

Dynamical Effects of Symmetry along a Reaction Path: Mode Specificity in the Unimolecular Dissociation of Formaldehyde

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Abstract: If there is a geometrical symmetry (i.e., C_s , C_{3v} , etc.) that is conserved along a reaction path (the steepest descent path in mass-weighted Cartesian coordinates from a transition state to reactants and to products), then it is shown that this leads to selection rules in the dynamical coupling between the reaction coordinate and the vibrational modes that are orthogonal to it: namely, states corresponding to different irreducible representations do not interact. Thus, even if one makes a statistical (i.e., transition-state theory) approximation to the dynamics within a given irreducible representation, i.e., a "symmetry-adapted transition-state theory", there can still be mode-specific effects between the different symmetries. The unimolecular decomposition of formaldehyde, $H_2CO \rightarrow H_2 + CO$, which has a planar reaction path, is taken as an example, and it is seen that the A' and A'' microcanonical rate constants differ by a factor of ~ 20 in the tunneling regime and still by a factor of 2 at $\sim 5-6$ kcal/mol above the classical threshold of the reaction.

I. Introduction

Symmetry plays an important role in many aspects of chemistry, e.g., in crystallography, in spectroscopy, and also in kinetics and reaction dynamics, which is the concern of this paper and for which there are several different kinds of symmetry effects. The "conservation of orbital symmetry"¹ of electronic wave functions influences whether a given reaction will have a high activation barrier or not and also influences its stereochemical aspects. Quite different from this are the effects caused by identical atoms in a reaction, i.e., the appearance of "symmetry numbers" or "statistical factors" in transition-state-theory rate constants.^{2,3}

The present paper discusses yet another kind of symmetry and its consequences for reaction dynamics, namely, the effect of a symmetry that is maintained along a reaction path. (Furthermore, as discussed in section IV, the symmetry that is maintained along the reaction path is the same as the symmetry of the transition state.) It is shown that such a symmetry implies selection rules in the coupling between the reaction coordinate and the transverse vibrational modes of the dynamical system, and this can in turn lead to mode-specific effects in the rate constants.

To keep the presentation physically transparent, it is first carried through in sections II and III for a specific reaction, the unimolecular dissociation of formaldehyde (in its ground electronic state),



which has recently been the focus of considerable experimental and theoretical interest.⁴ The reaction path in this case is planar,^{4a} i.e., C_s symmetry, and the first point of the paper (section II) is to show that this leads to a decoupling of the even (A') and odd (A'') vibrational states of the out-of-plane bending mode. Thus, even within a statistical approximation (i.e., microcanonical transition-state theory) for the dynamics one should take account of the fact that (due to symmetry) A' and A'' states do not interact. Section III thus introduces a "symmetry-adapted transition-state theory", i.e., a microcanonical transition-state-theory rate constant separately for A' and A'' states. For the formaldehyde reaction (eq 1.1), the symmetry-induced mode specificity, i.e., the difference between the rate constants (at the same total energy) for A' and A'' states, is quite significant; in the tunneling region, the A' rate constant is a factor of ~ 20 larger than the A'' rate constant, and it is still a factor of 2 larger at $\sim 5-6$ kcal/mol above the classical threshold of the reaction.

Section IV then shows how these ideas can be generalized. The basic result is that symmetry of the transition state (and thus the reaction path) leads to decoupling of states corresponding to different irreducible representations of the symmetry group so that, even if a statistical approximation (i.e., microcanonical transition-state theory) is assumed for the dynamics, one should calculate a distinct microcanonical transition-state-theory constant for each irreducible representation. In the limit of energies far above the reaction threshold, these different rate constants become equal, but as seen with the formaldehyde reaction (1.1), symmetry-induced mode specificity (i.e., difference in the rate constants) can be significant at chemically relevant energies.

II. Consequences of Reaction Path Symmetry for the Reaction Path Hamiltonian

It is useful to base the discussion of the reaction dynamics on the reaction path Hamiltonian as formulated by Miller, Handy, and Adams.⁵ This describes the polyatomic reactive system in terms of a reaction coordinate⁶ (the distance along the reaction path, the steepest descent path in mass-weighted Cartesian coordinates from the saddle point of the potential-energy surface, i.e., the transition state, back to reactants and forward to products) plus local normal-mode displacements about it. The overall picture

(1) R. B. Woodward and R. Hoffman, "The Conservation of Orbital Symmetry", Verlag Chemie, Weinheim/Bergstr., 1970.

