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Author
Miller, William H.

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William H. Miller

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

William H. Miller

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

and

Lehrstuhl für Theoretische Chemie
Technische Universität München
8046 Garching bei München, West Germany

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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 $\sim 20$ in the tunneling regime, and still by a factor of 2 at $\sim 5-6$ kcal/mole 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" of electronic wavefunctions influences whether a given reaction will have a high activation barrier, or not, and also 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)

\[ H_2CO \rightarrow H_2 + CO \]  

(1.1)

which has recently been the focus of considerable experimental and theoretical interest.\(^4\) The reaction path in this case is planar.\(^4a\)
i.e., $C_8$ 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 (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 ~5-6 kcal/mole 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 rate 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. This describes the polyatomic reactive system in terms of a reaction coordinate (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 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 is

\[
H(p_s, s, \{n_k, q_k\}, k=1,\ldots,F-1) = V_0(s) + \sum_{k=1}^{F-1} (n_k + \frac{1}{2}) \omega_k(s) \\
+ \frac{1}{2} \left[ p_s - \sum_{k,k'=1}^{F-1} Q_k p_{k'} B_{k,k'}(s) \right]^2 \\
+ \frac{1}{2} \left[ 1 + \sum_{k=1}^{F-1} Q_k B_k F(s) \right]^2,
\]

(2.1a)

where

\[
Q_k = \sqrt{\frac{2n_k + 1}{\omega_k(s)}} \sin q_k
\]

(2.1b)

\[
P_k = \sqrt{(2n_k + 1)\omega_k(s)} \cos q_k
\]

(2.1c)
Here \((s,p_s)\) are the reaction coordinate and its conjugate momentum (labeled as the \(F\)th degree of freedom) and \((n_k,q_k)\), \(k=1,\ldots,F-1\) are the classical action-angle variables \(^7\) for the \((F-1)\) vibrational modes orthogonal to the reaction path; \(n_k\) is the classical analog of the vibrational quantum number for mode \(k\), and \(q_k\) is the classical phase of the oscillator. \(F=3N-6\) is the number of degrees of freedom of the non-rotating system in its center of mass, 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

\[
B_{k,k'}(s) = L_k(s) \frac{3L_{k'}(s)}{\partial s}, \tag{2.2a}
\]

for \((k,k') = 1,\ldots,F, k\neq k'\), where \(L_k(s)\) is the \((3N\)-dimensional\) eigenvector of the projected force constant matrix \(^5\) for mode \(k\) at the distance \(s\) along the reaction path. \(L_k(s)\) is the normalized gradient vector itself, which by definition points along the reaction path. The elements \(B_{k,F}(s), k=1,\ldots,F-1\) depend on how the curvature of the reaction path couples into mode \(k\), and the elements

\[
B_{k,k'}(s), (k,k') = 1,\ldots,F-1, k\neq k', \]

are coriolis-like coupling elements. There are also diagonal coupling elements given by

\[
B_{k,k}(s) = -\frac{\omega'_k(s)}{2\omega_k(s)}, \tag{2.2b}
\]
for \( k=1, \ldots, F-1 \). A more detailed discussion of the reaction path Hamiltonian, its generalization to non-zero 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),

\[
B_{5,5}(s) = \frac{-\omega_5'(s)}{2 \omega_5(s)} \quad (2.4)
\]

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
and its square, and this means (via standard, semiclassical correspondence) 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 bend 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

\[
\text{HDCO} \rightarrow \text{HD} + \text{CO}
\]

which of course also has a planar reaction path.

To make contact with customary group theoretic language one notes that the planar, \( C_\sigma \) 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 \( C_\sigma \): \( A' \) (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

\[
\sin q_5 \cos q_5 = \frac{1}{4i} (e^{2iq_5} - e^{-2iq_5})
\]
$B_{k,k}$ never vanish, however, so that the quantum number for mode $k=5$ is not completely conserved, only its eveness or oddness is.
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 non-interacting states are mixed statistically. In microcanonical transition state theory, for example as it is used in the RRKM treatment of unimolecular reactions, 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, too, 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 standard\(^{10} \) separable harmonic approximation for the energy levels, these microcanonical rate constants are given by (including tunneling\(^{11} \))

\[
k_{A'}(E) = \frac{N_{A'}(E)}{2\pi\hbar \rho_{A'}(E)} \tag{3.1a}
\]

\[
k_{A''}(E) = \frac{N_{A''}(E)}{2\pi\hbar \rho_{A''}(E)} \tag{3.1b}
\]

