043                 DO 26 K=1,NF
0044                 SUMA=0.0D0
0045                 DO 25 J=1,NF
0046             25  SUMA=SUMA+B(J,I)*F(J,K)
0047             26  BF(I,K)=SUMA
0048                 DO 28 I=1,NA
0049                 DO 28 K=1,NA
0050                 SUMB=0.0D0
0051                 DO 27 J=1,NF
0052             27  SUMB=SUMB+BF(I,J)*B(J,K)
0053             28  FX(I,K)=SUMB
0054                 WRITE(6,18)
0055             18  FORMAT('1','CARTESIAN COORDINATE FX-MATRIX')
0056                 DO 29 I=1,NA
0057             29  WRITE(6,14)I,(FX(I,J),J=1,NA)
0058                 WRITE(7,19)((I,J,FX(I,J),J=1,NA),I=1,NA)
0059                 I=-2
0060                 WRITE(7,19)I
0061             19  FORMAT(4(2I3,1PD14.7))
0062                 GO TO 1
0063           1111  CALL EXIT
0064                 END
```

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```
      C  ************************************************************************
      C     CARTESIAN COORDINATE FORCE CONSTANT ROUTINE
      C  ************************************************************************
0001        IMPLICIT REAL*8 (A-H,O-Z)
0002        REAL*8 DD3(3,6,3,6),BC(4),BC3(4)
0003        REAL*8 ECC(7,3,6,7,3,6),D(7,3,6,3,6),DD(3,6,3,6),XK(6),YK(6),ZK(6),XKC(6),
           *,XKC(6),YKC(6),ZKC(6)
0004        DIMENSION X(6),Y(6),Z(6),R(15),DER(15),AG(6),R2(15),D1(3),D3(3),
           1 ALPH(3),RE(3),BETA(3),CC(3),AA(3),SIG(3),RSTR(3),ACS(6),DK(6),
           2 Y1(6),Y2(6),ASS(6),F(4),GF(4),RX(6),PX(6),PY(6),PZ(6),DX(6),
           3 DY(6),DZ(6),DPX(6),DPY(6),DPZ(6),DF(15,3),
           4,XX(20),YY(20),CO(11),XYZ(3),KC(3,6),KCR(4),KCC(4)
0005        DIMENSION APARM(5)
0006        COMMON X,Y,Z,R,DER,AG,R2,D1,ALPH,RE,D3,BETA,CC,AA,SIG,RSTR,TAU,
           1 RV,DIJ,CP,EE,ACS,ASS,RX,XII,                 V1,V2,V3,V4,BMAX,
           2 RSS,VR,PER,H,PX,PY,PZ,WH,WC,WBR,W,DT,DX,DY,DZ,DPX,DPY,DPZ,T,DF,
           3TEMP,RKT,START,APARM,PI,T3PI,EL6PI,S6PI,
           4III,JJJ,KKK,LLL,NV1,NV2,NV3,NV4,JJ,NI,KEE
0007        DATA XYZ/'X(','Y(','Z('/
      C////////////////////////////////////////////////////////////////////////
      C     THIS PROGRAM CALCULATES THE CARTESIAN COORDINATE FORCE CONSTANTS
      C     (THE SECOND DERIVATIVE OF A POTENTIAL ENERGY SURFACE NAMED "POT6" WITH
      C     RESPECT TO THE CARTESIAN COORDINATE COORDINATES OF THE CH5 SYSTEM) USING
      C     NUMERICAL PARTIAL DIFFERENTIATION TECHNIQUES.
      C////////////////////////////////////////////////////////////////////////
      C##################################################################################
      C
      C     ECC = CALCULATED ENERGY MATRIX, CAPABLE OF STORING 49 INCREMENTAL ENERGIES
      C           NEEDED FOR CALCULATION  OF EACH FORCE CONSTANT IN THE 18X18 MATRIX.
      C     D = FIRST DERIVATIVE MATRIX
      C     DD = SECOND DERIVATIVE MATRIX BY SEVEN POINT METHOD
      C     DD3 = SECOND DERIVATIVE MATRIX BY 3 POINT METHOD
      C     XK, YK, AND ZK = GEOMETRY COORDINATE CONSTANTS FOR RESETTING GEOMETRY
      C                      AFTER INCREMENTATION.
      C     XKC, YKC, AND ZKC = COORDINATE FOR RESETTING GEOMETRY TO A PREVIOUSLY
      C                         INCREMENTED GEOMETRY.
      C
      C##################################################################################
0008        A=0.75D0
0009        B=-0.15D0
0010        C=0.15D0/9.0D0
0011        KEE=-1
      C////////////////////////////////////////////////////////////////////////
      C     READ IN POT6 DATA
0012        CALL READ
0013        PI=2.0D0*DARSIN(1.0D0)
0014        T3PI=(2.0D0*PI)/3.0D0
0015        EL6PI=(11.0D0*PI)/6.0D0
0016        S6PI=(7.0D0*PI)/6.0D0
      C////////////////////////////////////////////////////////////////////////
      C     CALCULATE  DOUBLE PRECISION TETRAHEDRAL ANGLE NEEDED FOR  GEOMETRY CALCULA-
      C     TIONS.
0017        CALL TETRAH(TAU,PI)
      C     ZERO OUT MATRICES
0018        DO 1 KA=1,6
0019        XK(KA)=0.0D0
0020        YK(KA)=0.0D0
0021        ZK(KA)=0.0D0
```

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```
0022              XKC(KA)=0.0D0
0023              YKC(KA)=0.0D0
0024              ZKC(KA)=0.0D0
0025              DO 1 KX=1,3
0026              DO 1 IX=1,3
0027              DO 1 IC=1,6
0028              DD(KX,KA,IX,IC)=0.0D0
0029              DD3(KX,KA,IX,IC)=0.0D0
0030              DO 1 IJ=1,7
0031              D(IJ,KX,KA,IX,IC)=0.0D0
0032              DO 1 IJC=1,7
0033              FCC(IJ,KX,KA,IJC,IX,IC)=0.0D0
0034            1 CONTINUE
       C////////////////////////////////////////////////////////////////////////////////
       C
       C      THE INTEGER "IRC" TELLS THE PROGRAM WHETHER IT IS TO READ IN THE
       C      INTERATOMIC DISTANCES (IF IRC IS GREATER THAN OR EQUAL ZERO)
       C      OR IF THE PROGRAM IS TO READ IN THE CARTESIAN COORDINATES OF THE ATOMS (IF
       C      IRC IS LESS THAN ZERO).
       C      "RINK" IS THE INCREMENT SIZE.
       C
       C////////////////////////////////////////////////////////////////////////////////
0035              READ(5,770)IRC,RINK
0036          770 FORMAT(I2,D10.3)
0037              IF(IRC)3,2,2
0038            2 READ(5,771)(R(I),I=1,15)
0039          771 FORMAT(4D20.13)
0040              DR1=R(1)
0041              WRITE(6,772)(I,R(I),I=1,15)
0042          772 FORMAT(//,5X,'INTERATOMIC DISTANCES',/,15(7X,'R',I2,'=',1PD20.10,/))
                 *))
0043              GO TO 4
0044            3 READ(5,773)(X(I),Y(I),Z(I),I=1,6)
0045          773 FORMAT(3D20.13)
0046              WRITE(6,774)(I,X(I),Y(I),Z(I),I=1,6)
0047          774 FORMAT(1X,'ATOM',9X,'X',19X,'Y',19X,'Z',/,6(I4,2X,3D20.12,/),//)
0048              CALL DIST
0049              DR1=R(1)
0050              WRITE(6,772)(I,R(I),I=1,15)
0051            4 CONTINUE
0052              WRITE(6,775)
0053          775 FORMAT('1')
0054              IF(IRC)6,5,5
0055            5 CALL PLACE(DR1)
0056              Z(1)=DR1
0057              Z(6)=R(5)
0058              CALL DIST
0059              WRITE(6,772)(I,R(I),I=1,15)
0060            6 CONTINUE
0061              CALL ANGLE
0062              WRITE(6,777)(I,AG(I),I=1,6)
0063          777 FORMAT(5X,'HCH ANGLES THETA',/,1X,6('T',I1,'=',1PD17.10,1X)/)
0064              DO 7 I=1,6
0065              XK(I)=X(I)
0066              YK(I)=Y(I)
0067              ZK(I)=Z(I)
0068            7 CONTINUE
0069              WRITE(6,774)(I,XK(I),YK(I),ZK(I),I=1,6)
```

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```
0070              CALL PUT6
        C ///////////////////////////////////////////////////////////////////////////////
        C
        C      FACTOR TO CONVERT EV/(BOHR RADIUS)**2 TO MDYNE/ANGSTROM
0071              FACT=0.1602100U/(0.5291670D0*0.5291670D0)
0072              WRITE(6,775)
0073              E=EE+18.323200
        C >>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>
        C
        C      IJ = LABEL FOR SETTING INCREMENT FOR KX,KA COORDINATE FROM -3 TO +3 *
        C      INCREMENT SIZE.
