

THEORETICAL STUDIES OF THE VIBRATIONAL
PREDISSOCIATION OF THE $C_2H_4F_2$
VAN DER WAALS COMPLEX

By

ROBERT WILLIAM GRAHAM

Bachelor of Science

University of Oklahoma

Norman, Oklahoma

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Thesis Approved:

Leonid M. Raff

Thesis Adviser

J. Paul Serbin

Donald L. Thompson

W. W. Rindell

John F. Keld

Norman N. Rusham

Dean of the Graduate College

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CHAPTER I

INTRODUCTION

Recently, supersonic expansion techniques and the use of lasers have motivated a series of studies of various van der Waals complexes. Reactions occurring under matrix isolation conditions have been found to exhibit special effects not seen for the comparable solution or gas-phase reactions. For example, some reactions show site selectivity and structure specificity. In addition, due to the nature of matrix-isolated molecules having widely spaced rotational levels, intramolecular energy transfer is reduced. This gives rise to the localization of internal energy and increases the possibility of mode-selective rate enhancement.

Frei and Pimentel¹ have reported the results of several photochemically assisted reactions occurring under matrix isolation conditions. Their studies show significant differences in the rates of product formation upon induced irradiation of various modes. That is, they have observed mode-specific rate enhancement. The reaction of C_2H_4 with F_2 to form either 1,2-difluoroethane or $HF + CH_2 = CHF$ was found to increase two and five orders of magnitude as the photon wave number increases from 953 to 1896 cm^{-1} and 953 to 4209 cm^{-1} , respectively. The transition from 953 to 1896 cm^{-1} involve similar vibrational motions, therefore they postulated that any difference in quantum yields was probably associated with a barrier to reaction between these two photon energies and not due to mode specificity. They also found the transition to 2989 cm^{-1} , which involves an in-plane C-H stretch, gave a higher quantum yield than the transition to 1896 cm^{-1} , which involves an out-of plane motion. They found it unlikely that these differences in the quantum yields directly indicate mode specificity of the motions excited. However, they

also observed that excitation of the $\nu_2 + \nu_{12}$ combination band of C_2H_4 at 3076 cm^{-1} results in a quantum efficiency greater than that for excitation of ν_9 at 3105 cm^{-1} , which suggests the possibility of mode specificity being present.

Supersonic jet spectroscopy has been an important tool in probing the properties of van der Waals molecules. Due to the low temperatures created by these techniques, stable van der Waals molecules can be produced. Supersonic expansion leads to a simplification of the spectrum by depopulating the excited rotational and vibrational states. This is important because van der Waals bonds are weak and long with low frequency vibrations and large rotational constants. Spectroscopic studies give information about the structure but yield little information concerning the potential surface due to the limited number of levels probed.² Fortunately, this somewhat formidable problem has received much attention recently using various theoretical methods in generating potential surfaces.³

As a first-step in the study of matrix-isolation chemistry, we examine the photochemistry of van der Waals complexes. These complexes act as an intermediate between a bimolecular gas-phase system and one that is isolated in a matrix. A matrix-isolated system traps such a chemical intermediate whereas the bimolecular system reveals the weak bonding forces holding the complex together. Analysis of the reaction dynamics for a van der Waals complex using the same potential surface as that for the bimolecular system should reveal the onset of the dynamics associated with matrix-isolation reactions.

A great deal of the experimental measurements of unimolecular decay rates of van der Waals complexes has been reported by Levy and co-workers.⁴⁻¹³ For example, Levy *et al.*⁴ have determined I_2 He lifetimes as a function of the vibrational state of the I_2 He stretching mode. The method for preparing the van der Waals complexes involves the use of supersonic molecular beams or free jets. The cold environment produced by supersonic expansion allows the preparation and study of such van der Waals molecules. Excitation of the $I_2 \dots He$ molecules causes a significant amount of the complex to dissociate to $I_2 +$

He. In addition, there have been extensive studies¹⁴⁻¹⁹ on the dynamics of vibrational predissociation (VP) of other van der Waals complexes.

Beswick and Jortner²⁰ have reported studies of VP in X...BC van der Waals systems using a quantum mechanical collinear model with a single electronic potential surface. They found that for some of the van der Waals complexes of I₂, the vibrational predissociation mechanism depended upon initial quantum state, mass, and various interaction parameters.

A classical trajectory study on the He + I₂ collision reaction by Noid, Gray, and Rice²¹ found apparent erratic behavior in final vibrational energy vs initial vibrational phase angle, a so-called chattering region. In these regions they found a large number of smooth, regular, subdomains they call icicles. They found that these icicles led to a fast initial decay rate and suggest these icicles to be a non-statistical factor in the dynamics of the molecule. In continuing their²² study of HeI₂ molecule, they found that for low excitation states of the diatomic, decay modes exist only quantum mechanically, but for high excitation levels, dissociation acts classically. Most fragmentation of the van der Waals complex that occurs at low energy levels must therefore be attributed to tunneling.

Nesbitt and Hynes²³ have carried out quasiclassical trajectory calculations in studying highly vibrationally excited anharmonic oscillators, such as the van der Waals I₂...X systems. Vibrational energy transfer for highly excited oscillators was found to achieve maximum efficiency at a vibrational level of 80 but becomes progressively less efficient as the internal energy approaches the dissociation limit.

Woodruff and Thompson²⁴ examined the He...I₂ (B³π) molecule using quasiclassical trajectory calculations. They found that increasing the I₂ vibrational quantum number caused an increase in the rate of decay of He...I₂, similar to that found by Beswick and Jortner.²⁵

Noorbacha, Raff, and Thompson²⁶ have studied the dissociation dynamics of the RgI₂ van der Waals complexes (Rg = Ar, Kr, Xe). Three-dimensional quasiclassical

were used for computing the rates. Generally the dissociation of these complexes is non-RRKM in character, and is significantly influenced by "cage" effects.

Gerber, Buch, and Ratner²⁷ have used a time-dependent self-consistent field (TDSCF) method in combination with classical and semiclassical trajectory calculations to analyze the $I_2 \dots Ne$ van der Waals molecule energy transfer, dynamics, and predissociation rate. The TDSCF method includes formal separability of the modes, each of which is governed by a time-dependent potential which is an average of the full interaction potential over all other modes. They found TDSCF calculations were useful to analyze the dissociation dynamics of weakly coupled molecule. Good values for complex lifetime, fragment energy content, and vibrational level population of the final states were obtained.

Schatz, Buch, Ratner, and Gerber²⁸ have studied the dynamics of sequential dissociation processes of the type $XI_2(v)Y \rightarrow X + I_2(v)Y \rightarrow X + Y + I_2(v)$ ($X, Y = Ne, He$) using quasiclassical trajectory calculations and TDSCF methods. They use statistical RRKM-like models in analyzing the role of X atoms in promoting or impeding Y-atom dissociation in the $X-I_2-Y$ species as compared to I_2-Y ; and they compare quasiclassical trajectory and classical TDSCF methods to test the reliability of the latter approach in describing polyatomic molecule dissociation dynamics. The results of these two methods are in agreement for three and four-atom clusters and show that an increase in total molecular size gives rise to a faster dissociation of the first atom to leave the complex.

Quasiclassical trajectory calculations were used by Delgado-Barrio, Villareal, Mareca, and Albelda²⁹ in treating the $He \dots I_2$ van der Waals molecule. The incorporation of rotational degrees of freedom were shown to decrease the VP rate. Their results are in agreement with experimental, classical, and quantal results.⁷⁻⁹

Brady, Doll, and Thompson³⁰⁻³² have performed classical studies on the collision of a single atoms with small clusters of atoms and the dissociation of quasibound clusters of

atoms using classical trajectories. First-order decay rates were found to decrease exponentially as the total fixed energy decreases and as the impact parameter increases.

Theoretical studies of the $O_3...NO$ van der Waals complex were done by Arnold, Gettys, Thompson, and Raff³³ using quasiclassical trajectory calculations. The dynamics of the $O_3...NO$ complex to be very different from those previously found for the bimolecular gas-phase collision using the same potential energy surface.³⁴ They found significant vibrational rate enhancement as the internal energy content of the molecule is increased, and suggest that this rate enhancement is mode specific. However, vibrational excitation in the bimolecular reaction shows rate enhancement but no mode specificity. They also found the dissociation rate to be dependent upon the structure.

Collinear $A+BC$ exchange reactions have been analyzed by Agrawal and Raff³⁵ by treating the system via perturbation wave packet studies and time-dependent methods. The time-dependent methods and close-coupling probabilities obtained for two of the three surfaces used were found to be in good accord. Wave packet computations proved to be the optimum method for calculation of rate coefficients. Viswanathan, Raff and Thompson³⁶ studied the decomposition of the $He...I_2$ ($B^3\pi$) complex using similar methods.

In a later paper, Viswanathan, Raff and Thompson³⁷ computed rate coefficients and cross sections for $Ar_2 + X \rightarrow Ar...X + Ar$, $Ar_2 + X^* \rightarrow 2Ar + X$, and $Ar_2 + X \rightarrow Ar_2...X$ where $X = N_2, CO, CO_2$. They found dissociation cross sections to be independent of the vibrational energy transfer from X . For N_2 and CO , the rotational to vibrational energy transfer had some effect on Ar_2 dissociation, and translational to vibrational energy transfer showed N_2 to be the most effective in dissociating Ar_2 .

Adams³⁸ studied the vibrational predissociation of $Ar...BCl_3$ van der Waals complexes using Monte Carlo-RRKM methods. The results were in agreement with the experimental rate in that the van der Waals complex dissociates considerably faster upon single mode excitation, which implies a rapid internal energy redistribution.

It is the purpose of this paper to explore the effects of vibrationally exciting various modes of C_2H_4 in the $C_2H_4...F_2$ van der Waals molecule.

We present calculations of vibrational predissociation rates using quasiclassical trajectory methods. For the $C_2H_4...F_2$ van der Waals complex, it is found that increasing the C_2H_4 internal energy produces an increase in the rate of decay. The results also indicates some mode specific rate enhancement is present. In this case, the van der Waals complex $C_2H_4...F_2$ dissociates to C_2H_4 and F_2 and upon vibrational excitation of the ethylene molecule, we find a significant increase in the predissociation rate. Included are rates of decay of the unimolecular complex for excitation of the symmetric C–H stretch, torsional motion, and non-planar CH_2 rock, or the ν_1 , ν_4 , and ν_7 C_2H_4 modes, respectively.

The following sections describe the $C_2H_4F_2$ potential-energy surface, computational methods, and results.