where the \( N \)'s are the cumulative reaction probabilities for each symmetry,
\begin{align*}
N_{A'}(E) &= \sum_{n_1,n_2}^{\infty} \sum_{n_3,n_4=0}^{\infty} P_{1d}[E-V_0-\sum_{k=1}^{5} \hbar \omega_k(n_k + \frac{1}{2})] \quad (3.2a) \\
N_{A''}(E) &= \sum_{n_1,n_2}^{\infty} \sum_{n_3,n_4=0}^{\infty} P_{1d}[E-V_0-\sum_{k=1}^{5} \hbar \omega_k(n_k + \frac{1}{2})] \quad (3.2b)
\end{align*}

and the \( \rho \)'s are the density of states of the reactant molecule of the corresponding symmetry,

\begin{align*}
\rho_{A'}(E) &= \sum_{n_1,n_2,n_3}^{\infty} \sum_{n_4,n_6=0}^{\infty} \delta[E-\sum_{k=1}^{6} \hbar \omega_k(n_k + \frac{1}{2})] \quad (3.3a) \\
\rho_{A''}(E) &= \sum_{n_1,n_2,n_3}^{\infty} \sum_{n_4,n_6=0}^{\infty} \delta[E-\sum_{k=1}^{6} \hbar \omega_k(n_k + \frac{1}{2})] \quad (3.3b)
\end{align*}

Various quantities in the above expressions have their usual meaning: 
\( \{\omega_k\} \) and \( \{\omega_k^+\} \) are the frequencies of \( \text{H}_2\text{CO} \) and the transition state, respectively, \( V_0 \) is the barrier height, and \( P_{1d}(E_t) \) is the one dimensional tunneling probability as a function of the translational energy \( E_t \). 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

\[ \rho_{A'}(E) = \rho_{A''}(E) = \frac{1}{2} \rho(E) \quad , \tag{3.4} \]

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

\[
k_{A'}(E) = 2 P_{ld}(E-V_0^{ZP})/2\pi\hbar\rho(E) \tag{3.5a} \]

\[
k_{A''}(E) = 2 P_{ld}(E-V_0^{ZP} - \hbar\omega_k^+) / 2\pi\hbar\rho(E) \quad , \tag{3.5b} \]

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

\[ V_0^{ZP} = V_0 + \sum_{k=1}^{5} \frac{1}{2} \hbar\omega_k^+ \quad . \]

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

\[ k(E) = P_{ld}(E-V_0^{ZP})/2\pi\hbar\rho(E) \quad , \tag{3.6} \]

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,
and to depress the rate of the A" states because the effective activation energy is increased by the amount $\hbar \omega_j$,

$$k_{A''}(E) = 2k(E - \hbar \omega_j^+)$$  \hspace{1cm} (3.7b)$$

Figure 1 shows the A' and A" microcanonical rate constants for reaction (1.1) (J=0), as calculated from Eqs. (3.1)-(3.3) with the frequencies used in earlier work; one sees clearly how Eqs. (3.7) 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

$$k_{A',A''}(E) = k(E) \left( \frac{1 \pm \frac{1}{2} \frac{\hbar \omega_j^+}{E-V_0}}{1 \pm \frac{1}{2} \frac{\hbar \omega_j^+}{E}} \right)^{F-1}$$  \hspace{1cm} (3.8)$$

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 $E \gg \hbar \omega_j$, as is the case, the denominator is essentially unity, so that Eq. (3.8) gives the ratio
of rate constants as

\[
\frac{k_{A_1}(E)}{k_{A_2}(E)} = \left( \frac{1 + \lambda}{1 - \lambda} \right)^{F-1},
\]

(3.9a)

where

\[
\lambda = \frac{1}{2} \frac{\hbar \omega^+}{(E - V_0)}.
\]

(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

\[
E - V_0 = \frac{1}{2} \frac{\hbar \omega^+}{(2^{1/F-1} + 1)} \frac{(2^{1/F-1} + 1)}{(2^{1/F-1} - 1)},
\]

which for large \( F \) is well-approximated by

\[
E - V_0 = \frac{\hbar \omega^+}{2 \ln 2} (F-1)/2.
\]

(3.10)

For the present case \( \hbar \omega^+ \approx 2.3 \text{ kcal/mole} \), so that the RHS of Eq.
(3.10) is \( \sim 16-17 \text{ kcal/mole} \). Since the zero point energy of the
transition state is \( \sim 11 \text{ kcal/mole} \), Eq. (3.10) predicts that the
energy (relative to the classical threshold) at which \( k_{A_1} \) has fallen
to a factor of 2 greater than \( k_{A_2} \) is \( (E - V_0^{ZP}) \approx 5-6 \text{ kcal/mole} \), and
this is indeed seen in Figure 1.
Before concluding this discussion of the formaldehyde reaction (1.1), it is interesting to note that the usual photochemical excitation of formaldehyde actually prepares the molecule in a state of definite $C_5$ 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 ($v_4$ 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 $C_5$) 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 $S_0^\dagger$ 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 unimolecular transition $S_1 \rightarrow S_0^\dagger$ and the rate of 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, however, on the electric field dependence of the lifetimes offers 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"

\[
I + CH_3I \rightarrow ICH_3 + I
\]  

(4.1)

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

\[
Br + CH_3I \rightarrow BrCH_3 + I
\]  

(4.2)

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, symmetry-wise.

