Title
Polyatomic Reaction Dynamics

Author
Carrington, Tucker

Publication Date
1985-07-01

LBL-20048

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Lawrence Berkeley Laboratory

UNIVERSITY OF CALIFORNIA

Materials & Molecular Research Division

POLYATOMIC REACTION DYNAMICS

T. Carrington
(Ph.D. Thesis)

July 1985

Prepared for the U.S. Department of Energy under Contract DE-AC03-76SF00098

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LBL-20048

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Tucker Carrington

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Department of Chemistry, and Materials and Molecular Research Division
of the Lawrence Berkeley Laboratory, University of California
Berkeley, California 94720

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To the glory of God,

to whom I am thankful for loving parents and sisters

"Worthy art Thou, our Lord and our God, to receive glory and honor and power; for Thou didst create all things, and because of Thy will they existed, and were created."

Revelation 4: 11

Great are the works of the Lord;
They are studied by all who delight in them.
The fear of the Lord is the beginning of wisdom;
A good understanding have all those who do His
  commandments;
His praise endures forever.

Psalm 111: 2,10

Do you not know? Have you not heard?
The Lord is the Everlasting God, the creator of the ends
of the earth.

Isaiah 40: 28

Not to us, O Lord, not to us,
But to Thy name give glory
Because of thy lovingkindness, because of Thy truth.

Psalm 115: 1

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Acknowledgements

I am grateful for the support and guidance of Professor William H. Miller. It has been a privilege to work with and to accept the direction of a man with his extraordinary abilities. He has managed to both teach and lead me, and to allow me to explore and learn on my own. I very much appreciate his advice and direction.

I wish to thank the members of the Miller research group, from whom I have learned a great deal. I have benefited from numerous and stimulating discussions with John Tromp, Edwin Sibert, Mark Hermann, Peter Dardi, Shenghua Shi, Bruce Holmer, Lynn Hubbard, Steven Schwartz, Stephen Gray, Boyd Waite, Kim White, Beverly Ruf, Ralph Jaquet, and Koichi Yamashita. Kim White, Edwin Sibert, and Beverly Ruf proofread my thesis and Cheryn Gliebe helped me with the word processor and I am grateful for their help.

I would like to thank the members of both the Miller and Schaefer research groups who have helped me struggle with computers. I recognize that they have been very patient and kind and I am thankful.

I express my heartfelt appreciation to Professor Henry F. Schaefer who supported and sustained me during my very difficult second year.

A student's proclivities are affected to an extraordinary degree by his teachers. I have had the privilege of having excellent teachers and research advisors and for this I am grateful to God. I chose chemical physics largely because of the intrest and encouragement of an extraordinary man, Professor John C. Polanyi, and to him I am indebted.

Finally, I acknowledge my family who have supported and encouraged me. My partents have always been willing to bear my trials with me, and too often I have failed to share my joys with them and to express my appreciation for their love. I am deeply grateful for all they have done and endured on my behalf.

This work has been supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under Contract Number DE-Ac03-76SF0098, and by the National Science Foundation Grant CHE-79-20181.

Polyatomic Reaction Dynamics

Tucker Carrington

Abstract

It is difficult to study the reaction dynamics of polyatomic systems. One of the principal problems is the calculation of the Born-Oppenheimer potential energy surface. In this thesis several useful approximations to the full potential energy surface are proposed and applied. The reaction path approximation to the potential is used to study the vinylidene-acetylene rearrangement. The reaction path approximation is not sufficient when one or more of the vibrational degrees of freedom is strongly coupled to the reaction coordinate. In this case it is necessary to expand the potential about a two dimensional surface (the reaction surface) rather than about a one dimensional path (the reaction path). Assuming this form for the potential the reaction surface Hamiltonian is derived. An even better approximation to the full potential energy surface is obtained by expanding the potential about the reaction surface in internal coordinates. A Hamiltonian which allows two internal coordinates to undergo arbitrarily large amplitude displacements is developed and applied to studying malonaldehyde.

Chapter I Introduction

For many years theoretical chemists have pursued a complete understanding of A + B-C ---------→ A-B + C reactions. A variety of classical, semiclassical and quantum mechanical dynamical methods now exist for treating these problems[1] and quantum chemists are now able to calculate, from first principles, potential energy surfaces for these simple systems. It is quite difficult, however, to use the techniques that have been developed for three atom systems to study more complex reactions. Application of the methods that have been used on few-degree-of-freedom problems to study more complex processes requires an unmanageable amount of computation. It is important that dynamical models which require as input a relatively small number of ab initio calculations be developed.

To calculate the entire potential energy surface (i.e. the Born-Oppenheimer electronic energy) of a molecular system with N atoms requires an enormous amount of effort. The potential energy surface depends on 3N-6 coordinates and one would need about ten points on the surface to characterize its dependence on each of these coordinates. If each one of these calculations took only one second (and in fact they take much longer), then it would take $10^{3N-6} = 10^{21}$ s. $= 10^{13}$ years to calculate the potential energy surface for a molecule with nine atoms. If the calculation had been started when the universe was created it would not be finished today.

The reaction path Hamiltonian was developed to enable theoretical chemists to study the nuclear dynamics of polyatomic systems. Miller, Handy and Adams derived the Hamiltonian for a reacting system assuming that the potential energy surface was a multidimensional harmonic valley about the steepest descent path (in mass-weighted coordinates).[2] Many interesting chemical problems have been studied using the reaction path Hamiltonian. The vinylidene-acetylene rearrangement is studied using a method based on the reaction path Hamiltonian in Chapter II.

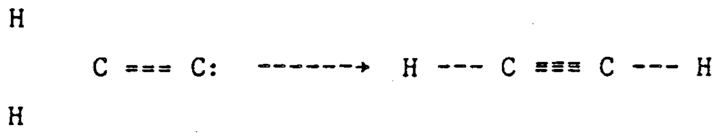
For some interesting problems a reaction path model is not sufficient. If one or more of the vibrational modes is strongly coupled to the reaction coordinate some regions of the reaction path will have large curvature and simple dynamical approximations based on a one dimensional model are precluded. In Chapter III a model is developed that is capable of treating problems with two strongly anharmonic degrees of freedom. The potential is expanded about a two dimensional surface (the reaction surface) rather than about a one dimensional path (the reaction path).

The reaction path and reaction surface Hamiltonians can be used to study the dynamics of polyatomic systems without extensive quantum chemistry calculations. The intramolecular dynamics of polyatomic molecules can also be studied by writing the kinetic energy in terms of internal coordinates (bond lengths and angles) and their conjugate momenta and approximating the potential with Morse and harmonic oscillators.[3] In Chapter IV a new Hamiltonian is derived for a molecular system with two strongly coupled degrees of freedom entirely in terms of internal coordinates and their conjugate momenta. This internal coordinate version of the reaction surface Hamiltonian combines advantages of the reaction surface idea with the desirable features of

internal coordinates. The new Hamiltonian is used to study proton transfer in malonaldehyde.

Chapter II The Vinylidene-Acetylene Rearrangement -- An Application of the Reaction Path Hamiltonian

The role of vinylidene as a reactive intermediate is not well understood. It is actually not known whether vinylidene exists as a distinct chemical entity. Even if there is a shallow minimum on the C_2H_2 potential energy surface at the vinylidene geometry, vinylidene may rearrange to form acetylene so quickly that it can not be detected.



$$\begin{matrix} H & & \\ & C \equiv C: & \longrightarrow \; H - C \equiv C - H \\ H & & \end{matrix}$$

If this is the case, it is unlikely that vinylidene is an important intermediate in organic reactions. Recent theoretical estimates of the height of the barrier separating vinylidene and acetylene[4,5,6] indicate that it is between 6.4[5] and 2.2[6] kcal/mole. On the basis of these calculations, electronic structure theorists estimate that the true barrier height is between four and zero kcal/mole. The rate constant for the unimolecular decomposition of vinylidene has been determined using RRKM theory. It was found that for a barrier height of four kcal/mole the rate constant varies from 10^{11} to $10^{13}s^{-1}$ as the excitation energy (i.e. the vibrational energy in excess of the zero point energy) varies from zero to six kcal/mole.[5]

Experimentally it is known that the radical anion H_2CC^- exists[7,8] as a stable species and that it has the vinylidene (ie., C_{2v}) equilibrium geometry.[9] Burnett, Stevens, Feigerle and Lineberger have done photodetachment experiments on H_2CC^-,

$$H_2CC^- \; + \; h\nu \; \dashrightarrow \; H_2CC: \; + \; e^- \; , \qquad (2.1)$$

and have observed vibrational structure.[10] They therefore conclude that vinylidene does exist and they estimate that its lifetime is about 10^{-14} s. They observe progressions in the CH_2 scissors mode and the C-C stretch. This structure is still evident at energies as high as 12 kcal/mole above the ground state of vinylidene. This implies that the lifetime does not decrease drastically if these modes are excited.

In this chapter the results of a new (more thorough) quantum chemistry calculation for the vinylidene acetylene system are presented, and on the basis of this information the lifetimes of individual quantum states of vinylidene are calculated using a multistate Feshbach description of the metastable states. The lifetime of vinylidene depends sensitively on the height of the barrier which separates vinylidene and acetylene on the potential energy surface. The two most recent theoretical calculations[5,6] of the barrier height gave quite different results. To obtain more accurate values of the barrier height and the vibrational frequencies of vinylidene and acetylene a rather large configuration interaction calculation was done using a triple zeta plus polarization basis set. Osamura et al.[5] determined the transition state geometry with a singles and doubles configuration interaction calculation and a double zeta plus polarization basis set. At this geometry they recalculated the electronic energy with a triple zeta plus polarization basis set and found that the barrier height dropped from 8.1 to 6.4 kcal/mole. This large change indicates that it might also be worthwhile to redetermine the transition state geometry with a triple zeta plus polarization basis set. It is also important to have accurate values of the vibrational frequencies of vinylidene and acetylene. The frequencies determine the zero-point correction to the barrier and directly affect the calculation of the lifetime.

The dynamics of the vinylidene rearrangement are studied using a detailed theory. The effect of coupling between the reaction coordinate motion and the other vibrational modes is included explicitly and lifetimes of individual quantum states of vinylidene are determined. The rate constant of the vinylidene rearrangement was previously determined using a statistical theory (microcanonical transition state theory).[5] Using the method described in this chapter one may determine how the lifetime varies upon excitation of various vibrational modes of vinylidene.

A. Potential Energy Calculations

The transition state geometry and the Born-Oppenheimer electronic energy were determined with a triple zeta plus polarization basis set and configuration interaction which included single and double excitations. The two lowest occupied self-consistent field (SCF) molecular orbitals were held doubly occupied in all configurations and the two highest lying virtual orbitals were deleted from the CI (these four orbitals are all localized in the core or carbon 1s region and are not expected to play a significant role in describing the valence electrons). Apart from these restrictions all single and double excitations relative to the Hartree-Fock reference configuration were included.

Analytic CI gradient methods[11] were used to locate the acetylene and vinylidene minima and the transition state. The geometries are shown in Figure 1. At each of the three stationary points the Cartesian force constant matrix was computed by finite differences of analytic gradients. The vibrational frequencies obtained by diagonalizing the force constant matrices calculated at the acetylene and vinylidene geometries are given in Table 1.

The triple zeta plus polarization CI bond lengths for vinylidene, acetylene, and the transition state are all smaller than the results obtained earlier with a double zeta plus polarization basis set.[5] The C-C bond lengths are 1.3% shorter for all three structures, and the C-H bond lengths decrease between 0.3% and 0.8%. The overall geometry of the transition state does not change a great deal. Accurate experimental values of the bond lengths of acetylene are available[12] and comparison of these values with the calculated ones provides an indication of the accuracy of the calculations. The triple zeta plus polarization values of the C-C and the C-H bond lengths in acetylene are 0.005 Å and 0.003 Å shorter than the experimental values.[17] The triple zeta plus polarization results are closer to the experimental numbers than the earlier double zeta plus polarization values were.

The triple zeta plus polarization CI calculation gives a barrier height of 6.3 kcal/mole. The Davidson correction for unlinked clusters[13] reduces the barrier height to 5.4 kcal/mole. These values are very close to the ones obtained by Osamura et al. and it is therefore reasonable to assume that further expansion of the basis set and better treatment of electron correlation will not make the barrier disappear completely. The true value of the barrier height is probably between two and four kcal/mole.

The known anharmonic frequencies (i.e., v=0 to v=1 energy differences) are compared with the triple zeta plus polarization frequencies in Table 1. The theoretical values of the acetylene frequencies are in better agreement with the experimental frequencies than the double zeta plus polarization values calculated previously. They are all between 3.6% and 7.5% higher than the experimental frequencies. Much of the discrepency between the experimental and theoretical values is due to the neglect of anharmonicity.

B. Dynamics of the Vinylidene-Acetylene Rearrangement

To study the dynamics of the vinylidene-acetylene rearrangement it is necessary to have a Hamiltonian. Miller, Handy and Adams[2] showed that if the potential energy surface is approximated by a multidimensional harmonic valley about the steepest descent path and if one neglects Coriolis coupling terms which couple the vibrational degrees of freedom to each other and to the reaction path then for total angular momentum J=0 the Hamiltonian is

$$H(p_s,s,P_k,Q_k) = \frac{\frac{1}{2}\left[p_s - \sum_{k,l=1}^{F-1} Q_k P_l B_{k,l}(s)\right]^2}{\left[1 + \sum_{k=1}^{F-1} Q_k B_{k,F}(s)\right]^2} +$$

$$\sum_{k=1}^{F-1} \left[\frac{1}{2} P_k^{\;2} + \frac{1}{2} w_k(s)^2 Q_k^{\;2}\right] + V_o(s). \qquad (2.2)$$

Here F is the number of internal degrees of freedom (for the vinylidene-acetylene system F=6), (s,p_s) are the reaction coordinate, the distance along the steepest descent path from the transition state, and its conjugate momentum, and (Q_k,P_k), k=1,......F-1 are the coordinates and momenta for motion orthogonal to the reaction path. $V_o(s)$ is the potential energy along the minimum energy path and $w_k(s)$ is the frequency of the kth transverse vibrational mode. The functions $B_{k,F}(s)$ couple the reaction coordinate to the vibrational modes and are related to the curvature of the reaction path and the $B_{k,l}(s)$ couple the vibrational modes to each other and are Coriolis-like couplings related to the twist of the vibrational modes about the reaction path. The functions $B_{k,1}(s)$ are given by

$$B_{k,1}(s) = \frac{\partial \mathbf{L}_k(s)}{\partial s} \cdot \mathbf{L}_k(s) \qquad (2.3)$$

where $\mathbf{L}_k(s)$ is the kth eigenvector of the projected Cartesian force constant matrix (the reaction path direction is projected out of the force constant matrix) at a distance s along the reaction path. The normalized gradient vector is denoted by $\mathbf{L}_F$. Detailed discussions of the development and applications of the reaction path Hamiltonian can be found in earlier work.[14] The quantities which specify the reaction path Hamiltonian in equation (1.2), i.e., $V_0(s)$, $w_k(s)$ and $B_{k,1}(s)$ are obtainable from quantum chemistry calculations along the reaction path.

It is useful to write the Hamiltonian in terms of action-angle variables (n_k,q_k), k=1..........F-1 for the vibrational modes. These are defined in the usual manner,

$$Q_k = \left[\frac{(2n_k + 1)}{w_k(s)} \right] \cos q_k,$$

$$P_k = -[(2n_k + 1)w_k(s)]^{1/2} \sin q_k.$$

In terms of these variables the reaction path Hamiltonian is

$$H(p_s, s, \mathbf{n}, \mathbf{q}) = \sum_{k=1}^{F-1} (n_k + \frac{1}{2})\, w_k(s) + V_o(s) +$$

$$\frac{\frac{1}{2}\left[p_s + \sum_{k,l=1}^{F-1} [(2n_k+1)(2n_l+1)w_l(s)/w_k(s)]^{1/2} \cos q_k \sin q_l\, B_{k,l}(s)\right]^2}{\left[1 + \sum_{k=1}^{F-1} [(2n_k+1)/w_k(s)]^{1/2} \cos q_k\, B_{k,F}(s)\right]^2} \tag{2.4}$$

where the diagonal elements $B_{k,l}$ are defined to be[2]

$$B_{k,l}(s) = - \frac{\frac{\partial w_k(s)}{\partial s}}{2w_k(s)} \tag{2.5}$$

It is quite difficult to calculate $V_o(s)$, $w_k(s)$ and $B_{k,l}(s)$ as functions of the reaction coordinate. For the vinylidene-acetylene system these quantites have been computed at the stationary points of the potential energy surface, i.e., the local minimum that is vinylidene, and the transition state (actually there are two symmetrically equivalent transition states) between vinylidene and acetylene. The functions $V_o(s)$, $w_k(s)$ and $B_{k,l}(s)$ are approximated by quadratic interpolation through these three points. For example, $V_o(s)$ is approximated by the polynomial

$$V_o(s) = As^2 + Bs^4 + Cs^6, \qquad (2.6)$$

with the coefficients A, B and C chosen so that the barrier height and the harmonic frequencies of vinylidene (s=0) and the transition states match the triple zeta plus polarization values given in the previous section. The frequencies are interpolated similarly,

$$w_k(s) = w_k + (w_k^{\ddagger} - w_k)\, s^2 / s^{\ddagger 2}, \qquad (2.7)$$

where w_k and $w_k^{\ddagger}$ denote the harmonic frequencies of the mode k at vinylidene (s=0) and the transition state ($s = \mp s^{\ddagger}$), respectively.

The $B_{k,l}(s)$ coupling functions occur at a higher order in perturbation theory than the $B_{k,F}$ functions and therefore it is probably a reasonable assumption to retain only the direct coupling between the reaction coordinate (labeled as mode F) and the vibrational modes. The interpolative approximation to these coupling functions is obtained by interpolating the eigenvectors and then using equation (2.3) to calculate $B_{k,F}(s)$. The result is

$$B_{k,F}(s) = (4s^{\ddagger 3})^{-1}[s^2(\mathbf{L}_k^l \cdot \mathbf{L}_F^r - \mathbf{L}_F^l \cdot \mathbf{L}_k^r) +$$

$$(s - s^{\ddagger})^2 \, (L_k^v \cdot L_F^l - L_F^v \cdot L_k^l) +$$

$$(s + s^{\ddagger})^2 (L_k^r \cdot L_F^v - L_F^r \cdot L_k^v)] \quad , \qquad (2.8)$$

where "l" and "r" label the eigenvectors of the "left" and "right " transition states, ($s= -s^{\ddagger}$ and $+s^{\ddagger}$) and "v" labels the eigenvectors of vinylidene ($s=0$).

The development of the reaction path Hamiltonian was motivated by the desire to study molecular dynamics without full potential energy surface calculations. Computing the reaction path and diagonalizing the force constant matrix along it is <u>much</u> easier than calculating an entire potential energy surface. Even this however, is an arduous job. The interpolative approximate version of the reaction path Hamiltonian described above is much easier to construct than the full reaction path Hamiltonian itself. Using this interpolative model $V_o(s)$, $w_k(s)$ and $B_{k,l}(s)$ can be calculated from quantum chemisty calculations (energies and force constant matrices) at stationary points on the potential energy surface. Quantum chemists frequently calculate energies and force constant matrices at stationary points and this interpolative procedure can be used to construct a Hamiltonian which characterizes the dynamics of a reacting system from this information. Although it may seem rather crude to base a dynamical study on three potential energy points, the semiclassical lifetimes we calculate depend on integrals of

$V_o(s)$, $w_k(s)$, and $B_{k,1}(s)$ and not on the quantities themselves. The functional forms are therefore probably not critical.