(2) For an excellent review, see P. Pechukas in "Dynamics of Molecular Collisions Part B" (Vol. 2 of Modern Theoretical Chemistry), Miller, W. H. Ed., Plenum Press, New York, N. Y., 1976, p 285 et seq.

(3) Some other works concerning symmetry in reaction kinetics are (a) R. G. Pearson, *Acc. Chem. Res.*, **4**, 152 (1971); (b) R. E. Stanton and J. W. McIver, Jr., *J. Am. Chem. Soc.*, **97**, 3632 (1975); (c) J. N. Murrell and K. J. Laidler, *Trans. Faraday Soc.*, **64**, 371 (1968); (d) E. W. Schlag, *J. Chem. Phys.*, **38**, 2480 (1963); (e) L. Salem, *Acc. Chem. Res.*, **4**, 322 (1971); (f) M. Quack, *Mol. Phys.*, **34**, 477 (1977).

(4) See, for example, (a) J. D. Goddard and H. F. Schaefer, *J. Chem. Phys.*, **70**, 5117 (1979); (b) J. C. Weisshaar and C. B. Moore, *ibid.*, **70**, 5135 (1979); (c) H. L. Selzle and E. W. Schlag, *Chem. Phys.*, **43**, 111 (1979), and many references to earlier work cited in these papers.

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

(6) A number of workers have contributed to the development of the reaction path description of reaction dynamics; for example, (a) G. L. Hofacker, *Z. Naturforsch.*, **A**, **18a**, 607 (1963); (b) S. F. Fischer, G. L. Hofacker, and R. Seiler, *J. Chem. Phys.*, **51**, 3951 (1969); (c) R. A. Marcus, *ibid.*, **45**, 4493, 4500 (1966); **49**, 2610 (1968); **53**, 4026 (1976); (d) S. F. Fischer and M. A. Ratner, *ibid.*, **57**, 2769 (1972); (e) P. Russegger and J. Brickmann, *ibid.*, **62**, 1086 (1976); **60**, 1 (1977); (f) M. V. Basilevsky, *Chem. Phys.*, **24**, 81 (1977); (g) K. Fukui, S. Kato, and H. Fujimoto, *J. Am. Chem. Soc.*, **97**, 1 (1975).

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of the potential surface is that of a (multidimensional) harmonic valley about the reaction path. For zero total angular momentum the classical version of the Hamiltonian is⁵

$$H(p_s, s, \{n_k, q_k\}, k = 1, \dots, F-1) = V_0(s) + \sum_{k=1}^{F-1} \left(n_k + \frac{1}{2} \right) \omega_k(s) + \frac{1}{2} [p_s - \sum_{k,k'=1}^{F-1} Q_k P_{k'} B_{k,k'}(s)]^2 / [1 + \sum_{k=1}^{F-1} Q_k B_{k,F}(s)]^2 \quad (2.1a)$$

where

$$Q_k = (2n_k + 1/\omega_k(s))^{1/2} \sin q_k \quad (2.1b)$$

$$P_k = ((2n_k + 1)\omega_k(s))^{1/2} \cos q_k \quad (2.1c)$$

Here (s, p_s) are the reaction coordinate and its conjugate momentum (labeled as the F th degree of freedom) and (n_k, q_k) , $k = 1, \dots, F-1$ are the classical action-angle variables⁷ for the $(F-1)$ vibrational modes orthogonal to the reaction path; n_k is the classical analogue of the vibrational quantum number for mode k , and q_k is the classical phase of the oscillator. The number of degrees of freedom of the nonrotating system in its center of mass is $F = 3N - 6$, where N is the number of atoms. $V_0(s)$ is the reaction profile, i.e., the potential energy along the reaction path, and $\{\omega_k(s)\}$ are the frequencies of the $(F-1)$ local normal modes. The coupling elements $\{B_{k,k'}(s)\}$, which couple the vibrational modes to each other and to the reaction coordinate, are given by

