

Conclusions

Poly(chlorotrifluoroethylene) is a suitable material for studying the IR spectra of hydrogen-bonded systems by the stretched-film method.

The results can be treated by assuming that the oriented gas model is valid. Carboxylic acids associate in a polymeric film in the same way as in the gas phase or in dilute solutions. Thus, the results can be compared with gas or solute values rather than with solid-state results.

Acknowledgment. We thank Mr. Lasse Kalervo, M.Sc. (Technical Research Centre of Finland), for performing measurements on the PE-983 spectrometer, and Mr. Leif Schauman, eng. (Bonsomer Oy, the Finnish representative of Allied Chemical), for generously providing samples of Aclar films.

Registry No. Poly(chlorotrifluoroethylene) (homopolymer), 9002-83-9; acetic acid, 64-19-7; benzoic acid, 65-85-0; acrylic acid, 79-10-7; propynoic acid, 471-25-0.

FEATURE ARTICLE

Reaction-Path Dynamics for Polyatomic Systems

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Recent advances in computational quantum chemistry are making it increasingly feasible to determine the minimum-energy paths for polyatomic reaction processes. (This is the steepest descent path, in mass-weighted Cartesian coordinates, through a transition state from reactants to products.) This paper reviews a methodology for basing a reaction *dynamics* on such a reaction path (plus harmonic fluctuations about it). Some of the applications of the approach are discussed, as well as its generalizations and extensions.

I. Introduction

Theoretical understanding of the dynamics of *simple* chemical reactions, i.e., the atom-diatom ($A + BC \rightarrow AB + C$) variety, has made enormous progress in the 20 or so years since molecular-beam experiments stimulated interest in such research. There now exist a variety of classical, semiclassical, and completely quantum-mechanical methodologies, of varying degrees of accuracy and applicability, for carrying out calculations of reaction cross sections, rate constants, product state distributions, and all other reaction attributes.¹ The need for the potential energy surfaces (i.e., the electronic energy in the Born-Oppenheimer approximation), which determine the motion of the atoms and thus the dynamics of the reactions, has also been one of the driving forces spurring recent developments in computational quantum chemistry.²

One would naturally like to extend these capabilities of dealing with the simplest chemical reaction to the realm of more complex reactions, i.e., those involving polyatomic molecules. In addition to the innate intellectual interest in doing so, there is the practical need caused by a literal avalanche of new molecular-beam and spectroscopic experiments that probe various microscopic features of polyatomic dynamics;³ these involve questions of laser-

induced, mode-specific chemistry, the nature of highly vibrationally excited polyatomic molecules, intramolecular vibrational energy redistribution, etc. The difficulty of dealing with the many degrees of freedom in a polyatomic system, however, is a formidable obstacle, not one of the least of these being the need to determine the potential energy surface of the system: if there are N atoms in the system, the potential surface depends on $3N - 6$ coordinates, so that determining it over a grid of points in the $3N - 6$ dimensional coordinate space would require calculation of the surface at the order of 10^{3N-6} points, a considerable number for $N > 3$.

One way to circumvent this dimensionality problem is to utilize the idea of a reaction path. This and the related notion of a reaction coordinate (the distance along the reaction path) are of course venerable ones in the theory of chemical reactions—they were central in the original development of transition-state theory—and they have also been useful in the description of simple atom-diatom reactions. In the 1960s, for example, some of the first quantum-mechanical reactive scattering calculations for collinear $A + BC \rightarrow AB + C$ reactions were carried out by using the "natural collision coordinates" introduced by Marcus⁵ and Hofacker.⁶ A number of other workers have

(1) See, for example: (a) R. B. Bernstein, Ed., "Atom-Molecule Collision Theory", Plenum Press, New York, 1979; (b) W. H. Miller, Ed., "Modern Theoretical Chemistry", Vols. I and II, Parts A and B, Plenum Press, New York, 1976.

(2) (a) D. G. Truhlar, Ed., "Potential Energy Surfaces and Dynamics Calculations", Plenum Press, New York, 1981; (b) H. F. Schaefer III, "The Electronic Structure of Atoms and Molecules", Addison-Wesley, Reading, MA, 1972.

(3) See, for example: (a) A. H. Zewail, Ed., "Advances in Laser Chemistry", Springer-Verlag, New York, 1978; (b) K. L. Kompa and S. D. Smith, Eds., "Laser-Induced Processes in Molecules", Springer-Verlag, New York, 1979.

(4) S. Glasstone, K. J. Laidler, and H. Eyring, "The Theory of Rate Processes", McGraw-Hill, New York, 1941.

(5) R. A. Marcus, *J. Chem. Phys.*, **45**, 4493, 4500 (1966); **49**, 2610 (1968).

(6) (a) G. L. Hofacker, *Z. Naturforsch. A*, **18**, 607 (1963); (b) S. F. Fischer, G. L. Hofacker, and R. Seiler, *J. Chem. Phys.*, **51**, 3941 (1969).

also contributed to various aspects of the reaction-path description of chemical reactions.⁷

The simplest definition of a reaction path is the minimum-energy path, called the "intrinsic reaction coordinate" by Fukui^{7d} and colleagues. This is the steepest descent path (in mass-weighted Cartesian coordinates⁸) from the transition state (i.e., the saddle point of the potential energy surface) down to products and back to reactants, and in practice one generates the minimum-energy path by first finding the transition state for the reaction and then following the gradient vector (the derivative of the potential energy surface, the Born–Oppenheimer electronic energy, with respect to mass-weighted Cartesian coordinates of the nuclei) forward and backward. This "gradient-following" algorithm is actually quite feasible even for sizable polyatomic systems because quantum chemistry methodology for computing gradients efficiently is becoming widespread.⁹ (There are some situations, however, for which it would be better to choose a reaction path which is not the minimum-energy path, but this will be discussed later.)

Determining the potential energy surface along a reaction path is an inherently one-dimensional problem (albeit one dimension along a space curve in the $3N - 6$ dimensional space), so that it avoids the overwhelming problem of trying to determine it in the full $3N - 6$ dimensional coordinate space. To determine the dynamics of the system, however, one needs more than just this information, the very least being an approximation to the potential energy surface in the vicinity of the reaction path. This is possible if one has the matrix of second derivatives of the potential energy surface, i.e., the force constant matrix, along the reaction path; one may diagonalize the force constant matrix, for example, at positions along the reaction path and thus determine local normal modes for motions in the $3N - 7$ dimensional space orthogonal to the reaction path. The approximation to the potential energy surface is thus that of a many-dimensional "harmonic valley" about the reaction path. Fortunately, computational quantum chemists are also making considerable progress in the analytic (i.e., nonfinite-difference) calculation of second derivatives of the potential energy surface,¹⁰ so that the possibility of such calculations is becoming feasible. In fact, one anticipates that these

quantum chemistry reaction-path calculations will become increasingly commonplace in coming years, and one of our goals has been to develop a framework for describing the dynamics of polyatomic systems based on this picture.