The simplest dynamical model of the unimolecular decay of vinylidene is obtained by assuming that the rearrangement occurs by tunneling and that the process is vibrationally adiabatic. This corresponds to neglecting all the coupling elements, including the $B_{k,F}$'s, so that the action variables n_k, $k=1,\dots\dots F-1$ are conserved. With this approximation, the reaction coordinate motion takes place in an effective potential V_n,

$$V_n(s) = V_o(s) + \sum_{k=1}^{F-1} \frac{h}{2\pi} w_k(s)\,(n_k + 1) \quad . \tag{2.9}$$

The lifetimes for the metastable states in the vinylidene well can be computed using the WKB approximation. The WKB expression for the lifetime of a state with energy E is

$$\tau = \frac{h}{2\pi\Gamma} \quad ,$$

where[15]

$$\Gamma = 2\left[\frac{\partial E(n_1,\dots\dots,n_F)}{\partial n_F} /2\pi\right] \ln(1 + e^{-2\Theta}) \quad , \tag{2.10}$$

Θ is the barrier penetration integral,

$$\Theta = \int_{s_2}^{s_3} [2(V_n(s) - E)]^{1/2} \, ds \quad , \qquad (2.11)$$

and the vibrational energy levels of vinylidene are obtained from the WKB quantization condition,

$$(n_F + 1)\pi = \int_{s_1}^{s_2} [2(E - V_n(s))]^{1/2} \, ds \quad . \qquad (2.12)$$

The factor of 2 in equation (2.10) is due to the existence of two equivalent barriers through which vinylidene may tunnel to decay. Figure 2 shows the vibrationally adiabatic potential, $V_n(s)$, and the bare potential, $V_o(s)$, and indicates the classical turning points which are the limits on the integrals in equations (2.11) and (2.12).

The effects of the coupling elements may be included by using a matrix version of the Feshbach approach.[16] Let P be the projection operator that projects onto the zeroth order (i.e., vibrationally adiabatic) metastable states. The complex eigenvalues $[E_r - i(\Gamma/2)]$ of the system, which give the energies (E_r) and the decay rates $(2\pi\Gamma/h)$ of the coupled system, are determined by the secular equation

$$\det(H_{PP} + H_{PQ}(E + i\varepsilon - H_{QQ})^{-1} H_{QP} - E) = 0 \quad , \qquad (2.13)$$

where Q = 1 - P, and the determinant is only over the P space. It is common[18] to neglect the real part of the optical potential (the second term in the arguement of the determinant), which is a level shift of the real part of the eigenvalues, and to use only the diagonal part of H_{QQ} in the imaginary part. Equation (2.13) then becomes

$$\det(H_{PP} - i\pi H_{PQ}\, \delta(E - H^{0}_{QQ})\, H_{QP} - E) = 0 \quad .$$

Written out more explicitly this reads

$$\det(H_{\mathbf{m},\mathbf{n}} - \frac{i}{2}\, \Gamma_{\mathbf{m},\mathbf{n}}(E) - E\delta_{\mathbf{m},\mathbf{n}}) = 0 \quad ,$$

where

$$\Gamma_{\mathbf{m},\mathbf{n}}(E) = 2\pi\langle \mathbf{m}|H\delta(E - H^{0}_{QQ})\, H|\mathbf{n}\rangle$$

$$= \sum_{l_1, l_2, \ldots l_{F-1}} 2\pi\rho \, \langle \mathbf{m}|H|\mathbf{l}E\rangle\langle \mathbf{l}E|H|\mathbf{n}\rangle \quad . \tag{2.14}$$

The states $|\mathbf{l}E\rangle$ are the Q space states. They have quantum numbers **l** for the vibrational modes and total energy E such that the energy in the reaction coordinate lies above the barrier. The real symmetric matrix **Γ** is a function of the energy E so equation (2.13) must be solved iteratively, and for one complex eigenvalue at a time. An initial value for the real part of the eigenvalue E_r is assumed and the matrix

$$H_{\mathbf{m},\mathbf{n}} - \frac{i}{2} \Gamma_{\mathbf{m},\mathbf{n}} (E_r) \tag{2.15}$$

is diagonalized, the real part of the appropriate eigenvalue is then taken as E_r and the process is repeated until converged values are obtained. The imaginary part of the eigenvalue gives the "width"

$$\Gamma = -2\mathrm{Im}(E_{\mathrm{complex}})$$

for that state.

The width matrix **Γ** describes a golden rule-like energy transfer decay mechanism. To see this explicitly consider the one state case. Equation (1.14) is then the determinant of a 1 x 1 matrix and the decay rate of the state **n** is given by

$$\Gamma_{\mathbf{n},\mathbf{n}}/\hbar = \sum_{l} \frac{2\pi\rho}{\hbar} \left|\langle n|H|lE\rangle\right|^2$$

with $E = E_{\mathbf{n}} = H_{\mathbf{n},\mathbf{n}}$, which is recognized as the Fermi golden rule. State **n** might, for example, correspond to a state with the reaction coordinate mode in its ground state $n_F = 0$ and some of the transverse modes in excited states $n_k > 0$ for some $k = 1,\ldots.F-1$. The state $|lE\rangle$ that is energetically degenerate with this state could be one for which $l_k = 0$ for $k = 1,\ldots.F-1$, but which has enough energy in the reactive coordinate to put it over the barrier. The decay mechanism that is described by $\mathbf{\Gamma}$ is energy transfer from the transverse vibrational modes to the reaction coordinate.

In addition to decay by transfer of energy from the transverse vibrational degrees of freedom to the reaction coordinate mode there is also the possibility of decay by tunneling. This decay mechanism is included by adding to the width matrix of equation (2.14) a diagonal (i.e., vibrationally adiabatic) tunneling width,

$$\Gamma_{\mathbf{m},\mathbf{n}}(E) = \delta_{\mathbf{m},\mathbf{n}}\, \Gamma_{\mathbf{n}}(E) + \sum_{l} 2\pi\rho \langle m|H|lE\rangle\langle lE|H|\mathbf{n}\rangle , \qquad (2.16)$$

where $\Gamma_{\mathbf{n}}(E)$ is the tunneling width given by equation (1.10). The matrix $\Gamma_{\mathbf{m},\mathbf{n}}$ of equation (2.16) describes unimolecular decay by both the energy transfer and the tunneling mechanisms.

The matrix elements of the Hamiltonian are computed semiclassically by using the Heisenberg correspondence relation,

$$H_{\mathbf{m},\mathbf{n}} = (2\pi)^{-F} \int_0^{2\pi} dq_1 \,\ldots\ldots\!\int_0^{2\pi} dq_F \,\exp(-i\Delta n\cdot\mathbf{q}) \;\; H_{Cl}(\bar{\mathbf{n}},\mathbf{q}) \quad , \tag{2.17}$$

where $\bar{\mathbf{n}} = \frac{1}{2}(\mathbf{n}+\mathbf{m})$, $\Delta n = (\mathbf{n}-\mathbf{m})$. The action angle variables n_F and q_F for the s degree of freedom are determined by the vibrationally adiabatic potential. The $B_{k,F}$ coupling element for the transverse mode which is the CH_2 scissors mode at the vinylidene geometry, is about an order of magnitude bigger than the $B_{k,F}$'s for any of the other modes. If only coupling elements for this mode, designated mode k=1, are retained, then there are off-diagonal elements in equation (2.17) only for k=1 and the reaction coordinate mode k=F. The classical Hamiltonian is expanded in powers of the coupling element $B_{1,F}$ and only the lowest non-zero term is kept for each matrix element. The diagonal elements in equation (2.17) are simply the vibrationally adiabatic eigenvalues $E(n_1,\ldots\ldots n_F)$ given by equation (2.12). To first order in the coupling element $B_{1,F}$ the off diagonal elements are

$$H^{n_2,\ldots\ldots n_{F-1}}_{m_1,m_F,n_1,n_F} = (2\pi)^{-2} \int_0^{2\pi} dq_1 \int_0^{2\pi} dq_F$$

$$\times \exp[-i\,\Delta n_1 q_1]\,\exp[-i\Delta n_F q_F]\,\frac{1}{2}\,p_s{}^2[-2\,B_{1,F}(s)]$$

$$\times \left[\frac{2\,\bar{n}_1 + 1}{w_1(s)}\right]^{\frac{1}{2}} \cos q_1 \quad . \tag{2.18}$$

It is apparent that $\Delta n_1 = \mp 1$ and $\Delta n_F = 0, \mp 2, \mp 4, \ldots\ldots$. (The superscripts in equation (2.18) are the diagonal quantum numbers) The q_1 integral in equation (2.18) is easy and the integration over q_F is done by using the definition of q_F to convert it to an integration over s,

$$q_F = \frac{\partial E(n)}{\partial n_F} \int_{s_1}^{s} dx\, \frac{1}{p_s(x)} \quad , \tag{2.19}$$

and equation (2.18) becomes

$$H^{n_2,n_3,\ldots n_{F-1}}_{m_1,m_F,n_1,n_F} = -[2\bar{n}_1 + 1]^{\frac{1}{2}} \left[\frac{\partial E(n)}{\partial n_F} \Big/ 2\pi\right] \times$$

$$\int_{s_1}^{s_2} ds \quad P_s(s) \quad \frac{B_{1,F}(s)}{[w_1(s)]^{\frac{1}{2}}} \quad \exp(-i\Delta n_F\, q_F(s)) \tag{2.20}$$

with $q_F(s)$ given by equation (2.19) and

$$p_s(s) = [2[E-V_{\mathbf{n}}(s)]]^{1/2} . \qquad (2.21)$$

Matrix elements second order in $B_{1,F}$ which are required when $\Delta n_1 = \mp 2$ are computed in a similar fashion.

To construct the width matrix $\mathbf{\Gamma}$ it is also necessary to have matrix elements between a discrete metastable state $|\mathbf{n}\rangle$ and a continuum state $|1E\rangle$. If $\Delta n_F q_F(s)$ is replaced by

$$(E - E_{\mathbf{n}}) \int_{s_1}^{s} dx \frac{1}{p_s(x)} \equiv \delta(s) , \qquad (2.22)$$

then these matrix elements are also given by equation (2.20). The density of states in equation (2.16) is given by

$$\rho = \frac{1}{2} \left[\frac{\partial E(\mathbf{n})}{\partial n_F} \right]^{-1} . \qquad (2.23)$$

Each zeroth order metastable state couples to only half the total continuum states because of the Δn_F = even selection rule and therefore there is a factor of ½ in front of the derivative in equation (2.23).

The final expression for the discrete-continuum matrix elements can also be obtained by substituting WKB wave functions into the golden rule formula for the decay rate. Both approaches give the decay rate for the one state case $|n_1=1,n_F=0\rangle \rightarrow |m_1=0,E\rangle$ as

$$\Gamma/\hbar = 2\left[\frac{\partial E(n)}{\partial n_F} / 2\pi\hbar \right] \left| \int_{s_1}^{s_2} ds \ \frac{1}{2} \ \left[\frac{\bar{2}n + 1}{w_1(s)} \right]^{1/2} p_s(s) e^{-i\delta(s)} \ B_{1,F}(s) \right|^2 .$$

This has the usual semiclassical form: the decay rate is equal to a frequency times a probability, but in this case there is an extra factor of two because there are two symmetrical barriers,

$$\Gamma/\hbar = 2(w_F/2\pi) P \quad .$$

In summary the lifetimes of individual vinylidene states are calculated by diagonalizing the complex symmetric matrix in equation (2.16). The width matrix is the sum of the Feshbach energy transfer part, given by equation (2.14), and the tunneling contribution given by equations (2.10) and (2.11). The matrix elements between discrete states and between discrete and continuum states are computed semiclassically via equations (2.17) - (2.23).

C. Results and Discussion

The lifetimes of the vinylidene states depend sensitively on the height of the barrier separating vinylidene and acetylene. We have therefore computed lifetimes for barrier heights of two, three and four kcal/mole, and the results are given in Table II. The numbers in the column labeled VA are the vibrationally adiabatic results (equation (2.10)) and the results of the full semiclassical model described in the last section are given in the column labeled SC.

Including the coupling between the zeroth order metastable states affects the lifetimes significantly for the four kcal/mole barrier. The SC values are in most cases not changed much if the Feshbach contribution to Γ is omitted, the most important contribution to the width matrix is therefore due to tunneling.

It is apparent that excitation of the reaction coordinate mode is more effective in promoting reaction than excitation of the scissors degree of freedom. Although it requires more energy to excite the scissors mode to $n_1=1$ than it does to excite the reaction coordinate mode to $n_F=1$, exciting the reaction coordinate mode has a bigger effect on the decay rate. This is of course what one would expect, we know that the coupling between the scissors mode and the reaction coordinate is weak and we have assumed that it can be treated approximately.

The $B_{k,F}$ coupling elements for the scissors mode are an order of magnitude bigger than the $B_{k,F}$ coupling elements for the other orthogonal degrees of freedom. The lifetimes of vinylidene states with these modes excited should therefore be given accurately by the simple vibrationally adiabatic approximation. The lifetime acutally <u>increases</u> (by about a factor of two) if the C-C stretch is excited. This is due to the fact that the frequency of the C-C stretch increases between vinylidene and the transition state and therefore the effective barrier height increases.

The results are consistent with the experimental results of Burnett et al.[10] The experimental values of the frequencies for the C-C stretch and the scissors modes agree well with the frequencies we have calculated. The widths of the lines in the photoelectron spectrum provide lower bounds on the lifetimes of the states of vinylidene. They estimate that the lifetime of vinylidene is about 0.013 ps. This limiting lifetime is considerably smaller than, and thus consistent with, all the lifetimes given in Table II.

The experimentalists[10] suggest that the linewidth they observe has contributions from sources other than the rearrangement of vinylidene to form acetylene. It is nevertheless interesting to determine what barrier height gives a lifetime of 0.013 ps.. It is clear from Table II that the vibrationally adiabatic approximation is quite good for low barriers, and using this approximation we find that a barrier height of 1 kcal/mole corresponds to a lifetime of 0.017 ps for the ground state of vinylidene. If the dynamical model is reliable the barrier height for the vinylidene-acetylene rearrangement must be greater than 1 kcal/mole. For a one kcal/mole barrier height, the vibrationally adiabatic potential for a state with one quantum in the scissors mode does not have a potential well at all. This state however is observed experimentally and therefore it seems certain that the barrier height is really larger than 1 kcal/mole. Burnett et al. report a line width of 50 meV but the real line width for decay of vinylidene is probably narrower than this.

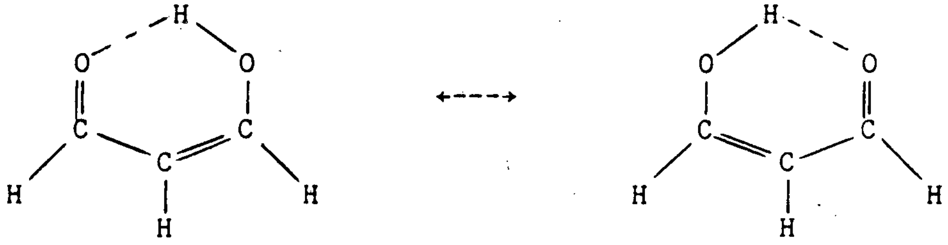
The calculations indicate that vinylidene does indeed exist. It appears to live at least 0.013 ps. and this lifetime is consistent with a barrier height of at least 1 kcal/mole. We estimate that the barrier height is actually between two and four kcal/mole and that the lifetime of the ground state of vinylidene is between 0.24 to 4.6 ps.. Exciting the CH_2 scissors mode decreases the lifetime by about a factor of two and exciting the C-C mode actually increases it.

Chapter III The Reaction Surface Hamiltonian

Significant progress towards understanding polyatomic reactions has been made by utilizing the idea of a reaction path.[2,14,19-21] By characterizing the entire potential energy surface as a multidimensional harmonic valley about the reaction path, this approach allows one to obtain what is often a good approximation to the dynamically important parts of the potential energy surface from a relatively modest number of quantum chemistry calculations. One does not require the entire potential energy surface of the N-atom system in 3N-6 dimensional space, but instead it is necessary only to determine it along a line, the reaction path, and to calculate the force constant matrix along the path. Usually the reaction path is chosen to be the steepest descent path in mass-weighted coordinates, and use is made of the ability of quantum chemists to evaluate the gradient of the potential energy surface. The central assumption is that one can circumvent the multidimensionality problem by assuming that the dynamics is dominated by motion along a one-dimensional path (in 3N-6 dimensional space).

Miller, Handy and Adams have derived the Hamiltonian for a reacting system in terms of the reaction coordinate (the distance along the reaction path), local normal modes for motion orthogonal to the reaction path and their conjugate momenta.[2] The dynamics of many interesting polyatomic systems can be studied by using this Hamiltonian. The vinylidene-acetylene isomerization disucussed in the last chapter is a good example of a system that can be adequately treated with the reaction path model.[22] Useful approximations can be based on a perturbative treatment of the coupling between the reaction coordinate motion and the transverse vibrations. Another standard approximation is vibrational adiabaticity. By assuming that the 3N-7 harmonic degrees of freedom orthogonal to the reaction path remain in the same adiabatic quantum state (or classically conserve their action variables) along the reaction coordinate, one can eliminate the harmonic degrees of freedom and obtain a reduced equation of motion for only the reaction coordinate degree of freedom.

The reaction path Hamiltonian is useful when the reaction coordinate is not strongly coupled to any of the orthogonal vibrations and when the potential is adequately described by a harmonic valley about the reaction path. If there are two strongly coupled non-harmonic degrees of freedom it is best to treat them both accurately. If there is strong coupling between the reaction coordinate and an orthogonal degree of freedom then some regions of the reaction path have large curvature. Large curvature and large coupling mean that no simple dynamical approximation will be useful. In addition, there are fundamental problems that are introduced by large curvature. Reaction path coordinates become multivalued and thus not well defined at distances farther from the reaction path than the local radius of curvature. Large curvature (i.e., small radius of curvature)[23] means that these multivalued regions are close to the reaction path and thus not in a region of configuration space that can be safely ignored. It is well known, for example, that reaction path coordinates are not suited to the description of the dynamics of heavy-light-heavy atom-diatom collinear reactions,[24] eg., I + HI --------→ IH + I. The problem is that, in this case, the reaction coordinate and the orthogonal vibration are strongly coupled and, as a result, the reaction path is very curved (and the skew angle is very small). There is no way of describing this sort of reaction without dealing with the full two-dimensionality of the system. These difficulties arise in all hydrogen atom transfer reactions, for example, the intramolecular hydrogen atom transfer in malonaldehyde



. (3.1)

The problems associated with the strong coupling between the reaction coordinate and a transverse degree of freedom can be avoided by treating the strongly coupled degrees of freedom separately.

It is not always satisfactory to assume that the potential energy surface is well described by a harmonic valley about the reaction path and to treat the coupling perturbatively. In this chapter an extension of the reaction path treatment is given where it is assumed that the dynamics is dominated by motion along a hypersurface (in 3N-6 dimensional space). The formulae are given explicitly for a two dimensional surface, which is called, in analogy to the reaction path, the reaction surface. This formulation should be useful when the dynamics of a polyatomic system, although not dominated by motion along a one-dimensional path, is dominated by motion along a surface. The key idea is that two degrees of freedom are allowed to undergo arbitrarily large amplitude motion, i.e., there are two reaction coordinate-like degrees of freedom, rather than just one. For atom transfer reactions (like equation (3.1)) it is natural to take these two large amplitude motion coordinates as r_1 and r_2, the lengths of the bond being broken and the bond being formed, although the methodology that is presented here is applicable for any choice of the two reaction parameters. The essential idea is that the important parts of the potential energy surface are treated accurately. Harmonic approximations are only introduced for the small amplitude degrees of freedom. Once the two most important degrees of freedom have been treated correctly for arbitrarily large displacements, it should be a good approximation to characterize the remaining degrees of freedom as harmonic motion.

The methodology is developed so that ab initio quantum chemistry calculations can be used as direct input, although it is of course not necessary that this always be done. The first step is to give a prescription for determining the reaction surface, i.e., for finding $\mathbf{a}(r_1,r_2)$, the nuclear Cartesian coordinates from which small amplitude displacements will be measured. The potential is assumed to be adequately described by an expansion about the reaction surface,

$$V(\mathbf{x}) = V\big(\mathbf{x} = \mathbf{a}\,(r_1,r_2)\big) + \frac{1}{2}\,\mathbf{d}\cdot\mathbf{K}\cdot\mathbf{d}\ , \qquad (3.2)$$

where r_1 and r_2 specify a point on the reaction surface, $\mathbf{a}(r_1,r_2)$ are the 3N nuclear coordinates of the reaction surface, **d** is a Cartesian displacement vector, and K is the force constant matrix evaluated on the reaction surface

$$\mathbf{K}(\mathbf{a}) = \left[\frac{\partial^2 \mathbf{V}(\mathbf{x})}{\partial \mathbf{x} \partial \mathbf{x}} \right]_{\mathbf{x}=\mathbf{a}} \tag{3.3}$$

There is no linear term in the Taylor series expansion in equation (3.2) because of the way the reaction surface is defined (see page 32).