        C      KX = 1, 2, OR 3 INDICATES THE X, Y, OR Z COORDINATE, RESPECTIVELY FOR
        C          ATOM NUMBER KA = 1 TO 6.
        C      IJC = LABEL FOR SETTING INCREMENT FOR IX,IC COORDINATE FROM -3 TO +3 *
        C      INCREMENT SIZE.
        C      IX = 1, 2, OR 3 INDICATES THE X, Y, OR Z COORDINATE, RESPECTIVELY FOR
        C          ATOM NUMBER IC = 1 TO 6.
        C
        C <<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<
0074              DO 311 KI=5,6
0075              DO 311 KX=1,3
0076              DO 300 IC=1,6
0077              DO 300 IX=1,3
0078              ECC(4,KX,KI,4,IX,IC)=E
0079              DO 31 IJ=1,7
0080              HX=RINK*(IJ-4)
0081              IF(KI.EQ.IC.AND.KX.EQ.IX)GO TO 301
0082              GO TO (21,23,25),KX
0083           21 X(KI)=XK(KI)+HX
0084              GO TO 26
0085           23 Y(KI)=YK(KI)+HX
0086              GO TO 26
0087           25 Z(KI)=ZK(KI)+HX
0088           26 CONTINUE
0089          301 CONTINUE
0090              DO 302 IA=1,6
0091              XKC(IA)=X(IA)
0092              YKC(IA)=Y(IA)
0093              ZKC(IA)=Z(IA)
0094          302 CONTINUE
0095              DO 30 IJC=1,7
0096              HC=RINK*(IJC-4)
0097              IF(KI.EQ.IC.AND.KX.EQ.IX)GO TO 303
0098              GO TO 304
0099          303 IF(IJ.GT.1.AND.IJ.LT.7)GO TO 30
0100              HC=RINK*(IJ+IJC-8)
0101          304 CONTINUE
0102              GO TO (305,306,307),IX
0103          305 X(IC)=XKC(IC)+HC
0104              GO TO 308
0105          306 Y(IC)=YKC(IC)+HC
0106              GO TO 308
0107          307 Z(IC)=ZKC(IC)+HC
0108          308 CONTINUE
        C ///////////////////////////////////////////////////////////////////////////////
        C      CONVERT FROM CARTESIAN COORDINATES TO PUT6 COORDINATES
0109              CALL DIST
0110              CALL ANGLE
```

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C ////////////////////////////////////////////////////////////////////////////////////
C        CALCULATE THE POTENTIAL ENERGY  CORRESPONDING TO THE MOLECULAR GEOMETRY.
0111            CALL PCT6
0112            ECC(IJ,KX,KI,IJC,IX,IC)=EE+16.3232D0
0113            DO 309 IA=1,6
0114            X(IA)=XKC(IA)
0115            Y(IA)=YKC(IA)
0116            Z(IA)=ZKC(IA)
0117        309 CONTINUE
0118         30 CONTINUE
0119            DO 310 IA=1,6
0120            X(IA)=XK(IA)
0121            Y(IA)=YK(IA)
0122            Z(IA)=ZK(IA)
0123        310 CONTINUE
0124         31 CONTINUE
0125            IF(IX.NE.KX.OR.IC.NE.KI)GO TO 71
C        STORE DUPLICATE ENERGY VALUES FOR DIAGONAL  ELEMENT FORCE CONSTANT CALCULA-
C        TION.
0126            DO 70 IJ=1,7
0127            DO 70 IJC=1,7
0128            KEC=IJ+IJC
0129            IF(IJ.EQ.1.OR.IJ.EQ.7)GO TO 70
0130            GO TO (52,52,53,54,55,56,57,58,59,60,61,62,63,64),KEC
0131         52 ECC(IJ,KX,KI,IJC,IX,IC)=ECC(1,KX,KI,1,IX,IC)
0132            GO TO 70
0133         53 ECC(IJ,KX,KI,IJC,IX,IC)=ECC(1,KX,KI,2,IX,IC)
0134            GO TO 70
0135         54 ECC(IJ,KX,KI,IJC,IX,IC)=ECC(1,KX,KI,3,IX,IC)
0136            GO TO 70
0137         55 ECC(IJ,KX,KI,IJC,IX,IC)=ECC(1,KX,KI,4,IX,IC)
0138            GO TO 70
0139         56 ECC(IJ,KX,KI,IJC,IX,IC)=ECC(1,KX,KI,5,IX,IC)
0140            GO TO 70
0141         57 ECC(IJ,KX,KI,IJC,IX,IC)=ECC(1,KX,KI,6,IX,IC)
0142            GO TO 70
0143         58 ECC(IJ,KX,KI,IJC,IX,IC)=ECC(1,KX,KI,7,IX,IC)
0144            GO TO 70
0145         59 ECC(IJ,KX,KI,IJC,IX,IC)=ECC(7,KX,KI,2,IX,IC)
0146            GO TO 70
0147         60 ECC(IJ,KX,KI,IJC,IX,IC)=ECC(7,KX,KI,3,IX,IC)
0148            GO TO 70
0149         61 ECC(IJ,KX,KI,IJC,IX,IC)=ECC(7,KX,KI,4,IX,IC)
0150            GO TO 70
0151         62 ECC(IJ,KX,KI,IJC,IX,IC)=ECC(7,KX,KI,5,IX,IC)
0152            GO TO 70
0153         63 ECC(IJ,KX,KI,IJC,IX,IC)=ECC(7,KX,KI,6,IX,IC)
0154            GO TO 70
0155         64 ECC(IJ,KX,KI,IJC,IX,IC)=ECC(7,KX,KI,7,IX,IC)
0156         70 CONTINUE
0157         71 CONTINUE
C ////////////////////////////////////////////////////////////////////////////////////
C        CALCULATE SEVEN POINT FIRST DERIVATIVES
0158            DO 75 IJ=1,7
0159            DEA=ECC(IJ,KX,KI,5,IX,IC)-ECC(IJ,KX,KI,3,IX,IC)
0160            DEB=ECC(IJ,KX,KI,6,IX,IC)-ECC(IJ,KX,KI,2,IX,IC)
0161            DEC=ECC(IJ,KX,KI,7,IX,IC)-ECC(IJ,KX,KI,1,IX,IC)
0162            D(IJ,KX,KI,IX,IC)=(A*DEA+B*DEB+C*DEC)/RINK
```

```
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0163         75 CONTINUE
      C //////////////////////////////////////////////////////////////////////////////////
      C    CALCULATE SEVEN POINT SECOND DERIVATIVES
0164            DDEA=D(5,KX,KI,IX,IC)-D(3,KX,KI,IX,IC)
0165            DDEB=D(6,KX,KI,IX,IC)-D(2,KX,KI,IX,IC)
0166            DDEC=D(7,KX,KI,IX,IC)-D(1,KX,KI,IX,IC)
0167            DD(KX,KI,IX,IC)=((A*DDEA+B*DDEB+C*DDEC)/RINK)*FACT
0168            WRITE(6,780)XYZ(KX),KI,XYZ(IX),IC,RINK
0169        780 FORMAT('1',1X,'THE ENERGY SETS AND FIRST DERIVATIVES USED TO CALCU
           1LATE THE SECOND DERIVATIVE WITH RESPECT TO:',//,1X,A2,I2,') AND ',A2,I2
           2A2,I2,') USING AN INCREMENT OF RINK =',1PD22.13,///)
0170            DO 76 IJ=1,7
0171            IXD=IJ-4
0172            WRITE(6,791)
0173        791 FORMAT(18X,'1*RINK',24X,'2*RINK',24X,'3*RINK')
0174            WRITE(6,792)(ECC(IJ,KX,KI,IA,IX,IC),IA=5,7)
0175        792 FORMAT(2X,'E+',2X,3(1PD30.15))
0176            WRITE(6,793)ECC(IJ,KX,KI,3,IX,IC),ECC(IJ,KX,KI,2,IX,IC),ECC(IJ,KX,KI
           1KI,1,IX,IC)
0177        793 FORMAT(2X,'E-',2X,3(1PD30.15))
0178            WRITE(6,794)XYZ(IX),IC,XYZ(KX),KI,IXD,D(IJ,KX,KI,IX,IC)
0179        794 FORMAT(6X,'DV/D(',A2,I2,')) AT (',A2,I2,')',I2,'*RINK)=',1PD25.15,
           1/)
0180         76 CONTINUE
0181            WRITE(6,795)XYZ(KX),KI,XYZ(IX),IC,DD(KX,KI,IX,IC)
0182        795 FORMAT(2X,'DDV/D(',A2,I2,')D(',A2,I2,')=',1PD25.15,///)
      C //////////////////////////////////////////////////////////////////////////////////
      C    CALCULATE 3 POINT SECOND DERIVATIVES
0183            EXY=ECC(4,KX,KI,4,IX,IC)
0184          . EPP=ECC(5,KX,KI,5,IX,IC)
0185            EMM=ECC(3,KX,KI,3,IX,IC)
0186            EPM=ECC(5,KX,KI,3,IX,IC)
0187            EMP=ECC(3,KX,KI,5,IX,IC)
0188            DHS=RINK*RINK
0189            EDD=(EPP+EMM-(2.0D0*EXY))/DHS
0190            EED=(EPM+EMP-(2.0D0*EXY))/DHS
0191            DD3(KX,KI,IX,IC)=(EDD-EED)/4.0D0
0192            DD3(KX,KI,IX,IC)=DD3(KX,KI,IX,IC)*FACT
0193            WRITE(6,797)
0194        797 FORMAT(//,5X,'SECOND DERIVATIVE BY 3 POINT METHOD',/)
0195            WRITE(6,795)XYZ(KX),KI,XYZ(IX),IC,DD3(KX,KI,IX,IC)
0196            IF(KX.EQ.IX.AND.KI.EQ.IC)GO TO 540
0197            GO TO 551
0198        540 CONTINUE
      C //////////////////////////////////////////////////////////////////////////////////
      C    SET-UP AND CALCULATE DIAGONAL FORCE CONSTANT MATRIX ELEMENTS BY POLYNOMIAL
      C    LEAST SQUARES FIT METHOD.
