NORMAL MODE ANALYSIS OF ISOTOPICALLY

DECOUPLED ICE, THE ISOLATED BENZENE

RADICAL ANION, AND THIN LAYER

TCNQ MOLECULAR SYSTEMS

By

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Bachelor of Science

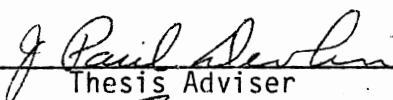Oral Roberts University

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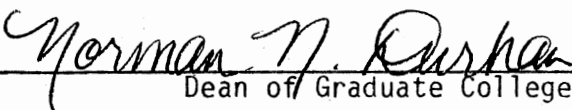
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CHAPTER I

REVIEW OF LITERATURE ON NORMAL MODE
ANALYSIS

Introduction

The nature of inter and intramolecular interactions can be studied by a detailed vibrational analysis. A normal coordinate analysis is frequently essential to a proper understanding of the vibrations of the molecular system in question. The present study attempts a normal coordinate analysis of the H_2O-D_2O system at low temperatures, the benzene radical anion under a D_{2h} point group symmetry, and the reinvestigation of (7,7,8,8-Tetracynoquinodimethane) TCNQ.

A normal mode is a mode of vibration for which the frequency and phase of motion of each atom within the molecule is the same. Each atom reaches its maximum displacement from the equilibrium position at the same time. Only the relative amplitudes of each atom's motion differs within a normal mode. Each molecule possesses 3N-6, 3N-5 for linear molecules, normal modes which linearly superimposed will completely describe the possible vibratory motions of the molecule. Each normal mode has a resonant frequency that can couple with the same frequency of electromagnetic radiation giving rise to unique infrared or Raman spectra for that molecule. Normal coordinate analysis attempts to correlate these absorbtion or scattering frequencies with the corresponding possible normal modes of vibration of the molecule and the force

constants between individual atoms that determine the resonant frequencies. These force constants give a quantitative picture of the forces holding a molecule together.

If the restoring forces between individual atoms are assumed to be classical and harmonic over the small vibratory displacements the problem is simplified. Dennison (1) reviewed many of the earlier methods used in solving for force constants from observed vibrational frequencies. However the complexity of solving the secular equation forbade applying the technique to even moderately sized molecules.

Wilson (2) developed a technique where the solution, according to the former restrictions, is a secular equation of the form

$$|FG - E\lambda| = 0 \tag{1-1}$$

where G is a matrix whose elements are related to the energy T of the molecule by.

$$2T = \sum_{tt'} (G^{-1})_{tt'} \dot{S}_t \dot{S}_{t'} \tag{1-2}$$

S_t is the tth internal coordinate. The matrix F is related to the potential energy V by

$$2V = \sum_{tt'} F_{tt'} S_t S_{t'} \tag{1-3}$$

E is the identity matrix and the λ's are constants related to the vibrational frequencies by

$$\lambda = 4\pi^2 \nu^2 \tag{1-4}$$

The G matrix may be evaluated from the geometry of the molecule (2). The λ's representing the fundamental frequencies of the molecule can be experimentally obtained. The goal of normal mode analysis is to take the empirical information and with the approximations implied in the technique determine the force constants and form of the normal modes of the molecule in question. Equation (1-1) can be rewritten (2) as

$$(GF - E\lambda_k)L_k = 0 \qquad k = 1,2,3,\ldots n \qquad (1-5)$$

where L_k is the kth column of the matrix L and 0 is the zero matrix of N rows and one column. L_k gives the linear transformation between the normal coordinate Q_k and the internal coordinates q_i as

$$Q_k = \sum_i l_{ki} q_i \qquad (1-6)$$

Using matrix notation equation (1-5) may be expressed

$$GFL = L\Lambda \qquad (1-7)$$

Here L is the matrix of eigenvectors diagonalizing the matrix GF by a similarity transformation. Λ is the diagonal matrix containing the eigenvalues λ_k.

The potential function giving the vibrational potential energy of a molecule may be expressed in many different ways. The general quadratic potential function given by

$$2V = \sum_{t,t'=1}^{3N-6} F_{tt'} S_t S_{t'} \qquad (1-8)$$

yields a matrix F such that all elements $F_{tt'}$ may contain nonzero values. In all but the simplest and more symmetric molecules this

causes an indeterminate secular equation since there are more force
constants to be evaluated than there are vibrational frequencies to
determine them. Therefore a more simple approximate force field must be
used for larger molecules. One such approximation is the modified val-
ence force field. Its predecessor the valence force field is given as

$$2V = \sum_i F_{ri} r_i^2 + \sum_j F_{\alpha j} \alpha_j^2 \qquad (1-9)$$

where r_i is the extension of bond i, and α_j the distortion of the
valence angle between two adjacent bonds. If the internal coordinates
are given as these r_i and α_j the matrix F becomes a diagonal matrix of
the appropriate F_{ri} and $F_{\alpha j}$. Often this potential function is too poor
an approximation so that it must be modified by including intuitively
selected cross-terms giving

$$2V = \sum_i F_{ri} r_i^2 + \sum_j F_{\alpha j} \alpha_j^2 + F_{rr'kl} r_k r_l$$

$$+ F_{\alpha\alpha'mn} \alpha_m \alpha_n + F_{raop} r_o \alpha_p \qquad (1-10)$$

where $k \neq l$, $m \neq n$, $o \neq p$

where k, l, m, o, p, are chosen so that F gives a meaningful potential
function without making the secular equation indeterminate.

L and F may be found from G and Λ, equation (1-7), but since the
solution is difficult to solve for analytically other ways are sought.
Iterative calcuations on equation (1-7) where F is varied between calcu-
lations is one technique. But unless the F matrix is varied in a sys-
tematic and logical fashion inefficiency and inconsistent F matrices may
result since (1-7) possesses no unique solution (3,4). Mann et al. (5)
first developed such a systematic way of varying F using linear least

squares. They were able to show that using the Jacobian of ν_i with respect to $F_{tt'}$ the linear least square corrections ΔF_{tt} of the F matrix elements may be computed from the Jacobian, the difference between the observed and calculated frequencies $\Delta\nu_i$, and a diagonal matrix P whose elements are $1/(\nu_{observed})^2$. Hisatune, Devlin, and Califano (6) used this technique in finding the potential functions for the nitrogen oxides, except they preferred to use $1/(\nu_{observed})$ for P the weight matrix because it gave more reasonable error distributions.

Overend and Scherer (7) developed a computerized linear least squares force constant evaluation using matrix notation in a manner similar to reference (5). They defined the matrices J and Z such that

$$\Delta\Lambda = JZ\Delta\Phi \qquad (1-11)$$

where $\Delta\Lambda$ is the difference between the observed and last calculated set of frequencies, $\Delta\Phi$ the force constant corrections due to $\Delta\Lambda$, J the Jacobian as previously defined, and Z the matrix for the linear transformation between a general quadratic force field and the force field to be evaluated. In this notation the linear least square corrections to the force constants becomes

$$(JZ)'P(JZ)(\Delta\Phi) = (JZ)'P(\Delta\Lambda) \qquad (1-12)$$

where P is the diagonal matrix of weighting factors.

Mann et al. (5) found J by varying F_{tt} by 0.01 millidyne/angstroms and then recalculating ν_i. The difference between the first and second calculated set of F_{tt} and ν_i gave the estimated derivative elements needed for J. This J was used in all other additional force constant adjustments on the molecule in question except for a final revaluation

of J on the last iterative cycle. Hisatune et al. (6) preferred to
revaluate J after 3 - 4 cycles. Overend and Scherer (7) calculated JZ,
from perturbation methods indirectly without explicitly evaluating J, by

$$(JZ)_{pr} = \sum_{i=1}^{n} \sum_{j=1}^{n} L_i{}^p L_j{}^p Z_{ij}{}^r \qquad (1-13)$$

Often in less symmetrical molecules the simplest force fields con-
tain more force constants than there are frequencies to determine them.
If the force constants are assumed to be invarient to isotopic substi-
tion, additional frequencies may he obtained from the isotopic analogs
of the molecule being examined. Thus if isotopic substition yields
sufficiently different vibrational frequencies a much larger and more
realistic potential function can be evaluated. Use of isotopically sub-
situted calculated G and Λ_{obs} to solve equation (1-12) is called an
overlay which was first programmed by Schachtschneider and Synder (8).

Several other approaches to evaluating force constants from the
secular equation have been suggested. Panchenko et al. (9) have sug-
gested a matching method to find F. Many authors have tried to simplify
F so that all elements may be calculated (10). But Overend (11) and
Averbukh (3) have cast serious doubts on these attempts. This has
prompted Shimanouchi and Nakagawza (12) to quote,

> The method of calculating normal frequencies, isotope fre-
> quency shifts, . . . and refining the values of these force
> constants by the method of least squares seems to be fairly
> well established (p. 217).

Since equation (1-7) has no unique L and F solution sometimes more
than one F matrix may be found that satisfactorily reproduces the vibra-
tional frequencies. Averbukh (3) has discussed the theoretical basis
for this and pointed out that the reproduction of an experimental set

of frequencies by a certain matrix F cannot serve as proof that this matrix F is the true potential function. McKean (4) studied several examples of F matrix multiplicity such as in the E species of NF_3, B_2 species in ketene, and diazomethane, and the A_g species of ethylene. He found that where chemical intuition and symmetric isotopic substition could not choose the correct F matrix sometimes asymmetric substitution would. Levin (13) found that of two F matrix solutions presented for NF_3 the correct force field could be determined by a vibrational band intensity calculation. Using the normal modes predicted by the two solutions, the dipole derivatives were calculated using the INDO and CNDO/2 molecular orbital programs. The resulting calculated band intensities were then compared with the experimental values.

In this study all normal mode calculations were made using a series of Fortran programs developed by Overend and co-workers. These programs were run on an IBM 370/168 or 370/158 computer with the Fortran IV (H extended) compiler under the optimization level OPT(2) and extended precision increase AUTODBL(DBLPAD4) parameter options unless otherwise noted. The former parameter optimizes the program for maximum speed in execution whereas the latter promotes all single precision variables to double precision and pads all necessary constants appropriately. The output from the H compiled program was compared with the output from the IBM Fortran G1 compiled program and found to be self consistent.

There are three programs to this series: OVEREND, WMAT, and ZMAT. WMAT calculates from the geometry of the molecule the corresponding G matrix elements and computes a W matrix (to be discussed later). ZMAT calculates the transformation matrix Z from Urey-Bradley space to internal coordinate space used in equation (1-11). OVEREND takes the

needed W and Z matrices plus the assigned observed frequencies and calculates the best F matrix to reproduce the observed frequencies using the least square method (7) previously mentioned. OVEREND also has overlay capabilities. Since the transformation matrix Z between valence force field space and internal coordinate space is trivial use of ZMAT or other like program was unnecessary.

The algorithm used by OVEREND was taken from a method developed by Miyazawa (14). The problem with solving equation (1-7) directly is that the GF matrix is not necessarily symmetric and hence can be very tedious and time consuming to solve even on the computer. But if the GF matrix can be transformed by an appropriate similarity transformation into a symmetric matrix, fast computer routines such as the Jacobi method can be used to find the eigenvalues of GF and eigenvectors L by the appropriate transformation. Using the notation of Miyazawa (14) and Schachtschneider (8) the method is shown below.

The matrix G may be diagonalized by

$$GA = AT \tag{1-14}$$

since the eigenvectors of a nondegenerate hermitian matrix are orthogonal

$$T = A'GA = BB \tag{1-15}$$

right multiply by A and left by A'

$$AA'GAA' = ABBA \tag{1-16}$$

since B is diagonal and B = B'

$$G = (AB)(AB)' \tag{1-17}$$

define a matrix W such that

$$W = AB = AT^{1/2} \qquad (1-18)$$

now rewrite equation (1-7) as

$$(AB)(AB)'FL = L\Lambda \qquad (1-19)$$

next multiply equation (1-19) by $(AB)^{-1} = B^{-1}A'$

$$(AB)^{-1}(AB)(AB)'FL = (B^{-1}A')L\Lambda \qquad (1-20)$$

$$(AB)'F(AB)(B^{-1}A')L = (B^{-1}A')L\Lambda \qquad (1-21)$$

or defining

$$C = (B^{-1}A')L = W^{-1}L \qquad (1-22)$$

$$W'FWC = C\Lambda \qquad (1-23)$$

now since W'FW is symmetric H may be defined

$$H = W'FW \qquad (1-24)$$

giving the resulting secular equation

$$HC = C\Lambda \qquad (1-25)$$

which can be solved by fast and accurate symmetric matrix diagonalization routines such as the Jacobi method. L may be found

$$L = WC \qquad (1-26)$$

Thus using W and F OVEREND can find L and Λ by finding H and C.

OVEREND then uses the linear least squares method of Overend and Scherer (7) to find an F from an initial given F such that the final F produces a calculated Λ that closely approximates the observed or vibrational frequencies.

OVEREND also has overlay capabilities. By combining equation (1-12) for a molucule in an overlay series a partitioned master equation can be derived of the form

$$\sum_{i=1}^{\nu} (J_i Z_i)'P_i(J_i Z_i)\Delta\Phi = \sum_{i=1}^{\nu} (J_i Z_i)'P_i \Delta\Lambda_i \qquad (1-27)$$

where the subscript i denotes the matrix for a single molecule or symmetry factored block. This form has the advantage of allowing an overlay series to be evaluated but can be broken up into its partioned parts for in-core storage and evaluation by a computer. Other forms could lead to necessarily large matrices.

Molecular Sytems

The first molecular system to be examined in this study was the thin layer condensed phase H_2O-D_2O matrix. The layer was prepared and examined by infrared and laser Raman spectroscopy as discussed by Devlin et al. (15,16). Two different types of thin layers were prepared; one where H_2O was codeposited with a large relative quantity of D_2O (5 percent H_2O) at 135°K and the other D_2O with a large relative quantity of H_2O (5 percent D_2O) at 135°K. After heating the samples to the necessary temperature the spectra were recorded. From these spectra the observed vibrational frequencies of D_2O, H_2O and HOD were deduced and used in a normal coordinate analysis of D_2O, H_2O, and HOD using WMAT

and OVEREND as described earlier. The data of D_2O and H_2O was combined in an isotopic overlay calculation.

The next sytem to be studied was the thin layer isolated benzene radical anion. The layer was prepared and examined by Devlin et al. (17). Two different types of benzene radical anions were observed; the ion paired benzene radical anion and the isolated benzene radical anion. The isolated benzene radical anion was assumed to have a quinoid electronic structure thus necessitating a D_{2h} point group symmetry. A normal coordinate analysis was made for benzene using a D_{2h} symmetry and TCNQ radical anion ring stretching force constants. The calculated frequencies were then compared with those observed from the thin layer isolated benzene radical anion for both C_6H_6 and C_6D_6.