This is obvioulsy a better approximation to the potential than a harmonic valley about a reaction path. For a two degree of freedom system (eg., collinear A + BC) this approximation is exact. It will certainly be more difficult to determine the quantities required to construct this reaction surface approximation than it is to determine the reaction path approximation to the potential. Application of the reaction surface model requires calculation of the potential energy surface and the force constant matrix over a two dimensional grid of (r_1,r_2) values. This is certainly more difficult than calculating these quantities along a line (which is all that is required for application of the reaction path model), but it should still be a feasible calculation for many interesting systems and it is considerably less demanding than having to determine the potential energy surface over a (3N-6) dimensional grid of values.

Normal coordinates for vibration orthogonal to the reaction surface are defined to be orthogonal to the surface (and to the six 3N dimensional vectors which correspond to infinitesimal rotations and translations of the entire reacting system). Removing the reaction surface coordinates from the vibrational part of the Hamiltonian not only facilitates a better approximation to the potential energy surface, it also simplifies treatment of coupling between rotation and large amplitude vibrations.

The reaction surface Hamiltonian is derived by making use of methods developed by spectroscopists to study the vibration-rotation spectra of floppy molecules.[25] The 3N-6 internal coordinates of the system are the two reaction coordinate-like variables r_1 and r_2 and 3N-8 local normal mode coordinates for motion orthogonal to the reaction surface. Euler angles are introduced in the usual way to describe the overall rotation of the molecular system. The Hamiltonian expressed in terms of these coordinates and their conjugate momenta is derived for general nonlinear geometries; modifications necessary for linear reaction surface geometries are also described.

All dynamics that involve strong coupling between only two degrees of freedom can be described exactly by the reaction surface model, because two degrees of freedom can undergo arbitrarily large amplitude motion. The dynamical phenomena that appear in collinear atom-diatom reactions will be described exactly. Many polyatomic reactions typically involve only two degrees of freedom in an intimate way and should be described accurately by this approach. In many chemical reactions one bond is broken while another is being formed, it seems intuitively obvious that an accurate description of these reactions will be obtained if these two important degrees of freedom are treated exactly.

A. Defintion of the Reaction Surface

In this section we will show how to determine the reaction surface. If mass-weighted coordinates are used, the reaction path is usually defined as the minimum energy path through the transition state from reactants to products. The reaction surface is defined analagously as the minimum energy surface subject to two constraints. One is at liberty to choose any two chemically interesting coordinates for the two constraint equations. For atom transfer reactions, such as Eqn. (3.1), it seems reasonable to pick the length of the bond being broken and the length of the bond being formed, but any two molecular parameters can be chosen as the two reaction parameters. The reaction surface is defined by minimizing the potential energy (i.e., the Born-Oppenheimer electronic energy) of the N atom system subject to the constraint of fixed values of r_1 and r_2. One minimizes the potential energy for a given pair of values (r_1,r_2), then changes r_1 and r_2 by a small increment and reminimizes the potential energy at the new pair of values (r_1,r_2) and repeats this process to obtain the potential energy over a two dimensional grid of (r_1,r_2) points. The Cartesian coordinates of the N atoms for these constrained minima are $a(r_1,r_2)$, these are the coordinates of the atoms on the reaction surface. At several points on the reaction surface it is also necessary to calculate the force constant matrix

$$\mathbf{K}(r_1,r_2) = \left[\frac{\partial^2 V}{\partial \mathbf{x} \partial \mathbf{x}}\right]_{\mathbf{x}=\mathbf{a}}$$

where $\mathbf{x} = x_{ia}$, $i = 1,\ldots N$, $a = x,y,z$ denote the 3N Cartesian coordinates. The potential energy on the reaction surface is denoted by

$$V_o(r_1,r_2) = V(\mathbf{a}) \tag{3.4}$$

Quantum chemists have developed techniques which enable them to calculate gradients of potential energy surfaces analytically, i.e., without using a finite difference approximation.[26] Using these methods, it is possible to calculate the reaction surface potential and the Cartesian coordinates of the nuclei on the reaction surface. If the increments are made systematically from one point on the two dimensional grid to another, then for most systems the minimizing geometry will change gradually and subsequent minimizations will be fairly easy. The reaction surface is of course independent of the coordinates that are used to perform the constrained minimization.

The constrained minimization procedure can be described by using Lagrange multipliers. Let $\mathbf{x}_i$ be a set of coordinates which determines the shape of the molecule. The x_i could be a set of (3N-6) internal coordinates or they could be Cartesian coordinates from which translation and rotation have been projected out; they give the configuration of the molecule but no information about overall translation or rotation. Let $R_1(x_i)$ and $R_2(x_i)$ be the functions that express r_1 and r_2 as functions of the coordinates x_i. To find the constrained minima one must solve the following equations

$$r_1 = R_1(\mathbf{x}),$$

$$r_2 = R_2(\mathbf{x}),$$

$$0 = \frac{\partial V(\mathbf{x})}{\partial \mathbf{x}} - l_1 \frac{\partial R_1(\mathbf{x})}{\partial \mathbf{x}} - l_2 \frac{\partial R_2(\mathbf{x})}{\partial \mathbf{x}} \qquad (3.5)$$

for $\mathbf{x}(r_1,r_2) = \mathbf{a}(r_1,r_2)$, $l_1(r_1,r_2)$, and $l_2(r_1,r_2)$ (l_1 and l_2 are Lagrange multipliers that have been introduced to accomplish the constrained minimization). It is also desirable to obtain equations which give the rate of change of the constrained minimum geometry, $a_i(r_1,r_2)$, with r_1 and r_2; that is to obtain equations which are the reaction surface analogue of the equation which defines the steepest descent reaction path. (The equation which defines the reaction path is

$$\frac{d\, a_{ib}(s)}{ds} \propto \frac{\partial\, V}{\partial\, a_{ib}} \,/\, m_i^{1/2} \qquad (3.6)$$

$i=1,\ldots,N$, $b=x,y,z$.) This is done by setting $x_i = a_i(r_1,r_2)$, treating l_1 and l_2 as functions of r_1 and r_2 and differentiating equation (3.5) implicitly, first with respect to r_1 and then with respect to r_2. The derivatives with respect to r_1 give three simultaneous linear equations for

$$\frac{\partial a(r_1,r_2)}{\partial r_1}, \quad \frac{\partial l_1(r_1,r_2)}{\partial r_1} \quad \text{and} \quad \frac{\partial l_2(r_1,r_2)}{\partial r_1}$$

the solution of which is as follows

$$\frac{\partial a(r_1,r_2)}{\partial r_1} = [\mathbf{A}^{-1} \frac{\partial R_1}{\partial a} \mathbf{M}_{22} - \mathbf{A}^{-1} \frac{\partial R_2}{\partial a} \mathbf{M}_{12}] / [\mathbf{M}_{11}\mathbf{M}_{22} - \mathbf{M}_{12}{}^2]$$

$$\frac{\partial l_1(r_1,r_2)}{\partial r_1} = - M_{22}/(\mathbf{M}_{11}\mathbf{M}_{22} - \mathbf{M}_{12}{}^2),$$

$$\frac{\partial l_2(r_1,r_2)}{\partial r_1} = M_{12}/(\mathbf{M}_{11}\mathbf{M}_{22} - \mathbf{M}_{12}{}^2),$$

where

$$\mathbf{M}_{i,j} = \frac{\partial R_i}{\partial a} \cdot \mathbf{A}^{-1} \cdot \frac{\partial R_j}{\partial a}, \qquad i,j = 1,2$$

$$\mathbf{A} = l_1 \frac{\partial^2 R_1}{\partial a \partial a} + l_2 \frac{\partial^2 R_2}{\partial a \partial a} - \frac{\partial^2 V}{\partial a \partial a} . \qquad (3.7)$$

The partial derivatives of $a_i(r_1,r_2)$, $l_1(r_1,r_2)$ and $l_2(r_1,r_2)$ with respect to r_2 are obtained from the derivatives with respect to r_1 by interchanging the subscripts 1 and 2. Equations (3.7) for the derivatives with respect to r_1 and the corresponding set of equations for the derivatives with respect to r_2 determine how the reacton surface geometry changes as r_1 and r_2 vary. They could be used to determine how the 3N Cartesian coordinates of the N-atom system change as the reaction surface variables r_1 and r_2 change, and they generalize the gradient-following algorithm used to construct the reaction path. To determine $a_i(r_1,r_2)$ over the entire two dimensional surface these equations must be integrated.

Clearly, determining the reaction surface will require more quantum chemistry calculations than determining a reaction path, this however, is the price that must be paid for a more accurate description of the reaction dynamics. It is much easier to locate the reaction surface and to calculate the potential as a function of position on this 2-D surface than it is to determine the entire 3N-6 dimensional potential energy surface.

B. Derivation of the Reaction Surface Hamiltonian

It has been shown that a reaction surface can be specified so that a good approximation for the entire potential energy surface is obtained efficiently from a relatively small number of quantum chemistry calculations. In this section the kinetic energy is derived in terms of the coordinates used to generate the approximate potential energy surface, three Euler angles for rotation of the N-atom system and their conjugate momenta. From the classical expression for the kinetic energy the classical and quantum mechanical reaction surface Hamiltonians are derived.

The Hamiltonian is obtained from a straightforward extension of the derivation of the original reaction path Hamiltonian.[2] The reaction path Hamiltonian itself is an application of the techniques developed by Hougen, Bunker and Johns to calculate vibration-rotation energy levels for triatomic molecules with large amplitude, floppy bending degrees of freedom.[25,27] Spectroscopists have also used these methods to study molecules where several internal coordinates undergo large amplitude motion.[28]

If the reaction parameters do not depend on the masses of the atoms (and r_1 and r_2 which we have chosen do not) then the reaction surface potential and the force constant matrices do not depend on the masses. Because the reaction surface is mass independent, unlike the reacton path (the steepest descent path in mass-weighted coordinates), which depends explicitly on the atomic masses, it is best to avoid introducing unnecessary dependence on the masses by not using mass-weighted coordinates (which were used in the derivation of the reaction path Hamiltonian). The masses, of course, will enter into the definition of the normal coordinates for vibration.

In the following derivation, the components of 3N dimensional Cartesian vectors will be represented by x_{ia}, where $i = 1,\ldots,N$ denotes atoms and $a = x,y,z$. Boldface vectors with an atomic subscript denote three dimensional vectors, i.e., the components of $\mathbf{x}_i$ are x_{ia}. The Einstein summation convention will be used for the small letters a, b and c (summation is implied over an index that occurs twice).

Let X_{ia} and x_{ia} be the Cartesian coordinates of the N atoms in a space-fixed system of axes and a molecule-fixed system of axes, respectively. The coordinates of the ith particle with respect to the moving and space-fixed axis systems are related by

$$X_i = R_{com} + S(\chi,\theta,\phi)^{-1} \cdot x_j \quad , \tag{3.8}$$

where R_{com} is a vector containing the space-fixed coordinates of the centre of mass of the N-atom system, and $\mathbf{S}(\chi,\theta,\phi)$ is the matrix of direction cosines which relates the orientations of the molecule- and space- fixed axis systems, and (χ,θ,ϕ) are the Euler angles. The coordinates in the molecule-fixed axis system are referred to a reference configuration (the reaction surface). Displacements from the reaction surface, $\mathbf{d}_i$ are given by

$$\mathbf{x}_i = \mathbf{a}_i(r_1,r_2) + \mathbf{d}_i \tag{3.9}$$

The molecule-fixed axis system is required to have its origin at the centre of mass,

$$\sum_{i=1}^{N} m_i \; a_i(r_1,r_2) = 0 \tag{3.10}$$

With equation (3.9) substituted into equation (3.8) there are 3N variables on the left-hand side (X_{ia}) and 3N+8 variables on the right-hand side (R_0, θ, ϕ, χ, d_{ia}, r_1, r_2). In order to have the same number of independent variables on both sides, it is necessary to introduce eight constraints for the 3N variables X_{ia}. The kinetic energy is simplified by choosing the constraints to be

$$\sum_{i=1}^{N} m_i \; d_i = \mathbf{0}, \tag{3.11}$$

$$\sum_{i=1}^{N} m_i \; a_i(r_1,r_2) \times \mathbf{d}_i = \mathbf{0}, \tag{3.12}$$

$$\sum_{i=1}^{N} m_i \frac{\partial a_i(r_1,r_2)}{\partial r_1} \cdot d_i = 0, \tag{3.13}$$

$$\sum_{i=1}^{N} m_i \frac{\partial a_i(r_1,r_2)}{\partial r_2} \cdot d_i = \mathbf{0} \; . \tag{3.14}$$

Relation (3.11) insures that the origin of the molecule-fixed system moves with the centre of mass. Relation (3.12), usually called the Eckart condition, assures that infinitesimal displacements do not contribute to the angular momentum. The displacements $\mathbf{d}_i$ are chosen to be orthogonal to the reaction surface, as indicated by relations (3.13) and (3.14). These conditions are satisfied by introducing, at each point on the reaction surface, normal coordinates defined so that they are orthogonal to the reaction surface and expressing the displacements

$\mathbf{d}_i$ in terms of the local normal mode coordinates. In terms of the normal mode coordinates Q_k, the displacements are given by

$$\mathbf{d}_i = m_i^{-\frac{1}{2}} \sum_{k=1}^{3N-8} L_{i,k}(r_1,r_2)\, Q_k$$

Throughout the rest of this chapter the indices k, l and m refer to normal modes, and the indices i and j refer to atoms. There are 3N-8 vibrational coordinates Q_k (for linear surface configurations there will be 3N-7). The elements of the (3N)x(3N-8) matrix $L_{ia,k}$ are functions of r_1 and r_2 and are subject to the condition that the columns of **L** be orthogonal to each other and to the reaction surface. This condition is satisfied by choosing $L_{ia,k}$ so that it is the iath component of the kth eigenvector of the projected force constant matrix. The projected 3N X 3N force constant matrix $\mathbf{K}^P(r_1,r_2)$ is defined by

$$\mathbf{K}^P(r_1,r_2) = (1 - \mathbf{P}(r_1,r_2))\cdot\mathbf{K}^M(r_1,r_2)\cdot(1-\mathbf{P}(r_1,r_2)).$$

where

$$\mathbf{K}^M_{ic,jb}(r_1,r_2) = \left[\frac{\partial^2 V(x)}{\partial x_{ic}\partial x_{jb}} \Big/ (m_i\, m_j)^{1/2}\right]_{x=a(r_1,r_2)} ,$$

and where $P(r_1,r_2)$ is the 3N X 3N matrix which projects onto the two directions tangent to the reaction surface at $a_{ia}(r_1,r_2)$. This projector is given by

$$P_{ic,jb}(r_1,r_2) = \sum_{n,m}^{2} m_i^{1/2} \frac{\partial a_{ic}(r_1,r_2)}{\partial r_n} \left[\mathbf{S}(r_1,r_2)^{-1}\right]_{n,m} \frac{\partial a_{jb}(r_1,r_2)}{\partial r_m} m_j^{1/2}$$

where $S(r_1,r_2)$ is the 2 X 2 overlap matrix of the two vectors $m_i^{1/2} \cdot da_{ib}(r_1,r_2)/dr_n$, $n = 1,2$,

$$S_{n,m}(r_1,r_2) = \sum_{i=1}^{N} m_i \frac{\partial a_i(r_1,r_2)}{\partial r_n} \cdot \frac{\partial a_i(r_1,r_2)}{\partial r_m} . \tag{3.15}$$

It was previously believed[2,44] that at each point (r_1,r_2) it was necessary to project out not only the two dimensional plane tangent to the reaction surface at (r_1,r_2), but also infinitesmal rotations and translations. Diagonalizing the Cartesian force constant matrix will always give six eigenvectors which correspond to translation and rotation and which are orthogonal to the vibrational eigenvectors. This is true whether or not the force constant matrix is calculated and diagonalized at an extremum. The eigenvalues which correspond to the translational and rotational eigenvectors will only, however, be zero at extrema.

At arbitrary geometries the projected force constant matrix will have two zero eigenvalues corresponding to the two vectors onto which P projects, at stationary points on the potential surface it will have in addition six other zero frequencies for the translational and vibrational degrees of freedom. At any point on the reaction surface there are 3N-8 eigenvalues, denoted $w_k(r_1,r_2)^2$, $k = 1,\ldots,3N-8$, which correspond to vibrations orthogonal to the reaction surface. The components of the corresponding eigenvectors are $L_{ia,k}$ $i = 1,\ldots,N$, $a = x,y,z$, $k = 1,\ldots,3N-8$.

In terms of the internal coordinates r_1, r_2 and Q_k, the potential energy is given by

$$V(r_1,r_2,Q_k) = V_o(r_1,r_2) + \sum_{k=1}^{3N-8} \frac{1}{2} w_k(r_1,r_2)^2 Q_k^2 , \tag{3.16}$$

where $w_k(r_1,r_2)^2$ are the vibrational eigenvalues of the projected force constant matrix. There are no terms linear in the normal coordinates because the reaction surface has been constructed so that $V_o(r_1,r_2)$ is the minimum value of the potential for fixed values of r_1 and r_2.

In their original paper Hougen, Bunker and Johns (HBJ) made it quite clear that the large amplitude coordinate they used (ρ) was the bend angle of the reference configuration and that this is not the same as the instantaneous value of the bend angle of the triatomic molecule. HBJ chose the large amplitude motion coordinate in this way so that equation (3.13) (with $r_1 = \rho$) would be satisfied. Other researchers who have applied these techniques to study various molecules[51,50] have defined the large amplitude coordinates so that equations like (3.13) are satisfied. To study NH_3, for example, ρ is chosen as the angle between the C_3 axis and an N-H bond <u>in the reference configuration</u>. Coordinates chosen in order to satisfy equation (3.13) are called "least squares coordinates" by Natanson[20e]. The large amplitude motion coordinates we use are the instantaneous values of the bond lengths r_1 and r_2. This means that, unlike HBJ-type large amplitude coordinates, our large amplitude coordinates do not automatically satisfy equation (3.13). We satisfy (3.13) by explicitly constructing normal modes which are orthogonal to the reaction surface and expressing displacements $\mathbf{d}_i$ from the surface in terms of these normal modes. It is because our large amplitude coordinates are the instantaneous values of r_1 and r_2 that there is no linear term in our expansion about the reaction surface.

Borrowing extensively from the spectroscopists and following the analysis of Wilson, Decius and Cross[29], we can derive the expression for the kinetic energy in terms of r_1, r_2, Q_k , their conjugate momenta and the three components of the angular momentum, J_x, J_y, and J_z. One obtains

$$2T = \sum_{k=1}^{3N-8} P_k^{\,2} + 2T^* , \qquad (3.17)$$

with

$$2T^* = (\mathbf{J}-\boldsymbol{\pi})\cdot(I^*)^{-1}\cdot(\mathbf{J}-\boldsymbol{\pi}) , \qquad (3.18)$$

where **J** and $\boldsymbol{\pi}$ are five dimensional vectors and $\mathbf{I}^*$ is a 5x5 matrix. $J = (J_x, J_y, J_z, p_{r_1}, p_{r_2})$, J_x, J_y and J_z are the x, y and z components of the total angular momentum vector for the reacting N-atom system and p_{r_1} and p_{r_2} are momenta conjugate to the reaction surface coordinates r_1 and r_2. The components of the vector $\boldsymbol{\pi}$ are

$$\pi_a = \sum_{k,l} B_{kl}^{a} Q_k P_l \qquad a = x,y,z,r_1,r_2 \tag{3.19}$$

with

$$B_{kl}^{a} = \sum_i e_{abc} L_{bi,k} L_{ci,l} \qquad a,b,c = x,y,z$$

$$B_{kl}^{r_1} = \sum_i \frac{\partial L_{ai,k}}{\partial r_1} L_{ai,l}$$

$$B_{kl}^{r_2} = \sum_i \frac{\partial L_{ai,k}}{\partial r_2} L_{ai,l} \, , \tag{3.20}$$

and P_l is the momentum conjugate to the normal coordinate Q_l. The permutation symbol (or the unit antisymmetric tensor) e_{abc} is useful for abbreviating many of the later expressions.