0199            DO 550 IK=1,7
0200            DO 550 IY=1,7
0201            IF(IK.GT.1.AND.IY.LT.7)GO TO 550
0202            KS=IK+IY-1
0203            KFC=KS-7
0204            XX(KS)=KFC*RINK
0205            YY(KS)=ECC(IY,KX,KI,IK,IX,IC)
0206        550 CONTINUE
0207            CALL LESQ(2,13,XX,YY,CO)
0208            WRITE(6,560)
0209        560 FORMAT(2X,'SECOND DERIVATIVE OF THE POLYNOMIAL LEAST SQUARES EQUATION FOLL
```

```
                         1ION FOLLOWS',/)
0210                     DDP=0.0D0
0211                     DDP=2.0D0*CO(3)*FACT
0212                     WRITE(6,795)XYZ(KX),KI,XYZ(IX),IC,DDP
0213            551 CONTINUE
0214            300 CONTINUE
0215            311 CONTINUE
0216                     KCX=0
0217                     DO 42 I=1,6
0218                     DO 42 KX=1,3
0219                     KCX=KCX+1
0220                     KC(KX,I)=KCX
0221             42 CONTINUE
0222                     WRITE(6,775)
0223                     WRITE(6,768)
0224            768 FORMAT(1X,'CARTESIAN COORDINATE FORCE CONSTANT MATRIX BY 3 POINT M
                        1ETHOD:')
0225                     KCT=0
0226                     DO 439 I=1,4
0227                     KCR(I)=0
0228                     KCC(I)=0
0229            439 BC(I)=0.0D0
0230                     KR=0
0231                     DO 445 KI=1,6
0232                     DO 445 KX=1,3
0233                     KR=KR+1
0234                     WRITE(6,761)KR
0235                     WRITE(6,760)((DD3(KX,KI,IX,I),IX=1,3),I=1,6)
0236                     KCT=0
      C ////////////////////////////////////////////////////////////////////////////
      C     CONSTRUCT AND PUNCH CARTESIAN COORDINATE FORCE CONSTANT MATRIX BY 7 POINT
      C     METHOD.
0237                     DO 444 I=1,6
0238                     DO 444 IX=1,3
0239                     IF(DABS(DD3(KX,KI,IX,I)).LE.0.1D-9)GO TO 441
0240                     KCT=KCT+1
0241                     KCR(KCT)=KC(KX,KI)
0242                     KCC(KCT)=KC(IX,I)
0243                     BC(KCT)=DD3(KX,KI,IX,I)
0244                     IF(KCT.EQ.4)GO TO 440
0245            441 IF(I.EQ.6.AND.IX.EQ.3)GO TO 440
0246                     GO TO 444
0247            440 CONTINUE
0248                     WRITE(7,763)(KCR(KCX),KCC(KCX),BC(KCX),KCX=1,4)
0249                     WRITE(6,763)(KCR(KCX),KCC(KCX),BC(KCX),KCX=1,4)
0250                     KCT=0
0251                     DO 442 IZ=1,4
0252                     KCR(IZ)=0
0253                     KCC(IZ)=0
0254                     BC(IZ)=0.0D0
0255            442 CONTINUE
0256            444 CONTINUE
0257            445 CONTINUE
0258                     WRITE(6,775)
0259                     WRITE(6,762)
0260            762 FORMAT(1X,'CARTESIAN COORDINATE FORCE CONSTANT MATRIX BY 7 POINT M
                        1ETHOD.')
0261                     NEND=-2
```

```
0262            765 FORMAT(I3)
0263                KR=0
0264                DO 44 KI=1,6
0265                DO 44 KX=1,3
0266                KR=KR+1
0267                WRITE(6,761)KR
0268            761 FORMAT(//1X,'ROW',I3)
0269                WRITE(6,760)((DD(KX,KI,IX,I),IX=1,3),I=1,2)
0270                WRITE(6,760)((DD(KX,KI,IX,I),IX=1,3),I=3,4)
0271                WRITE(6,760)((DD(KX,KI,IX,I),IX=1,3),I=5,6)
0272            760 FORMAT(/,1X,6(1X,1PD20.13))
0273            763 FORMAT(4(2I3,1PD14.7))
0274                DO 430 I=1,4
0275                KCR(I)=0
0276                KCC(I)=0
0277            430 BC(I)=C.0D0
0278                KCT=0
      C ////////////////////////////////////////////////////////////////////////////////////
      C     CONSTRUCT AND PUNCH CARTESIAN COORDINATE FORCE CONSTANT MATRIX BY 3 POINT
      C     METHOD
0279                DO 43 IC=1,6
0280                DO 43 IX=1,3
0281                IF(DABS(DD(KX,KI,IX,IC)).LE.0.1D-9)GO TO 431
0282                KCT=KCT+1
0283                KCR(KCT)=KC(KX,KI)
0284                KCC(KCT)=KC(IX,IC)
0285                BC(KCT)=DD(KX,KI,IX,IC)
0286                IF(KCT.EQ.4)GO TO 432
0287            431 IF(IC.EQ.6.AND.IX.EQ.3)GO TO 432
0288                GO TO 43
0289            432 WRITE(7,763)(KCR(KCX),KCC(KCX),BC(KCX),KCX=1,4)
0290                WRITE(6,763)(KCR(KCX),KCC(KCX),BC(KCX),KCX=1,4)
0291                KCT=0
0292                DO 433 I=1,4
0293                KCR(I)=0
0294                KCC(I)=0
0295            433 BC(I)=0.0D0
0296             43 CONTINUE
0297                IF(KX.EQ.3.AND.KI.EQ.6)WRITE(7,765)NEND
0298             44 CONTINUE
      C >>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>
      C     A SMALLER FORCE CONSTANT MATRIX IS NEEDED FOR CH3 FREQUENCY CALCULATION.
      C     CONSTRUCT AND PUNCH CH3 TRUNCATED FORCE CONSTANT MATRICES.
      C <<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<
0299                WRITE(6,766)
0300                WRITE(7,766)
0301            766 FORMAT(2X,'CARTESIAN COORDINATE FORCE CONSTANT SET FOR CH3. BY 7 PT. METH.
                   1T. METHOD')
0302                DO 45 I=1,4
0303                KCR(I)=0
0304                KCC(I)=0
0305                BC(I)=0.0D0
0306             45 CONTINUE
0307                KCT=0
0308                DO 48 KI=1,6
0309                DO 48 KX=1,3
0310                IF(KC(KX,KI).LT.4.OR.KC(KX,KI).GT.15)GO TO 48
0311                DO 47 IC=1,6
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0312                  DU 47 IX=1,3
0313                  IF(KC(IX,IC).LT.4.OR.KC(IX,IC).GT.15)GO TO 93
0314                  IF(DABS(DD(KX,KI,IX,IC)).LT.1.0E-10)DD(KX,KI,IX,IC)=0.0D0
0315                  IF(DD(KX,KI,IX,IC).EQ.0.0D0)GO TO 47
0316                  KCT=KCT+1
0317                  KCR(KCT)=KC(KX,KI)-3
0318                  KCC(KCT)=KC(IX,IC)-3
0319                  BC(KCT)=DD(KX,KI,IX,IC)
0320                  IF(IX.EQ.3.AND.IC.EQ.6)GO TO 49
0321                  GO TO 50
0322               49 IF(KX.EQ.3.AND.KI.EQ.6)GO TO 51
0323               50 CONTINUE
0324                  IF(KCT.NE.4)GO TO 47
0325                  GO TO 51
0326               93 IF(KCT.GT.0)GO TO 51
0327                  GO TO 47
0328               51 CONTINUE
0329                  WRITE(6,763)(KCR(I),KCC(I),BC(I),I=1,4)
0330                  WRITE(7,763)(KCR(I),KCC(I),BC(I),I=1,4)
0331                  DO 46 I=1,4
0332                  KCR(I)=0
0333                  KCC(I)=0
0334                  BC(I)=0.0D0
0335               46 CONTINUE
0336                  KCT=0
0337               47 CONTINUE
0338               48 CONTINUE
0339                  WRITE(6,765)NEND
0340                  WRITE(7,765)NEND
0341                  WRITE(6,767)
0342                  WRITE(7,767)
0343              767 FORMAT(2X,'CARTESIAN COORDINATE FORCE CONSTANT SET FOR CH3. BY 3 PT.