CHAPTER II

POTENTIAL-ENERGY SURFACE

We represent the potential-energy surface for the $C_2H_4...F_2$ van der Waals complex with the surface used by Raff³⁹ in the study of the bimolecular collision dynamics of the $C_2H_4 + F_2$ reaction. This surface consists of essentially twenty-nine different potential terms. The functional form for one bonding structure is

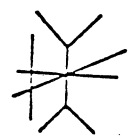
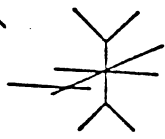
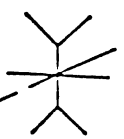
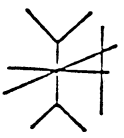
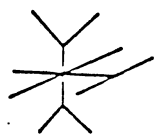
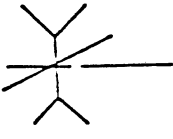
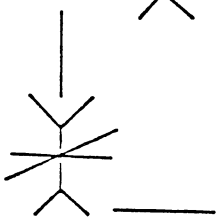
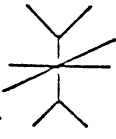
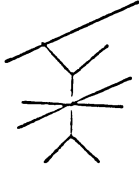
$$\begin{aligned}
 V_1 = & V^{CC}(R_{13}) + \sum_{i=14}^{21} V^{HF}(R_i) + \sum_{i=3}^4 V^{CH}(R_i) + \\
 & \sum_{i=11}^{12} V^{CH}(R_i) + V^{CF}(R_1) + V^{CF}(R_3) + \\
 & V^{FF}(R_{22}) + \sum_{i=1}^4 V^{CCH}(\theta_i) + \sum_{i=5}^6 V^{CCF}(\theta_i) + \\
 & V^{HCH}(\theta_7) + V^{HCH}(\theta_{10}) + \sum_{i=8}^9 V^{HCF}(\theta_i) + \\
 & \sum_{i=11}^{12} V^{HCF}(\theta_i) + V_T^{C_2H_4}(\phi_1) + V_T^{C_2H_3F}(\phi_2)
 \end{aligned}$$

The terms in Eq(1) are made up of bond stretching interactions plus bending potentials for each of the 12 angles along with torsional terms for the C_2H_4 and $CH_2 = CHF$ molecules. The $V^{\alpha\beta}(R_i)$ terms are bond stretching potentials for the bond whose distance is R_i . The $V^{\alpha\beta}(\theta_i)$ are the bending potentials for the angle θ_i . The ethylene torsional potential is $V_T^{C_2H_4}(\phi_1)$. The torsional potential for $CH_2 = CHF$ is $V_T^{C_2H_3F}(\phi_2)$. Hyperbolic tangent switching functions were used to achieve the correct asymptotic limits for the potential. All

terms in the potential were parameterized so that the potential could be fitted to the measured fundamental frequencies, equilibrium structures, heats of reactions, and the activation energy for the HF abstraction from 1,2-difluoroethane. Computed and measured values for vibration frequencies for ethylene and 1,2-difluoroethane, equilibrium structures and energies, and the heats of reaction were found to be in fair to good accord with experimental results. Certain geometries, fundamental frequencies, and barrier heights of transition states are unknown which therefore limits the accuracy of this potential. Nevertheless, this representation is reasonably accurate, simple in functional form, and can therefore serve effectively as a first approximation in analyzing the dynamics of the $C_2H_4...F_2$ van der Waals molecule.

The potential surface described previously has "van der Waals" minima for the $C_2H_4...F_2$ center-of-mass separations between 5.25 to 6.73 angstroms depending upon the structure. Table I gives the structures and stabilities of various $C_2H_4...F_2$ van der Waals complexes. Figures 1a-1i show the variation in potential as a function of separation for all structures investigated. As can be seen, structures 1 and 2 are predicted to be the most stable of all the complexes investigated. The values in Table I were calculated by holding all the bond lengths and bond angles fixed at their equilibrium positions while varying only the center-of-mass distance. Consequently, the fully relaxed structure can be expected to have somewhat greater stabilities than those given in Table I. Structures 1 and 2 have energies of 0.09154 and 0.07413 kcal/mole, respectively, below that for the separated molecules. The center-of-mass separation for 1 and 2 are 5.25 and 5.26 angstroms, respectively. The well depths are relatively small. This is not unexpected since the dispersion forces were not explicitly included in the potential surface formulation and there is no dipole-dipole interaction. In comparing this to the $O_3...NO$ system,³³ it is interesting to note that although dipole-dipole interactions are not explicitly included in the $O_3...NO$ surface formulation, the potential predicts structures with energies that are about what are expected for dispersion forces. Table I lists the structures and stabilities for nine

TABLE I
 STABILITIES AND STRUCTURES OF VARIOUS C₂H₄...F₂ VAN DER WAALS
 COMPLEXES

Notation	Structure	Well Depth (kcal/mole)	c.m.-c.m. dist (Angstroms)
1		0.09154	5.25
2		0.07413	5.26
3		0.04500	5.94
4		0.02250	5.95
5		0.02250	5.95
6		0.01250	6.69
7		*	*
8		0.01111	6.73
9		0.01111	6.73

* = Very unstable complex immediately dissociates; cm = center of mass.

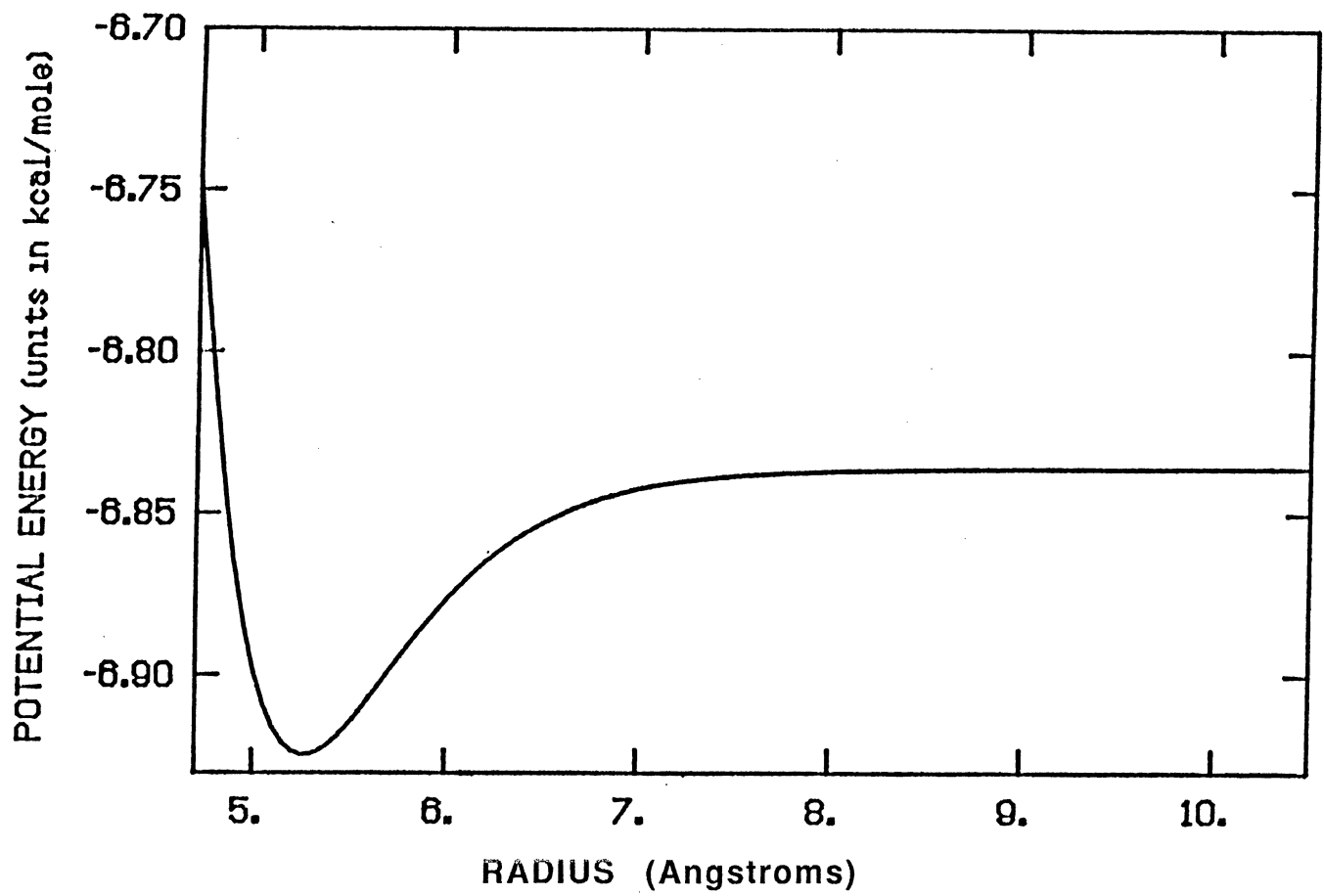


Figure 1a. Structure 1 - C₂H₄•F₂ Potential Energy vs. Center of Mass Radius Between F₂ and C₂H₄

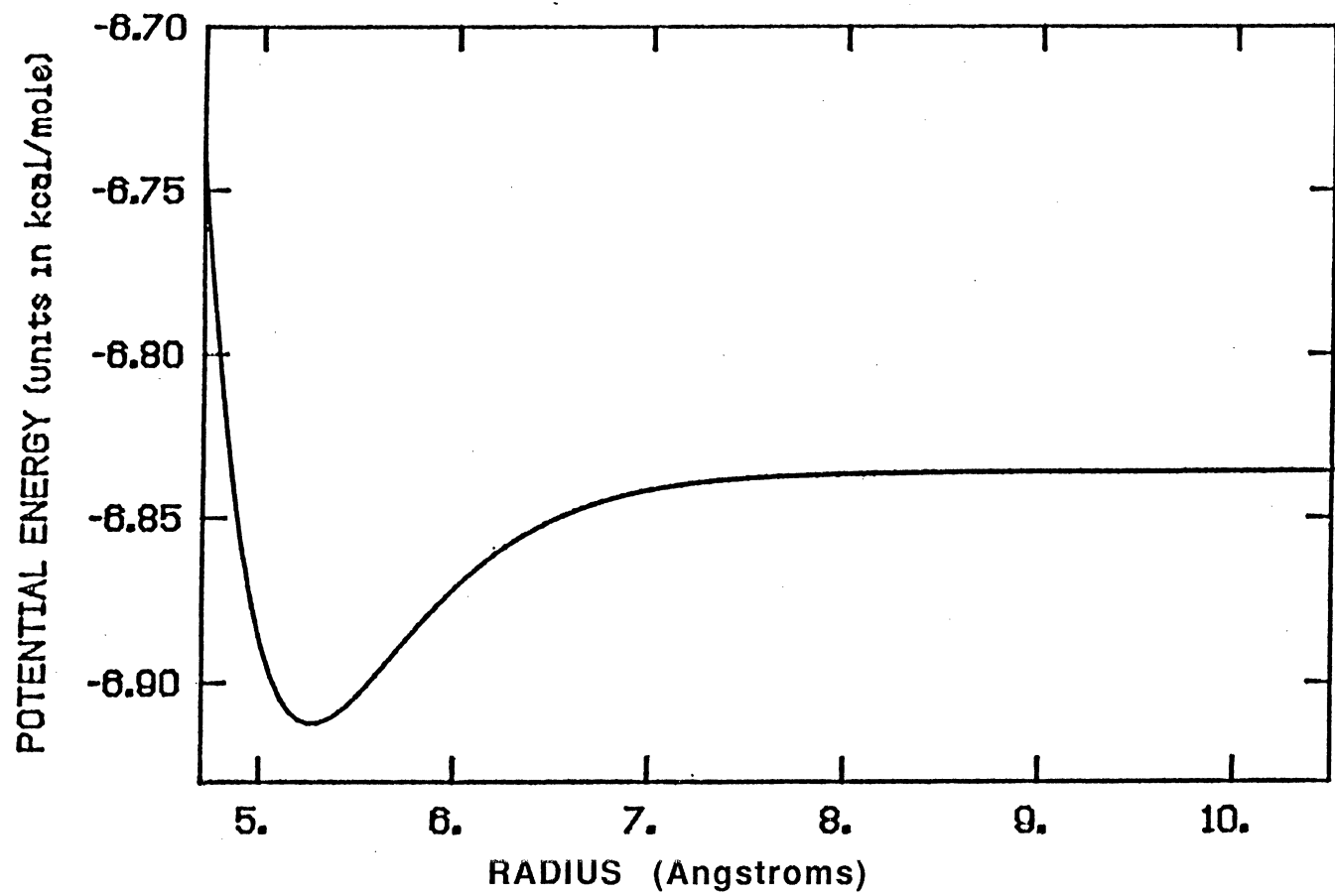


Figure 1b. Structure 2 - $C_2H_4 \cdot F_2$ Potential Energy vs. Center of Mass Radius Between F_2 and C_2H_4