The matrix I^* is defined by

$$I^*_{ab} = I_{ab} - \sum_{klm} B^a_{km} B^b_{lm} Q_k Q_l , \qquad (3.21)$$

The matrix I^* is given by

$$I^*_{ab} = I^o_{ab} + 2b_{ab} + c_{ab} \qquad (a,b = x,y,z,r_1,r_2) \qquad (3.22)$$

The matrices I^o, **b** and **c** are 5 X 5 matrices, the 2 X 2 blocks refer to the two coordinates r_1 and r_2, and the 3 X 3 blocks refer to the three spatial coordinates x, y and z,

$$I^o_{r_1 r_1} = \sum_i \left[\frac{da_{ai}}{dr_1} \right]^2 m_i$$

$$I^o_{r_2 r_2} = \sum_i \left[\frac{da_{ai}}{dr_2} \right]^2 m_i$$

$$I^o_{r_1 a} = e_{abc} \sum_i \frac{\partial a_{bi}}{\partial r_1} a_{ci} m_i$$

$$I^o_{r_2 a} = e_{abc} \sum_i \frac{\partial a_{bi}}{\partial r_2} a_{ci} m_i$$

$$I^{o}_{r_1 r_2} = \sum_i \frac{\partial a_{ai}}{\partial r_1} \frac{\partial a_{ai}}{\partial r_2} m_i = I^{o}_{r_2 r_1} \quad . \qquad (3.23)$$

The 3 X 3 block of I^o is the usual inertia tensor for the reference configuration $a_{ib}(r_1,r_2)$, the 2 X 2 block is the overlap matrix given above and the off-diagonal block is coupling induced by the angular momentum of the reference configuration in the molecule fixed axis system. Finally, the 5 X 5 matrices b and c are given by

$$b_{r_1 r_1} = -\sum_i \frac{d^2 a_{ai}}{dr_1^{\,2}} \sum_k L_{ai,k} \, Q_k \, m_i^{1/2}$$

$$b_{r_2 r_2} = -\sum_i \frac{d^2 a_{ai}}{dr_2^{\,2}} \sum_k L_{ai,k} \, Q_k \, m_i^{1/2}$$

$$b_{r_1 a} = -e_{abc} \sum_i \frac{da_{bi}}{dr_1} \sum_k L_{ci,k} \, Q_k \, m_i^{1/2} = b_{ar_1} \qquad (a=x,y,z)$$

$$b_{r_2 a} = -e_{abc} \sum_i \frac{da_{bi}}{dr_2} \sum_k L_{ci,k} \, Q_k \, m_i^{1/2} = b_{ar_2} \qquad (a = x,y,z)$$

$$b_{ab} = e_{ace} \, e_{bde} \sum_i a_{ci} \sum_k L_{di,k} \, Q_k \, m_i^{1/2} = b_{ba} \qquad (a=x,y,z)$$

$$b_{r_1r_2} = -\sum_k \sum_i \frac{d^2a_{ai}}{dr_1 dr_2} L_{ai,k} Q_k m_i^{½} = b_{r_2r_1}$$

$$c_{r_1r_1} = \sum_i \sum_{kl} \frac{dL_{ai,k}}{dr_1} \frac{dL_{ai,l}}{dr_1} Q_k Q_l$$

$$c_{r_2r_2} = \sum_i \sum_{kl} \frac{dL_{ai,k}}{dr_2} \frac{dL_{ai,l}}{dr_2} Q_k Q_l$$

$$c_{r_1a} = e_{abc} \sum_i \sum_{kl} L_{bi,k} \frac{dL_{ci,l}}{dr_1} Q_k Q_l = c_{ar_1}$$

$$c_{r_2a} = e_{abc} \sum_i \sum_{kl} L_{bi,k} \frac{dL_{ci,l}}{dr_2} Q_k Q_l = c_{ar_2}$$

$$c_{ab} = e_{ace} e_{bde} \sum_i \sum_{kl} L_{ci,k} L_{di,l} Q_k Q_l = c_{ba}$$

$$c_{r_1r_2} = \sum_{kl} \sum_i \frac{dL_{ai,k}}{dr_1} \frac{dL_{ai,l}}{dr_2} Q_k Q_l = c_{r_2r_1} . \tag{3.24}$$

The components of the angular momentum in molecule-fixed coordinates are

$$J_x = (J^2 - K^2)^{½} \cos q_K$$

$$J_y = (J^2 - K^2)^{1/2} \sin q_K$$

$$J_z = K \tag{3.25}$$

where J is the magnitude of the angular momentum, M is its projection onto the space fixed Z-axis and K is its projection onto the body-fixed z-axis.[2] The coordinates conjugate to these momenta are q_J, q_M and q_K. J and M are constants of the motion and the Hamiltonian is not a function of q_J or q_M. Because of the isotropy of space, the Hamiltonian is also independent of M. The classical Hamiltonian for total angular momentum J is given in terms of the coordinates (r_1, r_2, Q_k, q_K) and conjugate momenta $(p_{r_1}, p_{r_2}, P_k, K)$ by

$$H(r_1, p_{r_1}, r_2, p_{r_2}, Q_k, P_k, q_K, K) = T^* + V_o(r_1, r_2) +$$

$$\sum_{k=1}^{3N-8} \frac{1}{2} (P_k^2 + w_k(r_1, r_2)^2 Q_k^2) , \tag{3.26}$$

with T^* given by Equations (3.18) - (3.24).

C. Modifications for a linear reference geometry

These equations must be modified for points on the reaction surface which correspond to linear geometries of the reacting system. If, for example, the distances A--B and B--C are chosen as the two reaction coordinate-like degrees of freedom, then the minimum geometry for an atom-diatom reaction

A + BC -------→ AB + C will often be linear. Watson[30] first solved this problem for ordinary molecules and Miller, Handy and Adams[2] gave the necessary modifications for the reacton path case. The kinetic energy in terms of the coordinates and velocities is obtained as before, the only difference being that there are now only two rotational degrees of freedom and 3N-7 normal coordinates of vibration instead of 3N-8,

$$2T = \sum_{ab} I^{*}_{ab} w_a w_b + \sum_{k=1}^{3N-7} P_k^{2} ,$$

where $\mathbf{w} = (w_x, w_y, w_z, \partial r_1/\partial t, \partial r_2/\partial t)$) and w_x, w_y and w_z are angular velocities. When the reaction surface configuration is linear, $I^{o}_{r_n a} = 0$ and it is possible to show that

$$\sum_{k,l} \left[\sum_{m} B^{a}_{l,m} B^{b}_{k,m} \right] Q_k Q_l = c_{a,b} - b_{a,c} (I^{o})^{-1}_{c,d} b_{d,b} ,$$

and hence that

$$I^{*} = I^{o} + 2\,b + b\,(I^{o})^{-1}b \qquad (3.27)$$

$$I^{*\,-1} = (I^{o} + b)^{-1}\,(I^{o})\,(I^{o} + b)^{-1}$$

by using sum rules like those derived by Amat and Henry[55,51]. For a linear configuration both $\mathbf{I}^{o}$ and $\mathbf{b}$ are singular,

$$I^{o}_{ab} = D\,\varepsilon_{ab} \qquad (a,b = x,y,z)$$

where

$$D = \sum_{i} (a_{zi})^{2}\, m_{i}$$

and

$$\varepsilon_{ab} = \sum_{c} e_{azc}\, e_{bzc} = \delta_{ab} - \delta_{az}\delta_{bz}$$

and the z axis is taken as the molecular axis (i.e., $a_{bi} = \delta_{bz}\, a_{zi}$). The b matrix elements are,

$$b_{ab} = \sum_k \varepsilon_{ab} \sum_i m_i^{\frac{1}{2}} a_{zi} L_{zi,k} Q_k = b_{ba} \qquad (a,b = x,y,z)$$

$$b_{r_1 z} = 0 = b_{z r_1}$$

$$b_{r_2,z} = 0 = b_{z,r_2}$$

$$b_{r_1 x} = \sum_{k=1}^{3N-7} \sum_{i=1}^{N} L_{iy,k} \; m_i^{\frac{1}{2}} \frac{\partial a_{iz}}{\partial r_1} Q_k$$

$$b_{r_2 x} = \sum_{k=1}^{3N-7} \sum_{i=1}^{N} L_{iy,k} \; m_i^{\frac{1}{2}} \frac{\partial a_{iz}}{\partial r_2} Q_k$$

$$b_{r_1 y} = -\sum_{k=1}^{3N-7} \sum_{i=1}^{N} m_i^{\frac{1}{2}} L_{xi,k} \frac{\partial a_{iz}}{\partial r_1} Q_k$$

$$b_{r_2 y} = -\sum_{k=1}^{3N-7} {}_{i=1}^{N} m_i^{\frac{1}{2}} L_{xi,k} \frac{\partial a_{iz}}{\partial r_2} Q_k$$

$$b_{r_1 r_2} = -\sum_{k=1}^{3N-7} \sum_{i=1}^{N} m_i^{\frac{1}{2}} \frac{\partial^2 a_{zi}}{\partial r_1 \partial r_2} L_{zi,k} Q_k$$

$$b_{r_1 r_1} = -\sum_{k=1}^{3N-7} \sum_{i=1}^{N} m_i^{\frac{1}{2}} \frac{\partial^2 a_{zi}}{\partial r_1^{\,2}} L_{zi,k} Q_k$$

$$= -\sum_{k=1}^{3N-7}\sum_{i=1}^{N} m_i^{1/2} \frac{\partial a_{zi}}{\partial r_1}\frac{\partial L_{zi,k}}{\partial r_1} Q_k$$

$$b_{r_2r_2} = -\sum_{k=1}^{3N-7}\sum_{i=1}^{N} m_i^{1/2} \frac{\partial^2 a_{zi}}{\partial r_2^{2}} L_{zi,k} Q_k$$

$$(3.28)$$

Proceeding as before one obtains the same sort of kinetic energy expression

$$2T = \sum_{k=1}^{3N-7} P_k^{2} + T^{*} \qquad (3.29)$$

where T^* is given by equation (3.18) and I^* is given by equation (3.27), but for the linear configuration, the matrices **b** and $\mathbf{I}^{0}$ are four by four matrices. The matrices are constructed by taking the matrix elements given above and eliminating the columns and rows corresponding to the z degree of freedom. The z components of the vectors **J** and π are also removed. The indices of the vectors and matrices are (x,y,r_1,r_2).

D. Quantum Mechanical Hamiltonian Operator

The quantum mechanical operator corresponding to the classical Hamiltonian of Eqn. (3.26) can be obtained by using the Podolsky transformation,[31,29] where r_1, r_2 and Q_k are replaced by multiplicative operators and p_{r_1}, p_{r_2} and P_k are replaced by the differential operators

$$p_{r_n} \rightarrow \frac{\hbar}{i}\frac{\partial}{\partial r_n} \qquad n=1,2$$

$$P_k \rightarrow \frac{\hbar}{i}\frac{\partial}{\partial Q_k} \qquad k=1,\ldots,3N-8 \quad .$$

J_x, J_y and J_z are operators which obey the usual commutation relations for body-fixed angular momenta. If the volume element is

$$dr_1 dr_2 dQ_1 dQ_2 \ldots, dQ_{3N-8}\, d\chi d\phi d\theta \sin\theta$$

then the Hamiltonian operator is given by

$$H = \sum_{k=1}^{3N-8} \frac{1}{2}\left[\mu^{\frac{1}{4}} P_k \mu^{-\frac{1}{2}} P_k \mu^{\frac{1}{4}} + w_k(r_1,r_2)^2 Q_k^{\,2}\right] +$$

$$V_o(r_1,r_2) \quad + \quad \frac{1}{2}\,\mu^{1/4}\,(\mathbf{J}-\boldsymbol{\pi})\,\mu^{-1/2}\,(I^*)^{-1}\,(\mathbf{J}-\boldsymbol{\pi})\,\mu^{1/4} \qquad (3.30)$$

where

$$\mu \;=\; \det((I^*)^{-1}) \quad .$$

E. Elementary Dynamical Approximations

Starting from equation (3.26) or (3.29) for the kinetic energy in terms of the reaction surface variables and their conjugate momenta, one can obtain a hierarchy of zeroth order Hamiltonians to be used for perturbative calculations by neglecting various couplings. As a first approximation, it is reasonable to neglect the dependence of I^* on the normal coordinates Q_k. Because we have removed the large amplitude motion from the vibrational part of the problem this approximation is not too severe. The Q_k's will always be very small, this would not have been the case if we had not treated the reaction surface degrees of freedom separately. If in addition to neglecting the dependence of I^* on the Q_k, the π_a are assumed to be negligible then the term T^* becomes

$$T^* = \frac{1}{2}\,\mathbf{J}(\mathbf{I}^o)\mathbf{J} + \frac{1}{2}\,\mathbf{p}_r(\mathbf{S}(r_1,r_2))^{-1}\;\mathbf{p}_r \;+\; 2\sum_{n=1}^{2} p_{r_n}\; e_{abc} \sum_i \frac{\partial a_{bi}}{\partial r_n}\, a_{ci}\, m_i\, J_a \quad ,$$

(3.31)

where $\mathbf{p}_r$ is a two dimensional vector of momenta conjugate to the reaction surface variables. The Hamiltonian then has the form

$$H(r_1,r_2,p_{r_1},p_{r_2},Q_k,P_k,q_K,K)=H_{12}(r_1,r_2,p_{r_1},p_{r_2}) +$$

$$+ \sum_{k=1}^{3N-8} \frac{1}{2} (P_k{}^2 + w_k(r_1,r_2)^2 \; Q_k{}^2) +$$

$$H_{rot}(q_K, K,r_1,r_2) + H_{coup} , \qquad (3.32)$$

where

$$H_{12}(\mathbf{r},\mathbf{p}_r) = \frac{1}{2} \mathbf{p}_r \; S(r_1,r_2)^{-1} \mathbf{p}_r + V_o(r_1,r_2)$$

$$H_{rot}(q_K,K,\mathbf{r}) = \frac{1}{2} \; J \; \mathbf{I}^o(r_1,r_2)^{-1} \; J$$

$$H_{coup} = 2 \sum_{n=1}^{2} p_{r_n} \; e_{abc} \sum_i \frac{\partial a_{bi}}{\partial r_n} \; a_{ci} \; m_i \; J_a .$$

H_{12} is the Hamiltonian for the two reaction surface degrees of freedom on the two dimensional potential energy surface $V_o(r_1,r_2)$, H_{rot} is the

Hamiltonian for a rigid (in general asymmetric) rotor of molecular geometry $a_{ib}(r_1,r_2)$. H_{coup} is coupling due to the angular momemtum of the reference configuration. If $\boldsymbol{\pi}$, **b** and c (the **Q** dependence of I^* is in **b** and c) are neglected, one finds that the Hamiltonian of the entire system is the sum of a Hamiltonian for two dimensional motion on the reaction surface, a Hamiltonian for vibration orthogonal to this surface, a Hamiltonian for rigid rotation and a term which depends on the angular momentum of the reaction surface in the molecule-fixed axis system.

The orientation of the molecule-fixed axes with respect to the molecular system can be chosen to minimize the coupling term in equation (3.31) or to diagonalize the moment of inertia tensor on the reaction surface, but it is not possible to both minimize the coupling and to diagonalize the moment of inertia tensor simultaneously.

If the frequencies $w_k(r_1,r_2)$ are sufficiently slowly varying functions of r_1 and r_2, it is reasonable to assume that the 3N-8 vibrational degrees of freedom behave adiabatically. To do this the variables (Q_k,P_k) are replaced by the action-angle variables,

$$Q_k = [(2n_k + 1)/w_k(r_1,r_2)]^{1/2} \sin q_k ,$$

$$P_k = [(2n_k + 1)w_k(r_1,r_2)]^{1/2} \cos q_k . \qquad (3.33)$$

If derivatives of the frequencies with respect to r_1 and r_2 are neglected, the Hamiltonian becomes

$$H = \frac{1}{2}\,\mathbf{p}_r S(\mathbf{r})^{-1}\,\mathbf{p}_r + V_n(r_1,r_2) + H_{rot} + H_{coup}\,, \tag{3.34}$$

where V_n is the vibrationally adiabatic effective potential

$$V_n(r_1,r_2) = V_o(r_1,r_2) + \sum_{k=1}^{3N-8} \hbar w_k(r_1,r_2)\,(n_k + \tfrac{1}{2})$$

If the orientation of the molecule-fixed axes with respect to the molecule is chosen so that at each point (r_1,r_2) on the reaction surface the moment of inertia tensor is diagonal, and if rotation is also adiabatic, then H_{rot} also becomes a potential energy-type term. If the reaction surface geometry $\mathbf{a}_i(r_1,r_2)$ is a symmetric top (or if the energy levels of an asymmetric top are approximated by using a symmetric top model in the usual way),[32] then

$$H_{rot} = E_{JK}(r_1,r_2) = \frac{1}{2}\left[A(\mathbf{r}) + B(\mathbf{r})\right]\left[J(J+1) - K^2\right] + C(\mathbf{r})\,K^2 \tag{3.35}$$

where $A(r_1,r_2)$, $B(r_1,r_2)$ and $C(r_1,r_2)$ are the three principal rotation constants for geometry $a_{ib}(r_1,r_2)$, and C is the most distinct of the three. With this approximation for the rotational energy levels (and if the reaction surface geometry is a symmetric top there is no additional approximation), the complete Hamiltonian is equal to the sum of a Hamiltonian for a two dimensional problem in an effective potential and a coupling term.

It is important to remember that despite the drastic approximations we have made (neglecting $\boldsymbol{\pi}$, $\mathbf{b}$ and $\mathbf{c}$ completely), the coupling between the two reaction surface degrees of freedom is fully retained. The approximations introduced above all involve the neglect of coupling between the large amplitude motion coordinates and the other degrees of freedom; there have been no approximations to the direct interactions between the two large amplitude degrees of freedom. Equations (3.31) - (3.35) provide a zeroth order picture for the dynamics which includes all of the coupling between the two chosen coordinates r_1 and r_2. Two degrees of freedom are treated exactly and the effects of other degrees of freedom and rotation are treated in an approximate manner.

Both the "reduced dimensionality transition state" model of Bowman and the bending corrected rotating linear model used recently by Walker and Hayes,[33] which use collinear $A + B\text{-}C \longrightarrow A\text{-}B + C$ reactive scattering calculations to approximate the 3D process, can be derived from the zeroth order approximation to the reaction surface Hamiltonian given above. For linear configurations the coupling due to the angular momentum of the reference configuration is absent, and so for $\mathbf{J} = \mathbf{0}$, the zeroth order approximation to the reaction surface Hamiltonian implies that one should carry out collinear reactive scattering calculations on the effective collinear potential energy surface,

$$V_o(r_1,r_2) \;+\; \hbar w_b(r_1,r_2) \quad ,$$

where $w_b(r_1,r_2)$ is the bending frequency at the general collinear geometry (r_1,r_2). Bowman has done this calculation, and the results are in excellent agreement with the accurate values of full 3D scattering calculations. It is encouraging to see that the results obtained when the adiabatic bending energy is allowed to vary with both r_1 and r_2 are much better than the results one gets if the bending energy is only allowed to vary along the reaction path. This is a simple test, but it demonstrates that the reaction surface model will give more accurate results than the reaction path model.

It is clear that by neglecting either the Q_k dependence of I^* or $\boldsymbol{\pi}_a$ instead of both, or that by neglecting only certain components of $\boldsymbol{\pi}$, **b** and **c** one could obtain a better approximation to the Hamiltonian.

In addition to neglecting completely the Q_k depenedence of I^* one could choose to neglect some of the terms of the retained components of the **b** and **c** matrices. Each component b_{ab} and c_{ab} is a sum over normal coordinates Q_k. Contributions from the more strongly coupled vibrational modes could be kept and the others discarded.