                     1T. METHOD')
0344                  DO 85 I=1,4
0345                  KCR(I)=0
0346                  KCC(I)=0
0347                  BC(I)=0.0D0
0348               85 CONTINUE
0349                  KCT=0
0350                  DO 88 KI=1,6
0351                  DO 88 KX=1,3
0352                  IF(KC(KX,KI).LT.4.OR.KC(KX,KI).GT.15)GO TO 88
0353                  DO 87 IC=1,6
0354                  DO 87 IX=1,3
0355                  IF(KC(IX,IC).LT.4.OR.KC(IX,IC).GT.15)GO TO 92
0356                  IF(DABS(DD3(KX,KI,IX,IC)).LT.1.0D-10)DD3(KX,KI,IX,IC)=0.0D0
0357                  IF(DD3(KX,KI,IX,IC).EQ.0.0D0)GO TO 87
0358                  KCT=KCT+1
0359                  KCR(KCT)=KC(KX,KI)-3
0360                  KCC(KCT)=KC(IX,IC)-3
0361                  BC(KCT)=DD3(KX,KI,IX,IC)
0362                  IF(IX.EQ.3.AND.IC.EQ.6)GO TO 89
0363                  GO TO 90
0364               89 IF(KX.EQ.3.AND.KI.EQ.6)GO TO 91
0365               90 CONTINUE
0366                  IF(KCT.NE.4)GO TO 87
0367                  GO TO 91
0368               92 IF(KCT.GT.0)GO TO 91
```

```
0369              GO TO 87
0370          91 CONTINUE
0371              WRITE(6,763)(KCR(I),KCC(I),BC(I),I=1,4)
0372              WRITE(7,763)(KCR(I),KCC(I),BC(I),I=1,4)
0373              DO 86 I=1,4
0374              KCR(I)=0
0375              KCC(I)=0
0376              BC(I)=0.000
0377          86 CONTINUE
0378              KCT=0
0379          87 CONTINUE
0380          88 CONTINUE
0381              WRITE(6,765)NENU
0382              WRITE(7,765)NENU
0383        1111 STOP
0384              END
```

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      C ****************************************************************************
      C                   ABSOLUTE RATE THEORY ROUTINE
      C              CALCULATES KINETIC ISOTOPE EFFECTS USING
      C                 A MODIFICATION OF SUBROUTINE THERMO
      C                           ADAPTED FROM
      C               WOLFSBERG MODIFICATION OF SCHACHTSCNEIDER SD-9032-1
      C ****************************************************************************
0001          IMPLICIT REAL*8 (A-H,O-Z)
0002          DIMENSION SIG(18,18),W(18,18),DV(18),WT(10),RECORD(40),ARG(300),
             1NCO(300),NFO(300),Z(300),TEMS(18),TMOM(3),BEXC(2,40,18),RBEXC(18,40),
             20),ONUIM(2,40),OGTL(2,40),OGFR(2,40),SUMNU(2,40),MOPROB(2,40),SSUMNU(2,40)
             3NU(2,40)
0003          COMMCN SIG,W,DV,TEMS,TMOM,TMASS,RECORD,Z,BEXC,RBEXC,
             1 WT,ONUIM,OGTL,OGFR,SUMNU,SSUMNU,
             *ROTC,DV1,DV2,DV21,DV22,ASSM,
             2 NOTEM,NQ,KIND,NUMB,NOAT,N1UMB,N2UMB,NOPROB,NRO,NCO,NFO,MOPROB
             *,MO1,NROT
      C /////////////////////////////////////////////////////////////////////////
      C     THIS MAIN KOUTINE CONTROLS THE INPUT TO THERMO WHICH CALCULATES KINETIC
      C     ISOTOPE EFFECTS USING ABSOLUTE RATE THEORY.
      C /////////////////////////////////////////////////////////////////////////
0004       90 CONTINUE
      C    PRINT SUPPRESS CONTROL CARD
      C>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>
      C     IF NCO(1)=1 THEN THERMO WILL ONLY WRITE THE FINAL ISOTOPE EFFECT RESULTS
0005          NCO(1)=1
0006          NCO(1)=0
      C/////////////////////////////////////////////                <<<<<<<<<<<<
0007        2 FORMAT(I3)
      C     SAME CONTROL CARD AS USED IN THE WOLFSBERG MODIFICATION OF THE
      C     SCHACHTSCHNEIDER PROGRAM.
      C //////////////////////////////////////////////////////////////////////
      C     IND = INDICATOR OF NEW  FREQUENCY DATA SET WHEN EQUAL TO -09
      C     NOPROB = PROBLEM NUMBER OF DATA SET
      C     NQ = NUMBER OF FREQUENCIES
      C     NOAT = NUMBER OF ATOMS
      C     NOTEM = NUMBER OF TEMPERATURES TO BE READ IN
      C     KIND= ISOTOPIC CONFIGURATION (1= LIGHT ISOTOPE, 2= HEAVY ISOTOPE).
      C     NUMB = LABEL FOR FREQUENCY SET FROM 1 TO 40
      C     N1UMB = 0, IF KIND = 1; OTHERWISE,
      C     N1UMB = NUMB OF THE DATA SET THAT IS TO RATIOED WITH THE PRESENT DATA SET..
      C     N2UMB = 0 IF PRESENT DATA IS FOR REACTANTS OR KIND=1 DATA; OTHERWISE,
      C     N2UMB = NUMB OF THE KIND=2 REACTANT DATA TO BE RATIOED WITH
      C             THIS ISOTOPIC TRANSITION STATE DATA RATIO.
      C     NROT = INDICATES ROTATIONAL CORRECTION IS TO BE READ IN IF > ZERO.
      C     (NOTE: ROTATIONAL AND ASSM FACTORS ARE PLACED ON AN ADDITIONAL CARD
      C     AND PUT IMMEDIATELY AFTER THE SECOND LABEL CARD IN THE  LAST DATA SET
      C     BEFORE THE KIE IS CALCULATED.     )
      C     RCTC = EXPONENTIAL ROTATIONAL CORRECTION FACTOR.
      C     ASSM = AN ADDITIONAL EXPONENTIAL CORRECTION FACTOR.
      C     MO1 = IF>0 THEN DATA SET IS A CONTINUATION OF THE PREVIOUS  DATA SET.
      C           ( AS IF READING SECOND OF TWO OR MORE REACTANT DATA SETS).
      C ////////////////////////////////////////////////////////////////////////
0008       93 READ(5,4)IND,NOPROB,NQ,NOAT,NOTEM,KIND,NUMB,N1UMB,N2UMB,NROT,
             *MO1
0009        4 FORMAT(I3,I6,I3,8X,I3,9X,6I3,24X,I3)
0010          IF(NOPROB.EQ.7777)CALL EXIT
0011       91 IF(9+IND)90,92,90
```

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0012              92 CONTINUE
0013              97 READ(5,6)(RECORD(I),I=1,40)
0014               6 FORMAT(20A4)
0015                 ROTC=C.0D0
0016                 ASSM=0.0D0
0017                 IF(NROT.EQ.))GO TO 102
0018                 READ(5,11)ROTC,ASSM
0019              11 FORMAT(F12.6,48X,F12.6)
0020             102 IF(NOTEM)103,103,800
0021             800 IF(KIND-1)802,802,103
0022             802 IF(NUMB-1)804,804,103
        C      READ TEMPERATURES AT WHICH KIES ARE TO BE CALCULATED
        C      ONLY IF KIND=1 AND NUMB=1      *********************************************
0023             804 READ(5,10)(TEMS(I),I=1,NCTEM)
0024             103 CONTINUE
        C ////////////////////////////////////////////////////////////////////////////////
        C      READ CALCULATED FREQUENCIES FOR A GIVEN MOLECULAR ISOTOPIC CONFIGURATION.
0025                 DO 300 I=1,NQ
0026             300 DV(I)=0.0D0
0027                 READ(5,10)(DV(I),I=1,NQ)
0028              10 FORMAT(6F12.6)
        C ////////////////////////////////////////////////////////////////////////////////
        C      READ ATOMIC WEIGHTS BY ATCM NUMBER.