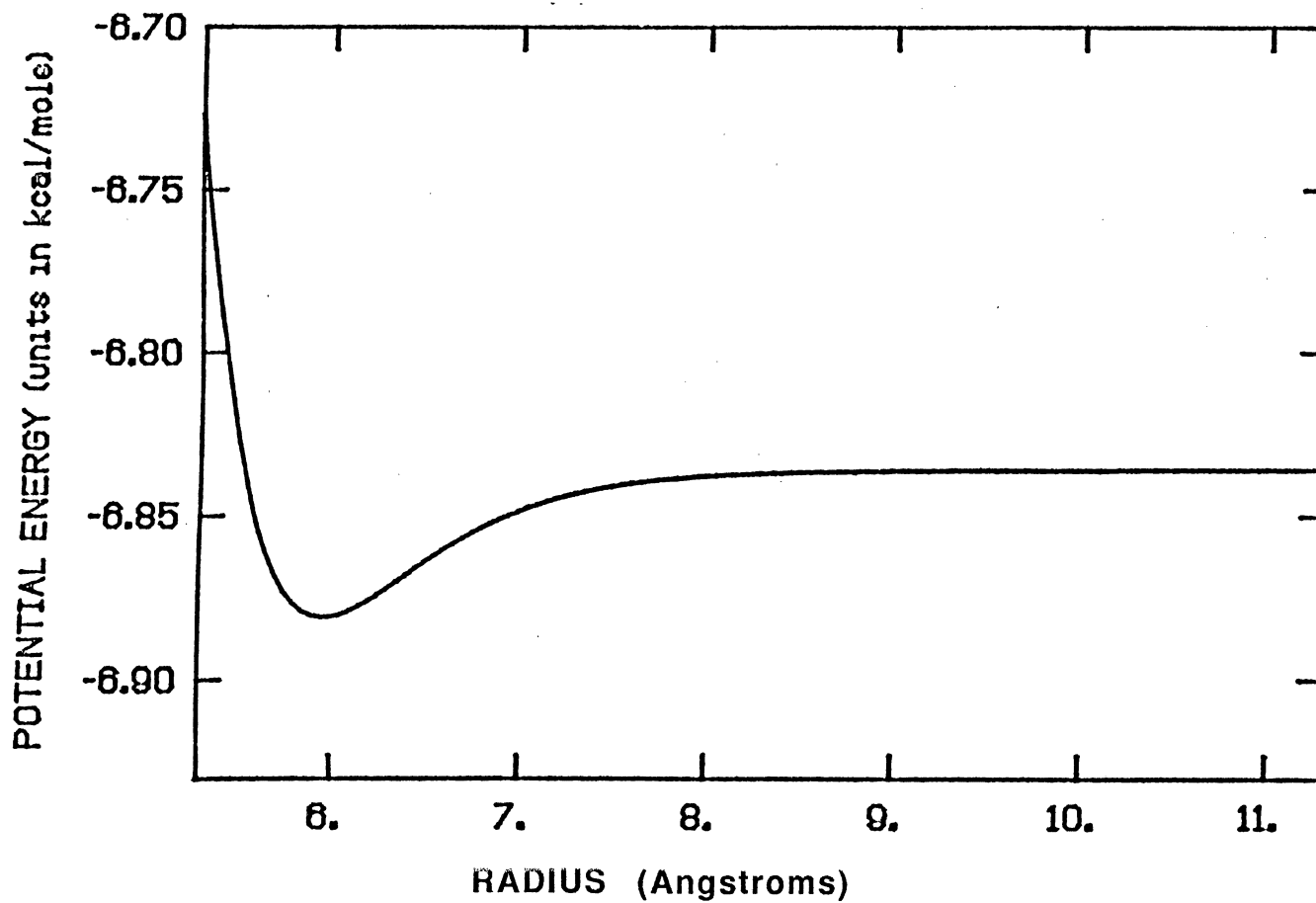


Figure 1c. Structure 3 - $C_2H_4 \cdot F_2$ Potential Energy vs. Center of Mass Radius Between F_2 and C_2H_4

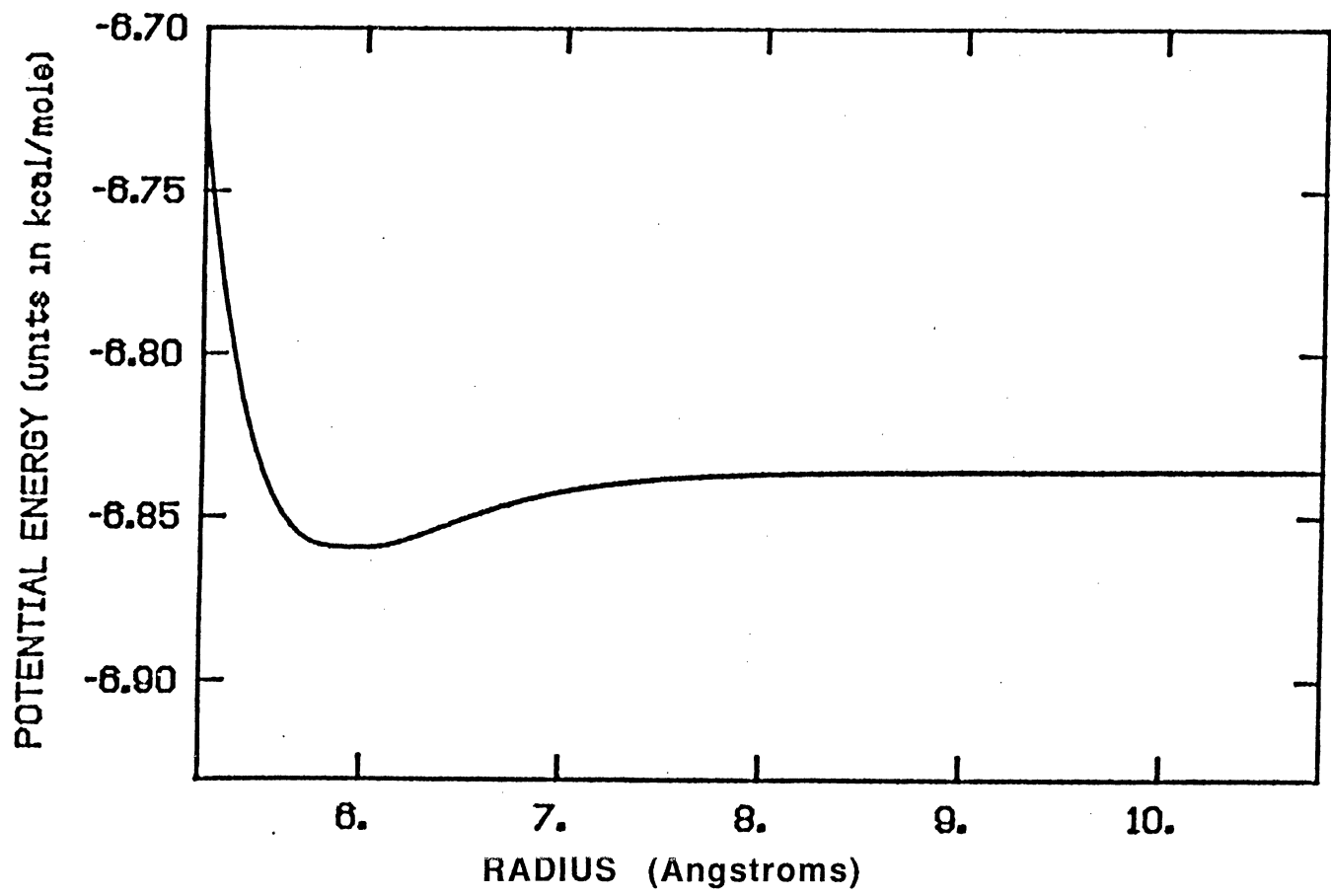


Figure 1d. Structure 4 - $C_2H_4 \cdot F_2$ Potential Energy vs. Center of Mass Radius Between F_2 and C_2H_4

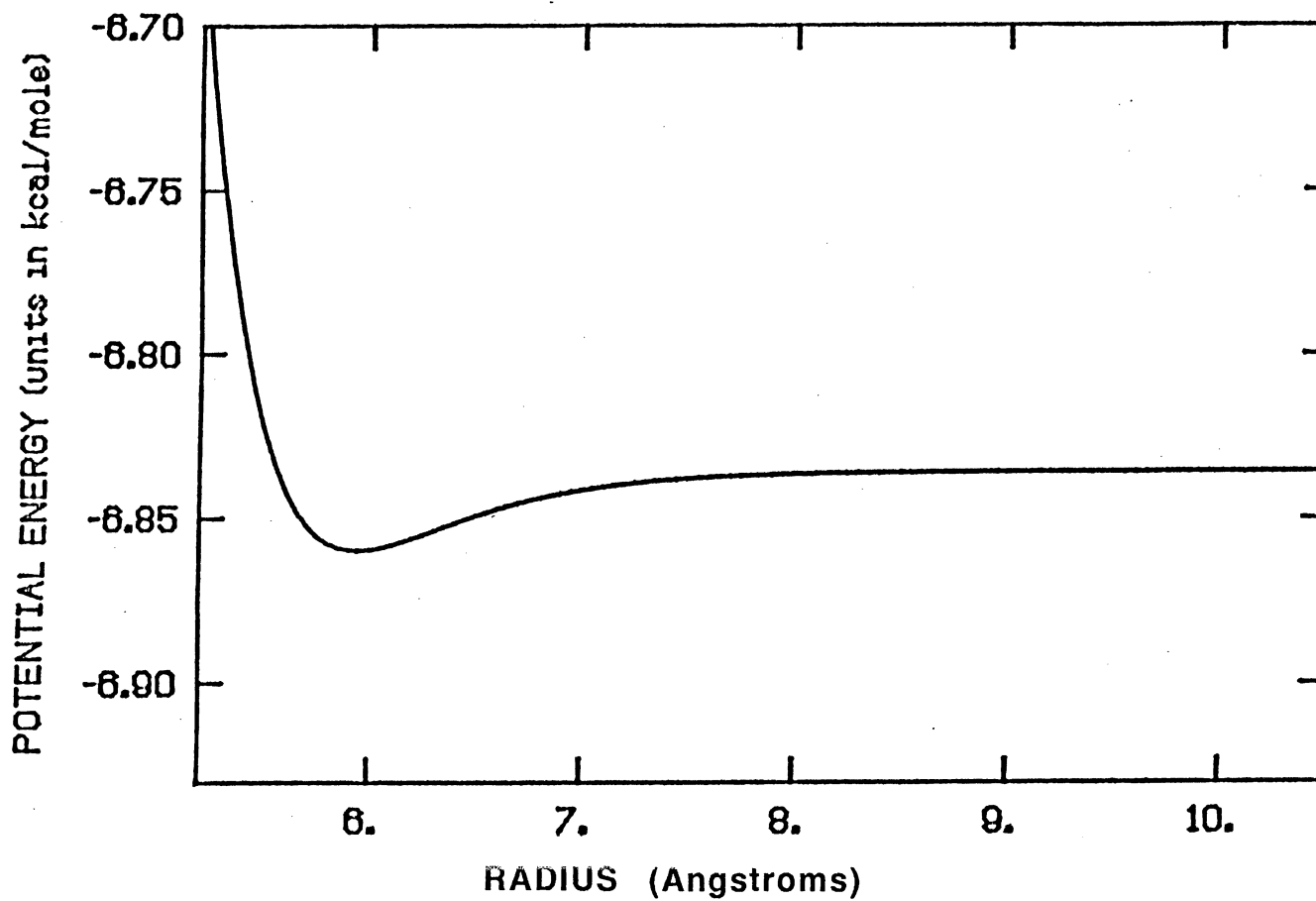


Figure 1e. Structure 5 - $C_2H_4 \cdot F_2$ Potential Energy vs. Center of Mass Radius Between F_2 and C_2H_4