The effects of **b**, **c** and $\boldsymbol{\pi}$ could be included by using perturbation theory. Since the potential energy is described correctly only to second order in Q_k, it makes sense to include the coupling terms only to second order in the small amplitude variables Q_k and P_k. If H_{coup} is neglected the pertubative expansion for T^* is,

$$T^* = T^*_o + T^*_1 + T^*_2, \tag{3.36}$$

where

$$T_o^* = \frac{1}{2} \mathbf{J} (\mathbf{I}^o)^{-1} \mathbf{J} + \frac{1}{2} \mathbf{p}_r (S(r_1,r_2))^{-1} \mathbf{p}_r$$

$$T^*_1 = -\mathbf{J} (\mathbf{I}^o)^{-1} \mathbf{b} (\mathbf{I}^o)^{-1} \mathbf{J}$$

$$T^*_2 = -\mathbf{J} (\mathbf{I}^o)^{-1} \boldsymbol{\pi} + \frac{3}{2} \mathbf{J} (\mathbf{I}^o)^{-1} \mathbf{b} (\mathbf{I}^o)^{-1} \mathbf{J} \ . \tag{3.37}$$

The matrix **c** does not appear in these equations because if $H_{coup} = 0$, $I_{r_n a}{}^o = 0$ and I^* is given by equation (3.27). Rayleigh-Schrodinger perturbation theory or distorted wave scattering theory could be used to include the effects of the perturbation terms.

F. Conclusions

The principal goal of this chapter was to derive a Hamiltonian adapted to studying the dynamics of polyatomic systems with two strongly coupled non-harmonic degrees of freedom. This Hamiltonian is given in equation (3.26). The Hamiltonian has been derived in terms of the reaction surface variables (r_1,r_2,Q_k) (and their conjugate momenta) to facilitate approximation of the potential energy surface. The kinetic energy in terms of these coordinates is exact, the potential energy is approximated by an expansion about the reaction surface. Because two degrees of freedom are allowed to undergo arbitrary large amplitude motion, the reaction surface Hamiltonian model will be able to provide an accurate description of a much wider class of dynamical phenomena in polyatomic systems than is possible with a reaction path model. H atom transfer reactions between two heavy molecular fragments where the reaction path typically has regions of large curvature have motivated this work, but the approach is developed generally and should have many useful applications.

We have treated the large and small amplitude coordinates separately; the special coordinates r_1 and r_2 are removed from the vibrational part of the problem. Because the Hamiltonian has been derived in a manner that facilitates the separation of the reaction surface degrees of freedom from the small amplitude vibrations it is natural to devise dynamical treatments based on a "system-bath" notion. The "system" is the two large amplitude degrees of freedom and the "bath" the remaining harmonic modes. Treating the system accurately - whether one is looking for eigenvalues, or calculating reactive scattering S matrices - is tantamount to dealing with a collinear atom-diatom system, something that can be dealt with quite accurately and efficiently using a variety of existing methods. The bath degrees of freedom will be dealt with approximately and the simplest approximation has been given above. Basing the system-bath description on the reaction surface Hamiltonian is a major advance over earlier work of Miller and Schwartz[34] where the two dimensional system itself was treated via a reaction path approximation, i.e., a reaction path plus one harmonic mode orthogonal to it.

All dynamical phenomena that appear in collinear atom-diatom systems will be described correctly by the reaction surface Hamiltonian. For bound two dimensional systems, questions of regular or chaotic spectra and the general nature of highly vibrationally excited states have received considerable attention.[35] Collinear (two dimensional) atom-diatom reactions exhibit both Feshbach (energy transfer), and potential (tunneling) resonances.[36] Model two dimensional potentials have been extensively studied to determine the extent of mode specificity, i.e., is the unimolecular decay rate a function only of the total energy or do states with the same energy decay at different rates?[37] Because the reaction surface Hamiltonian describes the dynamics of two dimensional systems exactly it is well suited to describing these phenomena in polyatomic systems and to studying the effects of the other degrees of freedom.

Many chemical reactions involve only two important degrees of freedom, the length of the bond being broken and the length of the bond being formed. If these two important degrees of freedom are treated accurately, it should be possible to study a great variety of interesting chemical phenomena.

Chapter IV A New Large Amplitude Motion Internal Coordinate Hamiltonian and Application to Malonaldehyde

Malonaldehyde is small enough that usefully accurate ab initio calculations can be performed, but large enough that its chemical properties are interesting and representative of larger polyatomics. Malonaldehyde contains a ring closed by a hydrogen bond, and it has been shown that two equivalent unsymmetrical planar equilibrium configurations exist in the vapour phase (see equation (3.1))[38]. Malonaldehyde has been studied carefully both experimentally and theoretically by several groups and is emerging as a prototype for the intramolecular dynamics of polyatomic molecules.[38,39,40]

A one dimensional cut between the two wells (which correspond to the two equilibrium configurations) through the potential energy surface has the form of a simple double well potential. Using a one dimensional semiclassical expression it is a straightforward matter to deduce the apparent barrier height from the observed splitting. Spectroscopists studying systems with double well potentials often assume a one dimensional model and determine a barrier height from the splitting between the lowest two energy levels.[41] In a polyatomic molecule intramolecular proton tunneling is not, however, a simple process involving only the motion of the proton, but a multidimensional process; the molecular framework must adjust as the proton tunnels[42], and there is direct coupling between the proton motion and the molecule's other degrees of freedom. If coupling to other degrees of freedom significantly alters the splitting then using a one dimensional formula to calculate the barrier height from the observed splitting will not be a reliable procedure. In this paper we devise a method for studying the effect of the other degrees of freedom on the splitting and apply it to malonaldehyde. It is reasonable to expect that coupling to other degrees of freedom will reduce the tunneling splitting (because the molecular framework must adjust as the proton tunnels). This is observed by Graf et al.[43] who conclude that the coupling of the proton with the motion of the nuclear framework is important.

Many polyatomic systems can be analaysed efficiently and accurately by using the idea of a reaction path. One assumes that the potential energy surface is well described by a multidimensional harmonic valley about the reaction path. This works well when the dynamics is dominated by motion along the reaction path. The reaction path is usually chosen to be the path of steepest descent. If the curvature of the path is not too big, quantum numbers for the vibrations orthogonal to the path are approximately conserved during the course of a reaction or molecular rearrangement. If however there are two strongly coupled degrees of freedom (and the curvature is big), it is necessary to treat them both accurately and to expand the potential about a two dimensional surface (called the reaction surface) rather than expanding about a one dimensional path.[44] The frequencies of the vibrational modes orthogonal to the reaction surface depend on the values of the two reaction surface coordinates (which have been removed from the vibrational part of the problem). Two coordinates which undergo large amplitude motion are described correctly for arbitrarily large displacements and the remaining degrees of freedom are treated as small amplitude (i.e. harmonic) motion. In this way the part of the problem that requires an accurate solution is separated from the part which may safely be treated approximately.

It is well known that proton transfer reactions involve two strongly coupled degrees of freedom.[45] A reaction surface rather than a reaction path model must be used to describe the dynamics. In order to explain the distinctive features of the spectrum of hydrogen bonded systems it is necessary to include the coupling between the two degrees of freedom, and it is too strong to be treated as a weak perturbation. Linear hydrogen bonds (where it is assumed that the proton is tansferred along a straight line) can be treated successfully either by solving a two dimensional problem exactly[46] or by an adiabatic separation of motions.[45,47,48] Kato et al. have studied malonaldehyde using a reaction path model. They include only coupling between the reaction coordinate and the other degrees of freedom due to the variation of the frequencies of the orthogonal modes along the reaction path. They demonstrate that the frequency of the OH stretch changes by about 1000 cm^{-1} between the equilibrium geometry and the transition state. This implies that the direct coupling between the reaction coordinate (which at the malonaldehyde equilibrium geometry corresponds to the O-O stretch) and the O-H stretch, which they have neglected, is quite strong. There is much less variation in the values of the other frequencies which indicates that the coupling between the reaction coordinate and these modes is fairly small. Accurate results for malonaldehdye will only be obtained by including the strong coupling between the important degrees of freedom. Indeed Kato et al. point out that the vibrationally adiabatic approximation they use will fail if the curvature of the reaction coordinate is large, and this is exactly the case for malonaldehyde. Proton transfer in malonaldehdye involves the motion of a light particle between two heavy ones. If only the two oxygen atoms and the hydrogen atom were involved and if the proton transfer was a linear process then the situation would be analogous to a heavy-light-heavy atom diatom problem. It is well known that reaction path coordinates are not useful for solving this sort of problem because of the large curvature of the reaction coordinate. In this case the dynamics is not dominated by motion along the reaction path, and the most dynamically important region of the potential energy surface for the calculation of the tunneling splitting is not the neighbourhood of the transition state, but is some part of the surface deep in the corner between the two wells.

In this chapter the proton transfer in malonaldehyde is studied by using an internal coordinate version of the reaction surface Hamiltonian. The two most important degrees of freedom are treated exactly and the effects of the other internal coordinates are included perturbatively. In Section A the calculation of the reaction surface potential is described. The Hamiltonian for a system with two strongly coupled degrees of freedom which are allowed to undergo large amplitude motion is derived entirely in terms of internal coordinates in Section B. The Hamiltonian is quite general and should be useful for a variety of problems. Once the reaction surface potential and the configuration of the molecule or reacting system on the reaction surface are known the Hamiltonian can be constructed from Wilson's G matrix. The calculations are described and the results are presented in Section C.

A. Calculation of the Reaction Surface

The reaction surface is obtained by minimizing the potential energy surface of the system subject to the constraint of fixed vlaues of r_1 and r_2 (the lengths of the bond being broken and the bond being formed). The Hondo program developed by Michel Dupuis and coworkers was used to minimize the potential energy for pairs of values (r_1,r_2) over a two dimensional grid. The Born-Oppenheimer electronic energy and the values of 3N-6 internal coordinates (N is the number of atoms, which in this case is nine) which specify the configuration of the molecule on the reaction surface were determined for more than one hundred values of (r_1,r_2). Because the surface is symmetric about the line $r_1 = r_2$ we can obtain energies and geometries for points with $r_1 < r_2$ from energies and geometries at points with $r_1 > r_2$ by reflection. This gives us a total of more than two hundred points on the surface. The force constant matrix $\frac{\partial^2 V}{\partial d_t \partial d_c}$ where d_t and d_c are internal coordinate displacements from the reaction surface was calculated at sixteen points. The calculations were done at the SCF level with a minimum basis set. The equilibrium geometries and energies that we obtained are identical with earlier results done at this level of theory.[57] The barrier we obtain is about six kcal/mole larger than the best available theoretical estimate[49] (an MP4 calculation at equilibrium and transition state geometries optimized at the MP2 level of theory), and the equilibrium frequencies are about five per cent higher than the best theoretical frequencies (which are SCF frequencies with a double zeta plus polarization basis set). The tunneling splitting in malonaldehyde certainly depends sensitively on the potential energy surface. The minimum basis SCF calculation can not be expected to provide anything more than the basic shape of the reaction surface. Accordingly, we have scaled our reaction surface so that the geometries of malonaldehyde at the stationary points of the reaction surface coincide with the MP2 geometries calculated by Frisch, Scheiner, Schaefer and Binkley,[49] and so that the electronic energy at the stationary points is equal to the values they obtained.

B. The Hamiltonian

The standard methods used to calculate the vibrational energy levels of polyatomic molecules[29] will not work satisfactorily if two or more degrees of freedom are strongly coupled. If vibrational displacements are large and the potential is strongly anharmonic, perturbative schemes based on a zeroth order picture, which does not include accurately the large amplitude motions, will not give reliable results. Hougen, Bunker and Johns[25](HBJ) originally developed an approach which uses perturbation theory to treat the effects of small amplitude vibrations but treats the large amplitude motions accurately. In the standard treatment of rigid moleucles the vibrational displacements of the atomic nuclei are measured with respect to a rigid reference configuration of the nuclei. Following HBJ several problems with large amplitude motions have been treated by defining a non-rigid reference configuration of the nuclei which follows the large amplitude motions.[27,50,51,28,52] In this way most of the anharmonicity is removed from the vibrational part of the problem. The derivation of the HBJ Hamiltonian essentially follows from the definition of the coordinates. The Cartesian coordinates of the atoms in the molecule-fixed frame are given by

$$\mathbf{R}_i = \mathbf{a}_i(\rho) + \mathbf{d}_i$$

where the $a_i(\rho)$ represent the reference configuration from which small amplitude Cartesian displacement vectors are measured.

Rectilinear displacements from the equilibrium geometry are not well suited to the description of large amplitude motion; this motion must be taken care of specially via the introduction of a non-rigid reference configuration. As the potential energy of a molecule or a reacting system depends only on the relative positions of the atoms and is most simply expressed in internal coordinates, it also makes sense to measure displacements from the reference configuration in terms of internal coordinates. Rather than specifying the instantaneous configuration of a molecule by giving 3N Cartesian components of a reference configuration and 3N Cartesian components for the displacement from that configuration[25], we specify the configuration by giving the values of the large amplitude curvilinear coordinates, the values of the small amplitude internal coordinates as a functions of the values of the large amplitude coordinates and internal coordinate displacements from this position. Instead of

$\mathbf{R}_i = \mathbf{a}_i(r_1,r_2) + \mathbf{d}_i$ where all the vectors have 3N Cartesian components we have $q_i = r_i$ for the large amplitude coordinates i = 1,2 and $q_i = a_i(r) + d_i$ $i=1,.....3N-8$ for the small amplitude coordinates with $a_i(\mathbf{r})$ the value of internal coordinate q_i when the large amplitude coordinates have the values r. The large amplitude coordinates are true curvilinear coordinates (in malonaldehyde we have chosen the length of the bond being broken and the length of the bond being formed) and the small amplitude coordinates are linearized internal coordinates. It would be simple to rewrite the Hamiltonian derived below for n rather than two large amplitude coordinates. The potential energy of a molecule is better represented by a quadratic expansion in displacements of internal coordinates from the equilibrium configuration than by a quadratic expansion in Cartesian displacements from the equilibrium configuration. It should also be true that the 3N-6 dimensional potential energy surface for a system undergoing some sort of large amplitude motion will be better described by a quadratic expansion in internal coordinate displacements about the reference configuration than by a Cartesian expansion about the same reference configuration. We have chosen the large amplitude coordinates so that

$$V = V_o(r_1,r_2) + \frac{1}{2}\, \mathbf{d}\, \mathbf{F}(r_1,r_2)\, \mathbf{d}$$

where **d** is a vector of 3N-8 internal coordinate displacements and **F** is a 3N-8 by 3N-8 matrix whose elements depend on the values of the reaction surface degrees of freedom r_1, r_2. An expansion in terms of internal coordinates is intuitively more appealing because it is easier to think of the force constant for a stretch changing as one moves from reactants to products, than it is to follow the evolution of the elements of the Cartesian force constant matrix.

If the total angular momentum is equal to zero, then the kinetic energy is given by

$$T = \frac{1}{2}\,(\mathbf{p}_r,\mathbf{p}_q) \begin{bmatrix} \mathbf{g} & \mathbf{G}_1 \\ \mathbf{G}_1 & \mathbf{G}_b \end{bmatrix} \begin{bmatrix} \mathbf{p}_r \\ \mathbf{p}_q \end{bmatrix} ,$$

$$= \tfrac{1}{2}\left[\frac{\partial \mathbf{r}}{\partial t} , \frac{\partial \mathbf{q}}{\partial t} \right] \begin{pmatrix} \mathbf{g} & \mathbf{G}_1 \\ \mathbf{G}_1 & \mathbf{G}_b \end{pmatrix}^{-1} \begin{pmatrix} \frac{\partial \mathbf{r}}{\partial t} \\ \frac{\partial \mathbf{q}}{\partial t} \end{pmatrix} = \frac{1}{2} \left[\frac{\partial \mathbf{r}}{\partial t} , \frac{\partial \mathbf{q}}{\partial t} \right] \begin{pmatrix} \mathbf{z} & \mathbf{x} \\ \mathbf{x} & \mathbf{y} \end{pmatrix} \begin{pmatrix} \frac{\partial \mathbf{r}}{\partial t} \\ \frac{\partial \mathbf{q}}{\partial t} \end{pmatrix} . \tag{4.1}$$

$\mathbf{p}_r$ is a two dimensional vector of momenta conjugate to the two reaction surface degrees of freedom r_1, r_2; p_q is a 3N-8 dimensional vector of momenta conjugate to the 3N-8 small amplitude internal coordinates. The matrices $\mathbf{g}$, $\mathbf{G}_b$, $\mathbf{G}_1$ $\mathbf{x}$, $\mathbf{y}$, and $\mathbf{z}$ all depend on the coordinates $\mathbf{r}$, $\mathbf{q}$. From equation (4.1) it is easy to obtain an expression for the kinetic energy of a system where r_1, r_2 undergo arbitrarily large displacements, without ever referring to the Cartesian coordinates of the atoms. The $\mathbf{r}$ and $\mathbf{q}$ coordinates are treated differently. Displacement vectors d are defined according to

$$\mathbf{q} = \mathbf{a}(r_1,r_2) + \mathbf{d} \quad . \tag{4.2}$$

Each of these vectors is a 3N-8 dimensional vector. The components of $\mathbf{a}$ are the values of the 3N-8 small amplitude internal coordinates on the reaction surface and the components of $\mathbf{d}$ are internal coordinate displacements from the reaction surface.

Normal coordinates Q are defined by the transformation

$$\mathbf{d} = L(r_1,r_2) \cdot \mathbf{Q} \tag{4.3}$$

There are 3N-8 normal coordinates and they represent vibrational motion orthogonal to the reference configuration. The matrix L is composed of the eigenvectors of $\mathbf{y}^{-1}$ $\mathbf{F}_b$, where the matrix $\mathbf{F}_b$ is part of the internal coordinate force constant matrix which is partitioned in the same way that the G matrix is (see eqn (4.1)),

$$\mathbf{F} = \begin{pmatrix} \mathbf{f} & \mathbf{F}_1 \\ \mathbf{F}_1 & \mathbf{F}_b \end{pmatrix}, \qquad (4.4)$$

and the matrix **y** is the lower right hand block of $\mathbf{G}^{-1}$,

$$\mathbf{y}^{-1} = (\mathbf{G}_b - \mathbf{G}_1^t \, \mathbf{g}^{-1} \, \mathbf{G}_1) \qquad (4.5)$$

The coordinates Q are chosen so that when $\frac{\partial \mathbf{r}}{\partial t} = 0$ the kinetic energy will be diagonal in $\frac{\partial Q}{\partial t}$. In a standard GF matrix calculation one can eliminate some internal coordinates from the problem (i.e. treat them as rigid) by setting the corresponding velocities equal to zero. To consturct normal modes for motion orthogonal to the surface (i.e. motion with $\frac{\partial r_1}{\partial t} = 0$ and $\frac{\partial r_2}{\partial t} = 0$), one should put $\frac{\partial r_1}{\partial t} = \frac{\partial r_2}{\partial t} = 0$ in equation (4.1) to obtain the correct G matrix. Determining the normal coordinates which represent motion orthogonal to the reference configuration is somewhat tricky. In the last chapter we suggested projecting the reaction surface out of the Cartesian force constant matrix to obtain a matrix whose eigenvectors would represent vibrations orthogonal to the reaction surface. It is simpler to determine the eigenvectors as we have suggested here, by diagonalizing $\mathbf{y}^{-1}\ \mathbf{F}_b$. To do this one needs to know only the G matrix for the molecular system (which is readily obtained from the tables of Wilson, Decius and Cross)[29] and there is no need to project out anything. The normal coordinates we have defined here are linear combinations of internal coordinate displacements, if for some reason it was preferable to work in Cartesian coordinates, as we did in the last chapter, the Cartesian eigenvectors which represent motion orthogonal to the reaction surface could be obtained from the matrix **L** (see equation (4.11)).

If the reference configuration is chosen so that the small amplitude coordinates do not vary with the large amplitude motion coordinates as originally suggested by Hougen, Bunker and Johns then $\mathbf{G}_1 = \mathbf{0}$ and our prescription for obtaining the local normal mode coordinates reduces to that of HBJ. If $G_1 = \mathbf{0}$ then $\mathbf{y}^{-1} = G_b$ and $\mathbb{L}$ is obtained by diagonalizing $\mathbf{G}_b\mathbf{F}_b$. Our reaction surface is defined so that all the small amplitude coordinates have their equilibirum values for each pair (r_1,r_2). This means that G_1 is not zero and to define local normal modes for vibration orthogonal to the surface we must diagonalize $\mathbf{y}^{-1}\ \mathbf{F}_b$ and not $\mathbf{G}_b\mathbf{F}_b$.