Motivated by these considerations, an explicit dynamical model, i.e., a reaction-path Hamiltonian, has been derived by Miller, Handy, and Adams.¹¹ This characterizes the dynamics as motion along the reaction path, plus harmonic deviations about it. It is essentially a polyatomic generalization of the natural collision coordinates for collinear $A + BC$ systems, and was obtained by adapting the "large amplitude motion" Hamiltonian developed by Hougen, Bunker, and Johns¹² to describe vibrational states of molecules with a "floppy" degree of freedom for which a harmonic treatment is not sufficiently accurate; for the reaction-path Hamiltonian this large amplitude motion coordinate is the reaction coordinate itself.

The reaction-path Hamiltonian thus provides a framework for at least beginning to deal with the dynamics of polyatomic reactions, and the purpose of this paper is to review what has been accomplished to date and to look ahead to what appears promising for future developments. Section II first describes the reaction-path Hamiltonian and the nature of the interactions that it incorporates. Various dynamical treatments based on it are described in section III, beginning with the very simplest approach (transition-state theory and variations) and proceeding to more dynamically based models, and finally describing an approach that can be as accurate as desired. Some of the applications that have been carried out to date are discussed in section IV, and section V discusses some of the possible future extensions and generalizations, as well as some of the limitations of a reaction-path approach.

II. Reaction-Path Hamiltonian

If (s, p_s) are the reaction coordinate (the mass-weighted distance along the reaction path) and its conjugate momentum, and (Q_k, P_k) , $k = 1, \dots, F - 1$ are the coordinates and momenta for normal-mode vibrations orthogonal to the reaction path ($F = 3N - 6$ are the number of degrees of freedom of the nonrotating N -atom system in its center of mass), then the classical version of the reaction-path Hamiltonian for total angular momentum $J = 0$ is given by^{11a}

$$H(p_s, s, \{P_k, Q_k\}) = \frac{1}{2} [p_s - \sum_{k,k'=1}^{F-1} Q_k P_k B_{k,k'}(s)]^2 / [1 + \sum_{k=1}^{F-1} Q_k B_{k,F}(s)]^2 + \sum_{k=1}^{F-1} [\frac{1}{2} P_k^2 + \frac{1}{2} \omega_k(s)^2 Q_k^2] + V_0(s) \quad (2.1)$$

Here $V_0(s)$ is the potential energy along the reaction path, as a function of the reaction coordinate, $\{\omega_k(s)\}$ are the local vibrational frequencies, and the coupling functions $\{B_{k,k'}(s)\}$ characterize the interaction between one vibrational mode and another, and between each vibrational mode and reaction coordinate (labeled as mode F).

The coupling functions are given explicitly by

(11) (a) W. H. Miller, N. C. Handy, and J. E. Adams, *J. Chem. Phys.*, **72**, 99 (1980); (b) other developments and applications of the reaction path Hamiltonian are in: W. H. Miller in "Potential Energy Surfaces and Dynamics Calculations", D. G. Truhlar, Ed., Plenum Press, New York, 1981, p. 265; (c) C. J. Cerjan, S.-h. Shi, and W. H. Miller, *J. Phys. Chem.*, **86**, 2244 (1982); (d) S. K. Gray, W. H. Miller, Y. Yamaguchi, and H. F. Schaefer, *J. Chem. Phys.*, **73**, 2733 (1980); (e) S. K. Gray, W. H. Miller, Y. Yamaguchi, and H. F. Schaefer, *J. Am. Chem. Soc.*, **103**, 1900 (1981); (f) Y. Osamura, H. F. Schaefer, S. K. Gray, and W. H. Miller, *ibid.*, **103**, 1904 (1981); (g) B. A. Waite, S. K. Gray, and W. H. Miller, *J. Chem. Phys.*, **78**, 259 (1983).

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

(7) (a) S. F. Fischer and M. A. Ratner, *J. Chem. Phys.*, **57**, 2769 (1972); (b) P. Russegger and J. Brickmann, *ibid.*, **62**, 1086 (1976); **60**, 1 (1977); (c) M. V. Basilevsky, *Chem. Phys.*, **24**, 81 (1977); **67**, 337 (1982); M. V. Basilevsky and A. G. Shamov, *ibid.*, **60**, 347 (1981); (d) K. Fukui, S. Kato, and H. Fujimoto, *J. Am. Chem. Soc.*, **97**, 1 (1975); K. Yamashita, T. Yamabe, and K. Fukui, *Chem. Phys. Lett.*, **84**, 123 (1981); K. Fukui, *Acc. Chem. Res.*, **14**, 363 (1981); (e) K. Ishida, K. Morokuma, and A. Komornicki, *J. Chem. Phys.*, **66**, 2153 (1977); (f) A. Nauts and X. Chapuisat, *Chem. Phys. Lett.*, **85**, 212 (1982); X. Chapuisat, A. Nauts, and G. Durand, *Chem. Phys.*, **56**, 91 (1981); (g) J. Pancir, *Collect. Czech. Chem. Commun.*, **40**, 1112 (1975); **42**, 16 (1977); (h) G. A. Natanson, *Mol. Phys.*, **46**, 481 (1982).

(8) If for some reason it is more convenient to use nuclear coordinates other than mass-weighted Cartesians, then the (unique) minimum-energy path can be defined as the "zero kinetic energy trajectory" that begins at the transition state. If the kinetic energy in terms of the coordinates $\{q_i\}$ is given by $\frac{1}{2} \sum_i \dot{q}_i G_{ij}(\mathbf{q}) \dot{q}_j$, then it is easy to show that this zero kinetic energy trajectory is determined by following the vector $-\mathbf{G}(\mathbf{q})^{-1} \partial V / \partial \mathbf{q}$ incrementally backward and forward from the transition state; see: (a) K. Fukui, *J. Phys. Chem.*, **74**, 4161 (1970); (b) H. F. Schaefer, *Chem. Br.*, **11**, 227 (1975).

(9) (a) P. Pulay in "Applications of Electronic Structure", H. F. Schaefer, Ed., Plenum Press, New York, 1977, p. 153; (b) J. W. McIver, Jr., and A. Komornicki, *J. Am. Chem. Soc.*, **94**, 2625 (1972); (c) B. R. Brooks, W. E. Laidig, P. Saxe, J. D. Goddard, Y. Yamaguchi, and H. F. Schaefer, *J. Chem. Phys.*, **72**, 4652 (1980).

(10) (a) J. A. Pople, R. Krishnan, H. B. Schlegel, and J. S. Binkley, *Int. J. Quantum Chem. Symp.*, **13**, 225 (1970); (b) 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); (c) P. Pulay, *ibid.*, **78**, 5043 (1983).

$$B_{k,k'}(s) = \mathbf{L}_k(s) \cdot (\partial \mathbf{L}_{k'}(s) / \partial s) \quad (2.2)$$

where $\mathbf{L}_k(s)$ are the eigenvalues of the projected force constant matrix. (The force constant matrix $K_{i,j}(s)$ itself

$$K_{i,j}(s) = \partial^2 V / \partial x_i \partial x_j \quad (2.3)$$

where $\{x_i\}$ are the mass-weighted Cartesian coordinates, must be modified, i.e., projected, to ensure that the normal-mode vectors $\mathbf{L}_k(s)$ are orthogonal to overall rotational eigenvectors and to the reaction path.) As has been discussed before,¹¹ the function coupling mode k to the reaction coordinate, $B_{k,F}(s)$, is the component of the reaction-path curvature in the direction \mathbf{L}_k ; the total curvature of the reaction path is given by

$$\kappa(s) = [\sum_{k=1}^{F-1} B_{k,F}(s)^2]^{1/2} \quad (2.4)$$

The coupling between one vibrational mode and another, $B_{k,k'}(s)$, is related to how much modes k and k' twist, or spiral, about the reaction path as s varies.