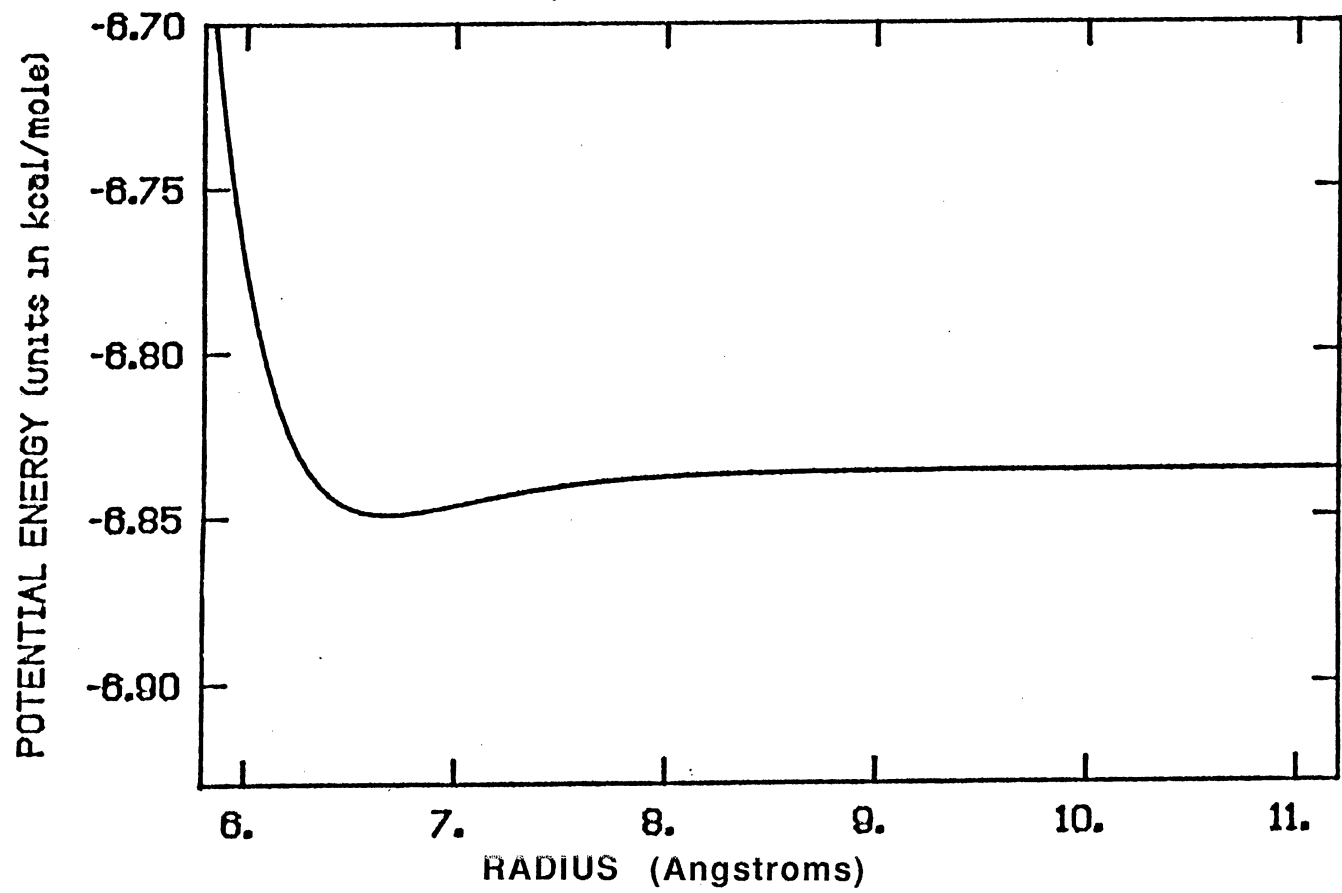


Figure 1f. Structure 6 - $C_2H_4 \cdot F_2$ Potential Energy vs. Center of Mass Radius Between F_2 and C_2H_4

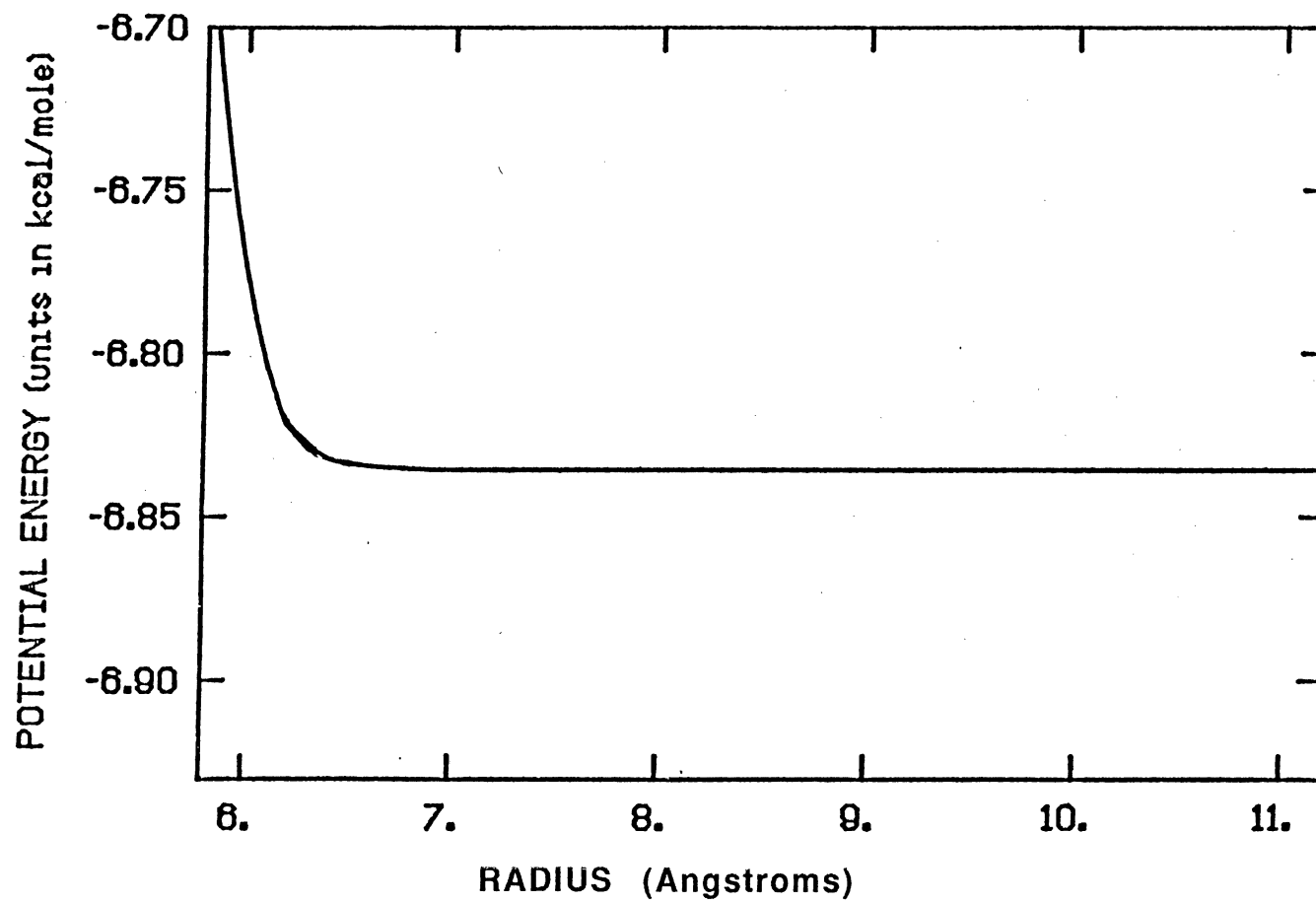


Figure 1g. Structure 7 - $C_2H_4 \cdot F_2$ Potential Energy vs. Center of Mass Radius Between F_2 and C_2H_4

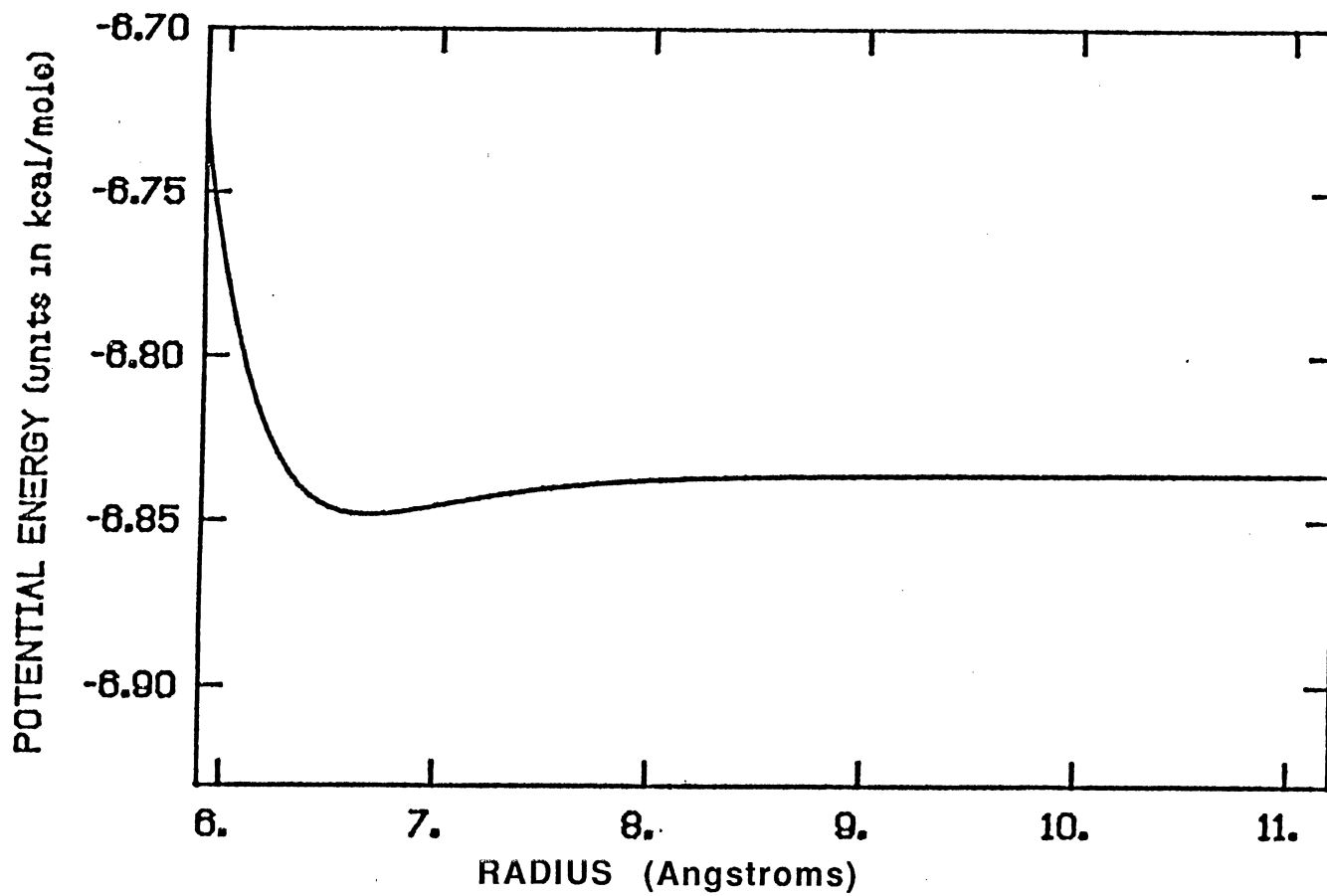


Figure 1h. Structure 8 - $C_2H_4 \cdot F_2$ Potential Energy vs. Center of Mass Radius Between F_2 and C_2H_4