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

for $(k, k') = 1, \dots, F, k \neq k'$, where $\mathbf{L}_k(s)$ is the $(3N-1)$ -dimensional eigenvector of the projected force-constant matrix⁵ for mode k at the distance s along the reaction path. $\mathbf{L}_F(s)$ is the normalized gradient vector, which by definition points along the reaction path. The elements $B_{k,F}(s)$, $k = 1, \dots, F-1$ depend on how the curvature of the reaction path couples into mode k , and the elements $B_{k,k'}(s)$, $(k, k') = 1, \dots, F-1, k \neq k'$, are coriolis-like coupling elements. There are also diagonal coupling elements given by

$$B_{k,k}(s) \equiv -\omega'_k(s) / 2\omega_k(s) \quad (2.2b)$$

for $k = 1, \dots, F-1$. A more detailed discussion of the reaction-path Hamiltonian, its generalization to nonzero total angular momentum, and its applications have been given in earlier papers.^{5,8}

Specializing now to the formaldehyde reaction (1.1), it was noted in the Introduction that the reaction path is planar. One has $F = 6$ here, and of the $F-1 = 5$ vibrational modes orthogonal to the reaction path, four ($k = 1, 2, 3, 4$) are in the plane of the four atoms and one ($k = 5$) is perpendicular to the plane. Since for all values of the reaction coordinate s the normal mode vectors $\mathbf{L}_k(s)$, $k = 1, 2, 3, 4$, and 6 correspond to atomic displacements in the plane, the vectors $\partial \mathbf{L}_k(s) / \partial s$, $k = 1, 2, 3, 4$, and 6 also have all atomic displacements in the plane. Then, since $\mathbf{L}_5(s)$ has all atomic displacements out of the plane, eq 2.2a shows that all the coupling elements $B_{5,k}(s)$ vanish for $k \neq 5$, i.e.,

$$B_{5,k}(s) = 0 \quad (2.3)$$

for $k = 1, 2, 3, 4$, and 6.

Therefore the only coupling of the out-of-plane mode $k = 5$ is that caused by the variation of its frequency with reaction coordinate, i.e., the diagonal coupling element from eq 2.2b,

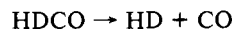
$$B_{5,5}(s) = -\omega'_5(s) / 2\omega_5(s) \quad (2.4)$$

The dependence of the Hamiltonian on the angle variable q_5 that goes with this coupling element is seen from eq 2.1 to be

$$\sin q_5 \cos q_5 = (e^{2iq_5} - e^{-2iq_5}) / 4i$$

and its square, and this means (via standard, semiclassical correspondence⁹) that the quantum mechanical Hamiltonian operator only has matrix elements in mode 5 with $\Delta n_5 = 0, \pm 2, \pm 4$, i.e., even and odd vibrational states of the out-of-plane bending mode are uncoupled.

It should be emphasized that it is the planar symmetry of the reaction path that leads to this decoupling of the even and odd out-of-plane vibrational states and that it has nothing to do with the identity of the two hydrogen atoms. Thus the situation is entirely the same for the reaction



which of course also has a planar reaction path.

To make contact with customary group theoretic language one notes that the planar, C_s , symmetry of the reaction path means that for each value of the reaction coordinate s the transverse vibrational modes will belong to one of the irreducible representations of C_s , A' (symmetric on reflection in the plane) or A'' (antisymmetric on reflection). Here the four in-plane modes $k = 1, 2, 3, 4$ are A' , and the out-of-plane mode $k = 5$ is A'' . (The reaction coordinate itself, $k = 6$, is A' ; it is always of the totally symmetric representation.) Since these symmetry classifications are maintained along the reaction path, the coupling elements $B_{k,k'}$ must vanish if k and k' belong to different irreducible representations. The diagonal coupling elements $B_{k,k}$ never vanish however, so that the quantum number for mode $k = 5$ is not completely conserved, only its evenness or oddness.

III. The Microcanonical Rate Constant

Even in a statistical theory, such as transition-state theory, one should take account of any quantities conserved by the Hamiltonian and not assume that noninteracting states are mixed statistically. In microcanonical transition-state theory, for example, as it is used in the RRKM treatment of unimolecular reactions,¹⁰ it is well recognized that since total angular momentum is a conserved quantity one should calculate a microcanonical rate constant for each value of J separately, $k_J(E)$, and then combine the rate constants for various J 's according to the appropriate experimental situation. (In many cases, one also averages over the total energy E , but in favorable situations experiments may determine the rate constant for a given energy E and a given total angular momentum J .)