The third system TCNQ was thoroughly investigated by Khatkale (18) who ran several normal coordinate analyses of the neutral, mono, di, and trianion salts of TCNQ using the same Z matrix transformation from modified valence space to internal coordinate space as was used by Girlando and Pecile (19). Serious discrepancies were found between Khatkale's and Pecile's force constant values for the final converged F matrix. Later investigation uncovered a difference between the Z matrices used by Khatkale and Pecile that prompted a new normal coordinate analysis of neutral TCNQ. The Z matrix of Khatkale was reconciled to agree with Pecile's and a normal coordinate analysis of thin layer neutral TCNQ was attempted using the observed frequencies of Girlando and Pecile (19).

CHAPTER II

NORMAL MODE ANALYSIS OF CONDENSED Ic
WATER SYSTEMS

Introduction

Water and its isotopes have been the subject of an enormous amount
of research. In particular much interest has been focused on the vibra-
tional frequencies of water and its isotopic analogs in the matrix iso-
lated and condensed phases.

At atmospheric pressure ice exists in three forms, ice Ia (amor-
phous), ice Ic (cubic), and ice Ih (Hexagonal). Ice Ia changes irre-
versibly to ice Ic at about 140°K and ice Ic changes irreversibly to ice
Ih at about 190°K. Thiel, Becker, and Pimental (20), Harvey and
Shurvell (21), and Tursi and Nixon (22) have examined and assigned the
frequencies of H_2O, D_2O, and HOD monomers, dimers, and higher polymers
isolated in nitrogen matrices. Haas and Hornig (23) explained the
spectra of dilute solutions of HOD frozen together with either H_2O or
D_2O. They first proposed that the width of the OH or OD stretch in ice
was due to intermolecular coupling of the O-H motion rather than hydro-
gen bonding. Hardin and Harvey (24) studied the infrared spectral
changes in the amorphous ice Ia to cubic ice Ic phase change.

The Raman spectra of thin layer Ia ice was reported by Li and
Devlin (25) using a beam trapping technique allowing improved polariza-
tion measurements. More recently other Rama measurements have been

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reported for amorphous and polycrystalline ice I and ice Ih by Rice et al. (26) and on single crystal ice Ih by Scherer and Snyder (27).

The infrared spectra of D_2O vibrationally decoupled in glassy H_2O and H_2O ice Ic was published by Devlin et al. (28,29) and the infrared spectra of amorphous and polycrystalline ice by Rice et al. (30). Since the OH stretching region of H_2O is highly coupled considerable effort has been devoted to finding the decoupled H_2O stretching and bending frequencies in ice Ia, Ic, and Ih by theoretical or matrix isolation techniques. Rice et al. (31,32,33) used theoretical methods to predict the decoupled frequencies and Devlin et al. (16) used molecular thin layer techniques.

From the results of their calculations Sceats and Rice suggested that the ν_3 and ν_1 stretching modes (ν_3 antisymmetric stretch, ν_1 symmetric stretch) for isolated H_2O in D_2O are weakly split about the ν_{OH} stretching mode frequency of HOD in ice Ic. Thus Fermi resonance of $2\nu_2$ with ν_1 pushes ν_1 into ν_3 yielding a single stretching band nearly concident with ν_{OH}. From the examination of spectra and spectral changes during proton exchange of H_2O isolated in a D_2O matrix of ice Ic Devlin et al. disagreed. The spectra was interpreted in terms of a higher ν_2 bending frequency such that Fermi resonance of ν_1 with $2\nu_2$ enhanced the spacing between ν_1 and ν_2. This problem prompted a normal mode analysis of the D_2O, H_2O, and HOD thin layer systems to determine which assignment is more reasonable.

Normal Mode Analysis

The bond lengths, angles, and masses used for H_2O, D_2O and HOD are shown in Table I. Figure 1 shows the internal coordinate system used

TABLE I

PARAMETERS USED FOR CREATING
WATER G MATRIX

Molecule	Bond length (OH) $\overset{o}{A}$	Bond angle (HOH) deg	At. mass
H_2O	0.96	104.5	H 1.00797
HOD	0.96	104.5	D 2.01400
D_2O	0.96	104.5	0 15.9994
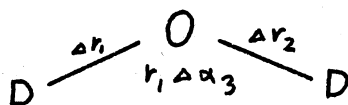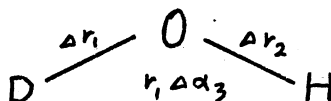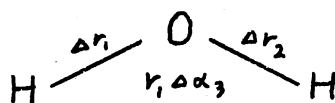
Figure 1. Internal Coordinates of Water Isotopes

for H_2O, D_2O, and HOD. Note that the bending coordinate $\Delta\alpha_3$ has been scaled by r_1 to make the bending and stretching force constant units consistent. Both H_2O and D_2O possess a C_{2v} point group symmetry while HOD possesses a planar symmetry. Under a C_{2v} symmetry D_2O and H_2O have two vibrations belonging to the A_1 irreducible representation (symmetric stretch and bend) and one vibration belonging to the B_1 irreducible representation (antisymmetric stretch). Since it would be necessary to perform overlay calculations on H_2O, D_2O, and HOD trial calculations were carried out on H_2O and D_2O using a C_{2v} symmetry and no symmetry. Both sets of symmetries gave the same results with like force constants for H_2O and D_2O. Since WMAT requires a U matrix containing the transformation between internal and symmetry coordinates U was set equal to I the identity matrix for HOD and the non-symmetrized H_2O and D_2O calculations. The symmetry coordinates used for C_{2v} H_2O and D_2O are shown in Table II.

TABLE II

SYMMETRY COORDINATES FOR WATER MOLECULE

Symmetry Specie	Symmetry Coordinate
A_1	$S_1 = (1/\sqrt{2})(\Delta r_1 + \Delta r_2)$
	$S_2 = r_1 \Delta\alpha_3$
B_1	$S_3 = (1/\sqrt{2})(\Delta r_1 - \Delta r_2)$

no redundancies

Several different force constant refinements and force fields were tried but only those yielding tenable results will be discussed. Three different types of force field refinements hereafter called set I, II, and III gave the best clues to unraveling the spectra. Since the calculations of Rice (33) on D_2O decoupled in H_2O ice Ic agreed with the conclusions of Devlin (16) the force constants from set I were calculated using only the Fermi resonance corrected D_2O observed frequencies (see reference 33). A valence force field was used

$$2V = \sum_{i=1}^{2} F_{rr}r_i^2 + F_{\alpha\alpha}\alpha_j^2 \qquad (2-1)$$

where F_{rr} was the OD stretching coordinate force constant and $F_{\alpha\alpha}$ the DOD bending coordinate force constant. These force constants were then transferred to H_2O without change and used to calculate the H_2O frequencies for H_2O decoupled (and isolated) in D_2O ice Ic. The results are shown in Table III. Set II force constants were likewise calculated by the modified valance potential function.

$$2V = \sum_{i=1}^{2} F_{rr}r_i^2 + F_{\alpha\alpha}\alpha_k^2 + F_{rr'}r_ir_j \qquad (2-2)$$

where $F_{rr'}$ was the stretch-stretch interaction force constant set equal to 0.06 millidynes/angstroms and not allowed to vary in the force field refinement. The value of $F_{rr'}$ was taken from Figure 3 of reference 33. The D_2O and H_2O frequencies calculated from the set II force constants are shown in Table IV.

For set III the potential function was the same as set II but F_{rr} and $F_{\alpha\alpha}$ were varied and $F_{rr'}$ constrained to 0.06 to fit the uncorrected

TABLE III

FORCE CONSTANTS AND CALCULATED FREQUENCIES
FOR SET I REFINEMENT

Symmetry		Obs. Freq.[a] (cm^{-1})	Calc. Freq. (cm^{-1})
D_2O			
A_1	ν_1	2392.0[b] (2367.0)	2386.8
	ν_2	1230.0	1230.1
B_1	ν_3	2444.0	2449.3
H_2O			
A_1	ν_1		3295.2
	ν_2		1688.5
B_1	ν_3		3342.5
		F_{rr} = 6.14 mdyne/ang $F_{\alpha\alpha}$ = 0.788 mdyne/ang	

[a]Reference 16
[b]Corrected for Fermi resonance with $2\nu_2$ on basis of calculations of
reference 33, value in parenthesis is actual observed frequency.

TABLE IV

FORCE CONSTANTS AND CALCULATED FREQUENCIES
SET II REFINEMENT

Symmetry		Obs. Freq.[a] (cm^{-1})	Calc. Freq. (cm^{-1})
D_2O			
A_1	ν_1	2392.0[b] (2367.0)	2383.2
	ν_2	1230.0	1230.2
B_1	ν_3	2444.0	2452.2
H_2O			
A_1	ν_1		3294.8
	ν_2		1686.3
B_1	ν_3		3346.4

$$F_{rr} = 6.161 \text{ mdyne/ang} \qquad F_{\alpha\alpha} = 0.785 \text{ mdyne/ang}$$
$$F_{rr'} = 0.06 \text{ mdyne/ang}$$

[a]Reference 16
[b]Corrected for Fermi resonance with $2\nu_2$ on basis of calculations of
reference 33, value in parenthesis is actual observed frequency.

(for any possible Fermi resonance) observed frequencies of decoupled D_2O and H_2O in an overlay calculation. The force constants calculated were transferred without change to HOD to calculate the decoupled HOD frequencies. The results are shown in Table V. Attempts to try an overlay calculation on H_2O, D_2O, and HOD failed due to a singularity encountered in inverting the JZ matrix for solving the normal linear least square equation (eq. 1-12). This usually results from an ill-conditioned JZ matrix that is difficult if not impossible to correct or improve.

Discussion

From the calculated frequencies of Tables III and IV several conclusions can be made concerning the decoupled H_2O observed frequencies. First using two very simple force fields an excellent fit of ν_2 and a reasonable fit of the stretching modes of D_2O are obtained. When these fields are transferred to decoupled H_2O an average 1687 cm^{-1} ν_2 bending mode and a sizable ν_1-ν_3 splitting (about 50 cm^{-1}) is predicted. This splitting is not in disagreement with the Sceats and Rice (33) prediction of concidence of ν_1 and ν_3 if Fermi resonance of ν_1 with $2\nu_2$ is included. But if the 1687 cm^{-1} ν_2 value is accepted the $2\nu_2$ value of 3374 cm^{-1} (ignoring anharmonicity), would be too high to have much Fermi resonance with ν_1, particularly to push ν_1 to a higher frequency, unless ν_1 is significantly higher than ν_3. This is in disagreement with the gas and crystal ν_1 values for D_2O. If Fermi resonance is present the tendency would apparently be to increase the ν_1-ν_3 splitting rather than decrease it.

Support for this conclusion can be drawn from the calculations of Table V. By taking the D_2O and H_2O overlay force constants, ignoring

TABLE V

FORCE CONSTANTS AND CALCULATED FREQUENCIES
SET III REFINEMENT

Symmetry		Obs. Freq. (cm^{-1})	Calc. Freq. (cm^{-1})
D_2O			
A_1	ν_1	2367.0	2338.8
	ν_2	1230.0	1251.1
B_1	ν_3	2444.0	2406.4
		Average Error = 1.50%	
H_2O			
A_1	ν_1	3200.0	3233.3
	ν_2	1732.0	1715.8
B_1	ν_3	3270.0	3284.0
		Average Error = 0.80%	
HOD			
	ν_{OH}	3270.0 (D_2O)	3260.0
	ν_{OD}	2418.0 (H_2O)	2372.0
	ν_2	1488.0[a]	1501.7
		Average Error = 1.10%	

F_{rr} = 5.934 mdyne/ang   Dispersion = 0.0677
$F_{\alpha\alpha}$ = 0.813 mdyne/ang   Dispersion = 0.4990
$F_{rr'}$ = 0.06 mdyne/ang   Constrained in refinement

[a]Average of observed HOD bending frequency for H_2O and D_2O matrices of 1510.0 (D_2O) and 1465.0 (H_2O).

any possible Fermi resonance in H_2O and D_2O, and transferring them to HOD we predict its frequencies to within the same average error as H_2O and D_2O. The one stipulation is that the average of the D_2O and H_2O matrix HOD ν_2 bending frequencies be compared to the calculated HOD ν_2 bending mode. This is not an unreasonable assumption since the HOD ν_2 bending mode can be expected and is observed to couple with an H_2O and D_2O matrix in some manner. The Table V calculation then gives reasonable results using a very simple force field and a ν_2 frequency of 1715.8 cm^{-1}, well above the value needed to rule out a Fermi resonance between ν_1 and $2\nu_2$ that would push ν_1 and ν_3 into an accidental degeneracy in the decoupled H_2O ice Ic spectra.

CHAPTER III

NORMAL MODE ANALYSIS OF MATRIX-ISOLATED

BENZENE RADICAL ANION

Introduction

The benzene negative anion has been studied by a variety of methods. Gardner (34) studied the UV spectra of benzene reduced with potassium in dimethoxyethane at -80°C. He found three major bands, one of which was attributed to solvated potassium. Graham and Duly (35) examined the absorption spectra of sodium isolated in solid benzene and claimed that the Na-C_6H_6 complex could not have higher than a C_{6v} symmetry on the basis of the active vibrational frequencies. In a follow-up paper McCoulough and Duley (36) extended their study of Na-C_6H_6 complexes to Na-C_6D_6 and mixed Na-C_6H_6 and Na-C_6D_6. They further concluded that Na atoms interact predominantly with one nearby benzene molecule.

Shida and Iwata (37) published the electronic spectra of the benzene anion radical produced by gamma ray irradiation induced reactions in a glassy solid solution of 2-methyl-tetrahydrofuran and benzene at 77°K. Their UV spectrum was similar to Gardner's (34) but as expected lacked the band attributed to solvated potassium.

The ESR spectra of the benzene-potassium, rubidium, and cesium ion pair was examined by Jones and Kuechler (38). They suggested an ion pair in which the metal anion is placed on the sixfold axis of benzene

anion but allowed to oscillate relative to and parallel to the benzene plane. Several calculational studies of the benzene radical anion have been done. Of the most recent is the work of Radom et al. (39) who used an ab initio molecular orbital calculation using the STO-3G and 4-31G basis sets and limited configuration interaction with STO-3G optimized structures. They found that the most stable structures for the benzene radical anion were two unique D_{2h} Jahn-Teller distortions from the D_{6h} neutral benzene symmetry. Figure 2 gives the parameters for these structures. The difference in calculated total energies for the two structures was negligible. Therefore Radom et al. suggested, especially in light of ESR results that all hydrogens are equivalent on the ESR time scale, that the benzene radical anion rapidly interconverts between the two D_{2h} structures shown in Figure 2.