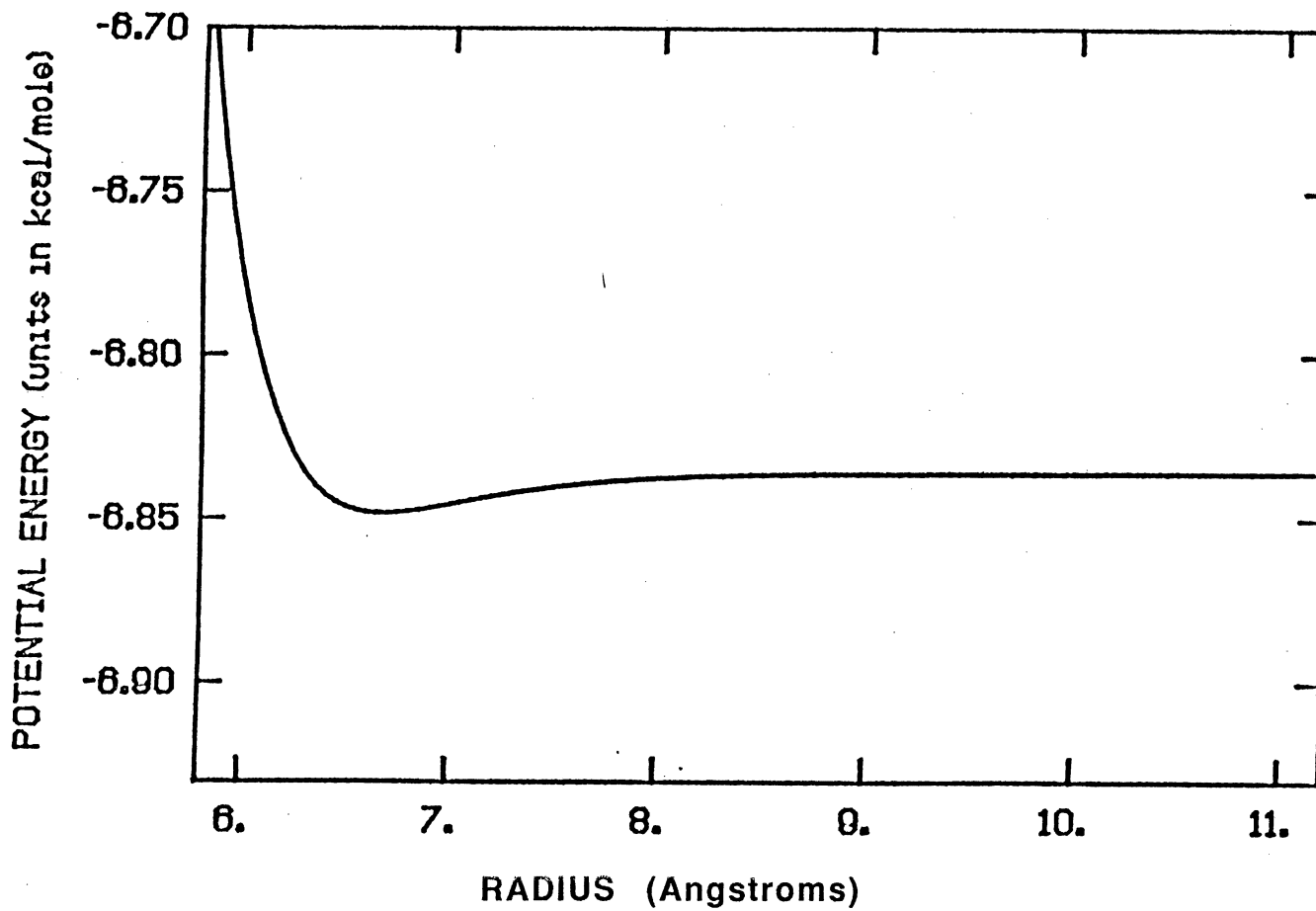


Figure 1i. Structure 9 - $C_2H_4 \cdot F_2$ Potential Energy vs. Center of Mass Radius Between F_2 and C_2H_4

$C_2H_4...F_2$ van der Waals complexes on the surface described. Structure 1 is the most stable complex. Overall energetic differences for the nine structures are all less than 0.09 kcal/mole. Structures 7, 8, and 9 were found to be the most unstable.

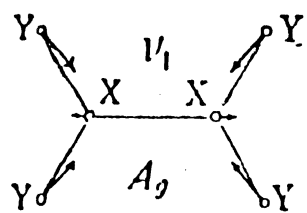
CHAPTER III

COMPUTATIONAL METHODS

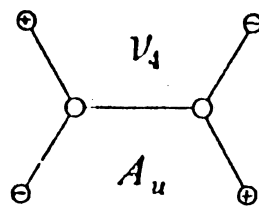
The dissociation dynamics of the $C_2H_4...F_2$ van der Waals complex have been studied using quasiclassical trajectory (QCT) calculations. The procedure used in the study of the $C_2H_4...F_2$ system is identical to that of Raff⁴⁰ in his treatment of the bimolecular collision dynamics of 1,2-difluoroethane. The only difference in this study is the initial-state and conditions of the problem.

For the following calculations, the initial configuration of the $C_2H_4...F_2$ complex is taken to be that of the van der Waals complex yielding the minimum equilibrium structure or greatest well depth. The structure found to best fit these requirements was structure 1. The vibrational motion of this system is described in terms of the normal modes for separated C_2H_4 and F_2 . Here, we have excited only various vibrational eigenstates for the C_2H_4 molecules. Initial conditions were to excite a particular mode with one quanta of energy while holding all others at zero point energy. We specifically examine the symmetric C–H stretch, torsional motion, and non-planar CH_2 rock shown in Figure 2a, 2b, and 2c, respectively. Fundamental vibrational frequencies and anharmonic constants were the same as those given by Raff.³⁹

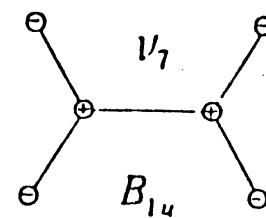
Phase averaging was the procedure used in selecting the proper initial conditions. The cumbersome method involves integrating over 260 vibrational periods of the V_1 symmetric stretch and storing the phases after each integration step. We then randomly selected a set of the vibrational phases from the stored data. Each trajectory was then initiated with different vibrational phases.



a.



b.



c.

Figure 2. Various Excited Modes of the Ethylene Molecule

The final state of the individual trajectories was determined by continuously monitoring the atom to atom separation and energy. All trajectories of the complex dissociated to F_2 and C_2H_4 . If the center-of-mass distance for the two molecules in this complex exceeded 8.0 a.u., the integration was terminated. If the trajectory did not meet these requirements within 1.35×10^{-12} s, it was terminated. The time limit of integration was such that more than 80% of the trajectories dissociated.

Plots for the time-variation of the center-of-mass separation of $C_2H_4-F_2$ with time for the four different excited states are shown in Figures 3a-3e. The faster decay rate seems reasonable. Due to the increase in energy into the system, we expect the molecule to come apart much faster. However, it is also interesting to note that the ground state and each of the excited modes exhibits a different magnitude in vibrational amplitude. The zero-point energy showing to be the greatest in magnitude, the non-planar CH_2 rock being the smallest, and the symmetric C-H stretch and torsional motion lying between the previous two. We also calculated that for a typical trajectory approximately eighty to a hundred vibrational cycles were completed before dissociation.

The numerical integration was carried out using a fourth-order Runge-Kutta-Gill routine with a fixed stepsize of 3.23×10^{-16} s. The integration accuracy was checked using back integration and energy conservation.

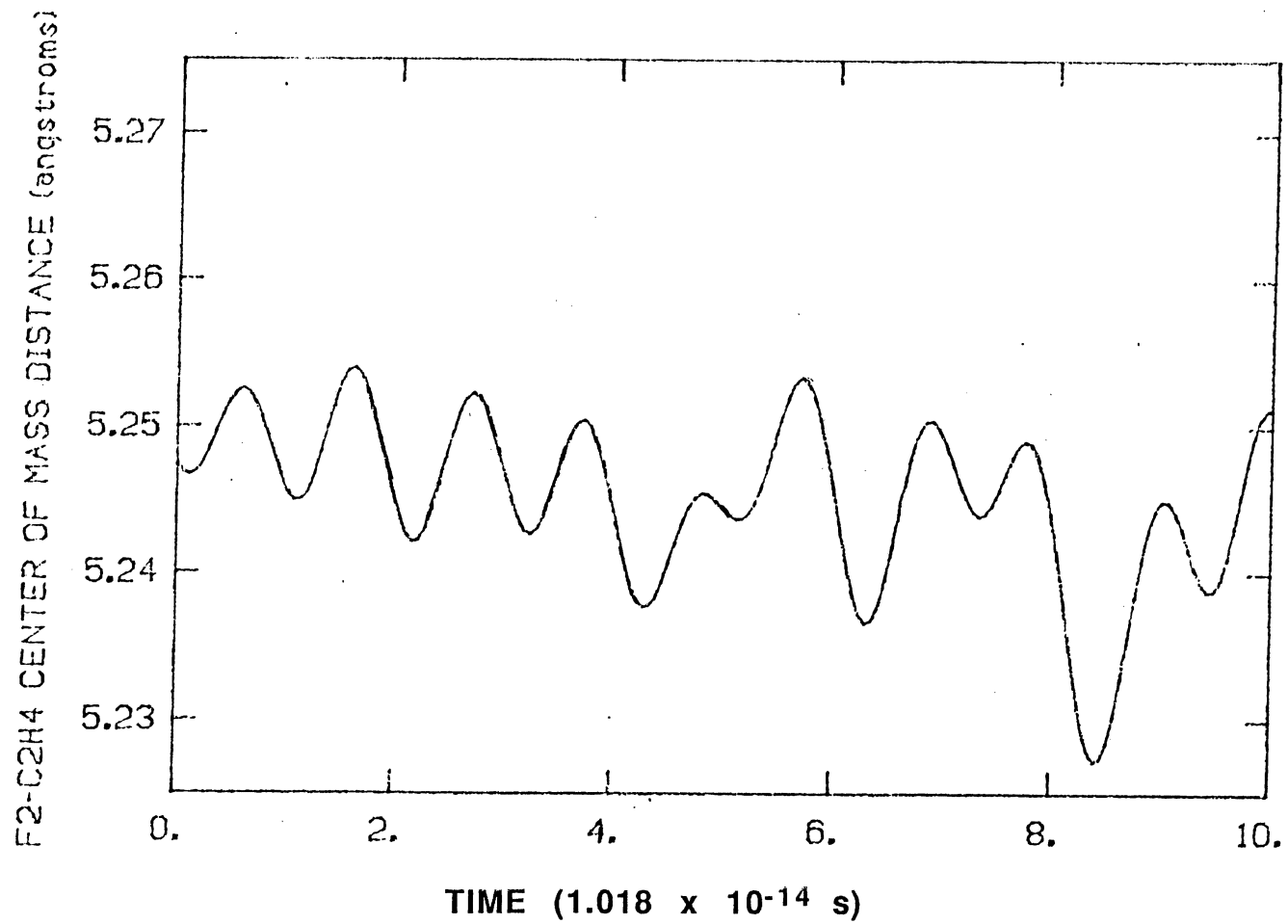


Figure 3a. F₂-C₂H₄ C.M. Variation with Time (Zero-Point Energy)