0029             324 READ(5,10)(WT(I),I=1,NOAT)
        C      READ MOMENTS OF INERTIA INTO TMOM(I).
        C      TMASS = MOLECULAR WEIGHT OF ISOTOPIC  CONFIGURATION.
0030                 READ(5,7)(TMOM(I),I=1,3),TMASS
0031               7 FORMAT(4E18.9)
0032                 IF(NOTEM)280,280,806
0033             806 CALL THERMO
0034             280 CONTINUE
0035                 GO TO 90
0036                 END
```

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0001            SUBROUTINE THERMO                                              321  359
      C //////////////////////////////////////////////////////////////////////////
      C      THERMO WITH BIGELEISEN DEFINITION OF F
      C      THIS ROUTINE CALCULATES (K1/K2) = MMI * EXC * ZPE
      C      AND COMPARES IT TO F(1/2)= VP * EXC * ZPE
      C      THE ROUTINE ALSO CALCULATES THE FIT TO THE LN  OF THE ARRHENIUS EQUATICN:
      C            LN(K1/K2) = LN(A1/A2) + (E1-E2)/(R*T)
      C //////////////////////////////////////////////////////////////////////////
0002            IMPLICIT REAL*8 (A-H,O-Z)
      C //////////////////////////////////////////////////////////////////////////
      C      TEMS = ARRAY FOR TEMPERATURES USED IN ISOTOPE EFFECT CALCULATIONS.
      C      DV = ARRAY FOR NORMAL MODE FREQUENCIES
      C      TMOM = ARRAY FOR PRINCIPAL MOMENTS OF INERTIA OF ISTOPIC MOLECULE.
      C      BEXC = ARRAY FOR VIBRATIONAL EXCITATION  TERM VALUES.
      C      DSUMU = ARRAY FOR ZPE TERM VALUES.
      C      WT = ARRAY FOR ISOTOPIC ATOMIC WEIGHTS.
      C      TMASFA = ARRAY FOR MMI TERM VALUES.
      C      TMASS =  MOLECULAR WEIGHT.
      C      OGFR =  LN(VIBRATIONAL PRODUCT FACTOR)
      C      SUMNU = ARRAY FOR THE SUMS OF THE ISOTOPIC  VIBRATIONAL FREQUENCIES.
      C      SSUMNU = ARRAY FOR  (SUMNU)**2.
      C      UNUIM = ARRAY FOR ISOTOPIC VALUES OF THE IMAGINARY FREQUENCIES.
      C      YOU = ARRAY FOR UNITLESS VIBRATIONAL ENERGY FACTORS.
      C      YOU = H*C*NU/(K*T)
      C      BTUN = ARRAY FOR BELL TUNNELING FACTORS.
      C      WTUN = ARRAY FOR WIGNER TUNNELING FACTORS.
      C //////////////////////////////////////////////////////////////////////////
0003            REAL*8 XL(40),YL(40),COEF(10)
      C //////////////////////////////////////////////////////////////////////////
      C THE FOLLOWING ARE ARRHENIUS EQUATION PARAMETERS.
      C      ARAT = ARRAY FOR RATIO OF PREEXPONENTIAL FACTORS.
      C      DE = ARRAY FOR DIFFERENCES IN ACTIVATION ENERGIES.
      C      SDY = STANDARD DEVIATION IN THE RATIO OF RATE CONSTANTS K1/K2.
      C      SDA = STANDARD DEVIATION IN ARAT.
      C      SDDE = STANDARD DEVIATION IN DE.
      C //////////////////////////////////////////////////////////////////////////
0004            REAL*8 BEXTUN(18),YDEV(18),BXQRAT(18),ARAT(4),DE(4),SDY(4),Y(4,18),
             2,SDA(40),SDDE(40),SY(4),SXY(4)
0005            DIMENSION TEMS(18),DV(18),TMOM(3),BEXC(2,40,18),WT(10),TMASFA(2,40  321  360
             1),OGIL(2,40),OGFR(2,40),SUMNU(2,40),RBEXC(18,40),RMASFA(40),DOGFR(  321  361
             240),RECORD(40),DSUMNU(40),MOPROB(2,40)   ,YOU(18),SIG(18,18),W(18,18  321  362
             38),RQRAT(18),SSUMNU(2,40),UNUIM(2,40),WTUN(18),BTUN(18),WRQRAT(18)  321  363
             4,BRQRAT(18),DSSUMN(40),REFFR(18),NRO(300),NCO(300),NFO(300),Z(300)
             5,OGIL(2,40)
0006            COMMON SIG,W,DV,TEMS,TMOM,TMASS,RECORD,Z,BEXC,RBEXC,
             1 WT,UNUIM,OGIL,OGFR,SUMNU,SSUMNU,
             *ROTC,DV1,DV2,DV21,DV22,ASSM,
             2 NOTEM,NQ,KIND,NUMB,NOAT,N1UMB,N2UMB,NUPROB,NRO,NCO,NFO,MOPROB
             *,MU1,NROT
0007            ALOG(XO)=DLOG(XO)
0008            SIGN(XO,YO)=DSIGN(XO,YO)
0009            EXP(XO)=DEXP(XO)
0010            SQRT(X)=DSQRT(X)
0011            SIN(XO)=DSIN(XO)
0012            ABS(XO)=DABS(XO)
0013            MOPROB(KIND,NUMB)=NUPROB                                        321  366
0014            DO 930 I=1,3                                                    321  366A
0015            IF (TMOM(I))928,928,930                                         321  366B
```

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     0016        928 TMOM(I)=1.0D0
     0017        930 CONTINUE                                                       32I 3660
     0018            TMAF=1.0D0
            C ////////////////////////////////////////////////////////////////////////////////
            C    MU1 ALLOWS FOR MORE THAN ONE REACTANT TO BE INCLUDED IN ALL TERMS.
            C    IF MU1 > 0 THEN THE DATA SET IS ASSUMED TO BE A PART OF THE PREVICUS CNE.
     C019            IF(MU1.GT.0)TMAF=TMASFA(KIND,NUMB)
            C ////////////////////////////////////////////////////////////////////////////////
            C    CALCULATE   MMI ELEMENT.
     C020        940 TMASFA(KIND,NUMB)=(TMOM(1)*TMOM(2)*TMOM(3))**0.5D0*TMASS**1.5D0*TM32I  367
                1AF
     0021            IF(MC1)951,950,951
     0022        950 OGTL(KIND,NUMB)=0.0D0
     0023        951 CONTINUE
     0024        952 DO 960 I=1,NOAT                                                 32I  369
     0025        956 OGTL(KIND,NUMB)=OGTL(KIND,NUMB)+1.5D0*ALOG(WT(I))             32I  370
     0026        960 CONTINUE                                                       32I  371
     C027            IF(MC1)965,964,965
     C028        964 OGFR(KIND,NUMB)=0.0D0                                          32I  372
     0029        965 CONTINUE
     C030        968 DO 980 I=1,NC                                                  32I 373
     0031        972 IF(0.1D0-DV(I))976,980,980                                     32I  374
     0032        976 OGFR(KIND,NUMB)=OGFR(KIND,NUMB)+ALOG(DV(I))                   32I  375
     0033        980 CONTINUE                                                       32I  376
     0034            IF(MU1)987,984,987
     0035        984 SUMNU(KIND,NUMB)=0.0D0                                         32I  377
     C036        986 SSUMNU(KIND,NUMB)=0.0L0                                        32I  378
     0037            ONUIM(KIND,NUMB)=0.0D0
     0038        987 CONTINUE
     C039        988 DO 999 I=1,NC
     0040        992 IF(0.1-DV(I))994,996,996                                       32I  380
     0041        994 SUMNU(KIND,NUMB)=SUMNU(KIND,NUMB)+DV(I)/2.0D0
     C042            GO TO 998
     0043        996 IF(-1.0-DV(I))998,998,997
     0044        997 ONUIM(KIND,NUMB)=-DV(I)
     C045        998 DVT=DV(I)**2
     0046        999 SSUMNU(KIND,NUMB)=SSUMNU(KIND,NUMB)+SIGN(DVT,DV(I))
     0047            IF(NCO(L).EQ.1)GO TO 904
     0048       1200 WRITE(6,1400)NOPROB,KIND,NUMB,(RECORD(I),I=1,20)
     0049       1400 FORMAT(38H1 THERMODYNAMIC QUANTITIES PROBLEM NO.18,15H  MOLECULE K32I  385
                1IND,I3,7H NUMBER,I3,/,12X,20A4)
     C050       1204 WRITE(6,1404)(TMOM(I),I=1,3),TMASS                             32I  387
     0051       1404 FORMAT(6HO IA= F12.6,6H  IB= F12.6,6H  IC= F12.6,8H  MASS= F12.6) 32I  388
     C052       1208 WRITE(6,1408)TMASFA(KIND,NUMB)                                32I  389
     0053       1408 FORMAT(27HO ((IA*IB*IC)**1/2)*M**3/2=E18.9)                    32I  390
     0054       1212 WRITE(6,1412)(DV(I),I=1,NQ)                                    32I  391
     0055       1214 WRITE(6,1414)SUMNU(KIND,NUMB),SSUMNU(KIND,NUMB)               32I  392
     0056       1412 FORMAT(21HO FREQUENCIES IN CM-1/(7F16.6))                     32I  393
     C057       1414 FORMAT(11HO SUM NU/2=E18.9,17HCM-1   SUM NU**2=E18.9,4HCM-2)  32I  394
     C058        904 DO 1590 L=1,NOTEM
     0059            IF(MU1)909,908,909
     C060        908 BEXC(KIND,NUMB,L)=1.0D0
     0061        909 CONTINUE
     0062        910 SUMU=0.0D0
            C ////////////////////////////////////////////////////////////////////////////////
            C    CALCULATE U FACTORS
     0063        912 DO 944 I=1,NQ                                                  32I  398
     C064        913 YOU(I)=1.4388D0*DV(I)/TEMS(L)
```

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0065          916 IF(0.1-UV(I))920,924,924                                          321  400
         C ////////////////////////////////////////////////////////////////////////
         C    CALCULATE EXC ELEMENT
0066          920 DEXC(KIND,NUMB,L)=BEXC(KIND,NUMB,L)*(1.0D0-EXP(-YOU(I)))          321  401
0067          924 CONTINUE                                                          321  402
0068          930 IF(0.1-UV(I))940,944,944                                          321  403
0069          940 SUMU=SUMU+YOU(I)/2.0D0                                            321  404
0070          944 CONTINUE                                                          321  405
0071              IF(NCO(1).EQ.1)GO TO 1550
0072         1216 WRITE(6,1416)TEMS(L)                                              321  406
0073         1416 FORMAT(15H0  TEMPERATURE=F12.6)                                   321  407
0074         1217 WRITE(6,1417)(YOU(I),I=1,NG)                                      321  408
0075         1417 FORMAT(24H0 THE VALUES OF U FOLLOW/(10F12.6))                     321  409
0076         1220 WRITE(6,1420)BEXC(KIND,NUMB,L),SUMU                              321  410
0077         1550 CONTINUE
0078         1420 FORMAT(19H EXCITATION FACTOR=F12.8,10H 1/2SUM U=F14.6)            321  411
         C ////////////////////////////////////////////////////////////////////////
         C    CALCULATE ISOTOPIC RATIOS.