The reader may recognize the similarity of the reaction-path Hamiltonian to the Born-Oppenheimer representation of the Hamiltonian for electronic and nuclear degrees of freedom of, for example, a diatomic molecule; there are indeed many parallels. The reaction coordinate s corresponds to the nuclear coordinate R , and the vibrational modes $k = 1, \dots, F-1$ to the electronic degrees of freedom. The normal-mode eigenvectors $\mathbf{L}_k(s)$, which are eigenvectors of the force constant matrix for fixed s , are analogous to the Born-Oppenheimer electronic eigenfunctions $\psi_n(q_{el}; R)$, which are eigenfunctions of the electronic Hamiltonian for fixed nuclear coordinate R . The eigenvalues of the force constant matrix (for a given value of s), the square roots of which are the frequencies $\{\omega_k(s)\}$, are analogous to the Born-Oppenheimer electronic energies $\epsilon_n(R)$ for a fixed value of the nuclear coordinate R . The frequencies $\{\omega_k(s)\}$ obey a noncrossing rule—i.e., frequencies for modes of the same symmetry cannot cross as a function of s —analogous to the Born-Oppenheimer electronic potential energy curves $\{\epsilon_n(R)\}$. Finally, one recognizes the analogue of the coupling functions in eq 2.2 to the electronically nonadiabatic coupling elements

$$\langle \psi_n | \partial \psi_{n'} / \partial R \rangle \quad (2.5)$$

that lead to transitions between Born-Oppenheimer states n and n' .

Another analogy with the nuclear-electronic system that is useful to exploit is the notion of a diabatic representation.¹³ This is an electronic basis in which the fixed-nuclei electronic Hamiltonian is not diagonal, but for which the nonadiabatic coupling elements, expression 2.5, are small and perhaps negligible; transitions from one electronic state to another then result from the off-diagonal terms of the fixed-nuclei Hamiltonian. It has been shown that there also exists such a representation of the reaction-path Hamiltonian,^{11b} i.e., one for which there are no coupling elements between different vibrational modes, but for which the potential energy is nondiagonal in the coordinates $\{Q_k\}$: the Hamiltonian in this diabatic representation is the same as that given by eq 2.1 with the modifications

$$B_{k,k'}(s) = 0 \quad (2.6a)$$

for $k, k' = 1, \dots, F-1$, and

$$\frac{1}{2} \sum_{k=1}^{F-1} \omega_k(s)^2 Q_k Q_{k'} \rightarrow \frac{1}{2} \sum_{k,k'=1}^{F-1} Q_k \Lambda_{k,k'}(s) Q_{k'} \quad (2.6b)$$

The diabatic frequencies $\{\tilde{\omega}_k(s)\}$

$$\tilde{\omega}_k(s) \equiv [\Lambda_{k,k}(s)]^{1/2}$$

are allowed to cross—i.e., undergo a local Fermi resonance—with the interaction between them determined by the off-diagonal term in the potential energy, $\Lambda_{k,k'}(s)$. This is the analogue of diabatic potential energy curves than can cross.

Finally, in some cases it may be desirable to generalize the above methodology even further and choose a reaction path that is actually not the minimum-energy path. Fortunately, the Hougen, Bunker, Johns¹² approach deals equally well with this situation, and the form of the reaction-path Hamiltonian is changed only slightly from that in eq 2.1. Thus, suppose this more general reaction path is specified by giving $\mathbf{a}(s) \equiv \{a_i(s)\}$, $i = 1, \dots, 3N$, the (mass-weighted) Cartesian coordinates of the N nuclei as a function of the distance s along the path. (We assume that the path is chosen so that the vector $\mathbf{a}'(s)$, which points along it, is orthogonal to overall rotational and translational eigenvectors.) If $\{\mathbf{L}_k(s)\}$, $k = 1, \dots, 3N-7$, are any set of $3N-7$ mutually orthogonal vectors which are also orthogonal to $\mathbf{a}'(s) \equiv \mathbf{L}_F(s)$ (and to overall rotational and translational eigenvectors), then a calculation like that carried out before^{11a} gives the Hamiltonian of eq 2.1 with the potential energy there

$$V_0(s) + \sum_{k=1}^{F-1} \frac{1}{2} \omega_k(s)^2 Q_k^2 \quad (2.7a)$$

replaced by the following

$$V_0(s) + \sum_{k=1}^{F-1} Q_k f_k(s) + \frac{1}{2} \sum_{k,k'=1}^{F-1} Q_k \Lambda_{k,k'}(s) Q_{k'} \quad (2.7b)$$

$$f_k(s) = \sum_{i=1}^{3N} (\partial V / \partial x_i)_{\mathbf{x}=\mathbf{a}(s)} L_{i,k}(s) \equiv (\partial V / \partial \mathbf{x}) \cdot \mathbf{L}_k \quad (2.8a)$$

$$\Lambda_{k,k'}(s) = \sum_{i,i'=1}^{3N} L_{i,k}(s) \left(\frac{\partial^2 V}{\partial x_i \partial x_{i'}} \right)_{\mathbf{x}=\mathbf{a}(s)} L_{i',k'}(s) \equiv \mathbf{L}_k^\dagger \cdot \frac{\partial^2 V}{\partial \mathbf{x} \partial \mathbf{x}} \cdot \mathbf{L}_{k'} \quad (2.8b)$$

Along this more general reaction path, therefore, there is a linear term in the transverse vibrational coordinates $\{Q_k\}$; only for the minimum-energy path is $f_k(s) \equiv 0$. Equations 2.7 and 2.8 also involve a more general vibrational representation, i.e., one which has both nonzero coupling elements $B_{k,k'}(s)$ in the kinetic energy and nonzero off-diagonal elements $\Lambda_{k,k'}$ in the potential energy. (The adiabatic representation has $\Lambda_{k,k'}(s) \equiv 0$ for $k \neq k'$, and the completely diabatic representation has $B_{k,k'}(s) \equiv 0$ for $k \neq k'$.) The reason that one might wish to choose a reaction path other than the minimum-energy path and this more general vibrational representation is to minimize the net coupling between the various degrees of freedom. For example, if one expands the kinetic energy in eq 2.1 to lowest order in the couplings, the reaction-path Hamiltonian is given in this more general case by

$$H(p_s, s, \mathbf{P}, \mathbf{Q}) = \frac{1}{2} p_s^2 + V_0(s) + \sum_{k=1}^{F-1} (\frac{1}{2} P_k^2 + \frac{1}{2} \Lambda_{k,k}(s) Q_k^2) + [-p_s^2 \sum_{k=1}^{F-1} Q_k B_{k,F}(s) + \sum_{k=1}^{F-1} Q_k f_k(s)] + [-p_s \sum_{\substack{k,k'=1 \\ k \neq k'}}^{F-1} Q_k P_{k'} B_{k,k'}(s) + \sum_{\substack{k,k'=1 \\ k \neq k'}}^{F-1} \frac{1}{2} \Lambda_{k,k'}(s) Q_k Q_{k'}] \quad (2.9)$$

By choosing the reaction path appropriately one may try to minimize the coupling terms linear in $\{Q_k\}$, the first square bracket in eq 2.9; i.e., one would try to have the

(13) See, for example, F. T. Smith, *Phys. Rev.*, **179**, 111 (1969).

gradient term in the potential energy approximately cancel the centrifugal (i.e., curvature coupling) term in the kinetic energy. Similarly, one could try to choose a vibrational representation to minimize the second square bracket in eq 2.9, i.e., a representation in which the nonadiabatic coupling in the kinetic energy is approximately canceled by nondiagonal terms in the potential energy.