The discussion in the previous section has shown that (at least for $J = 0$) even and odd (i.e., A' and A'') states of the out-of-plane vibrational mode, $k = 5$, are uncoupled, so one should calculate a microcanonical rate constant for A' and A'' symmetry separately. Within the standard¹⁰ separable harmonic approximation for the energy levels, these microcanonical rate constants are given by (including tunneling¹¹)

$$k_{A'}(E) = N_{A'}(E) / 2\pi \hbar \rho_{A'}(E) \quad (3.1a)$$

$$k_{A''}(E) = N_{A''}(E) / 2\pi \hbar \rho_{A''}(E) \quad (3.1b)$$

where the N 's are the cumulative reaction probabilities for each symmetry,

$$N_{A'}(E) = \sum_{\substack{n_1, n_2 \\ n_3, n_4=0}}^{\infty} \sum_{n_5=0, 2, 4}^{\infty} P_{1d} \left[E - V_0 - \sum_{k=1}^5 \hbar \omega_k^* \left(n_k + \frac{1}{2} \right) \right] \quad (3.2a)$$

$$N_{A''}(E) = \sum_{\substack{n_1, n_2 \\ n_3, n_4=0}}^{\infty} \sum_{n_5=1, 3, 5}^{\infty} P_{1d} \left[E - V_0 - \sum_{k=1}^5 \hbar \omega_k^* \left(n_k + \frac{1}{2} \right) \right] \quad (3.2b)$$

(7) H. Goldstein, "Classical Mechanics", Addison-Wesley, Reading, MA, 1950, pp 288-307.

(8) (a) S. K. Gray, W. H. Miller, Y. Yamaguchi, and H. F. Schaefer, *J. Chem. Phys.*, **73**, 2733 (1980); (b) W. H. Miller in "Potential Energy Surfaces and Dynamical Calculations", D. G. Truhlar, Ed., Plenum Press, New York, 1981, p 265; (c) S. K. Gray, W. H. Miller, Y. Yamaguchi, and H. F. Schaefer, *J. Am. Chem. Soc.*, **103**, 1900 (1981); (d) C. J. Cerjan, S.-h. Shi, and W. H. Miller, *J. Phys. Chem.*, **86**, 2244 (1982).

(9) This is a consequence of the Heisenberg correspondence relation; see, for example, W. H. Miller, *J. Chem. Phys.*, **64**, 2880 (1976).

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

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

and the ρ 's are the density of states of the reactant molecule of the corresponding symmetry,

$$\rho_{A'}(E) = \sum_{\substack{n_1, n_2, n_3 \\ n_4, n_6=0}}^{\infty} \sum_{n_5=0,2,4}^{\infty} \delta \left[E - \sum_{k=1}^6 \hbar \omega_k \left(n_k + \frac{1}{2} \right) \right] \quad (3.3a)$$

$$\rho_{A''}(E) = \sum_{\substack{n_1, n_2, n_3 \\ n_4, n_6=0}}^{\infty} \sum_{n_5=1,3,5}^{\infty} \delta \left[E - \sum_{k=1}^6 \hbar \omega_k \left(n_k + \frac{1}{2} \right) \right] \quad (3.3b)$$

Various quantities in the above expressions have their usual meaning: $\{\omega_k\}$ and $\{\omega_k^*\}$ are the frequencies of H_2CO and the transition state, respectively, V_0 is the barrier height, and $P_{1d}(E)$ is the one-dimensional tunneling probability as a function of the translational energy E . The fact that formaldehyde itself, i.e., the minimum point on the potential-energy surface, has higher symmetry than C_s is irrelevant for present purposes, for it is only C_s symmetry that is conserved along the reaction path and thus determines the quantities that are conserved by the reaction path Hamiltonian.

The most dramatic consequence of this dynamical symmetry appears in the tunneling regime of reaction 1.1 where only the ground state of the transition state contributes in eq 3.2. In this energy region it is not hard to show that

$$\rho_{A'}(E) \simeq \rho_{A''}(E) \simeq (1/2)\rho(E) \quad (3.4)$$

where $\rho(E)$ is the total density of reactants states computed without regard to A' and A'' symmetry (i.e., $\rho = \rho_{A'} + \rho_{A''}$), so that for the tunneling region eq (3.1) becomes

$$k_{A'}(E) \simeq 2P_{1d}(E - V_0^{ZP})/2\pi\hbar\rho(E) \quad (3.5a)$$

$$k_{A''}(E) \simeq 2P_{1d}(E - V_0^{ZP} - \hbar\omega_5^*)/2\pi\hbar\rho(E) \quad (3.5b)$$

where V_0^{ZP} is the barrier height plus zero point energy of the transition state,