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
\[ k_{\lambda}(E) = \frac{N_{\lambda}(E)}{2\pi\hbar \rho_{\lambda}(E)} , \quad (4.3) \]

where

\[ N_{\lambda}(E) = \sum_{n_1, \ldots, n_{F-1}=0}^{\infty} P_{\lambda}(n_1, \ldots, n_{F-1}) P_{\text{ld}}[E-V_0 - \sum_{k=1}^{F-1} \hbar \omega_k(n_k + \frac{1}{2})] \]

\[ \rho_{\lambda}(E) = \sum_{n_1, \ldots, n_F=0}^{\infty} P_{\lambda}(n_1, \ldots, n_{F-1}) \delta[E - \sum_{k=1}^{F} \hbar \omega_k(n_k + \frac{1}{2})] \quad , \quad (4.4a) \]

\[ (4.4b) \]

\[ (4.4b) \]

and \( \lambda \) 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 \( P_{\lambda}(n_1, \ldots, n_{F-1}) \) in Eq. (4.4) is the fraction that the state with quantum numbers \((n_1, n_2, \ldots, n_{F-1})\) is in the irreducible representation \( \lambda \). For the formaldehyde reaction it is quite trivial to determine this factor: for \( \lambda=A' \) \( P_{\lambda}(n_1, \ldots, n_5) = 1 \) 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. One simplifying observation is that \( P_{\lambda}(n_1, \ldots, n_{F-1}) \) is in general independent of the quantum numbers for the totally symmetry modes; this is the reason for omitting \( n_F \) as an argument of \( P_{\lambda} \) in Eq. (4.4b). One also has in all cases, the general relation
and from this one can easily show that the average microcanonical rate constant $k(E)$,

$$k(E) = \frac{\sum_{\lambda} \rho_{\lambda}(E) k_{\lambda}(E)}{\sum_{\lambda} \rho_{\lambda}(E)}$$

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 5 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 $(n_1, n_2, \ldots, n_7, n_8)$ is $A'$ or $A''$ if $(n_7+n_8)$ is even or odd, respectively; i.e., for $\lambda=A'$ $P_{\lambda}(n_7,n_8) = 1$ 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 non-zero 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 dependences associated with these couplings are
\[
\sin q_7 \cos q_7 = \frac{1}{4i} (e^{2iq_7} - e^{-2iq_7})
\]
\[
\sin q_8 \cos q_8 = \frac{1}{4i} (e^{2iq_8} - e^{-2iq_8})
\]
\[
\sin q_7 \cos q_8 = \frac{1}{4i} (e^{i(q_7+q_8)} - i(q_7+q_8) e^{-i(q_7-q_8)}
+ e^{-i(q_7-q_8)} )
\]

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

\[\Delta n_7 = 0, \pm 2, \pm 4 \quad , \quad \Delta n_8 = 0\]
\[\Delta n_8 = 0, \pm 2, \pm 4 \quad , \quad \Delta n_7 = 0\]
\[(\Delta n_7, \Delta n_8) = (1,1), (-1,1), (1,-1), (-1,-1), \ldots \quad ,\]

i.e., only matrix elements for which

\[\Delta(n_7+n_8) = 0, \pm 2, \pm 4, \ldots \quad .\]

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)-(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 \( k_{J,K,A}(E) \). (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 determine the microcanonical transition state theory rate constant for given values of \( K \) also, \( k_{J,K,A}(E) \).)

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 to 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 transition state theory" 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 (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 Miller\textsuperscript{16} 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 elements in Eq. (2.2)
and the frequencies along the reaction path that fully characterize the reaction path Hamiltonian. These quantities have been determined for the formaldehyde dissociation, and calculations for it like those of Waite and Miller are in progress.
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* Permanent address.


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. f. Naturforsch.* 18a, 607 (1963); (b) S. F. Fischer, G. L. Hofacker, and R. Seiler, *J. Chem. Phys.* 51, 3951 (1969);
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9. This is a consequence of the Heisenberg correspondence relation; see, for example, the discussion in W. H. Miller, J. Chem. Phys. 64, 2880 (1976).


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 $E$ 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 than indicated in Eq. (3.1), due to the two equivalent transition states (or equivalently, due to the symmetry number for $\text{H}_2\text{CO}$).
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