III. Dynamical Models

With a Hamiltonian one can begin to describe dynamics, and this section considers some of the dynamical models that have been based on the reaction-path Hamiltonian, beginning with the simplest approaches and proceeding to more rigorous ones.

A. *Transition-State Theory and Related Models.* The simplest dynamical models are statistical ones. The microcanonical flux, i.e., average flux for a given total energy, through a "dividing surface" that is perpendicular to the reaction path at distance s_0 along it, is given by

$$N(E, s_0) = \frac{2\pi\hbar}{(2\pi\hbar)^F} \int ds \int dp_s \int d\mathbf{P} \int d\mathbf{Q} \delta(E-H) \delta(s-s_0) \dot{s} h(\dot{s}) \quad (3.1)$$

where \dot{s} , the velocity along the reaction path, is given by Hamilton's equations

$$\dot{s} = \partial H / \partial p_s \quad (3.2)$$

the step function $h(\dot{s})$

$$h(\dot{s}) = \begin{cases} 1 & \dot{s} > 0 \\ 0 & \dot{s} < 0 \end{cases}$$

ensures that eq 3.1 is the "one-way flux" through the dividing surface. With the reaction-path Hamiltonian given by eq 2.1, it is a straightforward calculation to show that eq 3.1 and 3.2 give^{11b,14}

$$N(E, s) = [E - V_0(s)]^{F-1} / \{(F-1)! \prod_{k=1}^{F-1} \hbar \omega_k(s)\} \quad (3.3)$$

where s_0 has now been replaced simply by s . Remarkably, therefore, none of the coupling functions $B_{k,k'}(s)$ appear in the microcanonical flux; they have *not* been neglected in the calculation, they simply do not appear in the final result.

Transition-state theory corresponds to looking for the minimum (with respect to s) flux,¹⁵ the main bottleneck to the reactions; i.e.

$$N_{\text{TST}}(E) = \min_s N(E, s) \quad (3.4)$$

The thermal rate constant is given in terms of $N(E)$, the cumulative reaction probability—which is approximated in transition-state theory by the minimum of the microcanonical flux—by

$$\begin{aligned} k(T) &= (2\pi\hbar Q_0)^{-1} \int_0^\infty dE N(E) \exp(-E/kT) \\ &= \frac{kT}{h} \frac{1}{Q_0} \int_0^\infty dE N'(E) \exp(-E/kT) \end{aligned} \quad (3.5)$$

where Q_0 is the partition function (per unit volume) of reactants.

(14) As for most of the formulas given in this paper, eq 3.3 applies specifically to the case that total angular momentum $J = 0$. If rotation and vibration are assumed to be separable for purposes of "state counting", and if rotational energy is approximated as that of a symmetric top, then eq 3.3 is modified for $J > 0$ by replacing E by $E - \epsilon_{\text{rot}}(J, K)$ and summing the result over K from $-J$ to $+J$.

(15) For an excellent review, see P. Pechukas in "Modern Theoretical Chemistry", Vol. 2, Part B, W. H. Miller, Ed., Plenum Press, New York, 1970, p 285 et seq.

If there are several local minima of $N(E, s)$ as a function of s , then this corresponds to several "bottlenecks" of the reactive flux. If one assumes that microcanonical equilibrium is established locally in the regions between these bottlenecks—e.g., by existence of long-lived intermediates—then one can derive a "unified" statistical model.¹⁶ This model approximates the cumulative reaction probability as^{11b}

$$N(E) = \left[\sum_{k=1,3,\dots}^{2M+1} \frac{1}{N_k(E)} - \sum_{k=2,4,\dots}^{2M} \frac{1}{N_k(E)} \right]^{-1} \quad (3.6)$$

where for $k = 1, 3, 5, \dots, 2M+1$, $\{N_k(E)\}$, are the local minima of $N(E, s)$, and for $k = 2, 4, \dots, 2M$ they are the local maxima separating the local minima.

To apply these statistical theories one thus only needs the potential energy along the reaction path $V_0(s)$ and the frequencies $\{\omega_k(s)\}$ of the transverse modes. To locate the extrema of the flux $N(E, s)$ as a function of s one can show^{11b} that the equation

$$\partial N(E, s) / \partial s = 0 \quad (3.7)$$

is equivalent to the following one

$$E = \mathcal{V}(s) \quad (3.8a)$$

which involves the energy-independent function \mathcal{V}

$$\mathcal{V}(s) = V_0(s) - V_0'(s)(F-1) / \sum_{k=1}^{F-1} \frac{\omega_k(s)}{\omega_k(s)} \quad (3.8b)$$

To find the various extrema of the microcanonical flux one thus needs only to plot the function $\mathcal{V}(s)$ and look to see where it is equal to the energy E . This is a simple way to see how the reaction "mechanism" changes with energy. Typically, for example, at low energy E there is only one bottleneck, i.e., one minimum, in the flux, so that ordinary transition-state theory is a good approximation, while at higher energies there may be several minima. This latter situation is a herald, even within this statistical description, of more complex dynamics, i.e., "recrossing trajectories", which cause the breakdown of transition-state theory.¹⁵

B. *Symmetry-Adapted Transition-State Theory.* Statistical theories of the transition-state-theory variety are most often used to calculate thermal rate constants for bimolecular reactions, and for unimolecular reactions they are used in conjunction with some (usually simple) model for collisional excitation/deexcitation to determine the pressure dependence of the effective unimolecular rate constants.¹⁷ With the advent of laser-induced chemistry, however, there is increasing interest in applying them to more microscopic, state-specific dynamics.

With regard to such state-specific dynamics it has recently been emphasized¹⁸ that any symmetry a transition state possesses will lead to selection rules in the coupling between the various degrees of freedom. This is because the symmetry of the transition-state theory is conserved along the minimum-energy path.¹⁵ Thus, it is easy to see that the coupling functions given by eq 2.2 will be zero if modes k and k' belong to different irreducible representations of the symmetry of the transition state, and this leads to selection rules that are just what group theory mandates: states of different irreducible representations do not interact.

Thus, even if the dynamics of a reaction is sufficiently strongly coupled for a statistical approximation to be reasonable, if a state of a given symmetry is excited one

(16) W. H. Miller, *J. Chem. Phys.*, **65**, 2216 (1976).

(17) See, for example, P. J. Robinson and K. A. Holbrook, "Unimolecular Reactions", Wiley, New York, 1972.