$$V_0^{ZP} = V_0 + \sum_{k=1}^5 \frac{1}{2} \hbar \omega_k^*$$

If C_s symmetry were ignored, the rate in this tunneling region, $k(E)$, would be given by

$$k(E) \simeq P_{1d}(E - V_0^{ZP})/2\pi\hbar\rho(E) \quad (3.6)$$

so that the effect of taking C_s symmetry into account is to enhance the rate of the A' states by a factor of 2,

$$k_{A'}(E) \simeq 2k(E) \quad (3.7a)$$

and to depress the rate of the A'' states because the effective activation energy is increased by the amount $\hbar\omega_5^*$,

$$k_{A''}(E) \simeq 2k(E - \hbar\omega_5^*) \quad (3.7b)$$

Figure 1 shows the A' and A'' microcanonical rate constants for reaction 1.1 ($J = 0$), as calculated from eq 3.1–3.3 with the frequencies used in earlier work;¹¹ one sees clearly how eq 3.7a and 3.7b describe the tunneling region. There is approximately a factor of 20 difference between the two rate constants (at the same total energy) in this low energy region.

At energies sufficiently far above the classical threshold one can show that the two rate constants become equal, i.e., the effect of reaction path symmetry disappears. It is easy to see how this limit is approached if one uses the usual classical approximation to the various sums over states (i.e., replaces sums by integrals). It is not hard to show that this gives

$$k_{A',A''}(E) = k(E) \left(\frac{1 \pm \frac{1}{2} \frac{\hbar\omega_5^*}{E - V_0}}{1 \pm \frac{1}{2} \frac{\hbar\omega_5}{E}} \right)^{F-1} \quad (3.8)$$

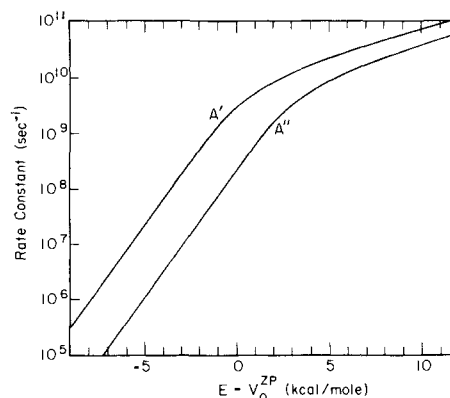


Figure 1. Microcanonical rate constant for the reaction $\text{H}_2\text{CO} \rightarrow \text{H}_2 + \text{CO}$ (for $J = 0$) for the symmetries A' and A'' as a function of total energy relative to V_0^{ZP} (the barrier height plus zero point energy of the transition state). The values plotted include an additional factor of 2 to that indicated in eq 3.1, due to the two equivalent transition states (or equivalently, due to the symmetry number for H_2CO).

where $k(E)$ is the ordinary classical rate expression (ignoring tunneling and C_s symmetry), and the “+” and “−” signs correspond to A' and A'' , respectively. For $E \gg \hbar\omega_5$, as is the case, the denominator is essentially unity, so that eq 3.8 gives the ratio of rate constants as

$$\frac{k_{A'}(E)}{k_{A''}(E)} \simeq \left(\frac{1 + \lambda}{1 - \lambda} \right)^{F-1} \quad (3.9a)$$

where

$$\lambda = \frac{1}{2} \hbar \omega_5^* / (E - V_0) \quad (3.9b)$$

As noted, therefore, for sufficiently high energy $\lambda \rightarrow 0$ and the ratio of rate constants, eq 3.9, approaches unity, but it may require a very high energy before this limit is effectively reached. Equation 3.9 shows, in fact, that the ratio of rate constants is still 2 at an energy given by

$$E - V_0 = \frac{1}{2} \hbar \omega_5^* \frac{(2^{1/F-1} + 1)}{(2^{1/F-1} - 1)}$$

which for large F is well approximated by

$$E - V_0 \simeq \hbar \omega_5^* (F - 1) / \ln 2 \quad (3.10)$$

For the present case $\hbar\omega_5^* \simeq 2.3$ kcal/mol, so that the right-hand side of eq 3.10 is ~ 16 – 17 kcal/mol. Since the zero point energy of the transition state is ~ 11 kcal/mol, eq 3.10 predicts that the energy (relative to the classical threshold) at which $k_{A'}$ has fallen to a factor of 2 greater than $k_{A''}$ is $(E - V_0^{ZP}) \simeq 5$ – 6 kcal/mol, and this is indeed seen in Figure 1.