From laser excitation spectra of symmetrically substituted chloro and fluorobenzene cations Sears, Miller, and Bondybey (40) supported the expected Jahn-Teller distortion of the benzene ring giving a splitting of approximately 250 cm^{-1} for the e' ring deformation mode.

Devlin et al. (17) have examined the Raman and infrared spectra of thin layer benzene codeposited with the alkali metals. From an examination of the Raman spectra of thin layer samples before and after bleaching with one watt of 4880 Å laser radiation they concluded that three species were present, neutral benzene, ion-paired benzene, and isolated benzene anion. The UV spectra of their samples were similar to Gardner's (34). By monitoring which Raman bands were resonantly enhanced with changing laser wavelength they were able to separate the isolated benzene anion frequencies from the ion-paired benzene anion frequencies. The resulting Raman spectrum for the isolated benzene anion was then

119.5°

1.352 Å

117.2°

1.434 Å

STRUCTURE I

120.5°

1.460 Å

122.8°

1.379 Å
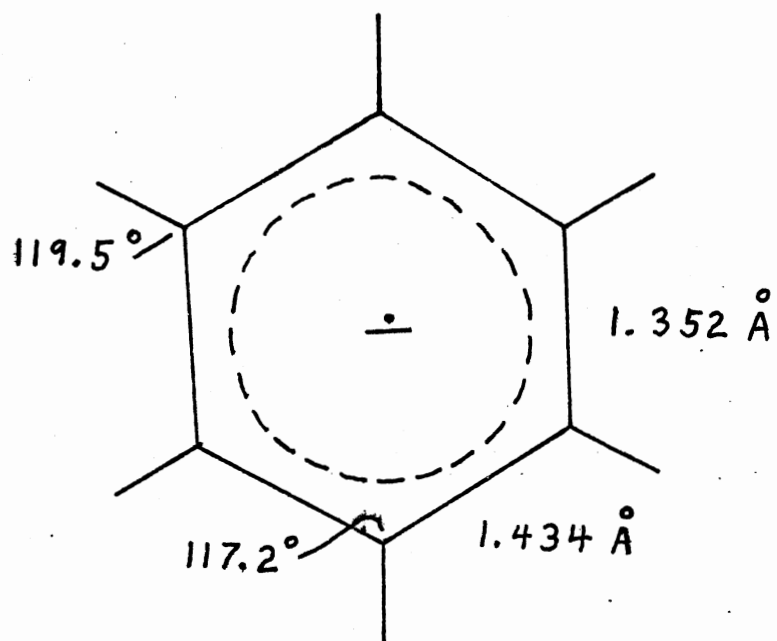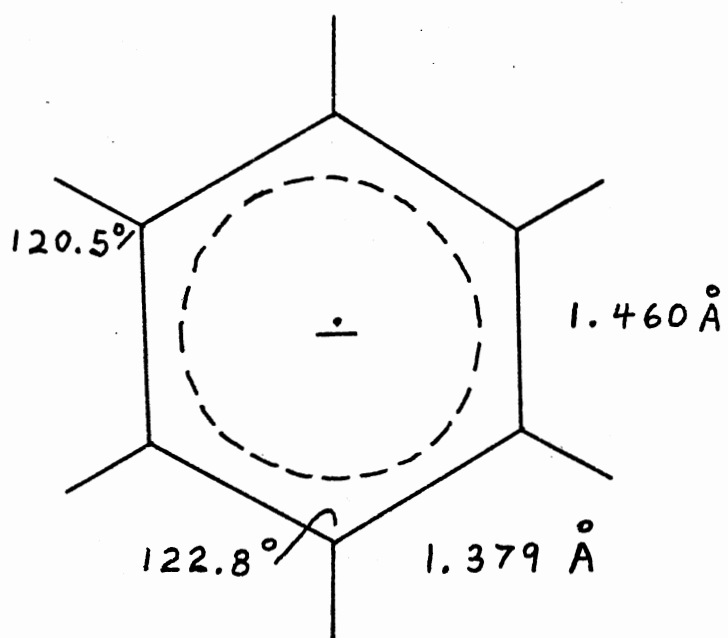
STRUCTURE II

Figure 2. Possible Structures for Benzene Radical Anion

correlated to a distorted benzene structure with a D_{2h} symmetry. From depolarizaiton measurements of three A_g and B_{3g} Raman bands of isolated benzene anions Devlin et al. suggested that the isolated benzene anion rapidly interconverts between two energy equivalent structures as first proposed by Hinde, Poppinger, and Radom (39). A closer examination of the isolated benzene anion Raman and infrared spectra revealed a benzene-like spectra with TCNQ-like splittings of the D_{6h} benzene E_g ring modes. This suggestion prompted a normal mode analysis of the D_{2h} isolated benzene anion system to test the validity of this idea.

Normal Mode Analysis

Since only eight C_6H_6 and six C_6D_6 isolated benzene anion frequencies could be assigned with some confidence a full force field determination would be unreasonable and underdetermined. Most of the observed frequencies were assigned to various ring stretching and C-H bending modes. Thus only calculations based on previously determined force constants, left unrefined, could be used to justify the assignments and the conclusions that the D_{2h} benzene anion distortions give rise to a TCNQ-like ring structure in the benzene ring. The calculational method was to find a suitable benzene force field, to modify it to include the two TCNQ-ring force constants for single and double carbon bonds, and to determine if the calculated frequencies correspond to the observed frequencies for the isolated benzene anion. The benzene force field chosen was a modified valence force field used by Scherer (41) in his analysis of the chlorinated benzenes. Scherer attempted to find how simple a potential function could adequately predict the frequencies of benzene and its deutero-isotope to within $10 - 15$ cm^{-1}. The simplicity without

a significant loss in accuracy of this function made it ideal as a benzene field. Since this force field contained only one value for the ring carbon-carbon bond it had to be modified to separate the six equal carbon-carbon stretching force constants into two sets of carbon-carbon stretching force constants to provide for the double and single bond character of the TCNQ-like ring structure. Next the two TCNQ carbon-carbon ring stretching force constant values of Girlando and Pecile (19) were transferred to the modified Scherer benzene force field and the resulting frequencies calculated.

The first step of the normal mode analysis was to reproduce the frequencies of benzene using Scherer's (41) nine parameter potential function with his Table 4ii force constants values under a D_{2h} molecular symmetry. The frequency fit and degeneracies produced from the correlation of the D_{6h} E_{2g} and E_{1u} modes with the D_{2h} A_g, B_{3g}, B_{1u}, and B_{2u} modes would provide a convenient check for errors as well as provide the necessary D_{2h} symmetry needed for the isolated benzene anion calculation.

Figure 3 gives the internal coordinate system used for the D_{2h} benzene calculations. The parameters and symmetry coordinates used throughout the benzene and isolated benzene anion calculations are shown respectively in Tables VI and VII. Table VIII gives the modified valence force field definitions and values used for the D_{2h} benzene and isolated benzene anion calculations. Since check calculations were run on Scherer's benzene force field using D_{6h} and D_{2h} symmetries the results are compared and displayed in Table IX.

After checking symmetries the next step involved taking Scherer's benzene force field and adding another carbon-carbon double bond
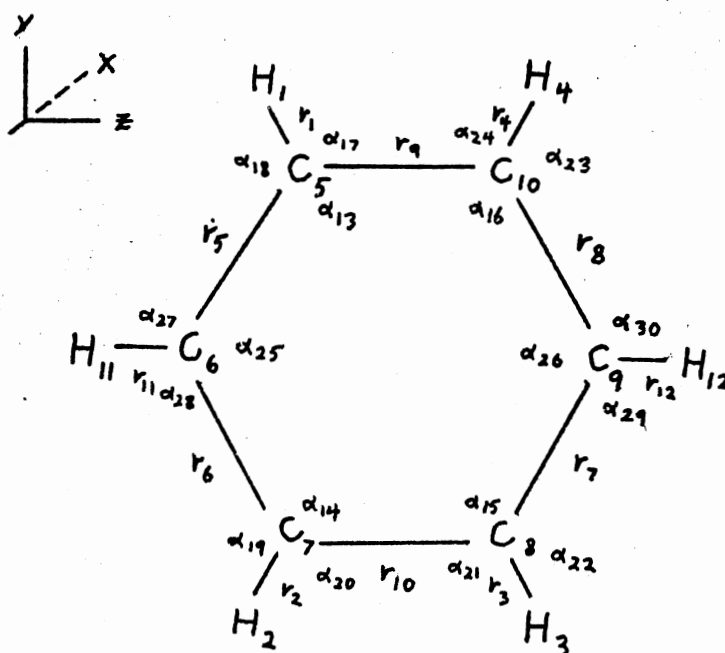
Figure 3. Internal Coordinates of D$_{2h}$ Benzene

TABLE VI

PARAMETERS FOR CREATING BENZENE AND
ISOLATED BENZENE ANION G MATRIX

Definition	Value
C - C bond	1.397 Å
C - H bond	1.08412 Å
C - C - C angle	120°
C - C - H(D) angle	120°
C atomic mass	12.01115
H atomic mass	1.007825
D atomic mass	2.0140

TABLE VII

SYMMETRY COORDINATES FOR D_{2h} BENZENE AND
ISOLATED BENZENE RADICAL ANION

Symmetry	Symmetry Coordinate
A_g	$S_1 = (1/\sqrt{4}) (\Delta r_1 + \Delta r_2 + \Delta r_3 + \Delta r_4)$
	$S_2 = (1/\sqrt{4}) (\Delta r_5 + \Delta r_6 + \Delta r_7 + \Delta r_8)$
	$S_3 = (1/\sqrt{2}) (\Delta r_9 + \Delta r_{10})$
	$S_4 = (1/\sqrt{2}) (\Delta r_{11} + \Delta r_{12})$
	$S_5 = (1/\sqrt{4}) (\Delta \alpha_{13} + \Delta \alpha_{14} + \Delta \alpha_{15} + \Delta \alpha_{16})$
	$S_6 = (1/\sqrt{4}) (\Delta \alpha_{18} + \Delta \alpha_{19} + \Delta \alpha_{22} + \Delta \alpha_{23})$
	$S_7 = (1/\sqrt{4}) (\Delta \alpha_{17} + \Delta \alpha_{20} + \Delta \alpha_{21} + \Delta \alpha_{24})$
	$S_8 = (1/\sqrt{4}) (\Delta \alpha_{27} + \Delta \alpha_{28} + \Delta \alpha_{29} + \Delta \alpha_{30})$
	$S_9 = (1/\sqrt{4}) (\Delta \alpha_{25} + \Delta \alpha_{26})$
B_{3g}	$S_{10} = (1/\sqrt{4}) (\Delta r_1 - \Delta r_2 + \Delta r_3 - \Delta r_4)$
	$S_{11} = (1/\sqrt{4}) (\Delta r_5 - \Delta r_6 + \Delta r_7 - \Delta r_8)$
	$S_{12} = (1/\sqrt{4}) (\Delta \alpha_{13} - \Delta \alpha_{14} + \Delta \alpha_{15} - \Delta \alpha_{16})$
	$S_{13} = (1/\sqrt{4}) (\Delta \alpha_{18} - \Delta \alpha_{19} + \Delta \alpha_{22} - \Delta \alpha_{23})$
	$S_{14} = (1/\sqrt{4}) (\Delta \alpha_{17} - \Delta \alpha_{20} + \Delta \alpha_{21} - \Delta \alpha_{24})$
	$S_{15} = (1/\sqrt{4}) (\Delta \alpha_{27} - \Delta \alpha_{28} + \Delta \alpha_{29} - \Delta \alpha_{30})$
B_{1u}	$S_{16} = (1/\sqrt{4}) (\Delta r_1 + \Delta r_2 - \Delta r_3 - \Delta r_4)$
	$S_{17} = (1/\sqrt{4}) (\Delta r_5 + \Delta r_6 - \Delta r_7 - \Delta r_8)$
	$S_{18} = (1/\sqrt{2}) (\Delta r_{11} - \Delta r_{12})$
	$S_{19} = (1/\sqrt{4}) (\Delta \alpha_{13} + \Delta \alpha_{14} - \Delta \alpha_{15} - \Delta \alpha_{16})$
	$S_{20} = (1/\sqrt{4}) (\Delta \alpha_{18} + \Delta \alpha_{19} - \Delta \alpha_{22} - \Delta \alpha_{23})$
	$S_{21} = (1/\sqrt{4}) (\Delta \alpha_{17} + \Delta \alpha_{20} - \Delta \alpha_{21} - \Delta \alpha_{24})$
	$S_{22} = (1/\sqrt{4}) (\Delta \alpha_{27} + \Delta \alpha_{28} - \Delta \alpha_{29} - \Delta \alpha_{30})$
	$S_{23} = (1/\sqrt{2}) (\Delta \alpha_{25} - \Delta \alpha_{26})$
B_{2u}	$S_{24} = (1/\sqrt{4}) (\Delta r_1 - \Delta r_2 - \Delta r_3 + \Delta r_4)$
	$S_{25} = (1/\sqrt{4}) (\Delta r_5 - \Delta r_6 - \Delta r_7 + \Delta r_8)$
	$S_{26} = (1/\sqrt{2}) (\Delta r_9 - \Delta r_{10})$
	$S_{27} = (1/\sqrt{4}) (\Delta \alpha_{13} - \Delta \alpha_{14} - \Delta \alpha_{15} + \Delta \alpha_{16})$
	$S_{28} = (1/\sqrt{4}) (\Delta \alpha_{18} - \Delta \alpha_{19} - \Delta \alpha_{22} + \Delta \alpha_{23})$
	$S_{29} = (1/\sqrt{4}) (\Delta \alpha_{17} - \Delta \alpha_{20} - \Delta \alpha_{21} + \Delta \alpha_{24})$
	$S_{30} = (1/\sqrt{4}) (\Delta \alpha_{27} - \Delta \alpha_{28} - \Delta \alpha_{29} + \Delta \alpha_{30})$

redundancies: 3 A_g, 1 B_{3g}, 3 B_{1u}, 2 B_{2u}

TABLE VIII

MODIFIED VALENCE FORCE FIELD FOR D_{2h} BENZENE AND ISOLATED BENZENE ANION

Symbol	Coordinate Type	Bond	Value[a]
		D_{2h} Benzene	
K_1	r_1r_1	C-H	5.06
K_2	r_5r_5	C-C	6.676
H_3	$\alpha_{13}\alpha_{13}$	C-C-C	1.05
H_4	$\alpha_{17}\alpha_{17}$	C-C-H	0.494
F_5	$r_9\alpha_{17}$	C-C,C-C-H	0.173
F_5	$r_9\alpha_{18}$	C-C,C-C-H	-0.173[b]
F_6	r_9r_{13}	C-C,C-C-C	-0.067
F_7	r_5r_9	C-C,C-C (ortho)	0.684
F_8	r_5r_8	C-C,C-C (meta)	-0.345
F_9	r_5r_7	C-C,C-C (para)	0.293
		Structure I (same but)	
K_2	r_5r_5,r_6r_6 r_7r_7,r_8r_8	C-C	5.50
K_{10}	$r_9r_9,r_{10}r_{10}$	C-C	7.50
		Structure II (same but)	
K_2	r_5r_5,r_6r_6 r_7r_7,r_8r_8	C-C	7.00
K_{10}	$r_9r_9,r_{10}r_{10}$	C-C	5.50

a: units: K in mdyne/$\overset{o}{A}$: H in mdyne-$\overset{o}{A}$/(radian)^2
    : F in mdyne/radian for stretch-bending
b: : Z-matrix elements set equal to -1.00