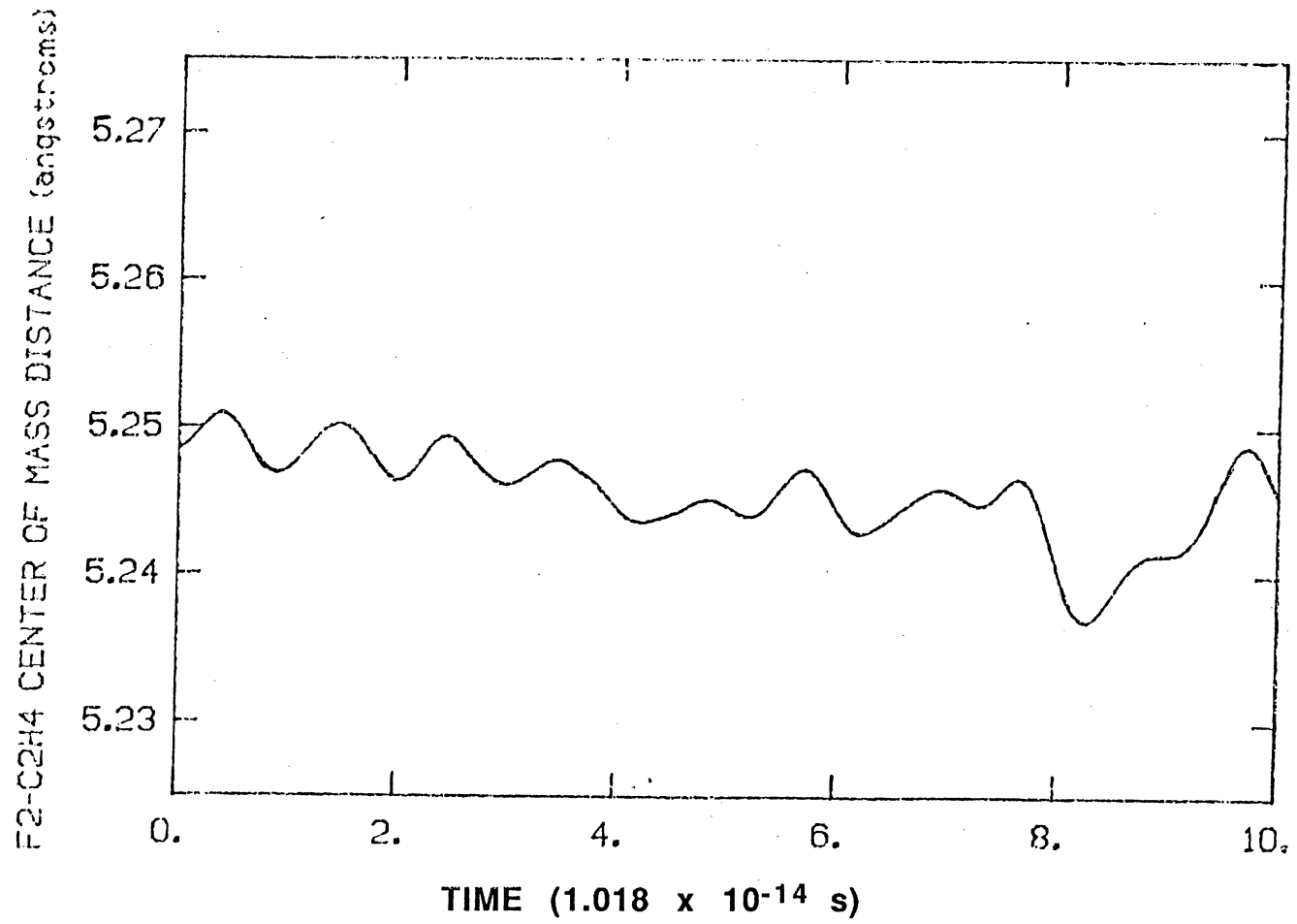


Figure 3b. F₂-C₂H₄ C.M. Variation with Time (Non-Planar CH₂ Rock)

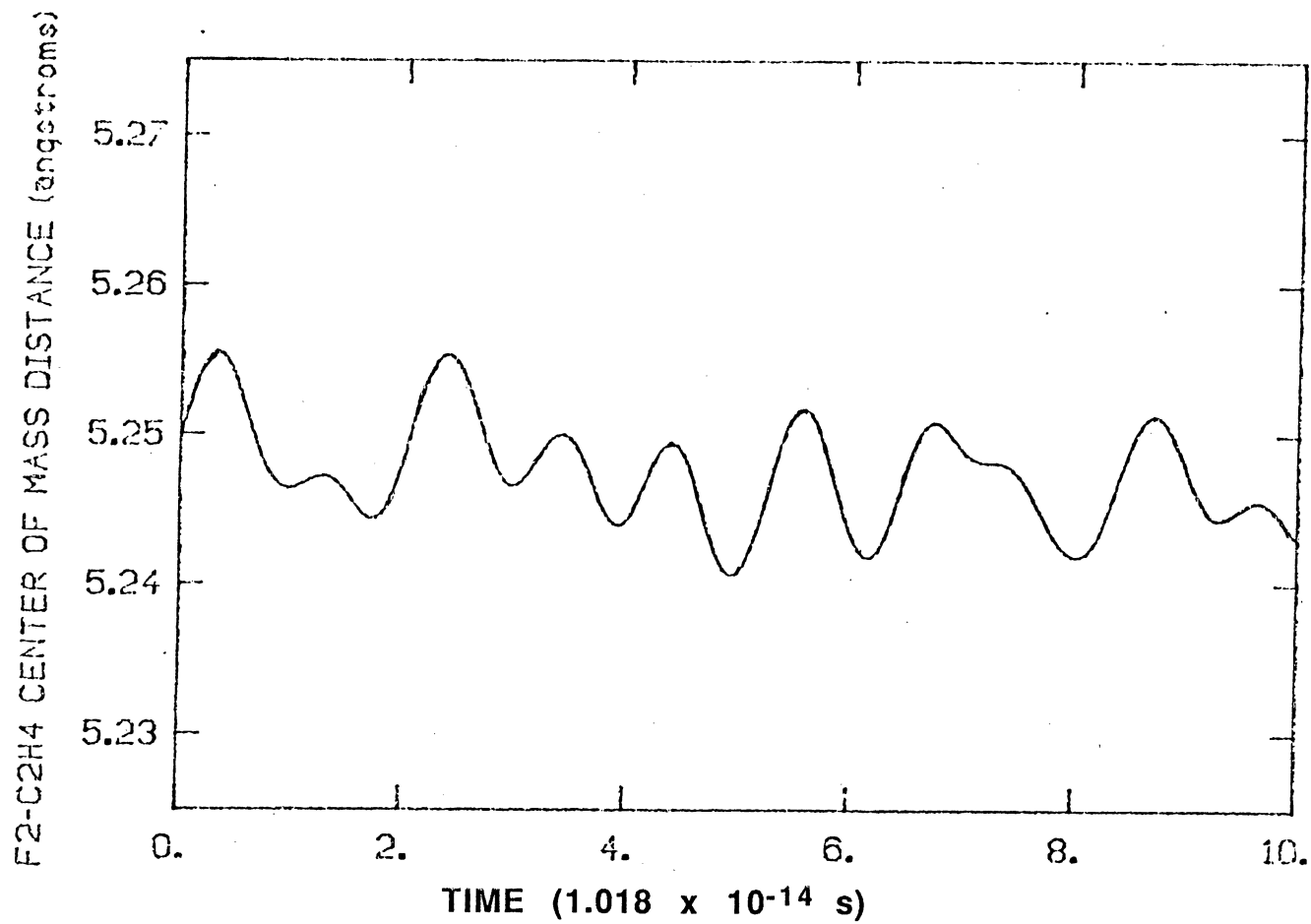


Figure 3c. F₂-C₂H₄ C.M. Variation with Time (Symmetric C-H Stretch)

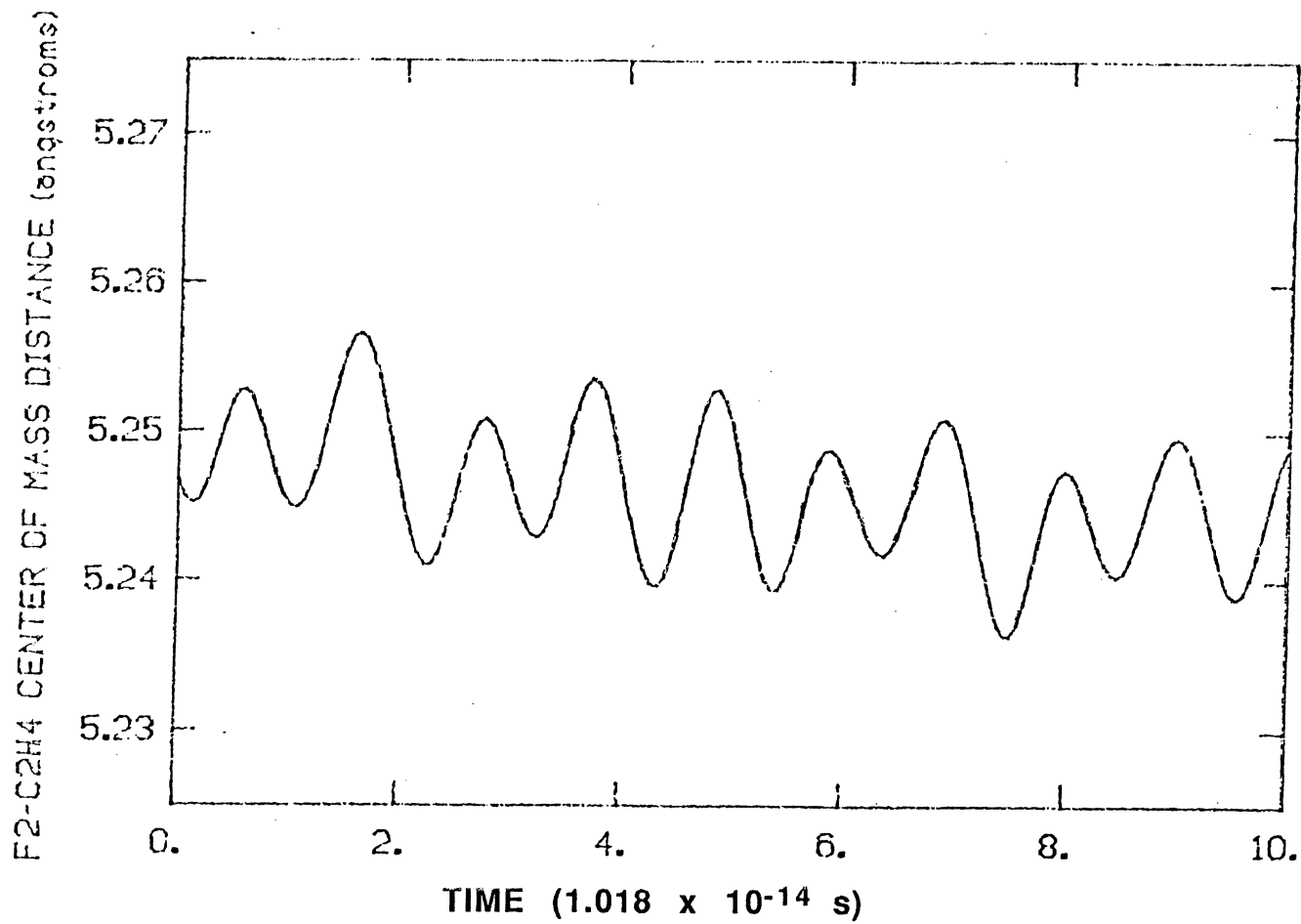


Figure 3d. F₂-C₂H₄ C.M. Variation with Time (Torsional Motion)