(18) W. H. Miller, *J. Am. Chem. Soc.*, **105**, 216 (1983).

should apply a symmetry-adapted transition-state theory¹⁸ which makes the statistical approximation separately for each irreducible representation. (This requires a quantum version of transition-state theory, however; the classical expression in section IIIA is not able to include these symmetry effects.) This will be discussed more specifically with regard to the unimolecular dissociation of formaldehyde in section IV. The important point is that the relevant symmetry group for these dynamical selection rules is *not* that of reactants (e.g., C_{2v} for formaldehyde, H_2CO) or products, but rather that of the transition state (C_s symmetry for the formaldehyde dissociation, $H_2CO \rightarrow H_2 + CO$, for which the transition state is planar). It should also be emphasized that this is a different symmetry aspect of transition-state theory than the usual symmetry numbers, statistical factors, etc.,¹⁵ that have received considerable attention over the years.

C. Semiclassical Perturbation-Infinite Order Sudden Approximation. Going beyond statistical approximations to more dynamically based treatments opens the door to a wide variety of possibilities, from simple approximate models to more accurate treatments that are capable (with sufficient effort) of arbitrary accuracy. Here I note one particular simple approximate model that has been developed and applied to a variety of different dynamical phenomena, namely, the semiclassical perturbation-infinite order sudden (SCP-IOS) model.¹⁹

The SCP-IOS model is the semiclassical approximation of Miller and Smith²⁰ applied to the reaction-path Hamiltonian. It has the appealing feature that it behaves qualitatively correctly both in the adiabatic limit, which is the situation if the transverse vibrational motion is much faster than motion along the reaction coordinate, and also in the sudden limit, which is the case if reaction-coordinate motion is much faster than transverse vibrational motion. For the case of a collinear atom-diatom reaction it becomes the Hofacker-Levine model.²¹

To illustrate how simple it is to apply, e.g., the probability of the vibrational transition $(n_1, \dots, n_{F-1}) \rightarrow (n'_1, \dots, n'_{F-1})$ in the transverse vibrational modes during motion from s_1 to s_2 along the reaction path is given by

$$P_{n_2 \leftarrow n_1}(E) = \prod_{k=1}^{F-1} |J_{\Delta n_k}(\gamma_k)|^2 \quad (3.9a)$$

where $J_{\Delta n_k}$ is the regular Bessel function of order Δn_k , and the "collision integrals" γ_k are given by

$$\gamma_k = \left| \int_{s_1}^{s_2} ds B_{k,F}(s) \{2[E - V_n(s)]\}^{1/2} [(2n_k + 1)/\omega_k(s)]^{1/2} e^{i\delta_k(s)} \right|$$

with

$$V_n(s) = V_0(s) + \sum_{k=1}^{F-1} (n_k + \frac{1}{2})\omega_k(s)$$

$$\delta_k(s) = \int_{s_1}^s ds' \omega_k(s') / [2[E - V_n(s')]]^{1/2}$$

$$n = \frac{1}{2}(n_1 + n_2) \quad (3.9b)$$

The collision integral γ_k is a measure of how much vi-

brational excitation is induced in mode k during motion from s_1 to s_2 : the Bessel function $J_{\Delta n_k}(\gamma_k)^2$ has its maximum at $\Delta n_k \simeq \gamma_k$, so that γ_k is the most probable vibrational quantum number change. A typical application of this expression would be to predict the product state distribution of an exothermic chemical reaction: with $n_1 = 0$, $s_1 = 0$, and $s_2 = \infty$, eq 3.9 gives the distribution of product internal degrees of freedom. Clearly the modes with the larger coupling element $B_{k,F}$ will be the ones excited most during motion from the transition state ($s_1 = 0$) to products ($s_2 = \infty$). Conversely, $s_1 = \infty$ and $s_2 = 0$ and $n_2 = 0$ corresponds to the time-reversed situation. In this case the modes k for which γ_k is large are the most effective promoting modes for the reaction; i.e., vibrational energy initially in such a mode will be converted with high probability into energy along the reaction coordinate at the transition state.

The SCP-IOS approximation has also been used to describe the effects of the curvature coupling elements on tunneling probabilities in, for example, the unimolecular dissociation of formaldehyde,^{11d,g} and it has also been used to determine the degree of mode specificity in state-selected unimolecular decomposition.²² If there were no coupling between the various modes of the polyatomic system, then the unimolecular decomposition would clearly be mode specific: i.e., different initial states with essentially the same total energy would decay at different rates because they would have various amounts of energy in the reaction coordinate and there would be no energy transfer among the various degrees of freedom. Conversely, to the extent that coupling between the modes causes efficient energy transfer among them, one expects more statistical behavior, i.e., the rate of decomposition depending essentially only on the total energy of the initial state and not on the particular initial state that is prepared. The degree of mode specificity in the state-specific unimolecular decay rates is thus a sensitive measure of the intermode coupling and thus a direct test of the way that the SCP-IOS, or any other model, is able to describe this.

Finally, it should be noted that Kato and Morokuma²³ have also developed a model for reaction-path dynamics that is similar in spirit to the SCP-IOS, but different in various specifics.

D. System-Bath Decomposition. One can construct a useful dynamical treatment of the reaction-path Hamiltonian capable of essentially arbitrary accuracy by exploiting the fact that reactions are typically local phenomena. That is, one expects the reaction coordinate to be strongly coupled to only a few of the transverse vibrational modes and more weakly coupled to the (perhaps many) remaining ones. It is thus natural to divide the complete polyatomic molecular system into a "system", which is the reaction coordinate and the few modes strongly coupled to it, and a "bath", which is the remaining transverse vibrational modes. The dynamics of the "system" is then to be treated accurately: if one is treating a reactive scattering problem, for example, one might perform a straightforward coupled-channel scattering calculation, which is feasible for a few degrees of freedom; if one is determining state-specific unimolecular decay rates, then a direct basis-set diagonalization of the Hamiltonian for the "system" is feasible, again because it is a system of only a few degrees of freedom.

The effect of the "bath" degrees of freedom is then included approximately, e.g., perturbatively or statistically. For the case of reactive scattering, Miller and Schwartz²⁴

(19) W. H. Miller and S.-h. Shi, *J. Chem. Phys.*, **75**, 2258 (1981).

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(21) G. L. Hofacker and R. D. Levine, *Chem. Phys. Lett.*, **9**, 617 (1971).

(22) B. A. Waite and W. H. Miller, *J. Chem. Phys.*, **76**, 2412 (1982).

(23) S. Kato and K. Morokuma, *J. Chem. Phys.*, **73**, 3900 (1980).

have developed the perturbative approach to including the "bath" and tested the approach by applying it to the three-dimensional version of the $\text{H} + \text{H}_2$ reaction. Here the "system" consists of the two collinear modes, and the two bending modes constitute the "bath". Accurate treatment of the "system" is equivalent to a collinear reactive scattering calculation, which they carried out, and then the coupling with the "bath" was included perturbatively. The results were quite good, so that one has some confidence in the approach in applying it to more interesting examples.