0079         1000 IF(KIND-2)1084,1004,1084                                          321  412
0080         1004 RMASFA(NUMB)=TMASFA(2,NUMB)/TMASFA(1,N1UMB)                       321  413
0081         1020 DOGTL=OGTL(1,N1UMB)-OGTL(2,NUMB)                                  321  414
0082         1024 TRFA=RMASFA(NUMB)*EXP(DOGTL)                                      321  415
0083         1028 DOGFR(NUMB)=OGFR(2,NUMB)-OGFR(1,N1UMB)                            321  416
0084         1032 PRODFA=EXP(DOGFR(NUMB))                                          321  417
0085         1035 TRRULE=PRODFA/TRFA                                               321  418
0086         1036 DSUMNU(NUMB)=SUMNU(1,N1UMB)-SUMNU(2,NUMB)                         321  419
0087              DSSUMN(NUMB)=SSUMNU(1,N1UMB)-SSUMNU(2,NUMB)
0088              IF(NCO(1).EQ.1)GO TO 1037
0089         1226 WRITE(6,1428)NUMB,NOPROB,N1UMB,MOPROB(1,N1UMB)                    321  420
0090         1428 FORMAT(56H1 THERMODYNAMIC QUANTITIES FOR MOLECULE OF KIND 2 NUMBER321  421
              113,12H PROBLEM NO.I8/42H WITH RESPECT TO MOLECULE OF KIND 1 NUMBER321  422
              213,12H PROBLEM NO.I8)                                             321  423
0091         1232 WRITE(6,1432)TRRULE                                              321  424
0092         1432 FORMAT(81H0 RATIO PRODUCT NU2/PRODUCT NU1 TO MASS FACTOR=1.0 (TELL321  425
              1ER-REDLICH) OK=NULL/NU2L=E18.9)                                   321  426
0093         1037 DO 1551 L=1,NUTEM
0094         1038 RBEXC(L,NUMB)=BEXC(1,N1UMB,L)/BEXC(2,NUMB,L)                      321  428
0095              DSUMU=1.4388D0*(SUMNU(1,N1UMB)-SUMNU(2,NUMB))/TEMS(L)
0096         1039 EXSUMU=EXP(DSUMU)                                                321  430
0097         1040 QRAT=RMASFA(NUMB)*RBEXC(L,NUMB)*EXSUMU                            321  431
0098         1044 EFFR=PRODFA *RBEXC(L,NUMB)*EXSUMU                                 321  432
0099              IF(NCO(1).EQ.1)GO TO 1551
0100         1236 WRITE(6,1436)TEMS(L)                                             321  433
0101         1436 FORMAT(15H0  TEMPERATURE=F12.6)                                   321  434
0102         1240 WRITE(6,1440)RMASFA(NUMB),RBEXC(L,NUMB),EXSUMU,DSUMU,Q            321  435
              1RAT                                                             321  436
0103         1440 FORMAT(66H Q2/Q1=MASS FACTOR (2/1)*EXCITATION FACTOR (1/2)*ZERO-PO321  437
              1INT (1-2)=E18.9,1H*E18.9/50X,1H*E18.9,10H (OR EXP  E18.9,2H)=E18.9321  438
              2)                                                               321  439
0104         1244 WRITE(6,1444)EFFR                                               321  440
0105         1551 CONTINUE
0106         1444 FORMAT(10H0 S2/S1 F=E18.9)                                        321  441
0107         1048 IF(N2UMB)1084,1084,1052                                          321  442
0108         1052 RRMAS=RMASFA(N2UMB)/RMASFA(NUMB)                                 321  443
0109         1056 RPROD=EXP(DOGFR(N2UMB)-DOGFR(NUMB))                              321  444
0110         1058 RATIO=RRMAS/RPROD
0111              WRITE(6,1600)
0112         1600 FORMAT('1',' ABSOLUTE RATE THEORY EQUATIONS FOLLOW ',//)
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0113          IF(NCO(1).EQ.1)GO TO 1060
0114     1252 WRITE(6,1452)MOPROB(2,N2UMB),MOPROB(2,NUMB)                      32I  446
0115     1452 FORMAT(81H0 RATIOS OF RATIOS OF THERMODYNAMIC QUANTITIES. IN THE N32I  447
             1UMERATOR 2 IS PROBLEM NO.I8/36H IN THE DENOMINATOR 2 IS PROBLEM NO32I  448
             2.I8,1H.)                                                         32I  449
0116     1256 WRITE(6,1456)RATIO                                               32I  450
0117     1456 FORMAT(19H0 Q RATIO/F RATIO= E18.9)                             32I  451
         C ////////////////////////////////////////////////////////////////////////
         C    CALCULATE FINAL RATIO TERMS FOR MMI, EXC, & ZPE.