In terms of the normal coordinates **Q** the potential energy is

$$V = V_o(r_1,r_2) + \sum_{k=1}^{3N-8} \frac{1}{2} w_k(r_1,r_2)^2 Q_k^{\ 2} \quad . \qquad (4.6)$$

To obtain the kinetic energy in terms of (r_1,r_2), Q_k, and their conjugate momenta one must transform equation (4.1). The relationship between the 3N-8 old coordinates q and the new coordinates Q is given by

$$\mathbf{q} = \mathbf{a}(r_1,r_2) + \sum_{l} L_l(r_1,r_2)\,\mathbf{Q}_l \qquad (4.7)$$

In terms of the old coordinates and momentum the kinetic energy is

$$T = \frac{1}{2}\,[\mathbf{p}_r,\ \mathbf{p}_q]\ G \begin{pmatrix} \mathbf{p}_r \\ \mathbf{p}_q \end{pmatrix} ,$$

and in terms of the new coordinates and momenta it is

$$T = \frac{1}{2}\ (\mathbf{p}_r,\mathbf{p}_Q)\ \left[(\Gamma^{-1})\ G\ (\Gamma^{-1})^t\right]\ \begin{matrix} \mathbf{p}_r \\ \mathbf{p}_Q \end{matrix} ,$$

where

$$\Gamma = \left(\begin{array}{cc|cccccc} 1 & 0 & 0 & 0 & 0 & 0 & 0\cdots\cdots\cdots 0 \\ 0 & 1 & 0 & 0 & 0 & 0 & 0\cdots\cdots\cdots 0 \\ \hline \mathbf{v}_1 & \mathbf{v}_2 & & & & L & & \end{array}\right),$$

$$\mathbf{v}_1 = \frac{\partial a}{\partial r_1} + \frac{\partial L}{\partial r_1}\cdot Q ,$$

$$\mathbf{v}_2 = \frac{\partial \mathbf{a}}{\partial r_2} + \frac{\partial \mathbf{L}}{\partial r_2} \cdot \mathbf{Q} \ . \qquad (4.8)$$

$\mathbf{v}_1$ and $\mathbf{v}_2$ are (3N-8) by 1 dimensional vectors. After doing the matrix multiplication one finds that .

$$T = \frac{1}{2} (\mathbf{p}_r, \mathbf{p}_Q) \left[\begin{array}{c|c} \mathbf{g} & \mathbf{g}\Gamma_1{}^t + G_1(L^{-1})^t \\ \hline \Gamma_1 \mathbf{g} + (L^{-1})^t \mathbf{G}_1{}^t & \begin{array}{l} \Gamma_1 \mathbf{g}\Gamma_1{}^t + \Gamma_1 \mathbf{G}_1 (L^{-1})^t + \\ (L^{-1})\mathbf{G}_1{}^t \Gamma_1{}^t + L^{-1} G_b (L^{-1})^t \end{array} \end{array} \right] \begin{array}{c} \mathbf{p}_r \\ \\ \mathbf{p}_Q \end{array}$$

where

$$\Gamma_1 = -\mathbb{L}^{-1} \cdot (\mathbf{v}_1 \mathbf{v}_2) \qquad (4.9)$$

$(\mathbf{v}_1\mathbf{v}_2)$ is a (3N-8) by 2 dimensional matrix composed of the two column vectors v_1 and v_2. The complete expression for the Hamiltonian in terms of the two special coordinates r_1 and r_2 and the 3N-8 small amplitude internal coordinates and their conjugate momenta is

$$H = T + V_o(r_1, r_2) + \frac{1}{2} \sum_{k=1}^{3N-8} w_k(\mathbf{r})^2 Q_k{}^2 \ . \qquad (4.10)$$

The Hamiltonian is derived completely in terms of internal coordinates without any reference to Cartesian coordinates. To construct the

Hamiltonian it is necessary only to know the G matrix for the molecule and the vector $\mathbf{a}(r_1,r_2)$ and $V_0(r_1,r_2)$. To construct an HBJ-type Hamiltonian in Cartesian coordinates one either needs to project the large amplitude motion coordinates out of the Cartesian force constant matrix[2,44], or to define the reference configuration so that only the large amplitude coordinates vary and to calculated **L** where

$$\mathbf{S} = \mathbf{L}\,\mathbf{Q}$$

(**S**, here is a vector of 3N-6 internal coordinates)
from the eigenvectors of **GF** and then to convert **L** to **l** where **l** is the matrix of eigenvectors of the Cartesian force constant matrix[27] via

$$\mathbf{l} = \mathbf{M}^{\frac{1}{2}}\,\mathbf{A}\;\;\mathbf{L} \qquad (4.11)$$

where **M** is a diagonal matrix of the atomic masses and **A** is the matrix which transforms 3N-6 internal coordinates to 3N Cartesian displacements[3]

$$\mathbf{d} = \mathbf{A}\,\mathbf{S}$$

To construct the Hamiltonian in equation (4.10) it is not necessary to define the large amplitude motion coordinates, as HBJ do, and to know **A**, nor is it necessary to project the large amplitude motion out of the Cartesian force constant matrix. HBJ also write out the Hamiltonian in terms of internal coordinates, but to do so they require the matrix **A** and the derivative of **A** with respect to the large amplitude coordinate, and even after converting to internal coordinates the reference configuration is still referred to a Cartesian axis system. The essential difference between our Hamiltonian and the standard one is that from the beginning we work in terms of internal coordinates, so that there are no traces of an original Cartesian coordinate system in our final result. To incorporate rotations, we would have to include Euler angles which determine the orientation of the molecule fixed Cartesian axis system with respect to the space fixed Cartesian axis system, but this is a different matter. The formula for the kinetic energy given in equation (4.9) does not depend on the choice of the reference configuration (or reaction surface). If we had chosen the reference configuration, as HBJ suggest, so that the small amplitude internal coordinates had constant values, then $\mathbf{G}_1$ and $\frac{\partial a}{\partial r_i}$ i=1,2 would be identically zero. This would simplify the form of the kinetic energy but introduce a linear term in the potential energy expansion.

The kinetic energy expression in equation (4.9) is exact for $\mathbf{J} = \mathbf{0}$. All applications of the reaction path Hamiltonian have been carried out for $\mathbf{J} = \mathbf{0}$ and Coriolis coupling terms like π_x, π_y, π_z in equation (3.18) and $b_{r_1,x}$, $b_{r_1,y}$, $b_{r_1,z}$ in equation (3.24) have always been neglected.[14] The Hamiltonian obtained in this chapter is exactly correct for $\mathbf{J} = \mathbf{0}$ -- no Coriolis-like couplings have been neglected.

The relationship between the internal coordinate large amplitude motion Hamiltonian derived in this chapter and the HBJ approach has been emphasized. It is also possible though, to view the development of this Hamiltonian as an extension of small amplitude internal coordinate methods.[2,57] Intramolecular vibrational energy transfer has been studied by several groups by expanding the potential to second order in internal coordinate displacements from the equilibrium configuration and expanding the (coordinate dependent) elements of Wilson's G matrix about the equilibrium configuration. The coordinate dependence of the G matrix elements couples the internal degrees of freedom, and the more complete the expansion of the G matrix elements is, the more accurately the coupling is treated. What we have done in this chapter is to include exactly the dependence of the G matrix on what we believe are the two most important degrees of freeom in the problem. The remaining coordinate dependence is treated by expanding the G matrix in essentially the standard way. Other workers have incorporated the coordinate dependence of the G matrix by expanding it about a point (the equilibrium configuration) we have expanded the G matrix about a two dimensional surface (the reaction surface) and thereby have included the functional dependence of the G matrix on the two reaction surface degrees of freedom accurately.

The exact Hamiltonian is of course too complicated to use in actual calculations, but it is now in a form in which it is amenable to realistic approximations. The $\mathbf{r}$ and $\mathbf{q}$ degrees of freedom are directly coupled by the G_1 matrix elements. They are also coupled by Γ_1 , this is coupling induced by motion along the reaction surface, it arises from the dependence of $\mathbf{a}$ and the local normal mode directions on r_1 and r_2. The most severe approximation would be to neglect G_1 and Γ_1 entirely. With this approximation

$$T = \frac{1}{2} (\mathbf{p}_r, \mathbf{p}_Q) \begin{bmatrix} \mathbf{g} & 0 \\ 0 & I \end{bmatrix} \begin{pmatrix} \mathbf{p}_r \\ \mathbf{p}_Q \end{pmatrix}, \qquad (4.12)$$

where I is a 3N-8 by 3N-8 identity matrix. Even if we drop both $\mathbf{\Gamma}_1$ and G_1 completely the strong coupling between the r_1 and r_2 degrees of freedom is still accounted for exactly because the zeroth order picture includes all coupling between r_1 and r_2. With $\mathbf{\Gamma}_1 = 0$ and $G_1 = 0$ the Hamiltonian is

$$H = \frac{1}{2} \mathbf{p}_r \mathbf{g} \mathbf{p}_r + V_o(r_1, r_2) + \sum_{k=1}^{3N-8} \left[\frac{P_k^2}{2} + \frac{1}{2} w_k(\mathbf{r})^2 Q_k^2 \right] . \qquad (4.13)$$

The frequencies of the orthogonal modes do not vary much with r_1 and r_2, therefore it is reasonable to assume that the orthogonal modes are adiabatic. With this additional assumption the Hamiltonian becomes

$$H = \frac{1}{2} \mathbf{p}_r \mathbf{g} \mathbf{p}_r + [V_o(\mathbf{r}) + (\mathbf{n} + \tfrac{1}{2}) \cdot \mathbf{w}(r_1, r_2) \hbar] . \qquad (4.14)$$

The Hamiltonian now depends on only two coordinates.

If $\mathbf{\Gamma}_1$ and G_1 are negelected in the off-diagonal blocks of the matrix in equation (4.9) but evaluated at $\mathbf{Q} = \mathbf{0}$ in the lower right hand corner of the matrix, then the Hamiltonian becomes

$$H = \frac{1}{2}\,\mathbf{p}_r\,\mathbf{g}\,\mathbf{p}_r + V_o(r_1,r_2) + \frac{1}{2}\,\mathbf{P}_Q\,\mathbf{A}\,\mathbf{P}_Q + \frac{1}{2}\,\mathbf{Q}\,\mathbf{\Lambda}\,\mathbf{Q} \ , \tag{4.15}$$

with $\Lambda_{i,j} = \delta_{i,j}\ w_i^{\ 2}(\mathbf{r})$ and

$$\mathbf{A} = \mathbf{\Gamma}_1^{\ o}\,\mathbf{g}\,(\mathbf{\Gamma}_1^{\ t})^o + \mathbf{\Gamma}_1^{\ o}\,\mathbf{G}_1^{\ o}\,(\mathrm{L}^{-1})^t +$$

$$(\mathrm{L}^{-1})\,\mathbf{G}_1^{\ o}\,(\mathbf{\Gamma}_1^{\ t})^o + \mathbf{L}^{-1}\,\mathbf{G}_b^{\ o}\,(\mathrm{L}^{-1})^t \ ,$$

where the o superscript means evaluated at $\mathbf{Q} = \mathbf{0}$. Remember that

$$\mathbf{L}^{-1}\,\mathbf{G}_b\,(\mathrm{L}^{-1})^t = \mathrm{L}^{-1}\,(\mathbf{y}^{-1} + \mathrm{G}_1\,\mathbf{g}^{-1}\,\mathrm{G}_1)\,(\mathrm{L}^{-1})^t \ ,$$

and therefore that

$$\mathbf{L}^{-1}\,\mathbf{G}_b^{\ o}\,(\mathrm{L}^{-1})^t = \mathbf{I} + \mathrm{L}^{-1}\,\mathrm{G}_1^{\ o}\,\mathbf{g}^{-1}\,\mathrm{G}_1^{\ o}\,(\mathrm{L}^{-1})^t \ .$$

If equation (4.15) is rewritten in terms of new coordinates $\mathbf{Z}$ given by

$\mathbf{X}^{-1}\ \mathbf{Q} = \mathbf{Z}$, where $\mathbf{X}$ is a matrix composed of the eigenvectors of $\mathbf{A}\ \mathbf{A}$, then (neglecting a small term introduced by the transformation, which is zero if the transverse motion is adiabatic) it becomes

$$H = \frac{1}{2}\ \mathbf{p}_r\ \mathbf{g}\ \mathbf{p}_r + V_o(r_1,r_2) + \frac{1}{2}\ \mathbf{P}_Z \cdot \mathbf{P}_Z + \frac{1}{2}\mathbf{Z} \cdot {}' \cdot Z \ , \tag{4.16}$$

where

$$\Lambda'_{ij} = \delta_{i,j}\ w_i'^{\,2} \qquad \text{and}$$

$w'^{\,2}_i$ are the eigenvalues of $\mathbf{A}\ \mathbf{A}$. This can be reduced to a two dimensional problem by assuming adiabaticity and one obtains

$$H = \frac{1}{2}\,\mathbf{p}_r\ \mathbf{g}\ \mathbf{p}_r + V_o(r_1,r_2) + (\mathbf{n} + \tfrac{1}{2}) \cdot \mathbf{w}'\ \hbar \tag{4.17}$$

If the $\mathbf{Q}$ motion is adiabatic and the additional coupling introduced (A-I) is small, then the Z motion should also be adiabatic and indeed the w_i' are also slowly varying functions of r_1 and r_2. Because there are only two degrees of freedom it is fairly easy to solve for the eigenvalues of the Hamiltonian in equation (4.17). A great deal of coupling has however been incorporated into the effective potential $V_o(r_1,r_2) + (\mathbf{n} + \tfrac{1}{2}) \cdot \mathbf{w}'\ \hbar$. The effects of G_1 and Γ_1 are partially included through the effective frequencies w'_i. Coupling introduced by the off-diagonal blocks in equation (4.9) and the **Q** dependence of Γ_1 and G_1 in the bottom right block can be included using perturbation theory.

C. Calculations and Results

A polynomial in r_1 and r_2 with fifteen terms which included terms of up to fourth order was fit to the reaction surface potential using the least squares method. This fit was scaled so that the geometry of malonaldehyde at the stationary points of the reaction surface coincided with the MP2 geometries calculated by Frisch, Scheiner, Schaefer and Binkley[49] and so that the electronic energy at those stationary points was equal to the MP4 values they obtained (at their MP2 geometries).

The 2 by 2 g matrix is given by

$$g = \begin{pmatrix} \frac{1}{m_H} + \frac{1}{m_O} & \frac{1}{m_H}\cos(\phi) \\ \frac{1}{m_H}\cos(\phi) & \frac{1}{m_H} + \frac{1}{m_O} \end{pmatrix}$$

where m_H is the mass of hdyrogen, m_O the mass of oxygen and ϕ is the angle between the bond lengths r_1 and r_2.[29]

We want to solve the two dimensional problem on the reaction surface exactly, so the full functional dependence of g must be retained. The angle ϕ is a function of the position on the reaction surface, $\phi = \phi(r_1,r_2)$. A polynomial in r_1 and r_2 with ten terms was fit to ϕ. The quantum mechanical energy levels of the two dimensional Hamiltonian

$$H = \frac{1}{2}\, \mathbf{p}_r \begin{bmatrix} \frac{1}{m_H} + \frac{1}{m_O} & \frac{1}{m_H}\cos(\phi) \\ \frac{1}{m_H}\cos(\phi) & \frac{1}{m_H} + \frac{1}{m_O} \end{bmatrix} \mathbf{p}_r + V_0(\mathbf{r})$$

were determined variationally.

Purely quantum mechanical terms in the Hamiltonian due to the fact that the determinate of **g** does not commute with $\mathbf{p}_r$ which are introduced when one transforms the classical Hamiltonian to a quantum mechanical Hamiltonian have been neglected. The exact quantum mechanical Hamiltonian is

$$H = \frac{1}{2}\, |\mathbf{g}(\mathbf{r})|^{1/4}\, \mathbf{p}_r\, |\mathbf{g}(\mathbf{r})|^{-1/2}\, \mathbf{g}(\mathbf{r})\, \mathbf{p}_r\, |\mathbf{g}(\mathbf{r})|^{1/4} + V_0(r_1,r_2) \quad , \tag{4.19}$$

where $|\mathbf{g}(\mathbf{r})|$ is the determinate of $\mathbf{g}(\mathbf{r})$. It is known that energy levels shift by only a small amount when the complete quantum mechanical Hamiltonian is used.[53] We are particularly interested in the splitting between the lowest two energy levels and it certainly seems reasonable to assume that the splitting is negligibly affected by the extra purely quantum mechanical terms.

We used products of harmonic oscillator basis functions centered in the interaction region to solve for the eigenvalues of the Hamiltonian in equation (4.18). To obtain convergence we used a basis set with 676 functions. Because the g matrix elements and the reaction surface potential are both written as polynomials in r_1 and r_2 the calculation of the Hamiltonian matrix elements can be done analytically.

The frequencies of the nineteen vibrational modes orthogonal to the reaction surface were computed at 16 points on the reaction surface by diagonalizing $\mathbf{y}^{-1}\,\mathbf{F}_b$. A fifteen term polynomial symmetric in r_1 and r_2 was fit to each of these frequencies. Frequencies which correspond to normal modes with different symmetries may cross, therefore one must fit the frequencies of each symmetry group separately. For each frequency the fit was then adjusted so that at the stationary points of the surface the frequency was equal to the best available theoretical frequency for malonaldehyde less 10%. The frequencies calculated by Frisch, Scheiner, Schaefer, and Binkley are done at the SCF level and SCF frequencies are typically about 10% too high. Assuming adiabaticity of the orthogonal degrees of freedom we then solved for the eigenvalues of

$$H = \frac{1}{2}\,\mathbf{p}_r\,\mathbf{g}(\mathbf{r})\,\mathbf{p}_r + \left[V_0(\mathbf{r}) + (\mathbf{n}=\mathbf{0} + \tfrac{1}{2})\,\hbar w(r_1,r_2)\right] . \tag{4.20}$$

$V_0(r_1,r_2) + \hbar w/2$ is an effective potential which includes approximately the contribution of the other modes.

As explained in the previous section the effect of additional coupling due to the dependence of **a** on **r** can be included by solving for the eigenvalues of

$$H = \frac{1}{2}\ \mathbf{p}_r\ \mathbf{g}\ \mathbf{p}_r + V_o(\mathbf{r}) + \frac{1}{2}\hbar\sum_{i=1}^{3N-8} w'_i \qquad (4.21)$$

To calculate the matrix **A** (which is required to compute the w'_i) as a function of **r** one needs to know $\mathbf{L}^{-1}$, $\partial\mathbf{a}/\partial r_1$, $\partial\mathbf{a}/\partial r_2$ and $\mathbf{G}_1{}^o$ as functions of r_1 and r_2. L^{-1} was determined at 16 points by diagonalizing $\mathbf{y}^{-1}\ \mathbf{F}_b$. $L^{-1}(r_2,r_1)$ was determined from $\mathbf{L}^{-1}(r_1,r_2)$ by symmetry, so that L^{-1} was known at a total of 32 points. A polynomial with ten terms was fit to each element of $\mathbf{L}^{-1}(r_1,r_2)$. The values of the internal coordinates on the reaction surface, **a** were fit with a fifteen term polynomial which was then differentiated to obtain $\frac{\partial\mathbf{a}}{\partial r_1}$ and $\frac{\partial\mathbf{a}}{\partial r_2}$. $\mathbf{G}_1{}^o$ was computed from the formulae of Wilson, Decius and Cross.[29] The frequencies $w'_i(r_1,r_2)$ obtained from diagonalizing ($\mathbf{A}\ \mathbf{A}$) were fit using the least squares method and the same polynomial form that was used to fit the frequencies $w_i(r_1,r_2)$.