TABLE IX

CALCULATED PLANAR FREQUENCIES OF BENZENE
USING SCHERER'S MVFF D_{2h} SYMMETRY

Symmetry	Obs. Freq. (cm^{-1})[a]	Calc. Freq. (cm^{-1})
A_g	3062.0	3055.4
	3047.0[b]	3054.1
	1595.0[b]	1590.3
	1177.0[b]	1185.8
	992.0	993.7
	607.0[b]	603.0
B_{3g}	3047.0[b]	3054.1
	1595.0[b]	1590.3
	1346.0	1338.5
	1177.0[b]	1185.8
	607.0[b]	603.0
B_{1u}	3057.0[b]	3053.6
	3048.0	3056.1
	1479.0[b]	1448.2
	1035.0[b]	1073.9
	1010.0[b]	1014.6
B_{2u}	3057.0[b]	3053.6
	1479.0[b]	1448.2
	1309.0	1303.7
	1146.0	1165.2
	1035.0[b]	1073.8

Average Error = 0.91%

[a]Scherer, J. R., Spectrochimia Acta, 20, 348, 1964, Table 1.
[b]Degenerate modes from D_{6h} symmetry split and assigned to D_{2h} according to correlation tables.

stretching force constant and using Girlando and Pecile's (19) ring

force constant of 5.5 millidynes/angstrom for the carbon-carbon single

bond and 7.5 millidyne/angstrom for the added carbon-carbon double bond

force constants. Or using Figure 3, bonds r_9 and r_{10} were assigned the

7.5 value and bonds r_5, r_6, r_7, and r_8 the 5.5 value instead of the

6.676 value used by Scherer (41). As a test of structure II an identi-

cal calculation was run except that the carbon-carbon stretching bond

values were reversed so that r_9 and r_{10} were assigned 5.5 and r_5, r_6,

r_7 and r_8 assigned 7.0 millidyne/angstrom. The 7.5 double bond force

constant was dropped to 7.0 to partially account for the double bond

value being assigned to four bonds instead of two. This helped keep the

total bond energy of structure II more consistent with the structure

I total bond energy. In both structural test calculations all other

stretching, bending, and interaction force constants were left to their

original Scherer benzene value. Table X gives the calculated frequen-

cies for the structure I calculation with the suggested assignments of

Devlin et al. (17). Table XI gives the calculated frequencies for the

structure II calculations.

Discussion

Scherer (41) using the Table 4ii force constants was able to calcu-

late the frequencies of benzene under a D_{6h} symmetry to within a one

percent error. The check calculation on benzene under a D_{2h} symmetry

shown in Table IX also reproduces the benzene frequencies to within a

one percent error. Notably all degenerate frequencies under D_{6h} sym-

metry still are degenerate under a D_{2h} symmetry to at least five signif-

icant digits in the check calculations. The calculated D_{2h} frequencies

TABLE X

CALCULATED PLANAR FREQUENCIES OF BENZENE
RADICAL ANION: STRUCTURE I

Symmetry	Obs. Freq. (cm^{-1})[a]		Calc. Freq. (cm^{-1})		Assig.
	$C_6H_6^-$	$C_6D_6^-$	$C_6H_6^-$	$C_6D_6^-$	
A_g	-	-	3055.8	2281.7	
	-	-	3052.9	2268.0	
	1586	1563	1613.6	1578.4	ring str.
	1152	-	1186.5	904.3	C-H bend [b]
	957	822	948.9	841.1	ring str.[b]
	616	587	602.7	582.0	ring def.
B_{3g}	-	-	3052.9	2271.2	
	1475	1428	1463.2	1431.6	ring str.
	1358	1190	1338.5	1041.1	C-H bend
	1303	-	1182.4	840.5	C-H bend
	648	615	592.6	573.1	ring def.
B_{1u}	-	-	3056.1	2276.2	
	-	-	3051.3	2265.5	
	-	-	1398.7	1259.9	
	-	-	1029.0	963.6	
	-	-	1014.6	799.1	
B_{2u}	-	-	3054.1	2275.4	
	-	-	1479.5	1387.8	
	-	-	1240.5	1147.9	
	-	-	1151.6	836.1	
	-	-	1033.8	809.0	

[a]Taken from reference 17
[b]Potential energy distribution shows these two assignments reversing
for C_6D_6

TABLE XI

CALCULATED PLANAR FREQUENCIES OF BENZENE
RADICAL ANION: STRUCTURE II

Symmetry	Obs. Freq. (cm^{-1})[a]		Calc. Freq. (cm^{-1})		Assig.
	$C_6H_6^-$	$C_6D_6^-$	$C_6H_6^-$	$C_6D_6^-$	
A_g	-	-	3055.8	2277.5	
	-	-	3052.9	2269.4	
	1475	1428	1523.1	1490.4	ring str.
	1152	-	1184.6	927.6	C-H bend [b]
	957	822	974.5	840.7	ring str.[b]
	616	587	596.6	576.6	ring def.
B_{3g}	-	-	3054.4	2279.3	
	1586	1563	1624.0	1590.0	ring str.
	1358	1190	1338.5	1041.1	C-H bend
	1303	-	1186.4	841.8	C-H bend
	648	615	605.2	584.2	ring def.
B_{1u}	-	-	3056.1	2276.2	
	-	-	3054.3	2275.9	
	-	-	1463.2	1352.4	
	-	-	1083.6	963.7	
	-	-	1014.6	817.2	
B_{2u}	-	-	3052.4	2269.2	
	-	-	1437.9	1345.9	
	-	-	1272.2	1197.9	
	-	-	1161.7	836.6	
	-	-	1030.6	802.6	

[a]Taken from reference 17
[b]Potential energy distribution shows these two assignments reversing
for C_6D_6

were not the same as Scherer's D_{6h} calculated frequencies but as mentioned before still within the same error as Sherer's. These minor differences can be traced to the different U matrices used by the Fortran program WMAT to introduce symmetry into the normal coordinate calculation and will be more fully discussed in Chapter 4. The good fit of Scherer's force field under a D_{2h} symmetry and resulting U matrix helps justify the use of this field for the benzene radical anion calculation.

Tables X and XI show that the structure I calculation matches the observed frequencies better, however structure II cannot be ruled out. This is especially true in light of the small number of observed frequencies available. Since the benzene A_g and B_{3g} Raman active modes usually involve considerable carbon ring distortion an examination of the deuteration shifts of these modes may show a preference for either of the two structures. Both structures give comparable deuteration shifts. Structure I gives 35, 108, and 21 cm^{-1} for the three A_g ring vibrations and 32 and 20 cm^{-1} for the two B_{3g} ring vibrations. Likewise structure II gives 33, 134, and 20 cm^{-1} for the A_g modes and 34 and 21 cm^{-1} for the B_{3g} modes. From the observed frequencies the shifts are 23, 135, and 29 cm^{-1} for the A_g modes and 47 and 33 cm^{-1} for the B_{3g} modes. So even though structure I gives a better overall fit structure II gives a slightly better deuteration shift prediction. The useful aspect of the calculation is that force constants from two different molecules can be combined without refinement to predict the ring and C-C-H bending modes of a third highly perturbed molecule with a reasonable amount of accuracy. This provides additional evidence that the benzene radical anion resembles benzene with a TCNQ-like ring distortion imposed upon it.

CHAPTER IV

NORMAL MODE ANALYSIS OF THIN LAYER TCNQ

Introduction

Conjugated ring systems have aroused much interest for many years.
In particular 7,7,8,8 tetracyanoquinodimethane (TCNQ) is known for its
role as a strong electron acceptor in charge-transfer complexes.

Takenaka (42) first interpreted the infrared, and laser Rama spec-
tra of neutral crystalline TCNQ and TCNQ-d_4. After making the vibra-
tional assignments he attempted a normal mode analysis utilizing a basic
Urey-Bradley force field, but found that it had to be modified by select
cross terms before a good fit of calculated and observed frequencies
could be obtained.

Girlando and Pecile (19) also interpreted the TCNQ spectra but uti-
lized polarized infrared and Rama data with particular attention to
Raman scattering geometries. Their interpretation postulated some
significant changes in the symmetry of several modes. This prompted
another normal mode analysis utilizing a modified valence force field.
From the neutral TCNQ analysis they extended their study to include a
spectra and normal mode analysis of the TCNQ radical anion (43).

Khatkale (18) used a standard vapor codeposition method to prepare
alkali metal salts of TCNQ. With this technique he formed the thin
layer mono, di, and trianion salts. A planar normal mode analysis was
made for neutral TCNQ, using a modified valence force field. The

resultant force field was then transferred to each anion and a new field calculated allowing only the stretching force constants to vary. Accordingly a comparison was made between the stretching force constants of each anion specie to determine the bonding changes occurring with each addition of an electron to neutral TCNQ.

Khatkale (18) was unable to reproduce the Girlando and Pecile (19) neutral TCNQ calculated frequencies using their modified valence force field and force constants. Thus he recalculated the neutral TCNQ valence force field using the same field definitions and diagonal stretching force constants as Girlando and Pecile, but resolved the differences by allowing select bending and interaction force constants to vary. Since publication of these two works it was found that Khatkale neglected an interaction term used by Girlando and Pecile. Therefore the MSK and GP neutral TCNQ force fields cannot be safely compared. Girlando and Pecile have also acknowledged that a minor mistake was made in transcribing for the computer the transformation matrix U between internal and symmetry coordinates (43,44). In addition, the value of an interaction force constant was misprinted in reference 19.

In view of these difficulties in arriving at a common set of neutral TCNQ force constants for a common modified valence force field, a new normal mode analysis was attempted using the modified valence force field definitions and observed frequencies of Girlando and Pecile (19).

Normal Mode Analysis

TCNQ belongs to the D_{2h} point group and all references cited used this symmetry. The first approach of the analysis was to reproduce the published values of Khatkale (18), change the Khatkale force field to

agree with the published force field of Girlando and Pecile (19), and then compare the calculated frequencies. Thus it was convenient to use the same internal coordinate system and G matrix parameters as used by Khatkale. Figure 4 and Table XII show the coordinates and parameters respectively. The coordinates and parameters used were checked against those used by Girlando and Pecile to the extent possible from the liter-ature and found to be consistent. The symmetry coordinates used were taken from the Khatkale calculations and are identical to those used by Takenaka (42). These coordinates are reproduced in Table XIII. The symmetry coordinates have the feature that all but three of the eleven planar mode redundancies have been eliminated by the proper linear com-bination of symmetry coordinates. The three remaining are left for the program WMAT to eliminate. To check Khatkale's symmetry (MSK U matrix) coordinates a new U matrix was constructed which contained eleven planar redundancies. This matrix, hereafter called the WBC U matrix was used to calculate a new symmetrized G matrix and used in subsequent select calculations. The symmetry coordinates used in this U matrix are shown in Table IV. The idea of repeating calculations with different U matrices that should give similar symmetrized G matrices and identical frequency predictions has also been advanced by Bertie, Andersen, and Wright (45). The modified valence force field used in this calculation and published by Girlando and Pecile (19) is shown in Table XV. The starred force constant definitions were those that Khatkale (18) omitted in his calculations.