0118     1060 DO 1552 L=1,NOTEM
0119     1064 RRBEXC=RBEXC(L,N2UMB)/RBEXC(L,NUMB)                             32I  453
         C    CALCULATE ZPE TERM
         C ////////////////////////////////////////////////////////////////////////
0120     1068 RRSUMU=EXP(1.4388D0*(DSUMNU(N2UMB)-DSUMNU(NUMB))/TEMS(L))       32I  454
0121     1072 RQRAT(L)=RRMAS*RRBEXC*RRSUMU                                    32I  455
0122     1076 REFFR(L)=RPROD*RRBEXC*RRSUMU
         C ////////////////////////////////////////////////////////////////////////
         C    CALCULATE TUNNELLING FACTORS
0123          WTUN(L)=1.0D0
0124          BTUN(L)=1.0D0
0125          BEXTUN(L)=1.0D0
0126          IF(ONUIM(2,NUMB))1080,1080,1078
0127     1078 WTUN(L)=(1.0D0+(1.0D0/24.0D0)*(1.4388D0*ONUIM(1,N1UMB)/TEMS(L))**2
             1)/(1.0D0+(1.0D0/24.0D0)*(1.4388D0*ONUIM(2,NUMB)/TEMS(L))**2)
0128          BTUN(L)=(CNUIM(1,N1UMB)*SIN((1.4388D0*ONUIM(2,NUMB))/(2.0D0*TEMS(L32I 4557
             1))))/(ONUIM(2,NUMB)*SIN((1.4388D0*ONUIM(1,N1UMB))/(2.0D0*TEMS(L)))
             2)
0129          UTUN1=1.4388D0*ONUIM(1,N1UMB)/TEMS(L)
0130          UTUN2=1.4388D0*ONUIM(2,NUMB)/TEMS(L)
0131          BETUN1=1.0D0+(UTUN1*UTUN1/24.0D0)+(7.0D0*(UTUN1**4)/5760.0D0)
0132          BETUN2=1.0D0+(UTUN2*UTUN2/24.0D0)+(7.0D0*(UTUN2**4)/5760.0D0)
0133          BEXTUN(L)=BETUN1/BETUN2
0134     1080 WRQRAT(L)=RQRAT(L)*WTUN(L)
0135          BRQRAT(L)=RQRAT(L)*BTUN(L)
0136          BXQRAT(L)=RQRAT(L)*BEXTUN(L)
0137     1260 WRITE(6,1436)TEMS(L)                                            32I  457
0138     1264 WRITE(6,1464)RRMAS,RRBEXC,RRSUMU,RQRAT(L)                       32I  458
0139     1464 FORMAT(51H0 Q RATIO=MASS FACTOR*EXCITATION FACTOR*ZERO-POINT=E18.932I  459
             1,1H*E18.9/50X,1H*E18.9,1H=E18.9)                               32I  460
0140     1268 WRITE(6,1468)RPROD,RRBEXC,RRSUMU,REFFR(L)                       32I  461
0141     1552 CONTINUE
0142     1468 FORMAT(54H0 F RATIO=PRODUCT FACTOR*EXCITATION FACTOR*ZERO-POINT=E132I  462
             18.9,1H*E18.9/50X,1H*E18.9,1H=E18.9)                            32I  463
0143     1270 WRITE(6,1470)MOPROB(2,N2UMB),MOPROB(2,NUMB)                     32I A463
0144     1470 FORMAT(60H1 RATIOS OF RATIOS OF Q'S. IN THE NUMERATOR 2 IS PROBLEM32I B463
             1 NO.I8/36H IN THE DENOMINATOR 2 IS PROBLEM NO.I8,1H.,/1H0,5X11HTEMP32I C463
             2ERATURE6X,7H0 RATIO7X,13HWIGNER TUNNEL,3X,14HTUNNEL Q RATIO,3X,11H32I D463
             3BELL TUNNEL,3X,14HTUNNEL Q RATIO,3X,'BTUN EXPAN.',2X,'TUNNEL Q RAT32I E463
             41O',/)                                                          32I F463
         C ////////////////////////////////////////////////////////////////////////
0145          ZL=0
0146          SX=0.0D0
0147          SX2=0.0D0
0148          DO 1510 I=1,4
0149          SY(I)=0.0D0
0150     1510 SXY(I)=0.0D0
0151          DO 1272 L=1,NOTEM                                               32I EJLO
0152          XL(L)=1.0D0/TEMS(L)
```

```
0153              YL(L)=ALOG(ABS(RQRAT(L)))
0154              IF(TEMS(L).LT.350.0D0)GO TO 1272
0155              X=1.0D0/TEMS(L)
0156              Y(1,L)=ALOG(ABS(RQRAT(L)))
0157              Y(2,L)=ALOG(ABS(WRQRAT(L)))
0158              Y(3,L)=ALOG(ABS(BRQRAT(L)))
0159              Y(4,L)=ALOG(ABS(BXQRAT(L)))
0160              ZL=ZL+1
0161              SX=SX+X
0162              SX2=SX2+(X*X)
0163              DO 1511 I=1,4
0164              SY(I)=SY(I)+Y(I,L)
0165         1511 SXY(I)=SXY(I)+(X*Y(I,L))
0166         1272 WRITE(6,1472)TEMS(L),RQRAT(L),WTUN(L),WRQRAT(L),BTUN(L
                 1),BRQRAT(L),BEXTUN(L),BXQRAT(L)
0167         1472 FORMAT(6X,4(F12.6,E19.9))
0168              IF(ZL.LE.0)GO TO 1482
0169              DNOM=(ZL*SX2)-(SX*SX)
0170              DO 1512 I=1,4
0171              ARL=((SX2*SY(I))-(SX*SXY(I)))/DNOM
0172              ARAT(I)=EXP(ARL)
0173              DESR=((ZL*SXY(I))-(SX*SY(I)))/DNOM
0174              DE(I)=DESR*1.9872D0
0175              SUMSDY=0.0D0
0176              DO 1513 L=1,NOTEM
0177              IF(TEMS(L).LT.350.0D0)GO TO 1513
0178              YCALC=DESR*(1.0D0/TEMS(L))+ARL
0179              YDEV(L)=YCALC-Y(I,L)
0180              SUMSDY=SUMSDY+(YDEV(L)*YDEV(L))
0181         1513 CONTINUE
0182              SDY(I)=DSQRT(SUMSDY/(ZL-2.0D0))
0183              SDB=SDY(I)*SQRT(SX2/DNOM)
0184              SDA(I)=EXP(SDB+ARL)-ARAT(I)
0185              SDDE(I)=SDY(I)*SQRT(ZL/DNOM)*1.9872D0
0186         1512 CONTINUE
0187         1481 FORMAT(/,1X,'ARRHENIUS EQUATION COEFFICIENTS CALCULATED FROM THEIR TEM
                 1 TEMPERATURE DEPENDENCE',/,2X,'PRE-EXP. RATIO =',E19.9,3(12X,E19.9),/,9X,'
                 2),/,9X,'DELTA E =',E19.9,3(12X,E19.9),/,1X,'STD.DEV. LN(QRAT)=',E1
                 39.9,3(12X,E19.9),/,5X,'STDEV A1/A2 =',E19.9,3(12X,E19.9),/,9X,'STD
                 4TDEV DE =',E19.9,3(12X,E19.9))
0188         1480 WRITE(6,1481)(ARAT(I),I=1,4),(DE(I),I=1,4),(SDY(I),I=1,4)
                 *,(SDA(I),I=1,4),(SDDE(I),I=1,4)
0189         1482 CONTINUE
0190              WRITE(6,1473)MOPROB(2,N2UMB),MOPROB(2,NUMB)
0191         1473 FORMAT(60H0 RATIOS OF RATIOS OF F'S. IN THE NUMERATOR 2 IS PROBLEM
                 1 NO.I8./36H IN THE DENOMINATOR 2 IS PROBLEM NO.I8,1H./1H010X11HTEMP
                 2ERATURE5X7HF RATIO)
0192              DO 1474 L=1,NOTEM
0193         1474 WRITE(6,1475)TEMS(L),REFFR(L)
0194         1475 FORMAT(1H 7XF12.6,E22.9)
0195              WRITE(6,1456)RATIO
0196              DDSSUM=DSSUMN(N2UMB)-DSSUMN(NUMB)
0197              WRITE(6,1476)DDSSUM
0198         1476 FORMAT(15HDODEL DEL NU**2=E22.9)
0199              WRITE(6,1580)MOPROB(1,N1UMB),MOPROB(2,NUMB)
0200         1580 FORMAT(/,40X,'TRANSITION STATE PROBLEM NO. RATIO OF ',I8,' /',I6,
                 */)
             C ////////////////////////////////////////////////////////////////////////
```

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```
      C      CALCULATE LINEAR LEAST SQUARES FIT TO K1/K2 VERSUS 1/T.
0201         CALL LESQ(1,L,XL,YL,COEF)
      C //////////////////////////////////////////////////////////////////////////////
      C      CALCULATE QUADRATIC LEAST SQUARES FIT TO K1/K2 VERSUS 1/T OR K1/K2 VERSUS
      C      1/(T**2)       .
0202         CALL LESQ(2,L,XL,YL,CCEF)
      C      ROTATIONAL AND ANHARMONIC CORRECTION TO Q RATIO  (I.E. REACTANT ZPE
      C      CORRECTION).