Another way of including the effect of the "bath" on the "system" dynamics exploits the fact that the "bath" consists of a set of uncoupled harmonic oscillators. Within classical mechanics, for example, the equations of motion for the "bath" degrees of freedom can be solved for in terms of the (unknown) trajectories of the "system", so that one obtains finally an equation of motion involving only the "system" trajectory. This equation of motion has the form of a generalized Langevin equation;^{11b} i.e., the "system" dynamics experiences frictional and random forces that are a result of coupling to the "bath". If the "system" consists of only two degrees of freedom, for example, then the overall description is that of a collinear reaction with friction. The analogy of the description to reactions in a condensed medium is obvious, and one expects that much of the methodology currently under development for describing reactions in solution²⁵ may be able to be borrowed, and vice versa.

The quantum-mechanical version of the generalized Langevin approach can be developed by using a Feynman path integral to describe the dynamics of the complete system. The "bath" degrees of freedom, being harmonic oscillators, can be immediately path integrated, and one obtains a reduced path integral involving only the "system" variables.²⁶ Work along these lines is being pursued.

IV. Applications

Several different research groups are pursuing applications based on a reaction-path description of polyatomic dynamics. Morokuma and colleagues^{7e} and Fukui et al.^{7d} have for quite a few years generated minimum-energy reaction paths (the "intrinsic reaction coordinate") and used these for qualitative discussions of reaction mechanisms. More recently they have utilized the reaction-path Hamiltonian to provide a more dynamical description; e.g., by calculating the frequencies $\{\omega_k(s)\}$ along the reaction path they see which ones vary significantly with s and thus are presumably strongly coupled to the reaction coordinate and exchange energy with it. (It would be more informative, of course, also to determine the coupling functions $B_{k,F}(s)$ and then compute the collision integrals γ_k of section IIIC, but this requires somewhat more computation.) Yamabe and Yamashita²⁷ have also recently carried out a number of calculations of this type.

Truhlar and colleagues²⁸ have also utilized the reaction-path Hamiltonian in some versions of their transition-state-theory calculations of bimolecular rate constants. They have based some of the ways that they include

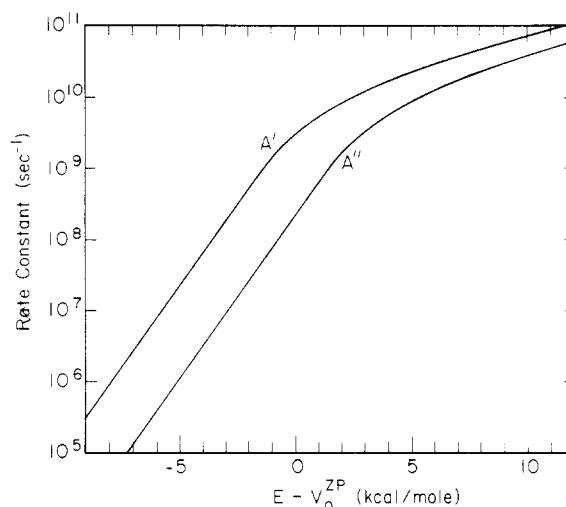


Figure 1. Symmetry-adapted microcanonical unimolecular decay rate for $\text{H}_2\text{CO} \rightarrow \text{H}_2 + \text{CO}$ on its ground-state potential energy surface, for $J = 0$. A' (A'') states are those even (odd) in the out-of-plane vibrational mode. E is the excitation energy in H_2CO , and V_0^{zp} the zero-point-energy-adjusted barrier height.

tunneling effects on it; they have also included (diagonal) anharmonicities in the transverse vibrational modes.

Below I discuss some of the applications that have been made and are in progress at Berkeley.

A. Tunneling in Unimolecular Reactions. The original motivation for Miller, Handy, and Adams' paper^{11a} was the desire to treat the unimolecular dissociation of formaldehyde



on its ground-state potential energy surface. Earlier transition-state-theory calculations²⁹ had suggested that tunneling plays an important role in the energy region of the origin of the $S_0 \rightarrow S_1$ photochemical excitation,³⁰ but these calculations neglected any coupling of the reaction coordinate to other degrees of freedom. Neglect of this coupling in the collinear $\text{H} + \text{H}_2$ reaction—the standard test case for tunneling in reactions—is known to give results wrong by 1–2 orders of magnitude, so it was not clear at all how meaningful these tunneling rates were for reaction 4.1.

A complete reaction-path calculation was thus carried out,^{11g} determining the frequencies $\{\omega_k(s)\}$ and all the coupling functions $\{B_{k,k}(s)\}$ which fully characterize the reaction-path Hamiltonian. Effects of these couplings on the microcanonical unimolecular rate constants were included within the SCP-IO approximation, and rather fortunately their effects on the rate constant were less than a factor of 2, so that it is believed that this approximation treatment is sufficient. (A similar treatment of tunneling in the $\text{H} + \text{H}_2$ reaction^{11c} brings the error from a factor of 10–100 down to within a factor of 2.)

The unimolecular dissociation of formaldehyde is also interesting because it should exhibit the symmetry-induced mode specificity discussed in section IIIB. Because the transition state, and therefore the entire reaction path for reaction 4.1, is planar, there is no coupling between A' and A'' states, i.e., those that are even and odd, respectively, on reflection in the plane. In this case this means simply that even and odd vibrational states of the out-of-plane vibrational mode are not coupled for total angular momentum $J = 0$. Thus, even if the dynamics is as strongly

(24) (a) W. H. Miller and S. Schwartz, *J. Chem. Phys.*, **77**, 2378 (1982); (b) S. Schwartz and W. H. Miller, *ibid.*, in press.

(25) See, for example, a review of this work in D. G. Truhlar, W. L. Hase, and J. T. Hynes, *J. Phys. Chem.*, **87**, 2664 (1983).

(26) R. P. Feynman and A. R. Hibbs, "Quantum Mechanics and Path Integrals", McGraw-Hill, New York, 1965, pp 68–73.

(27) K. Yamashita and T. Yamabe, *Int. J. Quantum Chem. Symp.*, in press; K. Yamashita, Ph.D. Thesis, Kyoto University, Kyoto, Japan, 1981.

(28) See, for example: (a) D. G. Truhlar and B. C. Garrett, *Acc. Chem. Res.*, **13**, 440 (1980); (b) A. D. Isaacson and D. G. Truhlar, *J. Chem. Phys.*, **76**, 1380 (1982).

(29) W. H. Miller, *J. Am. Chem. Soc.*, **101**, 6810 (1979).

(30) For a review of formaldehyde photochemistry, see C. B. Moore and J. C. Wiesshaar, *Annu. Rev. Phys. Chem.*, in press.

coupled as it can be—e.g., the classical trajectories of the system are “chaotic”—if a state of A' or A'' symmetry is initially excited, one should employ a symmetry-adapted statistical theory that involves only A' or A'' states.

Figure 1 shows such a symmetry-adapted microcanonical transition-state-theory calculation¹⁸ for the unimolecular dissociation of formaldehyde, and one sees that the degree of symmetry-induced mode specificity is quite pronounced (a factor of ~ 20) in the energy region below the classical threshold. (The origin of the $S_0 \rightarrow S_1$ photochemical excitation is an energy ~ 1 – 3 kcal/mol below the classical threshold, i.e., -1 to -3 kcal/mol on the energy scale in Figure 1). These results are for total angular momentum $J = 0$, for which the effect is most pronounced. Coriolis interactions mix rotation and vibration for $J > 0$ and will tend to diminish the effect, but not completely destroy it. A statistical (i.e., strong coupling) approximation to the rotation–vibration mixing predicts a³¹ factor of ~ 2 between the A' and A'' rate constants for $J > 0$.