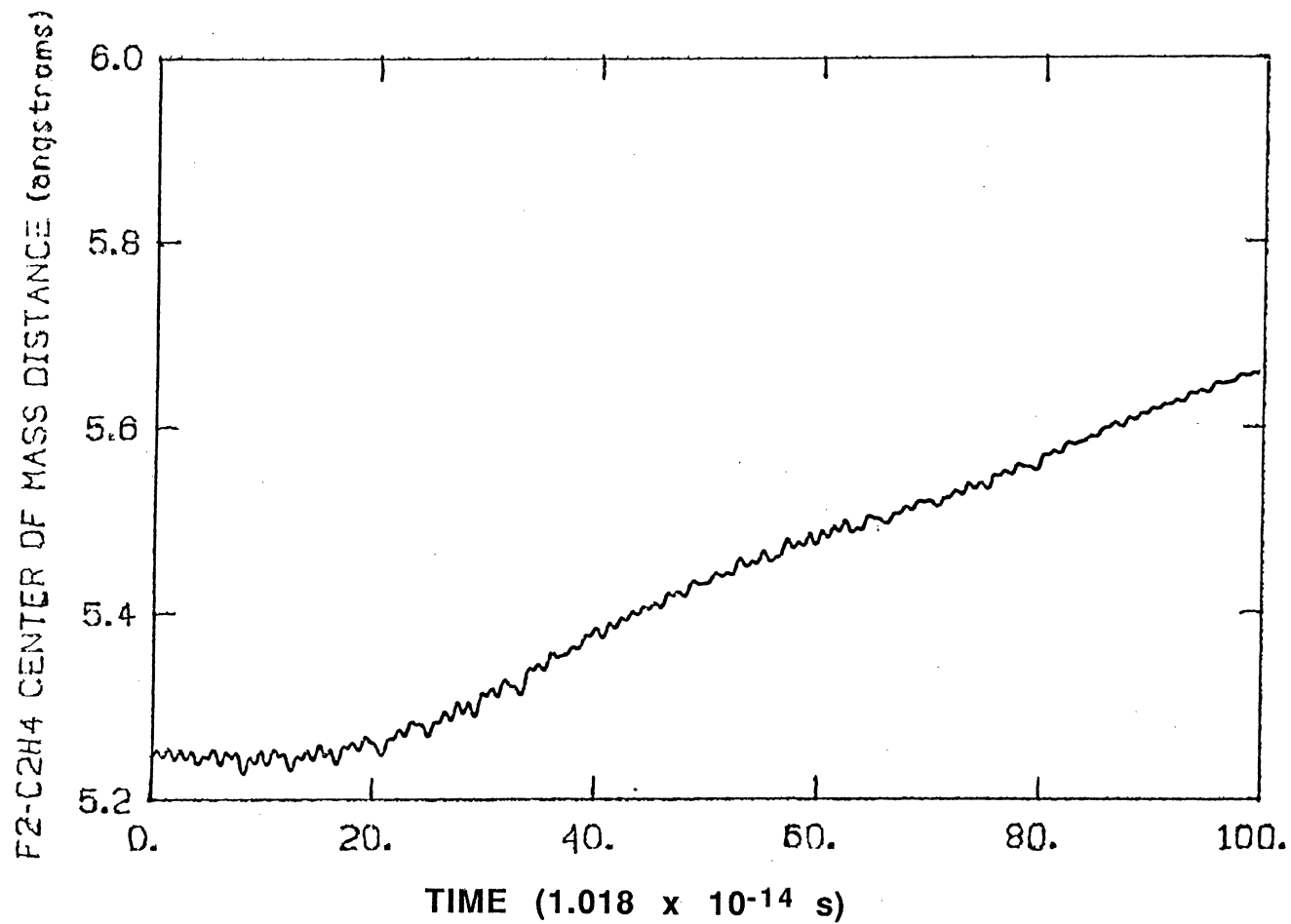


Figure 3e. F₂-C₂H₄ C.M. Variation with Time (Zero-Point Energy)

CHAPTER IV

RESULTS AND DISCUSSION

As discussed previously in the methods section, a trajectory was considered terminated if the integration time exceeded 1.35×10^{-12} s or if the center-of-mass distance exceeded 8.0 a.u. The internal energy of the dissociated species were then calculated and compared to their respective bond dissociation energies to determine the final products. All of the trajectories were found to dissociate to $C_2H_4 + F_2$. A total of two hundred trajectories were run for each of the different cases we examined. We let N_0 denote the total number of trajectories in a particular ensemble. The rate of decay for the van der Waals complex was determined by the equation $k = -\ln(N_t/N_0)/t$, where N_t is the number of nondissociated molecules at time t and k is the rate coefficient.

In Figures 4a-4d we show plots of $\ln(N/N_0)$ for the initially excited ν_0 , ν_1 , ν_4 , and ν_7 states, respectively, in the $C_2H_4...F_2$ van der Waals complex. There are basically three regions in each of these plots. The region up to about 4.3096×10^{-12} s corresponds to the first dissociation of F_2 and C_2H_4 molecules. This region is not linear due to the incomplete phase averaging over all vibrational phases. Following this is a region where the dynamics have properly taken over, thus giving a constant slope in which a least squares fit has been done to calculate the rate coefficients k for each of the plots. For Figure 4d an upper and lower bound were given in Table II. The third part of the plots is what appears to be a leveling off of the rate due to a nonstatistical sampling. The second region of these plots were fitted and the resulting decay rate coefficients are given in Table II. These rate coefficients are limited in their accuracy by the selection of the ranges fitted.

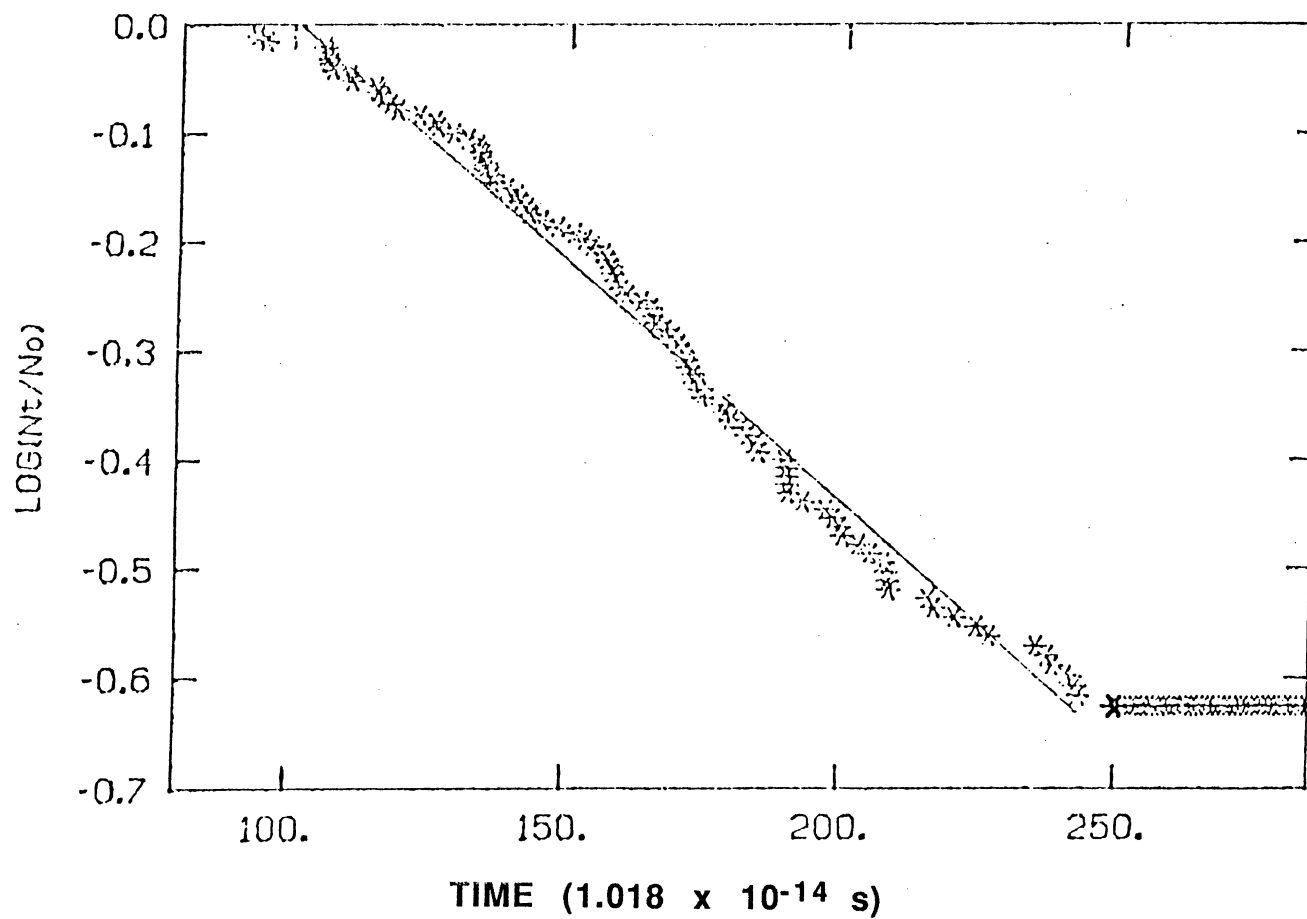


Figure 4a. Percent of Undissociated Trajectories at Time t (Zero Point Energy)

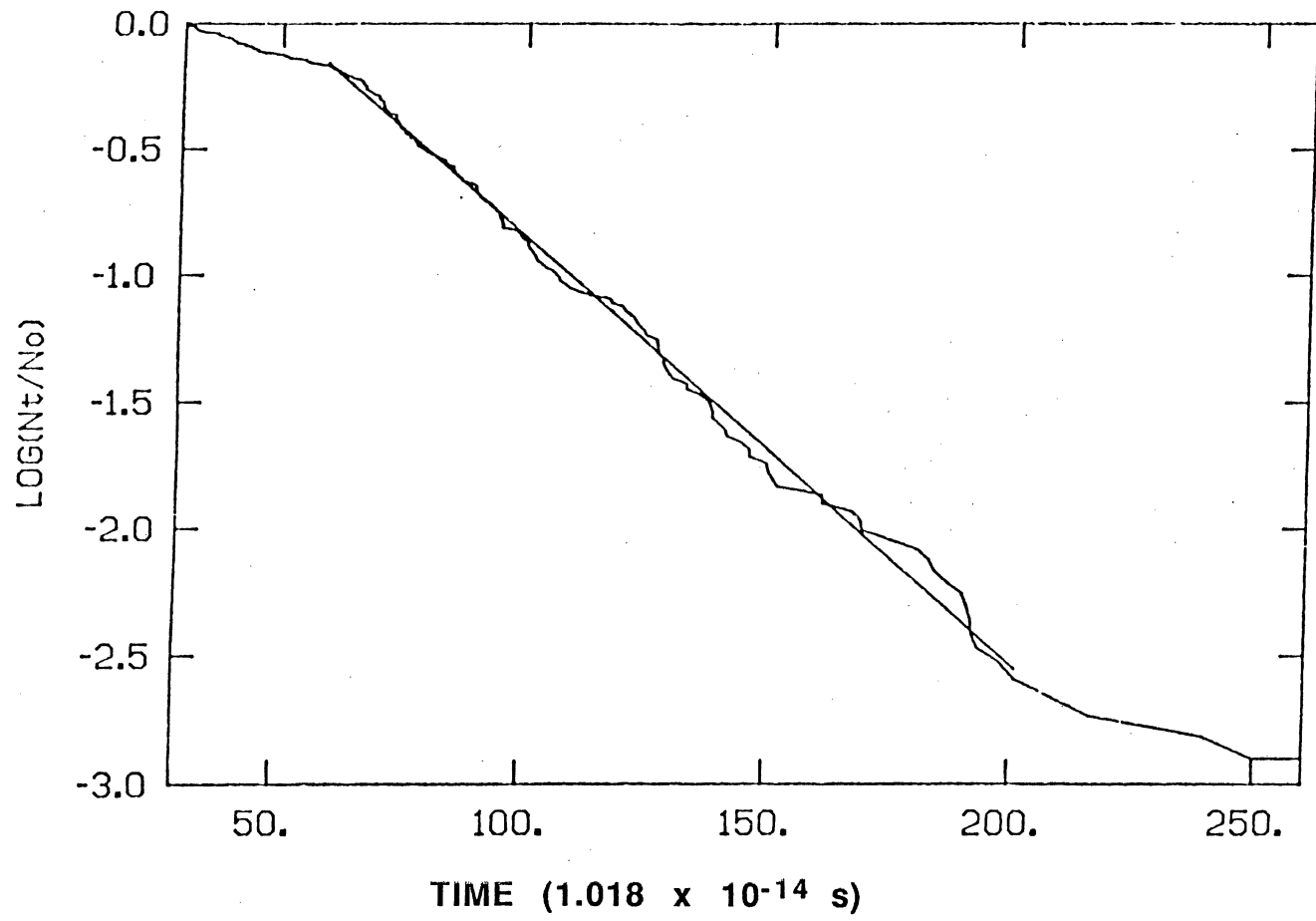


Figure 4b. Percent of Undissociated Trajectories at Time t (Non-Planar CH₂ Rock)