Before concluding this discussion of the formaldehyde reaction (eq 1.1), it is interesting to note that the usual photochemical excitation of formaldehyde actually prepares the molecule in a state of definite C_s symmetry (at least for $J = 0$), so that the “symmetry-induced mode specificity” discussed above should be relevant. This is because the photochemical excitation $S_0 \rightarrow S_1$ is to a definite vibrational state of the out-of-plane mode (ν_4 in usual spectroscopic designation, but mode $k = 5$ in the present paper). In the radiationless transition from S_1 back to S_0 (highly vibrationally excited), the overall symmetry of the molecule is conserved, and since the electronic symmetry (in C_s) of S_1 is A'' and that of S_0 is A' , the parity of the out-of-plane vibrational state must change. Thus, if an odd out-of-plane vibrational state of S_1 is excited, the out-of-plane state in S_0^* will be even, so that it is $k_{A'}(E)$ that is relevant in this case. Conversely, for excitation of an even out-of-plane vibrational state of S_1 , it is $k_{A''}(E)$ that is relevant for the unimolecular decay in S_0 .

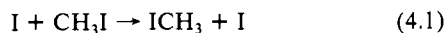
Unfortunately, however, the lifetimes that have been measured for the $S_0 \rightarrow S_1$ excitation appear to be a complicated combination of the rate of radiationless transition $S_1 \rightarrow S_0^*$ and the rate of

(12) E. W. Schlag, private communication.

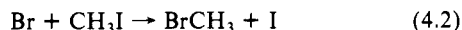
unimolecular decomposition in S_0 , and as yet it has not been possible to unravel the two processes to determine the rates of each process individually. The experiments by Weisshaar and Moore,¹³ however, on the electric field dependence of the lifetimes offer the promise of doing this.

IV. More General Discussion of Reaction Path Symmetry

It is now relatively easy to see how these ideas can be applied more generally. The situation is even more profound (and useful) by noting Pechukas' observation,² following Pearson,^{3a} that the symmetry of the transition state is the same as the symmetry that is maintained along the reaction path provided only that the reaction is indeed a reaction (and that the reaction path is "simple", i.e., does not bifurcate). That is, the "reaction"



is C_{3v} along the reaction path and D_{3h} at the transition state, but this "reaction" is really no reaction; i.e., the reactants and products are the same. The legitimate reaction



is C_{3v} along the reaction path and also at the transition state. The basic idea is that the transition state, a point on the reaction path, is not a *special* point on the reaction path, symmetrywise.

In general, therefore, one must first find the symmetry of the transition state, which, as noted above, is the symmetry along the reaction path. The microcanonical transition-state-theory rate constant for each irreducible representation of the symmetry group is then given by

$$k_\lambda(E) = N_\lambda(E) / 2\pi\hbar\rho_\lambda(E) \quad (4.3)$$

where

$$N_\lambda(E) = \sum_{n_1, \dots, n_{F-1}=0}^{\infty} \mathcal{P}_\lambda(n_1, \dots, n_{F-1}) P_{1d} \left[E - V_0 - \sum_{k=1}^{F-1} \hbar\omega_k^* \left(n_k + \frac{1}{2} \right) \right] \quad (4.4a)$$

$$\rho_\lambda(E) = \sum_{n_1, \dots, n_{F-1}=0}^{\infty} \mathcal{P}_\lambda(n_1, \dots, n_{F-1}) \delta \left[E - \sum_{k=1}^F \hbar\omega_k \left(n_k + \frac{1}{2} \right) \right] \quad (4.4b)$$

and λ denotes the particular irreducible representation (e.g., $\lambda = A'$ or A'' for the formaldehyde example, or A_1 , A_2 , or E for the C_{3v} case as in reaction 4.2). The factor $\mathcal{P}_\lambda(n_1, \dots, n_{F-1})$ in eq 4.4 is the fraction that the state with quantum numbers $(n_1, n_2, \dots, n_{F-1})$ is in the irreducible representation λ . For the formaldehyde reaction it is quite trivial to determine this factor: for $\lambda = A'$ $\mathcal{P}_\lambda(n_1, \dots, n_5) = 1$ or 0 for n_5 even or odd, respectively, and vice versa for $\lambda = A''$. If any of the irreducible representations are multidimensional (e.g., as in C_{3v}), then the determination of these factors is somewhat more complicated, but the machinery for doing so exists.¹⁴ One simplifying observation is that $\mathcal{P}_\lambda(n_1, \dots, n_{F-1})$ is in general independent of the quantum numbers for the totally symmetric modes; this is the reason for omitting n_F as an argument of \mathcal{P}_λ in eq 4.4b. One also has in all cases the general relation