B. Mode Specificity. Another interesting problem in polyatomic dynamics is the question of mode specificity. For the formaldehyde dissociation, reaction 4.1, for example, the question is whether the unimolecular decay rate depends on which particular metastable state of H_2CO is excited—i.e., one that has most of the energy in a C–H stretch, in a C–O stretch, or in the out-of-plane bend, etc.—or only on the total energy of excitation. The most recent calculations^{11g} suggest that at least for $J = 0$ the out-of-plane mode behaves mode specifically (in addition to the degree dictated by symmetry), i.e., that states which have most of their excitation in the out-of-plane mode dissociate more slowly than other states with essentially the same total energy.

Another interesting reaction for which the question of mode specificity arises is the unimolecular isomerization of vinylidene



Although the acetylene ($HC\equiv CH$) geometry is ~ 40 kcal/mol lower in energy than that of vinylidene, the latter is a local minimum on the potential energy surface.^{11f} The most recent quantum chemistry calculations³² give a barrier of ~ 2 – 4 kcal/mol for the vinylidene rearrangement; Figure 2 shows the potential energy vs. reaction coordinate in the vicinity of the vinylidene local minimum: the solid line is the bare potential $V_0(s)$, the dashed line is the vibrationally adiabatic potential for the ground state (i.e., including the zero-point vibrational energy of all the transverse modes), and the horizontal line indicates the lowest (and only) bound vibrational state in the vibrationally adiabatic potential.

Figure 2 is drawn for a “bare” barrier of 2 kcal/mol, the lower limit of the estimated value, and in this case the lifetime (with respect to tunneling to acetylene) is computed to be 0.2 ps, which corresponds to about three vibrational periods of motion in the potential well. This lifetime corresponds to an uncertainty principle spectral line width of ~ 23 cm^{-1} , which would preclude rotational structure, but certainly not vibrational structure. For a bare barrier height of 3 and 4 kcal/mol the lifetime increases to 2 and 30 ps, respectively.

The above lifetimes, however, all neglect coupling between the reaction coordinate and the other (transverse vibrational) modes of the polyatomic system. This means that the above lifetimes are probably reasonable estimates for the ground vibrational state of vinylidene, but a very

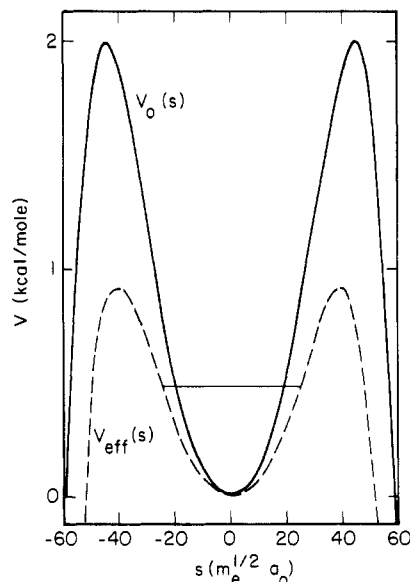
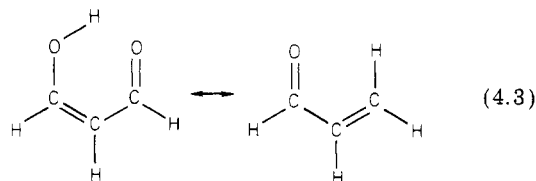


Figure 2. Potential along the reaction path for the rearrangement of vinylidene to acetylene, $H_2C=C: \rightarrow HC\equiv CH$; the solid curve is the “bare” potential $V_0(s)$, and the dashed curve the vibrationally adiabatic potential. The horizontal line shows the bound vibrational state in the vibrationally adiabatic potential.

interesting question arises if vinylidene is prepared with some vibrational excitation in one (or more) of the transverse vibrational modes. If there were no coupling between the reaction coordinate and these modes, then the lifetime would be independent of the vibrational energy in the transverse modes, whereas, if the coupling is strong, one expects the lifetime to decrease with the addition of vibrational energy in the transverse modes. The determination of the lifetime as a function of vibrational state in the transverse modes—for the bare barrier there is only one bound vibrational state in the reaction coordinate mode—should thus give significant insight into the intramolecular vibrational dynamics of this system and provide an excellent test of theoretical treatments of the reaction-path dynamics.

C. Other Potential Applications. It has also been noted^{11c} that a reaction-coordinate model is ideally suited to describing “local-mode” vibrational states in polyatomic molecules. This is essentially a direct application of the “large amplitude motion” approach of Hougen, Bunker, and Johns,¹² here the large amplitude motion, i.e., the reaction coordinate, being that of the anharmonic local-mode oscillator.

Another interesting application currently being pursued³³ is proton transfer in malonaldehyde³⁴



This is an example of tunneling splitting in a symmetric double-well potential, and the interesting feature from the point of view of the dynamics is the effect that coupling of the reaction coordinate to the transverse vibrational modes has on the tunneling splitting. If the tunneling

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proton were infinitely light compared to the heavier molecular framework, then the tunneling motion would occur "suddenly" and the slower degrees of freedom would contribute Franck-Condon factors

$$\Delta E_{\text{tun}} \simeq \Delta E_{\text{tun}}^{(0)} \times (\text{FC factors})$$

where $\Delta E_{\text{tun}}^{(0)}$ is the tunneling splitting (proportional to the tunneling rate) for frozen transverse modes. Coupling to the transverse vibrational modes thus reduces the tunneling splitting (because the Franck-Condon factors are less than unity); i.e., the tunneling rate is slowed down because the heavy molecular framework must "reorganize" itself as the proton tunnels. Although this qualitative picture is clearly oversimplified, it does indicate why coupling of the reaction coordinate to the transverse modes can modify the tunneling splitting significantly. A dynamical treatment based on the reaction-path Hamiltonian should be able to describe the phenomenon quantitatively.

V. Limitations and Future Directions

The purpose of this paper has been to show that many aspects of reaction dynamics in polyatomic systems are amenable to a reaction-path description, but limitations of this approach should also be noted. The most obvious of these is that in some situations the dynamical motion of the system will explore regions of the potential energy surface far away from the minimum-energy path, too far for a harmonic approximation to the surface about it to be accurate. This defect can be overcome, however, with the expenditure of additional effort. The only significant approximation in the Hamiltonian is that the potential energy has been expanded in the transverse vibrational coordinates $\{Q_k\}$ only to second order

$$V(s, \{Q_k\}) \simeq V_0(s) + \sum_{k=1}^{F-1} \frac{1}{2} \omega_k(s)^2 Q_k^2$$

there is essentially no approximation to the kinetic energy part of the Hamiltonian. One can therefore improve matters by keeping anharmonic terms, diagonal and off-diagonal, in the potential energy. This would be most important for low-frequency modes, for these would experience larger amplitude motion for which these terms would presumably be more important. Generating these higher order terms in the potential energy would require calculations of the potential energy surface at additional points, but this would not be an impossible task if anharmonic terms were needed for only a few low-frequency modes.