The next step in the normal mode calculation was to take the Table XV force field (with starred definitions) and use the force constants of Girlando and Pecile (19) along with the W matrix formed from the MSK U
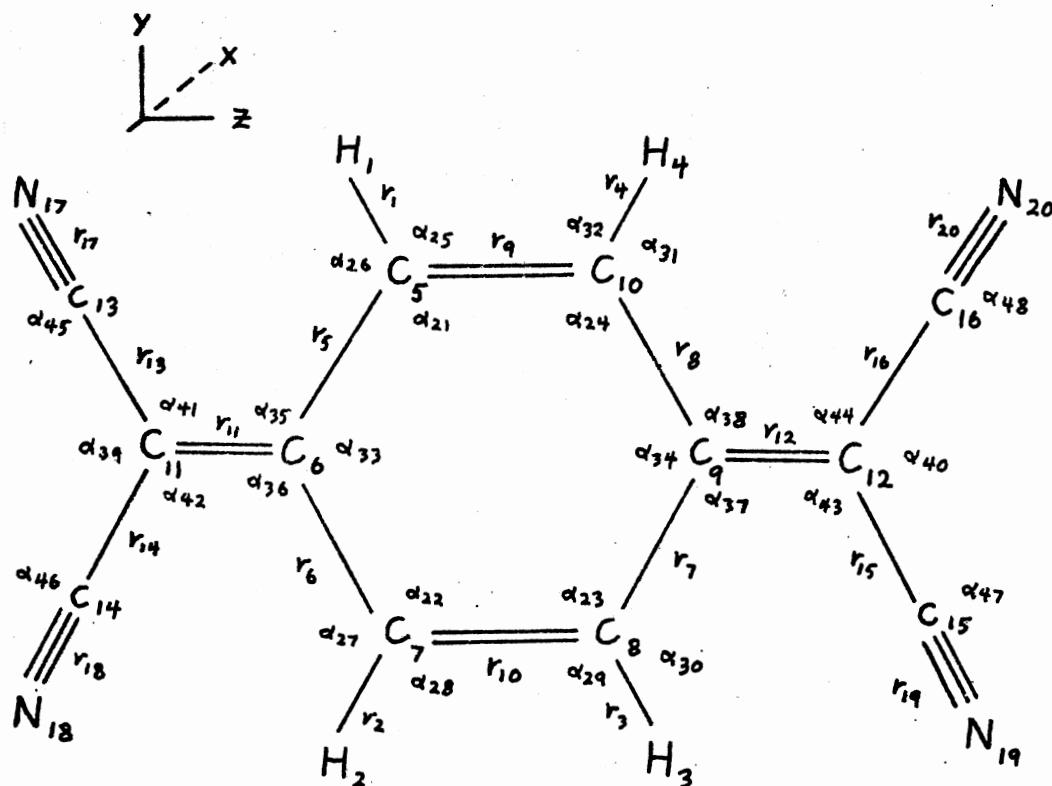
Figure 4. Internal Coordinates of D_{2h} TCNQ

TABLE XII

PARAMETERS USED FOR CREATING TCNQ
G MATRIX

Definition	Value[a]
C-C ring bond (r_5)	1.448 Å
C-C wing bond (r_{13})	1.441 Å
C=C ring bond (r_9)	1.346 Å
C=C wing bond (r_{11})	1.374 Å
C-N bond (r_{17})	1.140 Å
C-H bond (r_1)	1.08 Å
C=C-C angle ($\alpha_{21}, \alpha_{35}, \alpha_{41}$)	120°
C-C-C angle (α_{33}, α_{39})	120°
C-C-H, C=C-H angle (α_{25}, α_{26})	120°
C-C-N angle	180°
C atomic mass	12.011
H atomic mass	1.008
N atomic mass	14.007

[a]Reference 18

TABLE XIII

SYMMETRY COORDINATES USED BY KHATKALE[a]
(MSK) FOR D_{2h} TCNQ

Symmetry	Symmetry Coordinate
A_g	$S_1 = (1/\sqrt{4})\,(\Delta r_1 + \Delta r_2 + \Delta r_3 + \Delta r_4)$ $S_2 = (1/\sqrt{4})\,(\Delta r_{17} + \Delta r_{18} + \Delta r_{19} + \Delta r_{20})$ $S_3 = (1/\sqrt{2})\,(\Delta r_9 + \Delta r_{10})$ $S_4 = (1/\sqrt{2})\,(\Delta r_{11} + \Delta r_{12})$ $S_5 = (1/\sqrt{4})\,(\Delta r_5 + \Delta r_6 + \Delta r_7 + \Delta r_8)$ $S_6 = (1/\sqrt{4})\,(\Delta r_{13} + \Delta r_{14} + \Delta r_{15} + \Delta r_{16})$ $S_7 = (1/\sqrt{3})\,(\Delta\alpha_{39} + \Delta\alpha_{40}) + (1/\sqrt{12})$ $\quad (-\Delta\alpha_{41} - \Delta\alpha_{42} - \Delta\alpha_{43} - \Delta\alpha_{44})$ $S_8 = (1/\sqrt{3})\,(\Delta\alpha_{33} + \Delta\alpha_{34}) + (1/\sqrt{12})$ $\quad (-\Delta\alpha_{35} - \Delta\alpha_{36} - \Delta\alpha_{37} - \Delta\alpha_{38})$ $S_9 = (1/\sqrt{8})\,(\Delta\alpha_{25} - \Delta\alpha_{26} - \Delta\alpha_{27} + \Delta\alpha_{28}$ $\quad + \Delta\alpha_{29} - \Delta\alpha_{30} - \Delta\alpha_{31} - \Delta\alpha_{32})$ $S_{10} = (1/\sqrt{4})\,(\Delta\alpha_{45} + \Delta\alpha_{46} + \Delta\alpha_{47} + \Delta\alpha_{48})$ $S_{11} = (1/\sqrt{6})\,(\Delta\alpha_{21} + \Delta\alpha_{22} + \Delta\alpha_{23} + \Delta\alpha_{24})$ $\quad + (1/\sqrt{24})\,(-\Delta\alpha_{25} - \Delta\alpha_{26} - \Delta\alpha_{27} - \Delta\alpha_{28}$ $\quad - \Delta\alpha_{29} - \Delta\alpha_{30} + \Delta\alpha_{31} - \Delta\alpha_{32})$
B_{3g}	$S_{12} = (1/\sqrt{4})\,(\Delta r_1 - \Delta r_2 + \Delta r_3 - \Delta r_4)$ $S_{13} = (1/\sqrt{4})\,(\Delta r_{17} - \Delta r_{18} + \Delta r_{19} - \Delta r_{20})$ $S_{14} = (1/\sqrt{4})\,(\Delta r_5 - \Delta r_6 + \Delta r_7 - \Delta r_8)$ $S_{15} = (1/\sqrt{4})\,(\Delta r_{13} - \Delta r_{14} + \Delta r_{15} - \Delta r_{16})$ $S_{16} = (1/\sqrt{4})\,(\Delta\alpha_{41} - \Delta\alpha_{42} + \Delta\alpha_{43} - \Delta\alpha_{44}$ $S_{17} = (1/\sqrt{4})\,(\Delta\alpha_{35} - \Delta\alpha_{36} + \Delta\alpha_{37} - \Delta\alpha_{38})$ $S_{18} = (1/\sqrt{6})\,(\Delta\alpha_{21} - \Delta\alpha_{22} + \Delta\alpha_{23} - \Delta\alpha_{24})$ $\quad + (1/\sqrt{24})\,(-\Delta\alpha_{25} - \Delta\alpha_{26} + \Delta\alpha_{27} + \Delta\alpha_{28}$ $\quad - \Delta\alpha_{29} - \Delta\alpha_{30} + \Delta\alpha_{31} + \Delta\alpha_{32})$ $S_{19} = (1/\sqrt{8})\,(\Delta\alpha_{25} - \Delta\alpha_{26} + \Delta\alpha_{27} - \Delta\alpha_{28}$ $\quad + \Delta\alpha_{29} - \Delta\alpha_{30} + \Delta\alpha_{31} - \Delta\alpha_{32})$ $S_{20} = (1/\sqrt{4})\,(\Delta\alpha_{45} - \Delta\alpha_{46} + \Delta\alpha_{47} - \Delta\alpha_{48})$
B_{1u}	$S_{21} = (1/\sqrt{4})\,(\Delta r_1 + \Delta r_2 - \Delta r_3 - \Delta r_4)$ $S_{22} = (1/\sqrt{4})\,(\Delta r_{17} + \Delta r_{18} - \Delta r_{19} - \Delta r_{20})$ $S_{23} = (1/\sqrt{2})\,(\Delta r_{11} - \Delta r_{12})$ $S_{24} = (1/\sqrt{4})\,(\Delta r_5 + \Delta r_6 - \Delta r_7 - \Delta r_8)$ $S_{25} = (1/\sqrt{4})\,(\Delta r_{13} + \Delta r_{14} - \Delta r_{15} - \Delta r_{16})$ $S_{26} = (1/\sqrt{3})\,(\Delta\alpha_{39} - \Delta\alpha_{40})\,(1/\sqrt{12})$ $\quad (-\Delta\alpha_{41} - \Delta\alpha_{42} + \Delta\alpha_{43} + \Delta\alpha_{44})$ $S_{27} = (1/\sqrt{3})\,(\Delta\alpha_{33} - \Delta\alpha_{34})\,(1/\sqrt{12})$ $\quad (-\Delta\alpha_{35} - \Delta\alpha_{36} + \Delta\alpha_{37} + \Delta\alpha_{38})$ $S_{28} = (1/\sqrt{6})\,(\Delta\alpha_{21} + \Delta\alpha_{22} - \Delta\alpha_{23} - \Delta\alpha_{24})$ $\quad + (1/\sqrt{24})\,(-\Delta\alpha_{25} - \Delta\alpha_{26} - \Delta\alpha_{27} - \Delta\alpha_{28}$ $\quad + \Delta\alpha_{29} + \Delta\alpha_{30} + \Delta\alpha_{31} + \Delta\alpha_{32})$

TABLE XIII (Continued)

Symmetry	Symmetry Coordinate
	$S_{29} = (1/\sqrt{8}) \; (\Delta\alpha_{25} - \Delta\alpha_{26} - \Delta\alpha_{27} + \Delta\alpha_{28} - \Delta\alpha_{29} + \Delta\alpha_{30} + \Delta\alpha_{31} - \Delta\alpha_{32})$
	$S_{30} = (1/\sqrt{4}) \; (\Delta\alpha_{45} + \Delta\alpha_{46} - \Delta\alpha_{47} - \Delta\alpha_{48})$
B_{2u}	$S_{31} = (1/\sqrt{4}) \; (\Delta r_1 - \Delta r_2 - \Delta r_3 + \Delta r_4)$
	$S_{32} = (1/\sqrt{4}) \; (\Delta r_{17} - \Delta r_{18} - \Delta r_{19} + \Delta r_{20})$
	$S_{33} = (1/\sqrt{2}) \; (\Delta r_9 - \Delta r_{10})$
	$S_{34} = (1/\sqrt{4}) \; (\Delta r_5 - \Delta r_6 - \Delta r_7 + \Delta r_8)$
	$S_{35} = (1/\sqrt{4}) \; (\Delta r_{13} - \Delta r_{14} - \Delta r_{15} + \Delta r_{16})$
	$S_{36} = (1/\sqrt{4}) \; (\Delta\alpha_{41} - \Delta\alpha_{42} - \Delta\alpha_{43} + \Delta\alpha_{44})$
	$S_{37} = (1/\sqrt{4}) \; (- \Delta\alpha_{35} - \Delta\alpha_{36} - \Delta\alpha_{37} + \Delta\alpha_{38})$
	$S_{38} = (1/\sqrt{6}) \; (\Delta\alpha_{21} - \Delta\alpha_{22} - \Delta\alpha_{23} + \Delta\alpha_{24})$ $+ (1/\sqrt{24}) \; (- \Delta\alpha_{25} - \Delta\alpha_{26} + \Delta\alpha_{27} + \Delta\alpha_{28} + \Delta\alpha_{29} + \Delta\alpha_{30} - \Delta\alpha_{31} - \Delta\alpha_{32})$
	$S_{39} = (1/\sqrt{8}) \; (\Delta\alpha_{25} - \Delta\alpha_{26} + \Delta\alpha_{27} - \Delta\alpha_{28} - \Delta\alpha_{29} + \Delta\alpha_{30} - \Delta\alpha_{31} + \Delta\alpha_{32})$
	$S_{40} = (1/\sqrt{4}) \; (\Delta\alpha_{45} - \Delta\alpha_{46} - \Delta\alpha_{47} + \Delta\alpha_{48})$

Redundancies: 1 A_g, 1 B_{1u}, 2 B_{2u}

[a]Reference 18

TABLE XIV

WBC SYMMETRY COORDINATES USED FOR
D_{2h} TCNQ

Symmetry	Symmetry Coordinate
A_g	$S_1 = (1/\sqrt{4})\ (\Delta r_1 + \Delta r_2 + \Delta r_3 + \Delta r_4)$
	$S_2 = (1/\sqrt{4})\ (\Delta r_5 + \Delta r_6 + \Delta r_7 + \Delta r_8)$
	$S_3 = (1/\sqrt{2})\ (\Delta r_9 + \Delta r_{10})$
	$S_4 = (1/\sqrt{2})\ (\Delta r_{11} + \Delta r_{12})$
	$S_5 = (1/\sqrt{4})\ (\Delta r_{13} + \Delta r_{14} + \Delta r_{15} + \Delta r_{16})$
	$S_6 = (1/\sqrt{4})\ (\Delta r_{17} + \Delta r_{18} + \Delta r_{19} + \Delta r_{20})$
	$S_7 = (1/\sqrt{4})\ (\Delta \alpha_{21} + \Delta \alpha_{22} + \Delta \alpha_{23} + \Delta \alpha_{24})$
	$S_8 = (1/\sqrt{4})\ (\Delta \alpha_{25} + \Delta \alpha_{28} + \Delta \alpha_{29} + \Delta \alpha_{32})$
	$S_9 = (1/\sqrt{4})\ (\Delta \alpha_{26} + \Delta \alpha_{27} + \Delta \alpha_{30} + \Delta \alpha_{31})$
	$S_{10} = (1/\sqrt{2})\ (\Delta \alpha_{33} + \Delta \alpha_{34})$
	$S_{11} = (1/\sqrt{4})\ (\Delta \alpha_{35} + \Delta \alpha_{36} + \Delta \alpha_{37} + \Delta \alpha_{38})$
	$S_{12} = (1/\sqrt{2})\ (\Delta \alpha_{39} + \Delta \alpha_{40})$
	$S_{13} = (1/\sqrt{4})\ (\Delta \alpha_{41} + \Delta \alpha_{42} + \Delta \alpha_{43} + \Delta \alpha_{44})$
	$S_{14} = (1/\sqrt{4})\ (\Delta \alpha_{45} + \Delta \alpha_{46} + \Delta \alpha_{47} + \Delta \alpha_{48})$
B_{3g}	$S_{15} = (1/\sqrt{4})\ (\Delta r_1 - \Delta r_2 + \Delta r_3 - \Delta r_4)$
	$S_{16} = (1/\sqrt{4})\ (\Delta r_5 - \Delta r_6 + \Delta r_7 - \Delta r_8)$
	$S_{17} = (1/\sqrt{4})\ (\Delta r_{13} - \Delta r_{14} + \Delta r_{15} - \Delta r_{16})$
	$S_{18} = (1/\sqrt{4})\ (\Delta r_{17} - \Delta r_{18} + \Delta r_{19} - \Delta r_{20})$
	$S_{19} = (1/\sqrt{4})\ (\Delta \alpha_{21} - \Delta \alpha_{22} + \Delta \alpha_{23} - \Delta \alpha_{24})$
	$S_{20} = (1/\sqrt{4})\ (\Delta \alpha_{25} - \Delta \alpha_{28} + \Delta \alpha_{29} - \Delta \alpha_{32})$
	$S_{21} = (1/\sqrt{4})\ (\Delta \alpha_{26} - \Delta \alpha_{27} + \Delta \alpha_{30} - \Delta \alpha_{31})$
	$S_{22} = (1/\sqrt{4})\ (\Delta \alpha_{35} - \Delta \alpha_{36} + \Delta \alpha_{37} - \Delta \alpha_{38})$
	$S_{23} = (1/\sqrt{4})\ (\Delta \alpha_{41} - \Delta \alpha_{42} + \Delta \alpha_{43} - \Delta \alpha_{44})$
	$S_{24} = (1/\sqrt{4})\ (\Delta \alpha_{45} - \Delta \alpha_{46} + \Delta \alpha_{47} - \Delta \alpha_{48})$
B_{1u}	$S_{25} = (1/\sqrt{4})\ (\Delta r_1 + \Delta r_2 - \Delta r_3 - \Delta r_4)$
	$S_{26} = (1/\sqrt{4})\ (\Delta r_5 + \Delta r_6 - \Delta r_7 - \Delta r_8)$
	$S_{27} = (1/\sqrt{2})\ (\Delta \alpha r_{11} - \Delta \alpha r_{12})$
	$S_{28} = (1/\sqrt{4})\ (\Delta r_{13} + \Delta r_{14} - \Delta r_{15} - \Delta r_{16})$
	$S_{29} = (1/\sqrt{4})\ (\Delta r_{17} + \Delta r_{18} - \Delta r_{19} - \Delta r_{20})$
	$S_{30} = (1/\sqrt{4})\ (\Delta \alpha_{21} + \Delta \alpha_{22} - \Delta \alpha_{23} - \Delta \alpha_{24})$
	$S_{31} = (1/\sqrt{4})\ (\Delta \alpha_{25} + \Delta \alpha_{28} - \Delta \alpha_{29} - \Delta \alpha_{32})$
	$S_{32} = (1/\sqrt{4})\ (\Delta \alpha_{26} + \Delta \alpha_{27} - \Delta \alpha_{30} - \Delta \alpha_{31})$
	$S_{33} = (1/\sqrt{2})\ (\Delta \alpha_{33} - \Delta \alpha_{34})$
	$S_{34} = (1/\sqrt{4})\ (\Delta \alpha_{35} + \Delta \alpha_{36} - \Delta \alpha_{37} - \Delta \alpha_{38})$
	$S_{35} = (1/\sqrt{2})\ (\Delta \alpha_{39} - \Delta \alpha_{40})$
	$S_{36} = (1/\sqrt{4})\ (\Delta \alpha_{41} + \Delta \alpha_{42} - \Delta \alpha_{43} - \Delta \alpha_{44})$
	$S_{37} = (1/\sqrt{4})\ (\Delta \alpha_{45} + \Delta \alpha_{46} - \Delta \alpha_{47} - \Delta \alpha_{48})$