The effects of the coupling of the off-diagonal block (in equation (4.9)) were included by first order perturbation theory. $\mathbf{G}_1$ is expanded to first order about the reaction surface

$$G_1 = G_1 \Big|_{\mathbf{Q}=\mathbf{0}} + \frac{\partial G_1}{\partial Q} \Big|_{\mathbf{Q}=\mathbf{0}} \cdot \mathbf{Q} \qquad (4.22)$$

The constant term $G_1 \big|_{\mathbf{Q}=\mathbf{0}}$ does not affect the energy levels to first order. The G matrix elements coupling r_1 and r_2 with the six torsions were neglected. The matrix $\mathbf{\Gamma}_1$ was calculated by fitting $\mathbf{L}$ and differentiating the fit. The first order correction to the lowest two energy levels is given by

$$\int d\mathbf{r}\, dZ\, \Phi_{n=\mathbf{0}}(Z;r)\, \chi_{m=1,2}(\mathbf{r})\, \mathbf{p}_r\, [\mathbf{g}\, \mathbf{\Gamma}_1^t +$$

$$G_1 (L^{-1})^t](\mathbf{X}^{-1})^t\, \mathbf{p}_Z\, \Phi_{n=\mathbf{0}}\, (Z;r)\, \chi_{m=1,2}(\mathbf{r}) +$$

$$\int d\mathbf{r}\, dZ\, \Phi_{n=\mathbf{0}}(Z;r) \chi_{m=1,2}(\mathbf{r})\, \mathbf{p}_Z\, (\mathbf{X}^{-1})\, [\mathbf{\Gamma}_1\, \mathbf{g} +$$

$$\mathbf{L}^{-1} G_1]\, \mathbf{p}_r\, \Phi_{n=\mathbf{0}}\, (Z;r)\, \chi_{m=1,2}(\mathbf{r}) \quad . \qquad (4.23)$$

where $\mathbf{X}$ is the transformation matrix in equation (4.16)

and

$$[\mathrm{p}_Z \cdot \mathrm{p}_Z /2 \;+\; \frac{1}{2}\,(\mathbf{Z} \cdot \boldsymbol{\Lambda}' \cdot \mathrm{Z})]\Phi_{\mathbf{n=0}} \;=\; (\mathbf{n{=}0} + \tfrac{1}{2})\,\hbar w'(\mathbf{r})\;\Phi_{\mathbf{n=0}}(\mathrm{Z};r) \quad ,$$

and

$$[\,\frac{1}{2}\,\mathbf{p}_r\;\mathbf{g}\;\mathbf{p}_r \;+\; V_o(r_1,r_2) \;+\; \sum_{i=1}^{3N-8} \frac{1}{2}\,\hbar w'_i(\mathbf{r})]\;\chi_{1,2}(\mathbf{r}) \;=\; E_{1,2}\chi_{1,2}(\mathbf{r})$$

$E_{1,2}$ are the two lowest eigenvalues of the two dimensional problem.

In addition to direct coupling between the **r** and **Q** degrees of freedom due to the off-diagonal blocks of the matrix in equation (4.9), there is non-adiabatic coupling. We have determined the eigenvalues of the Hamiltonian in equation (4.10) approximately by neglecting the off-diagonal coupling and evaluating the matrices $\boldsymbol{\Gamma}_1$ and $\mathbf{G}_1$ at $\mathbf{Q} = \mathbf{0}$, (to obtain equation (4.16)), assuming adiabaticiy of the Z coordinates, solving the two dimensional problem exactly and then including the off-diagonal coupling with first order perturbation theory. It was assumed that the eigenvalues of equation (4.16) were given by

$$E_{1,2} \;=\; \varepsilon_{1,2} \;+\; (\mathbf{n} + \tfrac{1}{2}) \cdot w'\,\hbar \quad ,$$

where $\varepsilon_{1,2}$ are the eigenvalues of

$$H_{RS} = \frac{1}{2} \mathbf{p}_r \mathbf{g} \mathbf{p}_r + V_o(r_1, r_2) \quad ,$$

and that the eigenfuctions of equation (4.16) were given by

$$\Psi_{1,2,\, n} = \chi_{1,2}(\mathbf{r}) \, \Phi_{\mathbf{n}}(Z;r)$$

These approximate eigenvalues and eigenfunctions will be accurate if the non-adiabatic coupling is small.

If **n** = **n**′ then all the non-adiabatic coupling elements which depend on the first derivative are equal to zero and therefore the energy levels are not shifted by non-adiabatic coupling to first order. The off diagonal non-adiabatic coupling elements ($n \neq n'$) will only be large if the frequencies of the orthogonal modes vary appreciably as a function of their position on the reaction surface; this is not the case so the adiabatic approximation is certainly a good one.

If the reaction surface potential is scaled to reproduce the most reliable theoretical calculations available for malonaldehdye[49] we find that the zeroth order splitting (calculated using the Hamiltonian in equation (4.20)) between the two lowest energy levels is 70.0 cm^{-1}. Including the coupling in **A** (by solving for the eigenvalues of the Hamiltonian in equation(4.21) decreases the splitting to 60.2 cm^{-1}. This is considerably bigger than the experimental result of Baughcum et al.[38(d)] of 21.583264 cm^{-1}. If the reaction surface potential is scaled so that the barrier height is 6.8 kcal/mole, i.e. 2.5 kcal higher than the value predicted by Frisch, Scheiner, Schaefer, and Binkley then we find that the zeroth order splitting drops to 21.6 cm^{-1}. Coupling decreases it slightly to 17.1 cm^{-1}. To first order the effect of the off-block perturbation is to increase the splitting about 1 cm^{-1}, for both the surface scaled to the barrier height of FSSB and for the surface with the barrier height of 6.8 kcal/mole (2.5 kcal/mole higher than the value predicted by FSSB). The perturbation theory results depend somewhat on the way $\mathbf{L}^{-1}$, $\frac{\partial a}{\partial r_1}$, $\frac{\partial a}{\partial r_2}$ and $\mathbf{G}_1$ are fit. The effect of the off-block perturbation on the splitting is 1 ± 1 cm^{-1}.

It should be emphasized that even the zeroth order result includes the strong coupling between the two most important degrees of freedom exactly. The effects of the other degrees of freedom are relatively small because the most important part of the problem has been solved accurately.

D. Conclusions

It appears that a barrier height of 6.8 kcal/mole gives a splitting close to that observed by Baughcum et al. This is quite close to the value they obtain by working backwards from their experimental results. The agreement of our results with the microwave spectra is encouraging, however, it should be noted that the potential energy surface we use is approximate. Although our scaling procedure undoubtedly produces a surface which is pretty good, the basic topology of the reaction surface potential is still determined by an SCF mimimum basis set calculation.

Allowing the molecular framework to adjust as the hydrogen atom tunnels (by including the other modes adiabatically (via equation (4.20)) decreases the tunneling splitting as expected. If the effect of the direct coupling in the off-diagonal block and in the matrix A is included in the calculation the tunneling splitting decreases slightly. Our calculations show that the dynamics of the hydrogen atom exchange in malonaldehyde is dominated by motion on the reaction surface. We believe that many chemical phenomena involve only two strongly coupled large amplitude degrees of freedom and that treating this strong coupling accurately will be sufficient.

We have derived a Hamiltonian which will be useful for studying the dynamics of polyatomic systems where two internal coordinates interact strongly. The Hamiltonian is entirely in terms of internal coordinates and their conjugate momenta, and can be constructed easily if the Wilson G matrix for the molecule is known. We believe that it is simpler to construct this Hamiltonian than other Hamiltonians which have been proposed for studying problems with large amplitude motions[25,27,28,50,51,28,52] and that it will facilitate the study of many interesting problems.

Chapter V Conclusion

In order to study the dynamics of polyatomic systems one must make approximations. Much effort has been expended in the development of exact quantum mechanical and semiclassical methods for treating simple systems and it is now time to begin applying approximate versions of these theories to more complicated processes.

In order to study the nuclear dynamics of a polyatomic system one must know the Born-Oppenheimer electronic energy. Determining the entire potential energy surface for a large system is virtually impossible and it does not seem likely that computers will be big enough and fast enough to do the job in the near future. Clearly then, one must approximate the potential energy surface and several useful approximations have been proposed in this thesis. For many chemical systems the potential energy surface is adequately represented by a multidimensional harmonic valley about the steepest descent path. With this approximation for the potential, the full Hamiltonian has been derived by Miller, Handy and Adams.[2] The vinylidene-acetylene rearrangement was studied with this approximate Hamiltonian in Chapter II. It is not hard to upgrade this approximation, so that the potential is approximated by a multidimensional expansion about a two dimensional surface, and this was done in Chapter III. In Chapter IV it was noted that an expansion about the two dimensional surface (the reaction surface) in terms of internal coördinates gives a better representation of the full potential than an expansion in Cartesian coordinates and proton transfer in malonaldehyde was studied using this approximation to the potential.

The results presented here show clearly that it is fruitful to apply reaction path and reaction surface models to the study of polyatomic molecules. The reaction surface Hamiltonian and the internal coordinate large amplitude motion Hamiltonian derived in chapter IV should enable chemists to study many interesting polyatomic systems without inordinate computational effort.

References

1 See for example, R.B. Bernstein, Ed., Atom-Molecule Collision Theory, Plenum Press, New York, 1979.

2 W. H. Miller, N. C. Handy, and J. E. Adams, J. Chem. Phys. **72**, 99 (1980).

3 See for example, E. L. Sibert, William P. Reinhardt, and J. T. Hynes J. Chem. Phys. **81**, 1115 (1984).

4 C. E. Dykstra and H. F. Schaefer, J. Am. Chem. Soc. **100**, 1278 (1978).

5 Y. Osamura, H. F. Schaefer, S. K. Gray, and W. H. Miller, J. Am. Chem. Soc. **103**, 1904 (1981).

6 R. Krishman, M. J. Frisch, J. A. Pople, and P. V. R. Schleyer, Chem. Phys. Lett. **79**, 408 (1981).

7 G. C. Goode and K. R. Jennings, Adv Mass. Spectrom. Ion Phys. **6**, 797 (1974).

8 W. Lineberger, D. L. Albritton, F. C. Fehsenfeld, and E. E. Ferguson, J. Chem. Phys. **63**, 3238 (1975).

9 P. Rosmus, P. Botschwina, and J. P. Maier, Chem Phys. Lett. **84**, 71 (1981).

10 S. M. Burnett, A. E. Stevens, C. S. Feigerle, and W. C. Lineberger, Chem. Phys. Lett. **100**, 124 (1983).

11 B. R. Brooks, W. D. Laidig, P. Saxe, J. D. Goddard, Y. Yamaguchi, and H. F. Schaefer, J. Chem. Phys. **72**, 4652 (1980).

12 G. Herzberg, Electronic Structure of Polyatomic Molecules, Van Nostrand, Princeton, 1967, p.611.

13 E. R. Davidson, The World of Quantum Chemistry, eidted by R. Daudel and B. pullman, Reidel, Dordrecht, 1974, pp 17-30.

14 For development and applications of the reaction path Hamiltonian see (a) S. K. Gray, W. H. Miller, Y. Yamaguchi, and H. F. Schaefer, J. Chem. Phys. **73**, 2733 (1980); (b) S. K. Gray, W. H. Miller, Y. Yamaguchi, and H. F. Schaefer, J. Am. Chem. Soc. **103**, 1900 (1981); (c) B. A. Waite, S. K. Gray, and W. H. Miller, J. Chem. Phys. **78**, 259 (1983); (d) W. H. Miller, J. Phys. Chem. **87**, 3811 (1983).

15 W. H. Miller, Advan. Chem. Phys. **30**, 77 (1975).

16 H. Feshbach, Ann. Phys. (N.Y.) **5**, 357 (1958); **19**, 287 (1962).

17 W. J. Lafferty and R. J. Thibault, J. Mol. Spectrosc. **14**, 79 (1964).

18 D. F. Heller, M. L. Elert, and W. M. Gelbart, J. Chem. Phys. **69**, 4061 (1978).

19 R. A. Marcus, J. Chem. Phys. **45**, 4493, 4500 (1966); **49**, 2610 (1968); G. L. Hofacker, Z. Naturforsch. Teil A **18**, 607 (1963).

20 (a) P. Russegger and J. Brickmann, J. Chem. Phys. **62**, 1086 (1979); **60**, 1 (1977); (b) M. V. Basilevsky, Chem. Phys. **24**, 81 (1977); (c) A. K. Fukui, Acc. Chem Res. **14**, 363 (1981); (d) A. Nauts and X. Chapuisat, Chem. Phys. Lett. **85**, 212 (1982); X. Chapuisat, A. Nauts, and G. Durrand, Chem. Phys. **56**, 91 (1981) (e) G. A. Natanson, Mol. Phys. **46**, 481 (1982).

21 R. T. Skodje, D. G. Truhlar and B. C. Garrett, J. Phys. Chem. **85**, 3019 (1981).

22 T. Carrington, Jr., L. M. Hubbard, H. F. Schaefer, and W. H. Miller, J. Chem. Phys. **80**, 4347 (1984).

23 See for example, C. C. Rankin and J. C. Light, J. Chem. Phys. **51**, 1701 (1969).

24 See for example, J. Manz and J Romelt, Chem. Phys. Lett. **81**, 179 (1981); J.A. Kaye and A. Kuppermann, J. Chem. Phys. **77**, 573 (1981); **78**, 546 (1981); V. K. Babamov and R. A. Marcus, J. Chem. Phys. **74**, 1790 (1981); C. Hiller, J. Manz, W. H. Miller and J. Romelt, J. Chem. Phys. **78**, 3850 (1983) and B. C. Garrett, D. G. Truhlar, A. F. Wagner, and T. H. Dunning, Jr., J. Chem. Phys. **78**, 4400 (1983).

25 J. T. Hougen, P. R. Bunker, and J. W. C. Johns, J. Mol. Spectrosc. **34** 136 (1970).

26 B. R. Brooks, W. E. Laidig, P. Saxe, J. D. Goddard, Y. Yamaguchi, and H. F. Schaefer, J. Chem. Phys. **72**, 4652 (1980); J. A. Pople, R. Krishnan, H. B. Schlegel, and J. S. Binkley, Int. J. Quantum Chem. Symp. **13**, 225 (1970); Y. Osamura, Y. Yamaguchi, P. Saxe, M. A. Vincent, J. F. Gaw, and H. F. Schaefer, Chem. Phys.**72**, 131 (1982); Y. Yamaguchi, Y. Osamura, G. Fitzgerald, H. F. Schaefer, J. Chem. Phys. **78**, 1607(1983); P. Pulay, J. Chem. Phys. **51**, 1701(1983).

27 D. C. Moule and Ch. V. S. Ramachandra Rao, J. Mol. Spectrosc. **45**, 120 (1973).

28 J. C. D. Brand and Ch. V. S. Ramachandra Rao, J. Mol. Spectrosc. **61**, 360 (1976); P. Russegger, Chem. Phys. **41**, 299 (1979); P. Russegger, Chem. Phys. Lett. **69**, 362 (1980).

29 E. B. Wilson, Jr., J. C. Decius and P. C. Cross, Molecular Vibrations, McGraw-Hill, New York, 1955.

30 J. K. G. Watson, Mol. Phys. **15**, 479 (1968).

31 B. Podolsky, Phys. Rev. **32**, 812 (1928).

32 See for example, C. H. Townes and A. L. Shawlow, Microwave Spectroscopy, McGraw-Hill, New York, 1955, pp 83-109.

33 J. M. Bowman, G. -Z. Ju, and K. T. Lee, J. Chem. Phys. **75**, 5199 (1981); R. B. Walker and E. F. Hayes J. Phys. Chem. **87**, 1255 (1983).

34 W. H. Miller and S. Schwartz, J. Chem. Phys. **77**, 2378 (1982); J. Chem. Phys. **79**, 3759 (1983).

35 See for example, D. W. Noid, M. L. Koszykowski, and R. A. Marcus, Annu. Rev. Phys. Chem. **32**, 267 (1981).

36 See for example, V. K. Babamov and A. Kuppermann, J. Chem Phys. **77**, 1891 (1982).

37 See for example, B. A. Waite, and W. H. Miller, J. Chem. Phys. **73**, 3713 (1980); B. A. Waite, and W. H. Miller, J. Chem. Phys. **74**, 3910 (1981).

38 (a) W. F. Rowe, R. W. Duerst, and E. B. Wilson, J. Am. Chem. Soc. **98**, 4021 (1976); (b) S. L. Baughcum, R. W. Duerst, W. F. Rowe, Z. Smith, and E. B. Wilson, J. Am. Chem. Soc. **103**, 6296 (1981); (c) Z. Smith, E. B. Wilson, and R. W. Duerst, Spectrochim. Acta Part A **39**, 1117 (1983); (d)S. L. Baughcum, Z Smith, E. B. Wilson, and R. W. Duerst, J. Am. Chem. Soc. **106**, 2260 (1984) (e) P. Turner, S. L. Baughcum, S. L. Coy, and Z Smith, J. Am. Chem. Soc. **106**, 2265 (1984).

39 J. Bicerano, H. F. Schaefer, and W. H. Miller, J. Am. Chem. Soc. **105**, 2550 (1983).

40 C. J. Seliskar and R. E. Hoffmann, J. Mol. Spectrosc. **96**, 146 (1982).

41 See for example, H.-H. Limbach and J. Hennig, J. Chem. Phys. **71**, 3120 (1979); Y. Tomioka, M. Ito, and N. Mikami, J. Phys. Chem. **87**, 4401 (1983).

42 A. Sarai, Chem. Phys. Lett. **83**, 50 (1981); J. Chem. Phys. **76**, 5554 (1982).

43 F. Graf, R. Meyer, T.-K. Ha, and R. R. Ernst, J. Chem. Phys. **75**, 2914 (1981).

44 T. Carrington, Jr., and W. H. Miller, J. Chem. Phys. **81**, 3942 (1984).

45 See for example, G. L. Hofacker, Y. Marechal, and M. A. Ratner, in The Hydrogen Bond - Recent Developments in Theory and Experiments, Eds. P. Schuster et al., North-Holland Publ. Co., Amsterdam 1976, p 299.

46 See for example, R. Janoschek, in The Hydrogen Bond - Recent Developments in Theory and Experiments, Eds. P. Schuster et al., North-Holland Publ. Co., Amsterdam 1976, p 167;

47 N. D. Sokolov and V. A. Save'ev, Chem. Phys. **22**, 383 (1977).

48 S. Kato, H. Kato, and K. Fukui, J. Am. Chem. Soc. **99**, 684 (1977).

49 M. J. Frisch, A. C. Scheiner, and H. F. Schaefer, J. Chem. Phys. **82**, 4194 (1985).

50 D. Papousek, J. M. R. Stone, and V. Spirko, J. Mol. Spectrosc. **48**, 17 (1973).

51 K. Sarka, J. Mol. Spectrosc. **38**, 545 (1971).

52 For a fine descriptive review see, P. R. Bunker, Ann. Phys. Chem. **34**, 59 (1983); for a detailed review see P. Jensen, Comp. Phys. Rep. **1**, 1 (1983).

53 J. K. G. Watson, Mol. Phys. **15**, 479 (1968).

54 W. H. Miller, J. Phys. Chem. **83**, 960 (1979).

55 G. Amat and L. Henry, Cah. Phys. **12**, 273 (1958).

56 W. J. Bouma, M. A. Vincent, and L. Radom, Int. J. Quantum Chem. **14**, 767 (1978).

57 J. S. Hutchinson, J. Chem. Phys. **82**, 22 (1985).

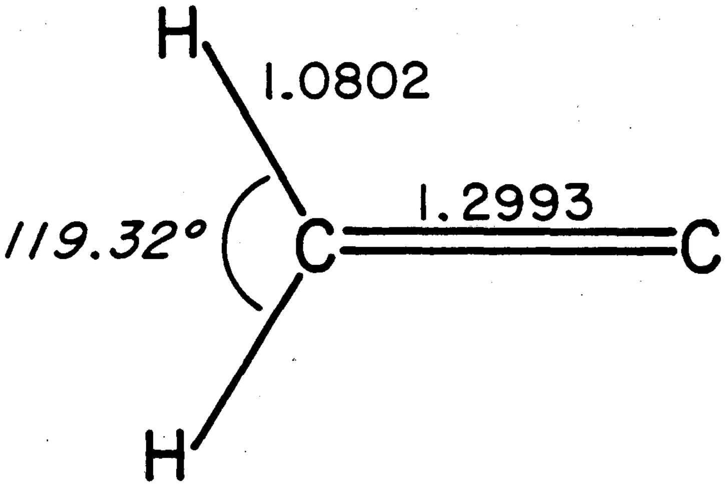
Table 1. Predicted Triple Zeta plus Polarization harmonic vibrational frequencies or vinylidene, acetylene and the transition state.