A more serious difficulty with a reaction-path description is the case that there is not just a single minimum-energy path of interest; e.g., the reaction path bifurcates. This is certainly possible and in fact probably quite common. One can clearly not base the definition of the coordinates $(s, \{Q_k\})$ on a minimum-energy path in this case. The only way to salvage the situation is to choose the reaction path for defining coordinates s (the distance along it) and $\{Q_k\}$ (transverse displacements) not to be the minimum-energy path, a possibility discussed at the end of section II. In simple situations one can see easily how to do this, but it is difficult to formulate a general criterion for the best way to do it.

Consider reaction 4.1, for example, the unimolecular decomposition of formaldehyde. The transition state is planar, and therefore the minimum-energy path starts out planar in going from the transition state toward products. Suppose at some further point along the reaction path the out-of-plane frequency goes to zero and then becomes imaginary as s increases further; i.e., the potential energy

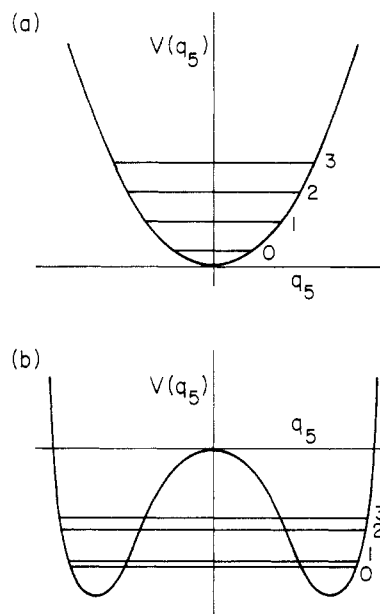


Figure 3. Sketch of the potential energy in the out-of-plane coordinate q_5 . (a) The minimum-energy path is planar. (b) The minimum-energy path has bifurcated, and there are now two symmetrically related nonplanar minimum-energy paths.

in the out-of-plane coordinate changes from that in Figure 3a to that in Figure 3b as s passes this point. (This does not happen for reaction 4.1, but it could have been the case.) At this point, in fact, the minimum-energy path bifurcates; there are two symmetrically related nonplanar minimum-energy paths for larger values of s . In this situation it is clear that the best thing to do is to retain the planar symmetry for defining the reaction path, which is now no longer a minimum-energy path but a path intermediate between the two minimum-energy paths. It is also clear that one must at least include diagonal anharmonicity in the out-of-plane coordinate so that the double-well potential in that degree of freedom is described qualitatively correctly (cf. Figure 3b). In any case such as this, i.e., that a bifurcation leads to symmetrically related minimum-energy paths (each of which is of lower symmetry than that of the minimum-energy path before bifurcation), one can overcome the difficulty in the above manner, i.e., by choosing the reaction path to be that of the higher symmetry. This path can be generated by following a *constrained* gradient, constrained to maintain the initial symmetry of the transition state. It is possible, though, that bifurcation of the minimum-energy path may not lead to symmetrically related minimum-energy paths. In such cases it seems reasonable that one would want to choose a reaction path that is in some sense intermediate between the different minimum-energy paths, but in this case there is no obvious way to give a unique prescription of the best way to choose it.

Finally, there may be cases for which a minimum-energy path exists but is not convenient to use to characterize the dynamics. It may, for example, have sharp changes in direction that cause large curvature coupling elements that are not really descriptive of the true dynamics. In this case it would be better to choose another, smooth reaction path between the initial and final configurations of interest, one chosen to minimize the coupling between the various degrees of freedom (as discussed at the end of section II). Since the reaction-path Hamiltonian is changed only slightly from the form that it has if the reaction path is the minimum-energy path, the dynamical approaches described in section II are essentially all applicable with

straightforward modifications.

In summary, therefore, it seems likely that the quantum chemistry calculation of reaction paths for polyatomic processes is going to become increasingly widespread in the immediate future, and, even though this does not provide as complete a description of the situation as one might like, it is enough to make a serious beginning at treating the microscopic reaction dynamics. This paper has reviewed some of the models and methodologies that can be utilized and some of the initial applications that have been made, but one expects both methodology and

applications to undergo rapid developments as computational quantum chemistry refines its techniques, and as modern experimental methods probe the microscopic dynamics of polyatomic systems even further.

Acknowledgment. Work described in this paper 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 No. DE-ACO3-76SF0098, and by the National Science Foundation Grant CHE79-20181.

ARTICLES

Influence of Structural Imperfections on the Photochemistry in Durene Crystals at Very Low Temperatures

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(Received: December 14, 1982)

Durene photodehydrogenation in the solid state yields duryl radicals. In doped crystals, the radicals are produced with $\lambda > 3000$ Å radiations absorbed by the guests in the high (120–300 K) temperature range, and with $\lambda < 2700$ Å radiations absorbed by the durene host in the low (2–40 K) temperature range. In the latter case, the reaction requires two photons and no substantial activation energy. The fluorescence spectra of duryl radicals produced below 40 K present a multisite structure which is nonreversibly modified by annealing the crystals. The simplified fluorescence spectra exhibited by the annealed samples correspond to radicals located in substitutional sites of the regular durene lattice. From the spectroscopic data obtained at very low temperatures, it is concluded that the durene photodehydrogenation takes place in the structural imperfections of the lattice where the excitation energy can be trapped. These physical defects are different in pure and in doped durene crystals.

Introduction

Photochemical reactions involving the release of hydrogen atoms are among the most widely investigated in the solid state because of the easy diffusion of hydrogen through the matrix, thus preventing the reverse recombination in the Franck-Rabinowitch cage. When aromatic compounds dispersed in organic rigid solutions are illuminated with UV light absorbed exclusively by the solute molecules, radicals can be generated from the solute and/or from the solvent molecules, as a result of the splitting of CH bonds. While the photodehydrogenation reaction is most likely limited to aromatic solutes having substituent groups, this reaction is generally observed with a great variety of solvent molecules such as aliphatic hydrocarbons, alcohols, or ethers frozen at 77 K. Many years ago it was established¹ that the trapped solvent radicals are produced through a two-photon mechanism with the second photon being absorbed by the aromatic molecule in the triplet state. Triplet-triplet transfer to a nearby solvent molecule subsequently leads to the dissociation of

a CH bond. The resulting radicals are identified by ESR techniques and optical spectroscopy. The reaction, which requires no thermal activation energy, was observed for a great number of aromatic molecules having triplet lifetimes of the order of seconds but not for fluoro- and chlorobenzene whose triplet lifetimes are about 3 orders of magnitude shorter.²

Dehydrogenation reactions can also be generated photochemically in molecular crystals where the well-defined spatial geometry of the system allows a more detailed study of the primary reaction steps. The host crystal durene (1,2,4,5-tetramethylbenzene) is particularly well suited for such investigations since hydrogen detachment from a methyl group produces the duryl (2,4,5-trimethylbenzyl) radical, easily identified by its characteristic green fluorescence.³ Our photochemical studies performed in durene crystals indicate that the mechanism producing

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