$$\sum_\lambda \mathcal{P}_\lambda(n_1, \dots, n_{F-1}) = 1 \quad (4.5)$$

and from this one can easily show that the *average* microcanonical rate constant $k(E)$,

$$k(E) \equiv \sum_\lambda \rho_\lambda(E) k_\lambda(E) / \sum_\lambda \rho_\lambda(E) \quad (4.6)$$

is the standard microcanonical transition-state expression without regard to symmetry.

To give another illustration of how the group theoretic reasoning and the dynamical arguments based on the reaction-path Hamiltonian are consistent, consider the case of a planar transition state, i.e., C_s symmetry, for a five-atom reaction. Of the $F - 1 = 3N - 7 = 8$ vibrational modes of the transition state, six will be of A' symmetry (i.e., in plane) and two will be A'' (out of plane). If modes $k = 7, 8$ are the A'' modes, then the state $(n_1, n_2, \dots, n_7, n_8)$ is A' or A'' if $(n_7 + n_8)$ is even or odd, respectively; i.e., for $\lambda = A'$ $\mathcal{P}_\lambda(n_7, n_8) = 1$ or 0 if $(n_7 + n_8)$ is even or odd, respectively, and vice versa for $\lambda = A''$.

To see this conservation of symmetry directly from the reaction-path Hamiltonian one notes that the only nonzero coupling elements of eq 2.2 involving modes $k = 7$ and 8 are $B_{7,7}$, $B_{8,8}$, and $B_{7,8}$. The angle dependencies associated with these couplings are

$$\sin q_7 \cos q_7 = (1/4i)(e^{2iq_7} - e^{-2iq_7})$$

$$\sin q_8 \cos q_8 = (1/4i)(e^{2iq_8} - e^{-2iq_8})$$

$$\sin q_7 \cos q_8 = (1/4i)(e^{i(q_7+q_8)} - e^{-i(q_7+q_8)} - e^{i(q_7-q_8)} + e^{-i(q_7-q_8)})$$

which imply that there will be matrix elements of the Hamiltonian involving these modes only for

$$\Delta n_7 = 0, \pm 2, \pm 4, \Delta n_8 = 0$$

$$\Delta n_8 = 0, \pm 2, \pm 4, \Delta n_7 = 0$$

$$(\Delta n_7, \Delta n_8) = (1, 1), (-1, 1), (1, -1), (-1, -1), \dots$$

i.e., only matrix elements for which

$$\Delta(n_7 + n_8) = 0, \pm 2, \pm 4, \dots$$

Thus the "evenness" or "oddness" of $(n_7 + n_8)$ is conserved, and this is the decoupling of the A' and A'' manifolds of states.

This discussion also suggests how rotation, i.e., $J > 0$, should be incorporated. First, if coriolis coupling is negligible along the reaction path, then vibrational-state symmetry is unaffected, and the only modification of eqs 4.3 and 4.4 is that the rotational energy is added to the transition state and to the reactant molecule, and the sums in eq 4.4 are augmented by a sum over K , the (unconserved) angular momentum projection quantum number; the rate constants are designated $k_{J,\lambda}(E)$. (If the reaction path is a symmetric top, as for reaction 4.2, then the projection quantum number K is also conserved, so that in this case one should also determine the microcanonical transition-state-theory rate constant for given values of K , $k_{J,K,\lambda}(E)$.)

If, on the other hand, coupling between rotation and vibration is strong, then one should utilize the composite symmetry of rotation and vibration. This is more complicated, but the methodology is essentially identical with that for ordinary stable molecules.¹⁵

In general, in fact, the procedure for counting states in eq 4.4 for each irreducible representation of the transition state is essentially the same as that for ordinary stable molecules. This is because the reaction coordinate itself is always of the totally symmetric representation—because the symmetry is maintained along the reaction path—so that this degree of freedom does not affect any of the symmetry aspects of the state counting.

V. Concluding Remarks

The main point of this paper has been to point out that when there is a symmetry maintained along the reaction path there are selection rules involving the dynamical coupling between the reaction coordinate and the vibrational modes orthogonal to it. Then even if one makes a statistical approximation to the dynamics within each separate manifold of states, there can be symmetry-induced mode-specific effects between states of different symmetry.