TABLE XIV (Continued)

Symmetry	Symmetry Coordinate
B_{2u}	$S_{38} = (1/\sqrt{4})\ (\Delta r_1 - \Delta r_2 - \Delta r_3 + \Delta r_4)$
	$S_{39} = (1/\sqrt{4})\ (\Delta r_5 - \Delta r_6 - \Delta r_7 + \Delta r_8)$
	$S_{40} = (1/\sqrt{2})\ (\Delta r_9 - \Delta r_{10})$
	$S_{41} = (1/\sqrt{4})\ (\Delta r_{13} - \Delta r_{14} - \Delta r_{15} + \Delta r_{16})$
	$S_{42} = (1/\sqrt{4})\ (\Delta r_{17} - \Delta r_{18} - \Delta r_{19} + \Delta r_{20})$
	$S_{43} = (1/\sqrt{4})\ (\Delta \alpha_{21} - \Delta \alpha_{22} - \Delta \alpha_{23} + \Delta \alpha_{24})$
	$S_{44} = (1/\sqrt{4})\ (\Delta \alpha_{25} - \Delta \alpha_{28} - \Delta \alpha_{29} + \Delta \alpha_{32})$
	$S_{45} = (1/\sqrt{4})\ (\Delta \alpha_{26} - \Delta \alpha_{27} - \Delta \alpha_{30} + \Delta \alpha_{31})$
	$S_{46} = (1/\sqrt{4})\ (\Delta \alpha_{35} - \Delta \alpha_{36} - \Delta \alpha_{37} + \Delta \alpha_{38})$
	$S_{47} = (1/\sqrt{4})\ (\Delta \alpha_{41} - \Delta \alpha_{42} - \Delta \alpha_{43} + \Delta \alpha_{44})$
	$S_{48} = (1/\sqrt{4})\ (\Delta \alpha_{45} - \Delta \alpha_{46} - \Delta \alpha_{47} + \Delta \alpha_{48})$

Redundancies: 4 A_g, 1 B_{3g}, 4 B_{1u}, 2 B_{2u}

TABLE XV

MODIFIED VALENCE FORCE FIELD AND
CONSTANTS FOR D_{2h} TCNQ

Symbol[a]	Coordinate Type	Bond	GP Value[b]	MSK Value[c]
K_1	$r_1\ r_1$	C-H	5.05	5.05
K_2	$r_5\ r_5$	C-C^R	5.46	5.46
K_3	$r_9\ r_9$	C=C^R	7.50	7.50
K_4	$r_{11}\ r_{11}$	C=C^W	6.90	6.90
K_5	$r_{13}\ r_{13}$	C-C^W	5.35	5.35
K_6	$r_{17}\ r_{17}$	C≡N	16.90	16.90
H_7	$\alpha_{21}\ \alpha_{21}$	C-C=C^R	.888	.966
H_8	$\alpha_{25}\alpha_{25} = \alpha_{26}\alpha_{26}$	(C-C-H)=(C=C-H)	.524	.335
H_9	$\alpha_{33}\ \alpha_{33}$	C-C-C^R	.913	1.034
H_{10}	$\alpha_{35}\ \alpha_{35}$	C-C=C^{R,W}	1.034	.564
H_{11}	$\alpha_{39}\ \alpha_{39}$	C-C-C^W	.728	.866
H_{12}	$\alpha_{41}\ \alpha_{41}$	C-C=C^W	.337	.924
H_{13}	$\alpha_{45}\ \alpha_{45}$	C-C≡N	.523	.758
F_{14}	$r_5\ r_6$	C-C^R,C-C^R	.157	.157
F_{15}	$r_5\ r_9$	C-C^R,C=C^R	.473	.608
F_{16}	$r_5\ r_{11}$	C-C^R,C=C^W	.646	1.29
F_{17}	$r_5\alpha_{21} = r_5\alpha_{33}$	(C-C^R,C-C=C^R)=(C-C^R,C-C-C^R)	.098	.098
F_{18}	$r_5\ \alpha_{35}$	C-C^R,C-C=C^{R,W}	.278	.647
F_{18}*	$r_5\ \alpha_{36}$	C-C^R,C-C=C^{R,W}	-.278	-
F_{19}	$r_5\ \alpha_{26}$	C-C^R,C-C-H	.108	.126
F_{19}*	$r_5\ \alpha_{25}$	C-C^R,C=C-H	-.108	-
F_{20}	$r_9\ \alpha_{21}$	C=C^R,C-C=C^R	.090	.090
F_{21}	$r_9\ \alpha_{25}$	C=C^R,C-C-H^R	.145^d	.317
F_{21}*	$r_9\ \alpha_{26}$	C=C^R,C-C-H^R	-.145^d	-
F_{22}	$r_{11}\ r_{13}$	C=C^W,C-C^W	.161	.161
F_{23}	$r_{11}\alpha_{35} = r_{11}\alpha_{41}$	(C=C^W,C-C=C^{R,W})=(C=C^W,C-C=C^W)	.242	.242
F_{24}	$r_{13}\ r_{14}$	C-C^W,C-C^W	.517	.517
F_{25}	$r_{13}\ \alpha_{41}$	C-C^W,C-C=C^W	.197	.197
F_{26}	$\alpha_{41}\alpha_{42} = \alpha_{39}\alpha_{41}$	(C-C=C^R,C-C=C^R)=(C-C-C^R,C-C=C^R)	-.045	-.045

a: units: K in mydne/Å, H in mdyne-Å/(radian)^2
       F in mdyne/radian for stretch-bending
b: : Reference 18
c: : Refernce 19
d: : Misprinted in ref. 19, correct value shown
*: : Force constant definition omitted by Khatkale reference 18
R: : ring
W: : wing

matrix symmetrized G matrix and attempt to reproduce Girlando and

Pecile's results. This was again repeated with the W matrix formed from

the WBC U matrix symmetrized G matrix. Using the W matrix formed from

the MSK symmetrized G matrix and the corrected force field of Table XV

with Girlando and Pecile's force constants large discrepancies were

still found in the calculated frequencies and published values of

Girlando and Pecile. Therefore it is suggested that there is still some

error larger than their U matrix error, or that some facet of their

force field is neglected in their published values (19).

When the calculation was repeated using the W matrix formed from

the WBC symmetrized G matrix the results were again quite different from

the Girlando and Pecile calculations. However while quite close to the

MSK symmetrized W matrix calculations there were still some significant

deviations between the MSK symmetrized and WBC symmetrized calculations.

Because of the WBC and MSK calculation discrepancy a series of test

calculations was performed using the program WMAT since the source of

the discrepancy should be found in the calculation of W from the sym-

metrized G matrix (see equations 1-14 through 1-18). The first test

calculation involved the computational precision. The IBM 370-168 com-

puter used has two Fortran compilers available. The G1, or "FORTGCG",

compiler will allow the program to be run in double precision only if

the program was originally written so. The other compiler, the H opti-

mization, or "FORTHCLG", compiler will allow the Fortran program to be

run as the G1 compiler, or with the extended precision features of the

compiler, AUTODBL(DBLPAD4). This feature, hereafter called FORTHCLG-

(DBLPAD4), allows a single precision written program to be compiled

and run as a double precision program without modifying the Fortran

statements. For the IBM 370-168 computer system single precision calcu-
lates with binary word lengths such that each number can be represented
accurately to seven digits in scientific notation. Double precision is
likewise accurate to eighteen digits. Check calculations were run under
both compilers with and without the extended precision feature and no
significant deviations were observed.

The program WMAT finds the W matrix by calculating the G matrix,
symmetrizing the G matrix with the inputted normalized U matrix, diag-
onalizing G to find the eigenvalues of G, and from the eigenvalues find-
ing the eigenvectors of G. Finally the eigenvalues and eigenvectors are
used to create W (see equation 1-18). Since the diagonalizing routine
does not preserve the order of the eigenvalues along the diagonal they
are rank ordered down the diagonal eigenvalue matrix. This order is
then preserved throughout the rest of the calculational procedure and
used to match the observed with the calculated frequencies in a least
squares refinement of force constants. If the G matrix is block fac-
tored by symmetry then each symmetry block is likewise rank ordered
independently of the other symmetry blocks. While calculating the W
matrix with the WBC eleven redundancy symmetrized G matrix it was found
that the diagonalizing routine, a Jacobi method, interchanged the order
of eigenvalues and eigenvectors nine and ten of the A_g symmetry block.
A check calculation on the same symmetrized G matrix using a different
diagonalizing technique, the Householder tridiagonalization method (46),
yielded the same eigenvalues. It was concluded that the interchanging
was due to very small residual values left in the off-diagonal elements
that, though large enough to cause extra Jacobi rotations and row
element eliminations, were too small to affect the eigenvalues and

eigenvectors obtained. The fault was corrected by interchanging eigen-values and eigenvectors nine and ten back into their proper sequence and continuing with the calculation. The interchanging fault was not observed when the W matrix was calculated with the MSK three redundancy symmetrized G matrix.

Since both the WBC symmetrized and MSK symmetrized W matrices were formed from the same unsymmetrized G matrix it was suspected that the discrepancy between the two lay in how the program reacted to the different U matrices used to symmetrize G.

Accordingly a series of calculations were made using the MSK and WBC U matrices for symmetrizing under different precisions and com-pilers. Khatkale's (18) force constants and force field definitions were used for this series. Table XVI shows the results of these calcu-lations. Six W matrices were constructed; three with the MSK three redundancy U matrix and three with the WBC eleven redundancy U matrix. Of the three constructed with the MSK U matrix, one was computed with the G1 compiler in single precision (FORTGCG), another with the H opti-mization compiler in single precision (FORTHCG), and the last with the H compiler in double precision (FORTHCLG(DBLPAD4)). Likewise of the three constructed with the WBC U matrix, one was computed with the G1 compiler in single precision (FORTGCG), another with the H optimization compiler in double precision (FORTHCLG(DBLPAD4)), and the last with the H optimization compiler in double precision with symmetry coordinates S_1, S_9, S_{10}, S_{11}, of the A_g symmetry block of the WBC U matrix inter-changed with each other. For the latter case it should be noted that since the order of the frequencies calculated is determined from the order of the G matrix eigenvalues which are each related to a

TABLE XVI

CALCULATED PLANAR FREQUENCIES[b] OF D_{2h}
TCNQ WITH DIFFERENT COMPILERS
AND U MATRICES

	MSK U Matrix			WBC U Matrix	
FORTGCG	FORTHCG	FORTHCLG (DBLPAD4)	FORTGCG	FORTHCLG (DBLPAD4)	FORTHCLG[a] (DBLPAD4,S)
A_g					
3051.87	3051.87	3051.90	3051.78	3051.81	3051.81
2229.49	2229.49	2229.18	2229.47	2229.48	2229.50
1614.18	1614.18	1614.18	1627.18	1627.19	1628.57
1457.40	1457.40	1457.40	1456.29	1456.29	1455.70
1208.61	1208.61	1208.61	1190.40	1190.41	1187.92
944.38	944.38	944.38	947.06	947.07	948.37
703.26	703.26	703.26	703.32	703.32	703.22
598.77	598.77	598.78	598.94	598.95	599.43
322.07	322.07	322.07	321.92	321.92	322.16
144.63	144.63	144.64	144.64	144.64	144.69
B_{3g}					
3051.87	3051.86	3063.59	3071.94	3071.96	3071.96
2226.42	2226.42	2226.83	2226.40	2226.41	2226.41
1446.01	1446.01	1518.35	1466.78	1466.78	1466.78
1352.95	1352.95	1262.97	1298.16	1298.16	1298.16
1197.96	1197.96	1174.07	1182.32	1182.33	1182.33
615.50	615.50	615.97	614.96	614.96	614.96
490.71	490.71	492.43	490.56	490.56	490.56
353.99	353.99	356.55	353.78	353.78	353.78
125.72	125.72	125.79	125.69	125.70	125.70
B_{1u}					
3054.46	3054.46	3054.47	3072.47	3072.49	3072.49
2229.49	2229.49	2229.49	2229.58	2229.59	2229.59
1547.39	1547.39	1547.39	1511.33	1511.33	1511.33
1392.22	1392.22	1392.22	1404.25	1404.25	1404.25
1001.61	1001.61	1001.61	1008.01	1008.01	1008.01
949.28	949.28	949.28	924.73	924.73	924.73
599.67	599.67	599.67	598.78	598.78	598.78
529.90	529.90	529.90	529.98	529.98	529.98
173.35	173.35	173.35	173.28	173.28	173.28

TABLE XVI (Continued)

	MSK U Matrix			WBC U Matrix		
FORTGCG	FORTHCG	FORTHCLG (DBLPAD4)	FORTGCG	FORTHCLG (DBLPAD4)	FORTHCLG (DBLPAD4,S)

B_{2u}

3049.92	3049.92	3049.92	3049.93	3049.95	3049.95
2226.28	2226.28	2226.28	2226.61	2226.60	2226.60
1535.31	1535.31	1535.32	1538.12	1538.12	1538.12
1339.67	1339.67	1339.67	1337.73	1337.74	1337.74
1228.88	1228.88	1228.88	1226.57	1226.57	1226.57
1135.77	1135.77	1135.77	1136.24	1136.24	1136.24
489.28	489.28	489.28	489.11	489.11	489.11
296.14	296.14	296.14	296.08	296.08	296.08
62.99	62.99	62.99	63.04	63.04	63.04

[a]Symmetry coordinates S_1, S_9, S_{10}, and S_{11} interchanged

[b]Force field definitions and force constant values taken from reference 18. Therefore FORTGCG frequencies agreed exactly with reference 18.

corresponding symmetry coordinate; then changing symmetry coordinate order within a symmetry block should make no difference on the vibrational frequencies calculated. This is valid as long as the same symmetry coordinate order is preserved throughout the calculation. WMAT forces this continuity by the rank ordering or the symmetrized G eigenvalues and eigenvectors in creating the W matrix.