0203  3300 IF(ROTC.EQ.0.0D0)GO TO 2221
0204       DO 3301 L=1,NOTEM
0205       RQR=RQRAT(L)*EXP(ROTC/TEMS(L))
0206       YL(L)=ALOG(ABS(RQR))
0207  3301 CONTINUE
0208       WRITE(6,3302)
0209  3302 FORMAT('1',1X,'LESQ FIT TO REACTANT ZPE CORRECTION',/)
0210       WRITE(6,3202)
0211       WRITE(6,3305)ROTC
0212  3305 FORMAT(/,1X,'ZPE CORRECTION FACTOR ROTC =',F12.6,/)
0213       CALL LESQ(1,L,XL,YL,COEF)
0214       CALL LESQ(2,L,XL,YL,CCEF)
0215  2221 IF(ASSM.EQ.0.0D0)GO TO 1084
0216       DO 3501 L=1,NOTEM
0217       RAR=RQRAT(L)*EXP(ASSM/TEMS(L))
0218       YL(L)=ALOG(ABS(RAR))
0219  3501 CONTINUE
0220       WRITE(6,3502)ASSM
0221  3502 FORMAT('1',1X,'LESQ FIT TO REACTANT ZPE CORRECTION',//,1X,'REACTANT
     *T CORRECTION FACTOR ASSM = ',F12.6,/)
0222       WRITE(6,3202)
0223  3202 FORMAT(1X,'THE COLUMNS LABELED X = 1/T , Y = LN( KIE ) AND EXP(Y) = KIE',/
     *= KIE',/)
0224       CALL LESQ(1,L,XL,YL,CCEF)
0225       CALL LESQ(2,L,XL,YL,COEF)
0226  1084 RETURN                                                    321  464
0227       END                                                       321  465
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```
0001          SUBROUTINE LESQ(M,NUMBER,X,Y,C)
C002          IMPLICIT REAL*8 (A-H,C-Z)
0003          DIMENSION X(40),Y(40),A(11,11),B(11),C(11),P(40)
      C ///////////////////////////////////////////////////////////////////////////
      C     LEAST SQUARES PROGRAM                                              TM
      C     X AND Y VALUES MUST BE PAIRED CORRECTLY.
      C     NUMBER = ACTUAL # X,Y DATA PAIRS
      C     M=DEGREE OF THE POLY.,MAX.=10                                      TM
      C     N=NO. OF EQUATIONS (=M+1)                                          TM
      C     X,Y=ARRAYS FOR THE DATA PAIRS                                      TM
      C     A= ARRAY FOR SUMS, WHICH BECOME CUEFF. INTHE SIMULTANEOUS EQTNS.   TM
      C     B=ARRAY FOR THE CONSTANT TERMS IN THE SIMULTANEOUS EQTNS.          TM
      C     C=ARRAY FOR THE UNKNOWNS, WHICH BECOME THE CUEFF. IN THE POLY.     TM
      C     P=ARRAY FOR THE POWERS OF THE X(I) FROM 1 TO 2*M.                  TM
      C ///////////////////////////////////////////////////////////////////////////
      C///////////////////////////////////////////////////////////////////////////
      C     SDY = STANDARD DEVIATION IN Y
      C     SDLY = STANDARD DEVIATION IN THE EXP(Y)
      C     SDA = STANDARD DEVIATION IN THE PREEXPONENTIAL FACTOR A1/A2.
      C     SDDL = STANDARD DEVIATION IN THE ACTIVATION ENERGY DIFFERENCES
      C///////////////////////////////////////////////////////////////////////////
      C     CALCULATE SUMS OF X POWERS                                         TM
0004          MX2=M*2                                                          TM
C005          DO 23 I=1,MX2                                                    TM
0006          P(I)=0.0D0
0007          DO 23 J=1,NUMBER                                                 TM
0008      23  P(I)=P(I)+X(J)**I                                               TM
      C     SUBSTITUTE INTO MATRIX A(11,11)                                    TM
C009          N=M+1                                                           TM
C010          DO 24 I=1,N                                                     TM
0011          DO 24 J=1,N                                                     TM
C012          K=I+J-2                                                         TM
0013          IF(K)26,26,25                                                   TM
0014      25  A(I,J)=P(K)                                                     TM
C015          GO TO 24                                                        TM
0016      26  A(1,1)=NUMBER                                                   TM
0017      24  CONTINUE                                                        TM
      C     SUM UP Y VALUES                                                    TM
0018          B(1)=0.0D0
0019          DO 21 J=1,NUMBER                                                TM
C020      21  B(1)=B(1)+Y(J)                                                  TM
0021          DO 22 I=2,N                                                     TM
C022          B(I)=0.0D0
0023          DO 22 J=1,NUMBER                                                TM
0024      22  B(I)=B(I)+Y(J)*X(J)**(I-1)                                      TM
C025          NM1=N-1                                                         TM
C026          DO 300 K=1,NM1                                                  TM
0027          KP1=K+1                                                         TM
C028          L=K                                                             TM
0029          DO 400 I=KP1,N                                                  TM
0030          ATEMP=DABS(A(I,K))-DABS(A(L,K))                                 TM
C031          IF(ATEMP)400,400,401                                           TM
0032      401 L=I                                                             TM
0033      400 CONTINUE                                                        TM
0034          IF(L-K)500,500,405                                             TM
0035      405 DO 410 J=K,N                                                    TM
0036          TEMP=A(K,J)                                                     TM
C037          A(K,J)=A(L,J)                                                   TM
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0038         410 A(L,J)=TEMP                                                    TM
0039             TEMP=B(K)                                                      TM
0040             B(K)=B(L)                                                      TM
0041             B(L)=TEMP                                                      TM
0042         500 DO 300 I=KP1,N                                                 TM
0043             FACTOR=A(I,K)/A(K,K)                                           TM
0044             A(I,K)=0.0D0
0045             DO 301 J=KP1,N
0046         301 A(I,J)=A(I,J)-FACTOR*A(K,J)                                    TM
0047         300 B(I)=B(I)-FACTOR*B(K)                                          TM
0048             C(N)=B(N)/A(N,N)                                               TM
0049             I=NM1                                                          TM
0050         710 IP1=I+1                                                        TM
0051             SUM=0.0D0
0052             DO 700 J=IP1,N                                                 TM
0053         700 SUM=SUM+A(I,J)*C(J)                                            TM
0054             C(I)=(B(I)-SUM)/A(I,I)                                         TM
0055             I=I-1                                                          TM
0056             IF(I)800,800,710                                              TM
0057         800 WRITE(6,791)
0058         791 FORMAT(1X,'LEAST SQUARES POLYNOMIAL COEFFICIENTS OF THE FORM C1 +
                1C2*X + C3*X**2 + ...')
0059             WRITE(6,901)(I,C(I),I=1,N)
0060         901 FORMAT(5(2X,2HC(,I3,2H)=,D17.10))
0061             WRITE(6,902)
0062         902 FORMAT(//,11X,'X',15X,'X**2',16X,'Y',15X,'YCALC',13X,'DEVY',13X,'E
                *XP(Y)',12X,'DEVEXP',/)
0063             DEYSQ=0.0D0
0064             DYSQ=0.0D0
0065             SUMSQX=0.0D0
0066             SUMX=0.0D0
0067             DO 900 NC=1,NUMBER
0068             YICALC=0.0D0
0069             DO 889 I=1,N
0070         889 YICALC=YICALC+(C(I)*X(NC)**(I-1))
0071             DEVY=Y(NC)-YICALC
0072             DYSQ=DYSQ+(DEVY*DEVY)
0073             XSQ=X(NC)*X(NC)
0074             EXPY=DEXP(Y(NC))
0075             DEXPY=EXPY-DEXP(YICALC)
0076             DEYSQ=DEYSQ+(DEXPY*DEXPY)
0077             WRITE(6,904)X(NC),XSQ,Y(NC),YICALC,DEVY,EXPY,DEXPY
0078         904 FORMAT(2X,7(D18.10))
0079             SUMSQX=SUMSQX+XSQ
0080             SUMX=SUMX+X(NC)
0081         900 CONTINUE
0082             IF(NUMBER.LT.3)RETURN
0083             SUMXSQ=SUMX*SUMX
0084             DNM=(NUMBER*SUMSQX)-SUMXSQ
            C     CALCULATE STANDARD DEVIATIONS
0085             SDY=DSQRT(DYSQ/(NUMBER-2))
0086             SDEY=DSQRT(DEYSQ/(NUMBER-2))
0087             WRITE(6,903)SDY,SDEY
0088         903 FORMAT(//,' STD. DEV. IN Y =',D18.10,20X,'STD. DEV. IN EXP(Y) =',D18.10)
                *18.10,////)
0089             SDB=SDY*DSQRT(SUMSQX/DNM)
0090             SDA=DEXP(C(1)+SDB)-DEXP(C(1))
0091             SDDE=SDY*DSQRT(NUMBER/DNM)*1.9872D0
```

```
FORTRAN IV G LEVEL  21              LESQ            DATE = 76247        23/04/44

 0092            WRITE(6,910)SDA,SDDE
 C093        910 FORMAT(/,1X,'SDA=',1PD18.10,20X,'SDDE=',1PD16.10)
 0094            WRITE(6,905)SUMSQX,SUMXSQ,DNM
 0095        905 FORMAT(/,1X,'SUM(X**2)=',D18.10,5X,'(SUMX)**2 =',D18.10,5X,'N*SUM(
                *X**2)-(SUMX)**2 =',D18.10,//)
 C096            RETURN
 0097            END
```

VITA *2*

Terry Don Marriott

Candidate for the Degree of

Doctor of Philosophy

Thesis: KINETIC ISOTOPE EFFECTS IN THE CH_4 + H $\rightleftarrows$ CH_3 + H_2 SYSTEM. PREDICTIONS OF THE LMR SIX-BODY POTENTIAL-ENERGY REACTION HYPERSURFACE

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