With the additional observation that the symmetry that is maintained along the reaction path is precisely the symmetry of the transition state, one is able to employ a "symmetry-adapted

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transition-state theory⁷ by knowing only the transition state, its symmetry, and its other usual properties (i.e., frequencies and moments of inertia).

Finally, although it has been emphasized that reaction-path symmetry can induce mode-specific effects between states of different symmetry, without more detailed dynamical calculations there is no way to know that there might not also be mode specificity *within* a given irreducible representation. For the formaldehyde reaction (eq 1.1), for example, it is possible that the rate constant might not be a smooth function of the total energy even within the A' or the A'' manifold. The kind of detailed dynamical calculations that can answer this question have been carried out by Waite and Miller¹⁶ for model problems, and depending on the nature of the coupling one can obtain statistical or mode-specific behavior within a given symmetry. To carry out calculations of this type for the formaldehyde reaction requires the coupling

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elements in eq 2.2 and the frequencies along the reaction path that fully characterize the reaction-path Hamiltonian. These quantities have been determined¹⁵ for the formaldehyde dissociation, and calculations for it like those of Waite and Miller are in progress.

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Registry No. Formaldehyde, 50-00-0.

Semiconductor Electrodes. 48. Photooxidation of Halides and Water on n-Silicon Protected with Silicide Layers

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Abstract: The electrochemical and photoelectrochemical behavior of n-type silicon electrodes coated with noble metal silicides and RuO₂ in aqueous solutions containing various redox couples was investigated. Iridium silicide coated n-Si electrodes, n-Si(Ir), and RuO₂-modified n-Si(Ir) electrodes can photogenerate I₂, Br₂, and Cl₂ with high stability and efficiencies (>5%). The photooxidation of water on these electrodes is also feasible.

Interest in the stabilization of small band gap n-type semiconductors against photocorrosion in photoelectrochemical (PEC) cells is based on the goal of photogenerating highly oxidizing species (e.g., Br₂, O₂, Cl₂, etc.) on these semiconductor electrodes. Because of its wide use and availability, small band gap n-Si has been of special interest. While naked n-Si is easily photooxidized in aqueous solutions to produce an insulating SiO₂ layer, stable n-Si photoelectrodes can be achieved by coating the photoanode with a thin gold or platinum layer overcoated with a thick polypyrrole film^{1,j,k} or derivatizing the n-Si surface before coating with a polypyrrole film.¹¹ However, the photogeneration of highly oxidizing species, such as Br₂, Cl₂, or O₂, on these electrodes cannot be accomplished because of the instability of polypyrrole in the potential range where the oxidation of Br⁻, Cl⁻, or H₂O takes place.² We have recently demonstrated³ that Pt silicide coated n-Si electrodes can be employed to fabricate fairly stable PEC

cells with aqueous solutions containing various redox couples, e.g., Fe^{2+/3+}, I^{-/I₃⁻}, Fe(CN)₆^{3-/4-}.

There is a wealth of information concerning thin-film-semiconductor reactions and the nature of semiconductor/metal interfaces, especially metal thin films on silicon.⁴ We report here a study of the electrochemical (EC) and PEC behavior of platinum and iridium silicide coated n-Si electrodes and suitably modified forms of these electrodes in aqueous solutions containing halide ions. We demonstrate that iridium silicide coated n-Si electrodes, denoted n-Si(Ir), and RuO₂-modified n-Si(Ir) electrodes (which are similar to the RuO₂-modified ITO coated n-Si electrodes described recently^{1m}) can photogenerate I₂, Br₂, and Cl₂ without noticeable decomposition with efficiencies above 5%. The photooxidation of water is also described.

Experimental Section

Silicides were prepared by procedures similar to those reported previously.^{3,4a} n-Si single crystals (0.4-0.6 ohm cm) donated by Texas Instruments were cleaned ultrasonically in trichloroethylene, acetone, and methanol. Immediately prior to vacuum deposition of metal, the n-Si crystals were etched twice with 48% HF solution for 10-20 min. The etched crystals were then rinsed thoroughly with distilled water and methanol and dried under vacuum. The metal films were deposited by flash evaporation of a known amount of metal on the n-Si crystals at a pressure of 10⁻⁶ torr. The thickness of the metal film deposited on silicon wafers was estimated from the optical density of a metal film deposited

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