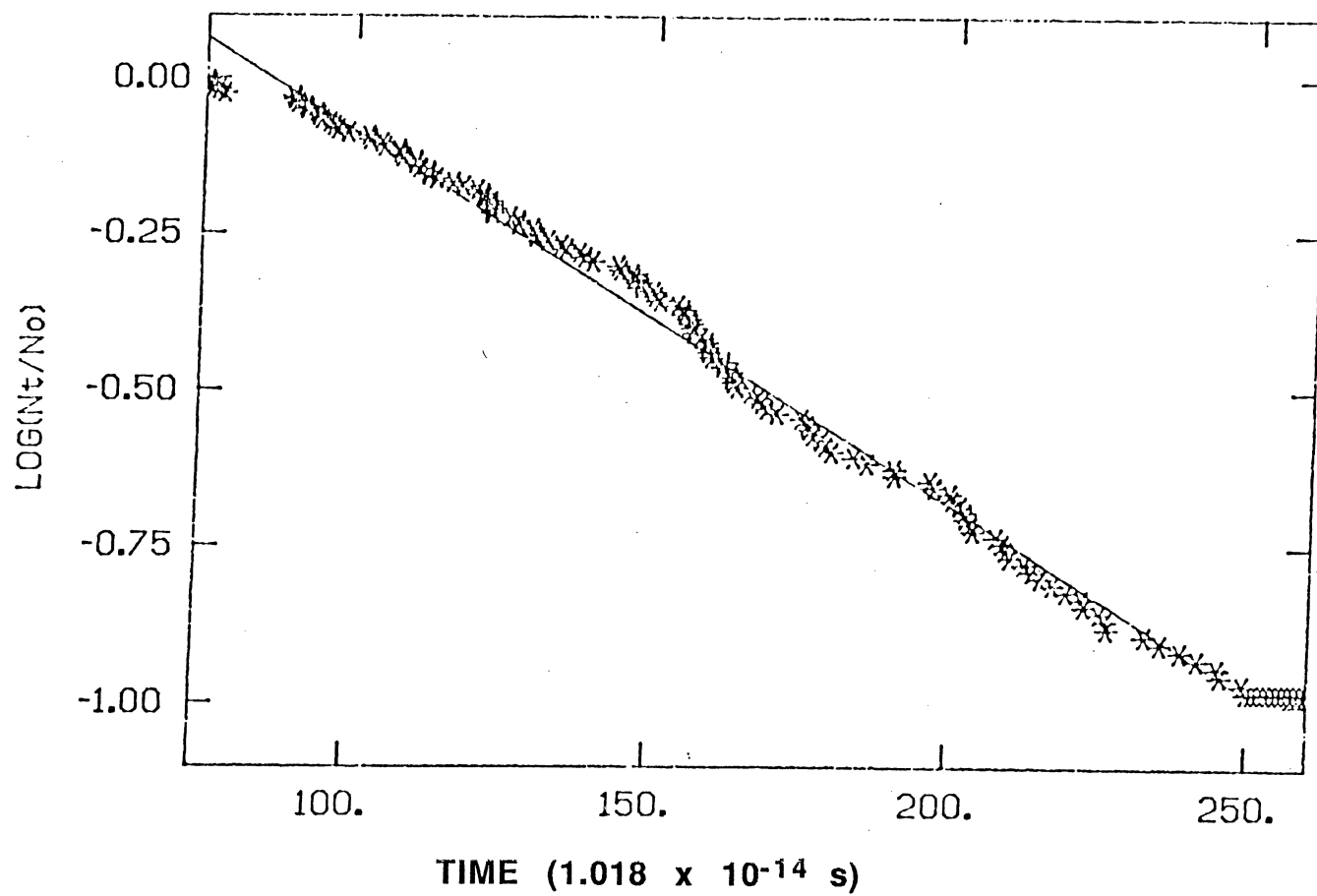


Figure 4c. Percent of Undissociated Trajectories at Time t (Torsional Motion)

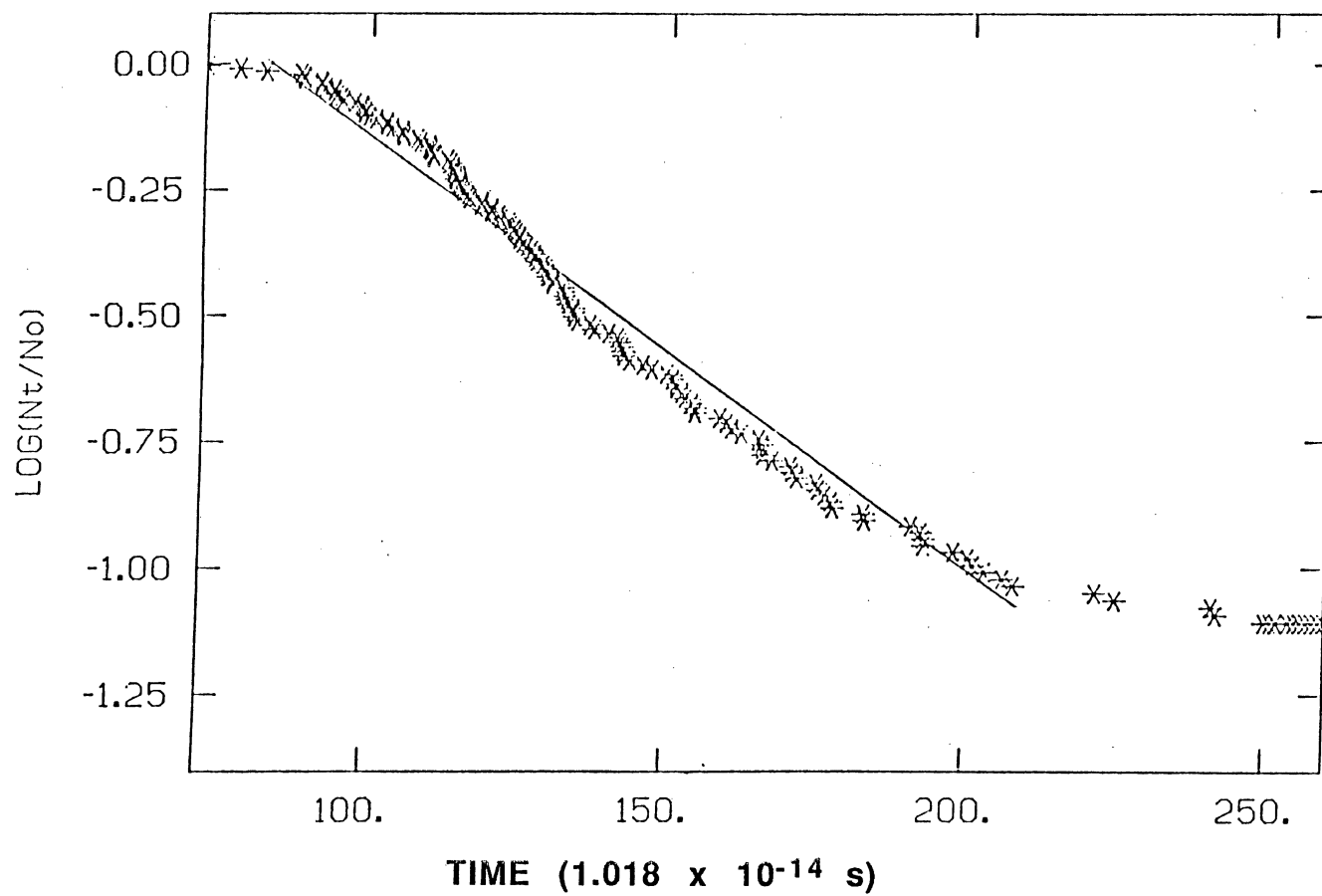


Figure 4d. Percent of Undissociated Trajectories at Time t (Symmetric C-H Stretch)

As it can be seen from Table II, we observed different rate constants for these four vibrational quantum states. The nonplanar rock excitation exhibited a rate four times greater than that of zero point energy, and approximately three times greater for both the torsional motion and symmetric stretch.

TABLE II
RATES FOR FOUR DIFFERENT VIBRATIONALLY
EXCITED STATES OF C₂H₄

Excited Mode	Rate (k) s ⁻¹ *
None	7.72 x 10 ¹¹
C-H Symmetric Stretch	1.59 x 10 ¹²
Upper bound to CH Symmetric Stretch	4.12 x 10 ¹²
Lower bound to CH Symmetric Stretch	6.82 x 10 ¹¹
Torsional Motion	1.11 x 10 ¹²
C ₂ H ₄ Nonplanar Rock	3.14 x 10 ¹²

All rates given in inverse seconds.

We have stated earlier that the van der Waals complex C₂H₄...F₂ is always found to dissociate to C₂H₄ + F₂. The results we have obtained indicate that the reaction coordinate is affected by exciting various modes in the complex. We notice the complex crosses over the critical dividing surface and moves to product configuration space at a much faster rate for the excited modes. In contrast to the gas-phase bimolecular reaction, the van der Waals molecule's internal energy has does not have sufficient time to diffuse intramolecularly and we therefore are able to observe mode specificity among with vibrational rate enhancement.

CHAPTER V

SUMMARY

The reaction and dissociation dynamics for the $C_2H_4...F_2$ van der Waals complex have been studied using quasiclassical trajectory calculations. The potential-energy surface³⁹ used in these calculations was effective in studying the dissociation dynamics of the $C_2H_4...F_2$ van der Waals complex. The initial state of the complex was determined to be that of structure 1 in Table I. We have presented calculations of VP rates for the symmetric C-H stretch, torsional motion, and non-planar CH_2 rock. The rate coefficients were obtained from the decay plots.

The effect of vibrationally exciting different modes for structure 1 in Table I has been determined. We find that increasing the C_2H_4 internal energy produces an increase in the rate of decay. We also find that the rate is dependent upon the particular mode of excitation. The results indicate that vibrationally exciting various modes of the ethylene molecule gives rise to different rates of decay. The different VP rates indicate mode specificity for vibrationally assisted reaction of the $C_2H_4...F_2$ van der Waals complex.

In conclusion, we presume the mode specificity and rate enhancement are due to the van der Waals molecule's inefficiency diffusing energy intramolecularly in the given time period.

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VITA

Robert William Graham

Candidate for the Degree of

Master of Science

Thesis: THEORETICAL STUDIES OF THE VIBRATIONAL PREDISSOCIATION OF
THE $C_2H_4F_2$ VAN DER WAALS COMPLEX

Major Field: Chemistry

Biographical:

Personal Data: Born in Louisville, Kentucky, August 24, 1962.

Education: Graduated from Canton High School, Canton, Massachusetts, May, 1980; received Bachelor of Science Degree from the University of Oklahoma in May, 1985. Completed requirements for the Master of Science degree at Oklahoma State University in May, 1987.

Professional Experience: Graduate Teaching Assistant, Oklahoma State University, Stillwater, Oklahoma, 1985-1987.

Membership in Honorary and Professional Society: Member of Phi Lambda Upsilon, Honorary Chemical Society.