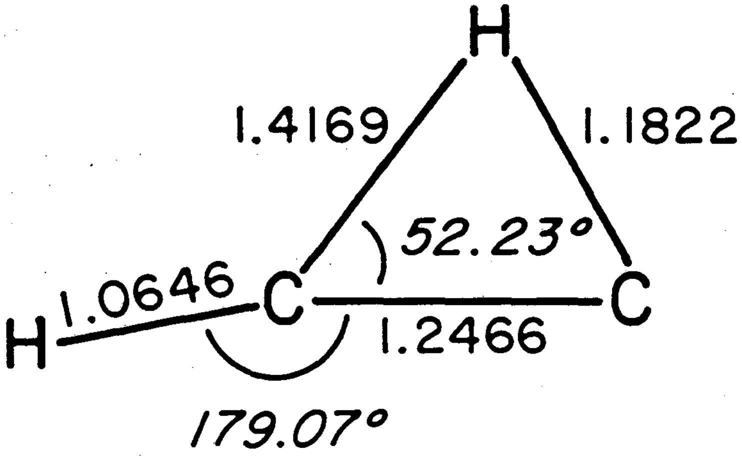
Species	Frequency cm^{-1}	Experiment	Normal-mode description
Vinylidene	3312		CH asym. str.
	3217		CH sym str.
	1719	1650 ∓ 120	CC stretch
	1289	1120 ∓ 100	CH$_2$ scissors
	800		out of plane
	422		CH$_2$ rock
Transition state	3469		CH stretch
	2673		CH stretch
	1898		CC stretch
	951		CCH bend
	607		out-of-plane
	1012i		reaction coordinate
Acetylene	3605	3373	CH asym. str.
	3492	3295	CH sym. str.
	2102	1974	CC stretch
	788	729	CCH bend
	654	612	CCH bend

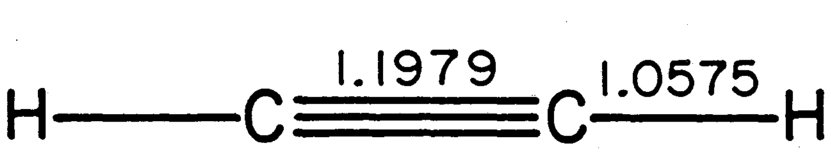
a Reference 12
b Reference 10

Table 2 Vinylidene lifetimes

Classical barrier height (kcal/mole)	Vinylidene State		Excitation energy (kcal/mole)	Lifetime (ps)	
	n_F	n_1		VA	SC
2	0	0	...	0.27	0.24
	0	1	3.5	0.12	0.12
3	0	0	...	3.2	0.76
	0	1	3.8	0.70	0.47
	1	0	1.8	0.21	0.18
4	0	0	...	4.7	4.6
	0	1	3.5	9.1	1.8
	1	0	1.1	1.3	0.31
	1	1	5.4	0.34	0.29







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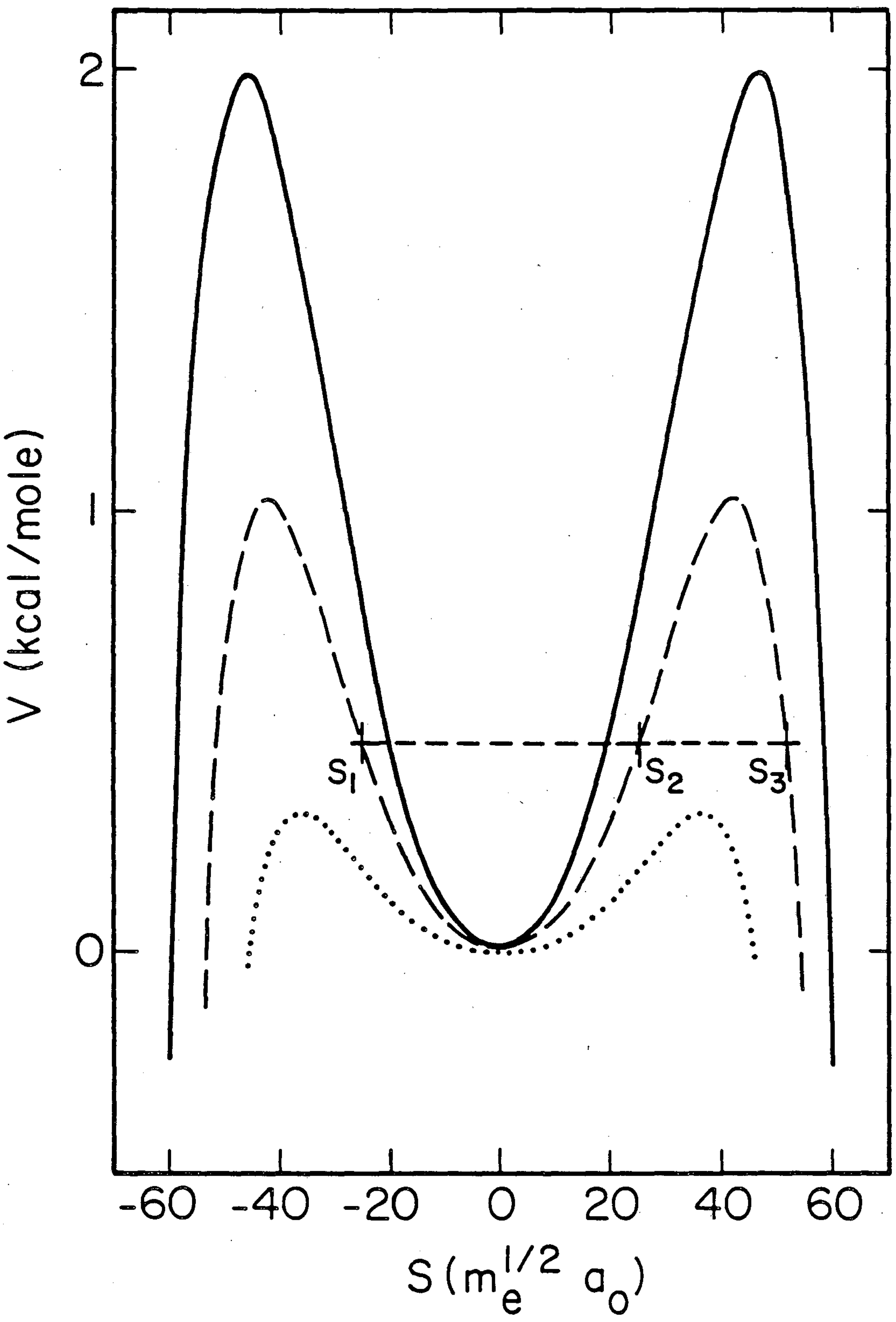

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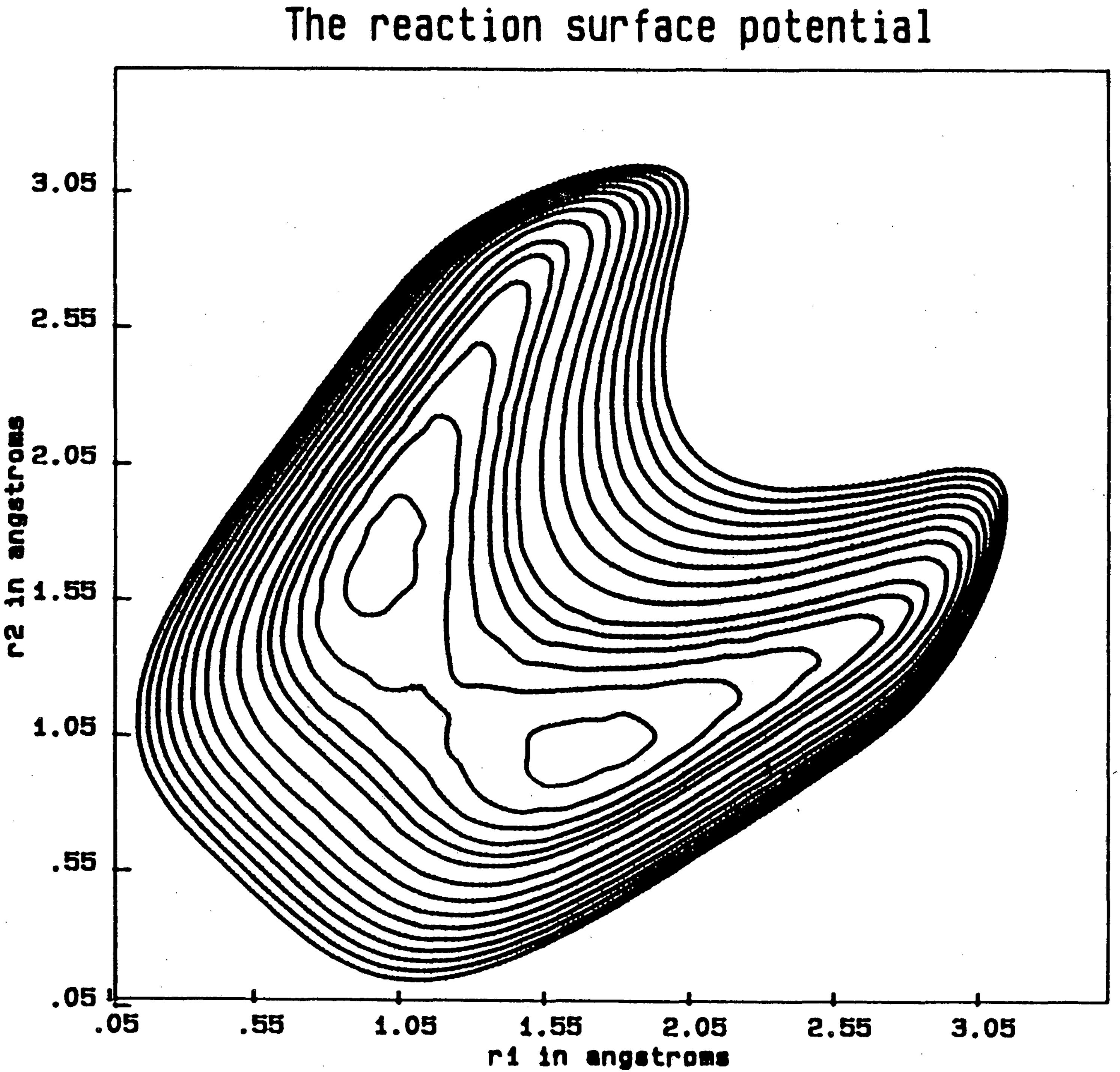
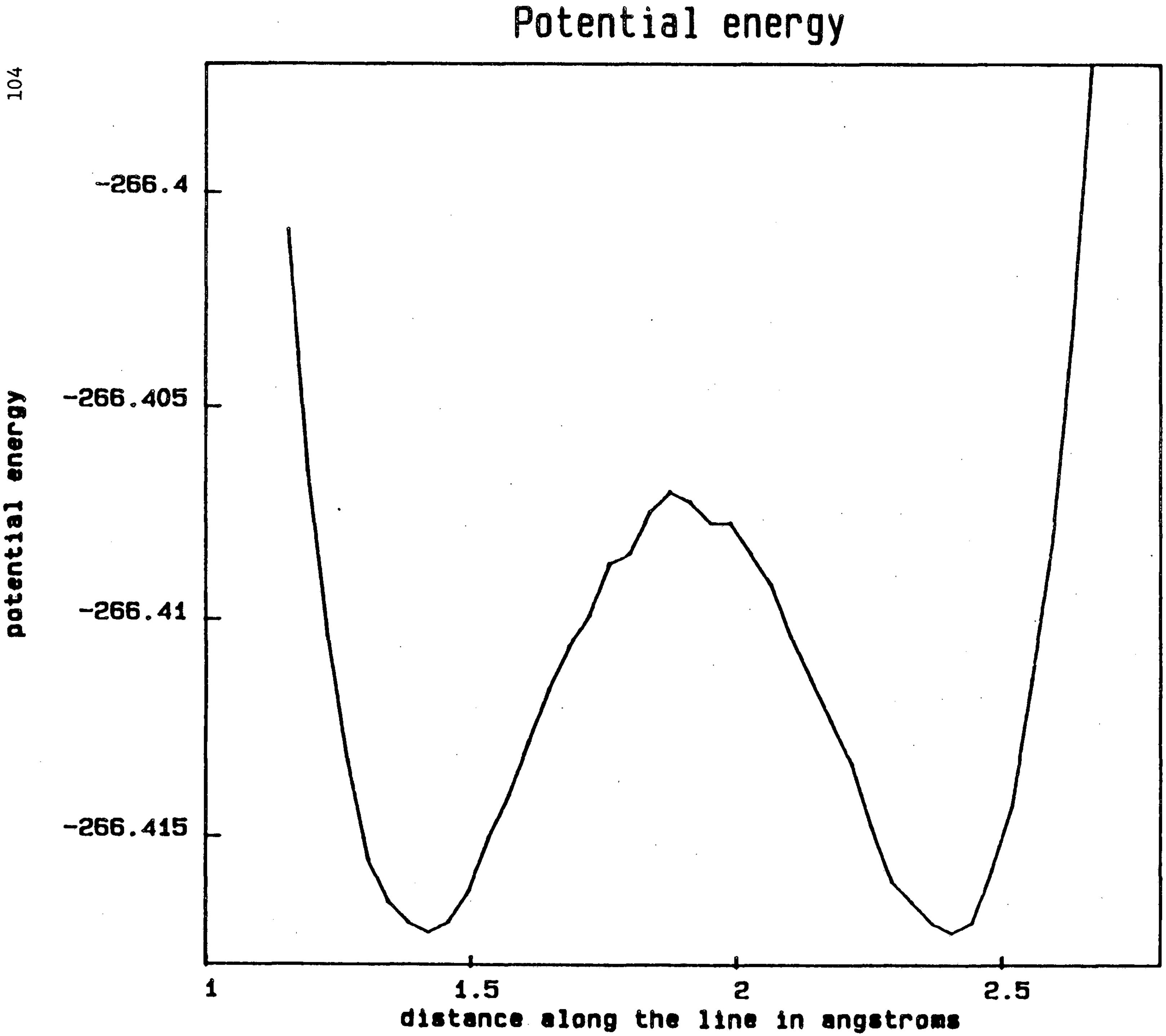

The reaction surface potential
3.05
2.55
2.05
1.55
1.05
.55
.05
.05
.55
1.05
1.55
2.05
2.55
3.05
r2 in angstroms
r1 in angstroms


Potential energy
potential energy
-266.4
-266.405
-266.41
-266.415
1
1.5
2
2.5
distance along the line in angstroms

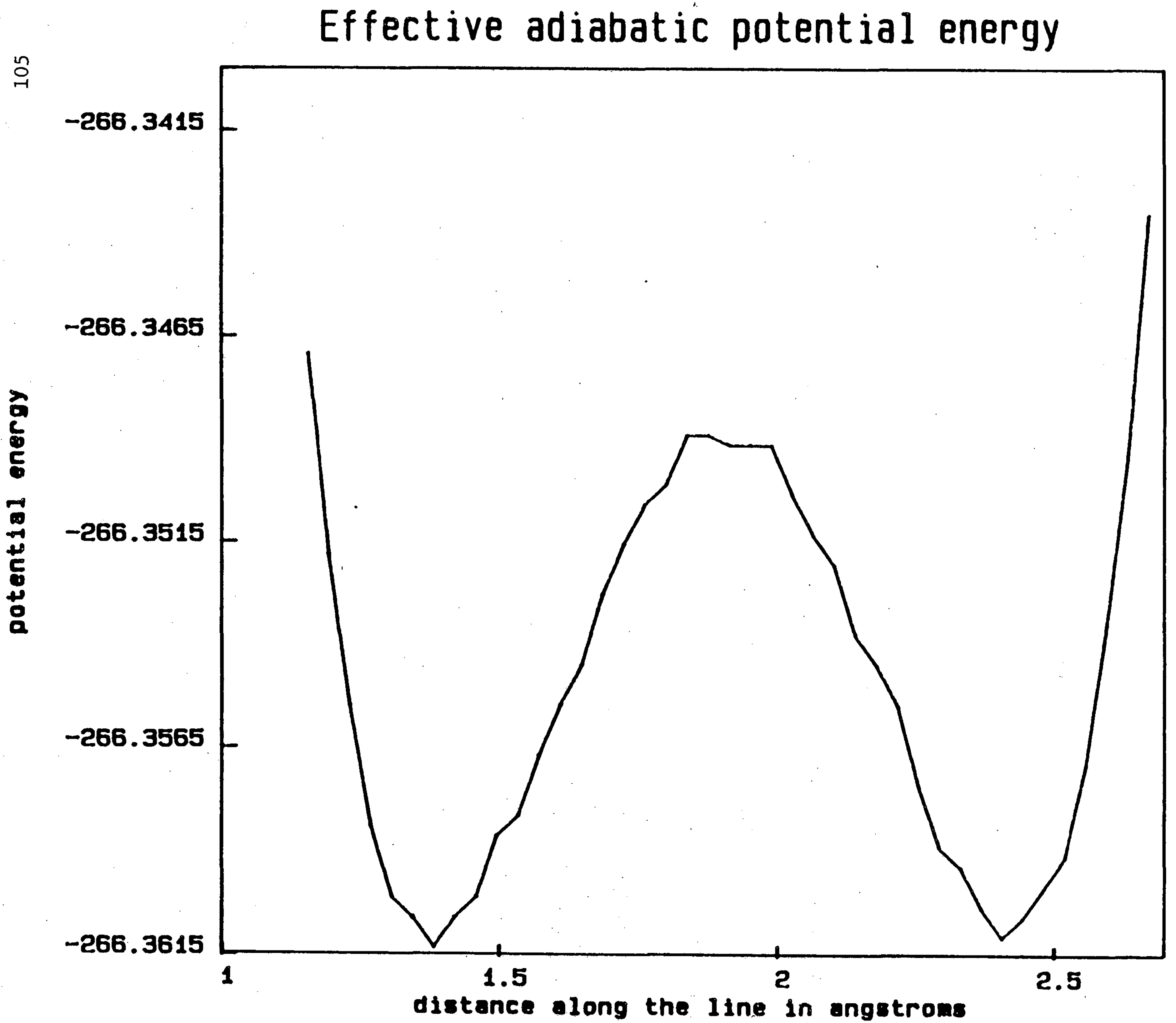

Effective adiabatic potential energy
potential energy
-266.3415
-266.3465
-266.3515
-266.3565
-266.3615
1
1.5
2
2.5
distance along the line in angstroms

Figure Captions

Figure 1. Triple zeta plus polarization configuration interaction geometries for vinylidene, acetylene, and the transition state. Distances are in Å .

Figure 2. The potential energy as a function of the reaction coordinate in the vicinity of vinylidene (s=0) and the two symmetrically equivalent planar transition states. The solid curve is the potential $V_0(s)$ (from equation (1.6)) for a barrier height of two kcal/mole, and the dashed curve is the vibrationally adiabatic potential (equation (1.9)) for the ground state n=0. The dotted curve is the vibrationally adiabatic potential with one vibrational quantum of excitation in the CH_2 scissors mode. The horizontal line indicates the ground vibrational state in the vibrationally adiabatic potential (n=0), and the classical turning points are indicated.

Figure 3. The reaction surface potential energy surface. The contours are -266.42,-266.415,-266.41,-266.405,-266.40,-266.395,-266.39,-266.38,-266.37,-266.37,-266.36,-266.35,-266.34,-266.33,-266.32,-266.31,-266.30.

Figure 4. A plot of the potential along a straight line between the two wells.

Figure 5. A plot of the effective adiabatic potential along a straight line between the two wells.

LAWRENCE BERKELEY LABORATORY
TECHNICAL INFORMATION DEPARTMENT
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720