It has been suggested by Bertie, Andersen, and Wright (45) that unless the U matrix is orthogonal by the definition of $U^+ U = I$, where I is the identity matrix, that programs using the formalism of Schachtschneider (47) will yield incorrect results. Since Schachtschneider's programs, and WMAT and OVEREND both use the method of Miyazawa (14) it was though worthwhile to construct a Fortran program ORTHOG to check the orthogonality of U matrices inputted in the manner used by WMAT. The orthogonality was checked using the definitions given previously to compute I and then examining the resulting identity matrix I to see if it was identity to the precision of the inputted data. Both the WBC and MSK U matrices proved orthogonal. However it was noted that the MSK U matrix had significantly more off-diagonal precision induced terms in the identity matrix than the WBC U matrix. Precision induced is defined to be less than 10^{-6} for IBM single precision and 10^{-17} for IBM double precision.

From the results of Table XVI it was concluded that the WBC U matrix symmetrized FORTHCLG(DBLPAD4) W matrix yielded the most reliable and consistent results. Since a more consistent W matrix, and improved force field definition was available, a new linear least square refinement of the TCNQ force field was undertaken. The force field definitions of Girlando and Pecile (Table XV) and the WBC symmetrized

FORTHCLG(DBLPAD4) compiled with W matrix were utilized in this refinement. Several different strategies in refining the force constants were tried but the following gave the most tenable result. The initial set of force constants used were those found by Khatkale (18) listed in Table XV. All diagonal stretching and bending force constants were constrained to their initial values and all interaction force constants were allowed to vary. The observed frequencies of Khatkale (18) were used and since no thin layer deuterated TCNQ frequencies were available, the calculation was restricted to the h isotope. Table XVII and Table XVIII lists the final converged set of force constants from the refinement and the resulting calculated vibrational frequencies. For comparison purposes the frequencies calculated using the WBC U matrix symmetrized FORTHCLG(DBLPAD4) W matrix and the Girlando and Pecile (19) force constant set are also shown in Table XVIII.

Discussion

When the WMAT and OVEREND programs were originally written in-core memory space in computers was at a premium. Hence the logic and precision used reflect this limitation. Much effort was directed in writing the program toward using tapes as intermediate storage memories and otherwise reducing the size of matrices to be handled. With newer computers and virtual memory storage, matrix size ceased to be the liability that it once was. Therefore it is not unexpected that problems in the diagonalization routines used in WMAT and OVEREND that could show up with large matrices would not be prevalent until recent years. The swapping of eigenvalues and eigenvectors nine and ten in the WBC U matrix could be one such problem. TCNQ has 48 internal planar

TABLE XVII

FORCE CONSTANTS FROM WBC LEAST SQUARE
REFINEMENT OF D_{2h} TCNQ

Force Constant[b]	Value[a]	Force Constant	Value[c]	Dispersion
K_1	5.05	F_{14}	.313	.28
K_2	5.46	F_{15}	.290	.16
K_3	7.50	F_{16}	.920	.25
K_4	6.90	F_{17}	-.0465	.09
K_5	5.35	F_{18}	.289	.09
K_6	16.90	F_{19}	.0827	.027
H_7	.966	F_{20}	.148	.17
H_8	.335	F_{21}	.208	.041
H_9	1.034	F_{22}	.165	.58
H_{10}	.564	F_{23}	.247	.34
H_{11}	.866	F_{24}	.435	.19
H_{12}	.924	F_{25}	.160	.09
H_{13}	.758	F_{26}	-.0427	1.4

[a]Held invariant in refinement
[b]See Table XVI for force constant definitions and units
[c]Allowed to vary in linear square refinement

TABLE XVIII

CALCULATED PLANAR FREQUENCIES FROM LEAST
SQUARE REFINEMENT OF D_{2h} TCNQ

Symmetry	Obs. Freq. (cm^{-1})[a]	Calc. Freq. (cm^{-1}) GP	WBC	Dispersion[b]
A_g	3048.0	3052.0	3050.8	0.8
	2229.0	2229.2	2227.0	5.7
	1602.0	1676.1	1612.3	12.0
	1454.0	1450.0	1457.0	11.3
	1207.0	1294.1	1206.4	11.1
	948.0	922.5	940.3	9.6
	711.0	720.1	725.4	10.1
	602.0	531.0	594.1	8.3
	334.0	315.6	325.9	3.8
	144.0	121.3	144.8	1.3
B_{3g}	3060.0	3064.7	3072.3	0.5
	2223.0	2225.4	2229.1	6.2
	1451.0	1541.5	1462.3	12.4
	1323.0	1371.2	1309.0	9.0
	1187.0	1182.1	1190.9	11.4
	609.0	603.7	607.2	7.8
	519.0	448.0	489.3	2.9
	-	358.2	354.3	0.9
	-	101.6	126.2	2.1
B_{1u}	3065.0	3066.2	3073.4	0.6
	2228.0	2229.3	2228.0	5.7
	1545.0	1601.8	1533.4	12.6
	1405.0	1454.5	1390.2	11.2
	998.0	986.7	999.3	12.3
	962.0	959.3	959.3	11.0
	600.0	559.5	593.7	8.7
	549.0	475.3	523.1	5.8
	146.0	143.5	173.2	0.5

TABLE XVIII (Continued)

Symmetry	Obs. Freq. (cm^{-1})	Calc. Freq. (cm^{-1}) GP	WBC	Dispersion
B$_{2u}$	3053.0	3049.8	3048.5	0.8
	2228.0	2225.5	2229.3	6.3
	1540.0	1598.1	1525.8	11.5
	1354.0	1404.9	1352.2	11.9
	-	1246.7	1234.1	8.2
	1125.0	1131.4	1114.3	12.2
	498.0	386.1	489.1	1.4
	-	285.9	295.2	1.9
	-	58.6	63.6	0.9

Average Error = 4.70% GP and 1.43% WBC

[a]Reference 18
[b]Disperson applicable to WBC calc. only
The GP calc. freg. are the results of using the best WBC W matrix
using the WBC sym. coord. in a zero order (no refinement) calc. with
the force constants of reference 19 (latter corrections included).

coordinates which would yield a 48 by 48 G matrix with redundancies

included. Simply multiplying two such matrices together would provide

enough computer operations for two well known computational errors to

occur, truncation and catastrophic cancellation. The first type of

error results from the inability of a finite computer representation to

fully represent a long or irrational base two number. This type of

error can often be improved by increasing the computer word length, ie.

use of double precision. The second type of error occurs when the very

small difference between two numbers which correspondingly loses signi-

ficant digits in multiplied or scaled so that all of its digits whether

significant or not are forced to be meaningful. Increasing computer

precision does not necessarily improve this type of error. Changing

the algorithm is usually the best solution if the defective part of the

algorithm can be found or changed. The problem with this type of error

is that it can often be very dependent on the input data. One set of

data may yield excellent results and another terrible. Numerical anal-

ysis books are numerous with examples of these errors and how to spot

them (48).

By using the extended precision feature of the IBM Fortran H opti-

mization compiler it was found that the calculated frequencies of WMAT

and OVEREND can be trusted to at least four to five significant figures

in single precision. This does not preclude the possibility of anhar-

monic vibrations, mixing of symmetries, castrophic cancellation, or

other theoretical problems affecting the frequency predictions.

The Jacobi method of diagonalization seeks to search each row of

the matrix to be diagonalized for the maximum sized element, eliminate

it with a trigometric transformation and then eliminate the next largest

sized element and so on until all off-diagonal elements are zero and the eigenvalues lie on the diagonal. If during the trigometric transformation truncation errors are produced, these small valued elements could cause extra row element eliminations and a corresponding eigenvalue and eigenvector order scrambling. Thus it is not unlikely that with this sort of diagonalization routine the larger the matrix to be diagonalized, the greater the chance of this problem. This possibility was given further credence when attempts to find TCNQ W matrices with no symmetry (U = I identity matrix) yielded a horribly scrambled eigenvalue order even though their numerical value was correct. However if the order of the eigenvalues along the diagonal is restored, by using added Fortran code, the calculation may proceed as normal. This was done for the WBC U matrix symmetrized calculations.

Table XVI shows the results of the series of calculations designed to ascertain the discrepancy between the WBC and MSK U matrix symmetrized W matrices. The G and F matrices were kept constant throughout the calculation and were identical to those used by Khatkale (18) in his calculation. Hence the frequencies predicted under the MSK U matrix and FORTGCG compiler with single precision are identical with his.

If the MSK U matrix symmetrized W matrix calculated frequencies in Table XVI are examined it can be seen that the H and G IBM Fortran compilers give identical results. But if the calculation is done in double precision (FORTHCLG(DBLPAD4)) significant deviations occur in the B_{3g} symmetry block. However in the WBC U matrix symmetrized W matrix calculations no such significant deviations are seen between the FORTGCG single precision calculation and the FORTHCLG(DBLPAD4) double precision calculation. This suggested that possibly the MSK U matrix is sensitive,

or that the predicted frequencies of the W matrix so symmetrized may be highly correlated or sensitive to small errors encountered in the W matrix. This could be caused by catastrophic cancellation or some other unknown factor. However it should be noted that for the WBC U matrix symmetrized W matrix there is a small change in some frequencies in the A_g block when symmetry coordinate order is changed within a symmetry block. For example the FORTHCLG(DBLPAD4) A_g 1190.41 cm^{-1} frequency is changed to 1187.92 cm^{-1} with FORTHCLG(DBLPAD4,S) and symmetry coordinates S_1, S_9, S_{10}, and S_{11} interchanged. But this frequency showed the maximum amount of change (2.5 cm^{-1}). This is in stark contrast to 90, 72, and 23 cm^{-1} changes seen in the MSK symmetrized W matrix calculations when double precision FORTHCLG(DBLPAD4) is used instead of single precision FORTGCG. Interestingly in the B_{3g} symmetry the major U matrix induced differences between the FORTHCLG(DBLPAD4) MSK U matrix and FORTGCG WBC U matrix calculations also correspond with the precision induced differences in the MSK symmetrized calculations. On the basis of these observations it was decided that the MSK symmetrized calculations were definitely unreliable in the B_{3g} symmetry block and probably so everywhere they differ from the WBC symmetrized calculations as can be seen in Table XVI between the MSK FORTHCLG(DBLPAD4) frequencies and the WBC FORTGCG frequencies. Therefore the WBC symmetrized, FORTHCLG-(DBLPAD4) compiled W matrix was chosen as the most reliable, and used in the subsequent least square refinement of the Girlando and Pecile (19) force field definitions.

Fortran program ORTHOG was written to check the orthogonality of the MSK and WBC U matrices. It was hoped that such a check would reveal any sensitivity of the U matrices by examination of the identity matrix

produced. Both matrices proved orthogonal, but the MSK U matrix pro-
duced significantly more precision induced off-diagonal errors than the
WBC U matrix. Since the U matrix elements can be inputted up to six
significant figures in WMAT, the U matrix can at best be orthogonal to
six significant figures. Thus it is conceivable that several multipli-
cations of U could induce errors of more than 10^{-6}, if the slight non-
orthogonality errors overlapped. The MSK U matrix was more numerically
complex due to the linear combinations used to eliminate redundancies.
This may explain why the slightly larger WBC U matrix had fewer off-
diagonal errors when checked with ORTHOG.

As with all large linear least square refinements of force fields
the converged results may not represent the true solution since the
normal mode force constant problem can have multiple solutions (3). The
resulting force constants should have reasonable error limits or disper-
sions, be chemically reasonable, and correspond with other similar force
constant calculations. Since the stretching and bending force constants
are identical to Khatkale's (18), discussion on these is left to refer-
ence (18). Accordingly attention will be focused on the interaction
force constants F_{14}-F_{26} of Table XVII. F_{14} and F_{15} the C-C,C-C ring and
C-C,C=C ring interaction force constants have values of .313 and .290
respectively. Scherer (41), Zerbi and Sandroni (49), and Di Lauro,
Neto, and Califano (50) in their respective calculations on benzene,
biphenyl, and 1,3 cyclohexadiene obtained values ranging from .684 to
.7716 for aromatic ortho ring stretching interactions with ring C=C,C-C
ortho interactions. Girlando and Pecile's and Khatkale's values range
from .157 to .608. Since TCNQ is non-aromatic the highly coupled

nature of aromatic ring interactions can be expected to be higher than for TCNQ as the present calculations show.

Examining the ring stretch-bend interaction force constants F_{17} (-.0465) and F_{20} (.148) it can be seen that they lie in the same range for aromatic carbon bond stretch-bend interactions as do aromatic ring stretch-bends do. Scherer (41) gives .056 for benzene in his Table 4i. But interestingly if all the stretch-bend interactions around the benzene carbon atom are included using the method of Scherer (41) then the carbon stretch-bend interaction force constant becomes -.067 (see Scherer (41) Table 4ii). This is analogus to the Khatkale (19) calculations where when the $F_{18}*$ definition is omitted Khatkale finds .098 for the $(C-C^R, C=C-C^R) = (C-C^R, C-C-C^R)$ interaction. In the present calculations when the $F_{18}*$ definition is included the interaction becomes negative as did Scherer's. However it should be noted that for both F_{17} and F_{20} the dispersions are quite high. Zerbi and Sandroni (49) found .226 for the biphenyl ring stretch-bend interaction.

F_{19} and F_{21} show the interaction between the C-H in plane bend and the C-C and C=C bond stretch by which the C-C-H bend is defined. For F_{21} the carbon bond is a single bond or a low bond order in neutral TCNQ. For F_{19} the carbon bond is double. So it should not be unexpected that an aromatic C-H stretch-bend interaction should fall between the F_{19} and F_{21} interaction constants value. F_{19} is .0827 and F_{21} .208 for TCNQ from Table XVII. For the aromatic values Scherer (41) gives .173, Zerbi and Sandroni (49) .088, and Di Lauro, Neto, and Califano (50) found .0918 for 1.3 cyclohexadiene. All are within the F_{19} and F_{21} values. But in a later benzene calculation using a considerably more complex force field Painter and Koenig (51) found .0723 for the benzene

C-H stretch-bend interaction though the reported dispersion (.0615) was rather large.

F_{26} the ortho carbon ring bend-bend interaction constant has maintained a small negative value throughout the Girlando and Pecile, Khatkale, and present TCNQ calculations. A quick check of Scherer's (41), and Painter and Koenig's (51) benzene calcuations show -.022 (averaged valence force field from Urey-Bradley field, figure 2, reference 41) and -.1459 respectively. The negative value of F_{26} is also consistent in spite of its very large dispersion in the great TCNQ calculations.

In concluding it should be said that, the TCNQ valence force constants presented in Table XVII are, (1) consistent with some previous conjugated and aromatic ring system force field calculations, (2) do not have unreasonable dispersions throughout the force constants, and (3) result from a more reliable W matrix and consistent force field definition. Regardless, the calculation was not an overlay calculation using deuterated TCNQ frequencies, and still contains some large dispersions on some interaction constants. Also it is known that force constant values and, particularly, interaction force constants are often dependent upon the number and type of force field definitions used in constructing the F matrix. Because of the errors and W matrix problems present in the presently published neutral TCNQ force field refinements, Table XVII is presented as an improved, rather than definitive, force field refinement of the neutral TCNQ problem.

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APPENDIX A

INPUT INSTRUCTIONS FOR FORTRAN PROGRAM

WMAT

INPUT INSTRUCTIONS FOR FORTRAN PROGRAM

WMAT

1. Problem Control Cards

   Card A

   IND   = -09, indicating the start of a problem,
             in columns 1-3

   Card B   columns

   1) NOPROB = the problem number, not equal to 7777   1-6
   2) NISQ   = the number of isotopes   7-9
   3) NOAT   = the number of atoms in the molecule   10-12
   4) NSYM   = the number of symmetry blocks in the   13-15
               molecule
   5) NIC   = the number of internal coordinates   16-18
   6) NRC   = the number of symmetry coordinates   19-21
               including redundancies
   7) NRED   = the number of redundancies   22-24
               NSC=NRC-NRED
   8) NICV   = the number of internal coordinates   25-27
               vectors, NICV-NIC if no linear
               bending coordinates are included
               (add one internal coordinate vector
               for each linear bending coordinate
               if analysis is nonplanar, however
               for planar analysis NICV=NIC)
   9) IFW   = 1 if W matrix is required   29
            = 0 if not
   10) IFDU = 1 if the eigenvalues of G are   31
                  required in full
            = 0 if not
   11) IFB   = 1 if B is to be printed   33
            = 0 if not
   12) IFPB = 1 if B is to be punched on cards   35
            = 0 if not

2. Dimension of the symmetry blocks are given in pairs of integers, in the order of the block within the U matrix. Each pair specifies the number of symmetry coordinates and then (second integer in pair) the number of redundancies included in that block. This information is used in modifying the G matrix, so that each block should be separately defined even if it will contain no zero eigenvalue in the

diagonalized G matrix. If there is only one symmetry block skip this card. FORMAT (12(2I3))

3. Record card. May include name of molecule, date, etc. One card must be included. FORMAT (24A3)

4. The X matrix is punched in 18 column fields, 4 per card. First three columns give the row number identifying the cartesian axes, X=1, Y=2, Z=3. Columns 4-6 give the column number of the X matrix, the atom number (as defined in setting up coordinate system), and columns 7-18 give the X, Y, or Z elements with the decimal point between columns 12-13 or punched. The row number following the last element is set equal to -1. FORMAT (4(2I3,F12.6))

5. Vector of 8 numbers - NI, NCOD, N1, N2, N3, N4, N5, and N6 where NI gives the number assigned to the internal coordinate, NCOD, the code identifying the type of coord, and N1-N6 the numbers of the atoms (as defined in 4.) defining the coordinate.

Type	Code	N1	N2	N3	N4	N5	N6
Stretching	1	I	J				
Bending	2	I	J	K		IX	JX
Out of Plane Wag	3	I	J	K	L	IX	JX
Torsion	4	I	J	K	L	IX	JX
Linear Bend	5	NO2	I	J	K	IX	JX
In Plane Wag	6	I	K	K	L	IX	JX

IX and JX give the bond distance by which the coordinate is to be weighted. If IX=JX, not equal to zero, the weighting factor is set equal to 1.0. Note that for the linear bending type N1=NO2, the number of the bending coordinate perpendicular to N1. If doing a planar analysis set NO2 equal to a dummy (ie. if NIC=12 then NO2 > NIC would work) internal coordinate number without further defining it. I, J, K, L are defined as follows for the following internal coordinate vectors.

Stretching - I and J equal end atom numbers
Bending - I and K equal end atom numbers, and J equals middle
          atom number
Out of Plane Wag - I equals end atom number, J equals apex
                   atom number, and K and L equal anchor atom
                   numbers
Torsion - I and L equal end atom numbers where I is nearest
          the observer, and J and K equal the central atom
          numbers where J is nearest the observer
Linear Bend - N1=NO2 the number of the second coordinate,
              I and K equal the end atom numbers, and J
              the central atom number
In Plane Wag - I equals the end atom number, J the apex atom
               number, and K and L the anchor atom numbers

The internal coordinate vector is punched in 24 column fields 3 columns for each of the 8 elements in the order NI, NCOD, N1, N2, N3, N4, N5, N6. There are three vectors per card. FORMAT (3(8I3))

6. A, the cartesian coordinates of a point giving the orientation of the linear bending coordinate, one for each linear bending pairs. The three coordinates are punched in order (X,Y,Z). For planar analysis the points should lie in the molecular plane. Write elements of A in 12 column fields, one point per card. The format pertaining to this card is FORMAT (3F12.6).

7. The U matrix in 18 column fields, 4 per card, similar to the X matrix, the row number first, column number second, followed by the appropriate matrix element. The row number following the last element is set equal to -3. Zero elements need not be entered in X or U. FORMAT (4(2I3,F12.6))

8. The atomic masses are punched in 12 column fields, 6 per card, decimal between columns 6 and 7 or punched. The masses are punched in order 1 to NOAT. FORMAT (6F12.6)

Instruction 8. is repeated for each isotope of a molecule. Problems may be stacked but following the last problem insert two cards, the first with -09 in columns 1-3 and the second with 7777 in columns 3-6 (I6 field). These control cards will stop the entire program.

These data are transferred from card to tape 3 for input, or where card input is preferred, assign INPUT, 3, 03. (Note: Program is presently set up to use cards and uses standard unit numbers 5, 6, and 7 for reading, writing, and punching.)

Notes: During compilation of the G matrix, the elements which are outside of the factored blocks are tested against 0.00001 and are replaced by zero in the upper triangular section only, unless one element is found to equal or exceed the limit, where then the check is abandoned and the element and its position indices are written on the output, followed by the partly modified G matrix. The program then continues with the next isotope or molecule.

APPENDIX B

INPUT INSTRUCTIONS FOR FORTRAN PROGRAM

OVEREND

INPUT INSTRUCTIONS FOR FORTRAM PROGRAM

OVEREND

Overend Output Summary

Operation	Calling Parameters	Output Codes	Remarks
Calculation of Normal Coordinates	IFP=0 IFSEL=0	A	
Zero-order Calc.	IFP=1 IFSEL=0	A,B,C	
Refinement:	IFP=1 IFSEL=1		
a) Incomplete		G (each cycle) A, B, C, D, E (last cycle)	
b) Divergence		G (each cycle) A, B, C (last cycle)	On diverg. orig. F.C. recalled and zero-order calc. done
c) Convergence		G (each cycle) A, B, C, D, E, F (last cycle)	

Table of Output Codes

A - F matrix (each molecule): a calc. and L (each isotope)
B - Potential energy distribution (each isotope)
C - Intrisic force constants, their uncorrected and relative
    dispersions in internal force constant space and their
    transformation to Urey-Bradley force constant space
D - Final Urey-Bradley force constants and their dispersions
E - Urey-Bradley force constant co-error matrix
F - Frequency parameters co-error matrix (each isotope)
G - SUMMD, Urey-Bradley force constants and their corrections

In the OVEREND program used in the present thesis the WRITE state-
ments to D, E, G, and part of C have been eliminated to save needless
Urey-Bradley output since all calculations were done in internal coordi-
nate space with modified valence force fields.

Overend Input

1. Problem Control Card   Columns

    1) NOPROB = number of the problem set equal to 7777   1-6
    2) NM   = number of molecules (excluding isotopes)   7-9
    3) NC   = total number of force constants supplied   10-12
    4) NA   = number of force constants to be adjusted   13-15
    5) NL   = the total number observed frequencies   16-18
    6) NPMAX = the maximum number of perturbations to   19-21
                be executed. If IFP=0 set NPMAX=1
    7) IFDU   = 1 if intermediate results are to be   22-23
                   dumped in full
              = 0 if not
    8) IFP   = 1 if a perturbation is desired   24-25
              = 0 if not
    9) IFSEL = 1 if force constants are to be adjusted   26-27
              = 0 if not (when IFP=0 then IFSEL=0)
   10) FIW   = 1 if weighting elements are input   28-29
              = 0 if not (elements of the weight matrix
                   are then set equal to 1.0)
   11) IFCON = 1 if convergence constants are input   30-31
              = 0 if not
   12) CON   = convergence scaling factor   32-37
                (decimal between 35 and 36 or punched)
   13) OSC   = oscillation scaling factor   38-43
                (decimal in 41 and 42 or punched)
   14) IFCH   = 1 if the matrix FB is to be written on   44-45
                   tape (first perturbation)
              = 0 if not

Note: Leave 12) and 13) blank when IFCON=0, program then assigns 0.75
       to CON and 0.4 to OSC.

2. Record of molecules, isotopes, etc. to be punched on one card. FORMAT (24A3)

3. List of equivalent force constants. This lists the force constants in ascending order, each number referring to the force constant whose value is to replace the original value given in the following array. If any constant is made equivalent to another, only the constant named in the list may appear in NFSEL. Punched in integers in 3 column fields. FORMAT (24I3)

4. Initial force constants punched in order 1 to NC, 6 fields per card of 12 columns, the decimal between columns 6 and 7 or punched. FORMAT (6F12.6)

5. NFSEL. Integers in ascending order denoting the force constants to be adjusted, punched in 3 column fields. If no force constants are to be adjusted (IFSEL=0), no blank card should be included. FORMAT (24I3)

6. Parameters for the Molecule   Columns

    1) NISQ = the number of isotopes included   1-3
    2) NI   = the number of internal coordinates   4-6
    3) NS   = the number of symmetry coordinates   7-9
             without redundancies
    4) NF   = the number of force constants   10-12
    5) NSYM = the number of symmetry blocks   13-15
             If NSYM>1, a second parameter
             card follows, with the dimension
             of each symmetry block in order
             corresponding to U matrix and to
             frequencies, punched as integers
             in 3 column fields. FORMAT (24I3)

FORMAT (5I3)

7. NFMOL. Integer in ascending order 1 to NC denoting the force constants of the molecule, punched in 3 column fields. FORMAT (24I3)

8. Observed frequencies. Entered in decreasing order in each factored block, in order 1 to NS. If a frequency is unknown or uncertain, enter a zero. Punched in 6 fields per card of 12 columns each. The decimal is between column 6 and 7 or punched. For overlay calculations repeat 8 again with the new frequencies for the new isotope. FORMAT (6F12.6)

9. Weighting elements. Only needed for least square refinement when IFW=1. Entered in order 1 to NS corresponding to the observed frequencies. Use same format as observed frequencies. If IFW=0 program assigns 1.0 to each weight element, and no blank cards should be supplied. For overlay calculations with IFW=1 include weight elements after each set of corresponding isotope frequencies, ie. not stacked after the previous isotope weight element set but in this order:

frequencies isotope 1, weight elements isotope 1, frequencies isotope 2, weight elements isotope 2, etc. FORMAT (6F12.6)

10. Z matrix. Non-zero elements, are entered with three indices, NC1 given the F matrix row number, NC2 the F matrix column number, NFOR the number of the force constant. Only the upper right half of the symmetric matrix is entered so NC2 must always be greater than or equal to NC1. The Z elements are punched in 4 fields per card of 18 columns, NC1 in columns 1-3, NC2 in columns 4-6, and NFOR in columns 7-9 and the appropriate Z element in columns 10-18 with the decimal between columns 12 and 13 or punched. The row number after the last element is set to -4. Do not repeat Z for extra isotopes or overlay calculations. FORMAT (4(3I3F9.6))

11. W matrix. four elements per card in 18 column fields. Row number in columns 1-3, column number in columns 4-6, elements in columns 7-18 with the decimal between columns 12 and 13 or punched. Only non-zero elements are entered. For extra isotopes and no overlay repeat 11 for that isotope. For overlays likewise repeat W in the same order as was used in 8. The row number after the last element for each W matrix set equal to -2.

12. Include a card with -09 in columns 73-75. This stops the reading of card sections 6-11 onto device with unit number set equal to 3. (Disk in this thesis' program)

13. The program may be continued with a new problem starting at 1 again or stopped by including a card with 7777 in columns 3-6.

Notes: 11 is repeated for each isotope of the molecule unless a overlay calculation is being performed, then 8, 9, and 11 are repeated as described in each section. 1-5 are read into the computer but 6-11 are copied onto unit number 3 which may be defined to be a tape drive or disk drive by the appropriate job control language. This is done because 6-11 are read repetitively by the program.

VITA 2

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Candidate for the Degree of

Master of Science

Thesis: NORMAL MODE ANALYSIS OF ISOTOPICALLY DECOUPLED ICE, THE ISOLATED BENZENE RADICAL ANION, AND THIN LAYER TCNQ MOLECULAR SYSTEMS

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