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Symmetry-Adapted Transition State Theory:

Non-Zero Total Angular Momentum

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Abstract

It is shown how non-zero total angular momentum is incorporated in a recently proposed symmetry-adapted transition state theory. The analysis is carried through explicitly for the unimolecular dissociation of formaldehyde, $\text{H}_2\text{CO} \rightarrow \text{H}_2 + \text{CO}$, for which the transition state is planar, i.e., C_s symmetry. The main qualitative result for this example is that mode-specificity between A' and A'' states--i.e., the difference of the rate constant ratio $k_{A'}/k_{A''}$ from unity--diminishes with increasing J but does not completely disappear even in the limit $J \rightarrow \infty$.

I. Introduction.

It has recently been pointed out¹ that any geometrical symmetry that a transition state may possess, which would also give the symmetry maintained along the reaction path,² will lead to selection rules in the dynamics of the reaction. These selection rules are the usual ones given by group theory--i.e., states corresponding to different irreducible representations of the appropriate symmetry group are uncoupled--and they can also be deduced by analysis of the reaction path Hamiltonian³ for the system. Thus even if the reaction dynamics is as strongly coupled as it can possibly be, so that a statistical theory such as transition state theory would be expected to be a good approximation for determining the rate constant for the reaction, one should take account of these selection rules and apply the statistical approximation separately to each different irreducible representation.

This "symmetry adapted transition state theory" has been applied¹ to the unimolecular dissociation of formaldehyde,

which has a planar transition state,⁴ i.e., C_s symmetry, and for total angular momentum $J=0$ it was seen that the microcanonical transition state theory rate constants for A' and A'' states (the two irreducible representations of C_s), differ by a factor of ~ 20 in the tunneling region which is important for this reaction. That is, there is a symmetry induced mode-specificity that cannot be destroyed no matter how strongly coupled the dynamics might be. (The microcanonical rate constants for A'/A'' symmetry are the average rate constants at a given

total energy for these symmetries; for individual states there may be even more mode-specificity than this dictated by symmetry.) It should also be noted that this symmetry feature is completely different from the role of symmetry numbers, or statistical factors,^{2,5} in transition state theory; i.e., it has nothing to do with the identity of the two H atoms and, for example, applies equally to the case $\text{HDCO} \rightarrow \text{HD} + \text{CO}$.

The purpose of the present paper is to show how rotation, i.e., total angular momentum $J > 0$, is handled in symmetry-adapted transition state theory. For the formaldehyde reaction (1.1), for example, it is clear that even (A') and odd (A'') out-of-plane vibrational states are coupled by coriolis interactions for $J > 0$, so that A'/A'' vibrational symmetry is no longer conserved. What is necessary, of course, is to consider the composite symmetry of the ro-vibrational states. Section II carries out this analysis for reaction (1.1), from which it is easy to see how one would proceed in general. For reaction (1.1) the main observation is that the degree of mode-specificity diminishes as J increases, but does not totally disappear.

In concluding the Introduction I would like to say what a privilege it is to be able to contribute to this special issue honoring Henry Eyring. I did not have the pleasure of knowing him well personally, but his work has obviously been an inspiration to all of us working in the theory of chemical reaction dynamics.

II. Application to Formaldehyde Dissociation.

As is usual in transition state theory, one approximates the energy levels of the reactants and the "transition state" by a simple separable-mode approximation, in the hope that the various densities of states will not depend sensitivity on approximations to individual energy levels. For the present situation it is also necessary to determine the symmetry of the various states in order to separate them into the different non-interacting irreducible representations. As noted in the Introduction, this will be carried out here specifically for reaction (1.1), which has a planar transition state, i.e., C_s symmetry. The notation follows closely that used before.⁶

For total angular momentum J the energy levels of the transition state are thus approximated as

$$E_{\tilde{n}, J, K_a}^{\dagger} = \epsilon_{\tilde{n}}^{\dagger} + \epsilon_{J, K_a}^{\dagger} \quad , \quad (2.1)$$

where the first term is the vibrational energy for the 5 vibrational modes $\tilde{n} \equiv (n_1, n_2, n_3, n_4, n_5)$, mode 5 being the out-of-plane (A'') mode; in practice a harmonic approximation is usually used for $\epsilon_{\tilde{n}}^{\dagger}$. The second term in Eq. (2.1) is the rotational energy, approximated as that of a symmetric rotor,⁷

$$\epsilon_{J, K_a}^{\dagger} = \frac{1}{2} (B^{\dagger} + C^{\dagger}) J(J+1) + [A^{\dagger} - \frac{1}{2} (B^{\dagger} + C^{\dagger})] K_a^2 \quad . \quad (2.2)$$

Here the a-axis, with rotation constant $A^{\dagger}$, is the "almost" symmetric rotor axis of the transition state, i.e., the in-plane axis that points almost along the CO bond. The rotation constant $A^{\dagger}$ is thus the

large one ($A^\dagger \approx 9 \text{ cm}^{-1}$), and $B^\dagger$ and $C^\dagger$ are small and almost equal ($B^\dagger \approx C^\dagger \approx 1 \text{ cm}^{-1}$).

The symmetry of the vibrational state is easy to ascertain: it is A' (A'') if the out-of-plane vibrational quantum number n_5 is even (odd). The rotational state symmetry, however, is more difficult to deal with. Asymmetric rotor states designated as $J_{K_a K_c}$, where K_a and K_c denote the conserved projections in the prolate and oblate limits, respectively, are A' (A'') in C_s symmetry if K_c is even (odd).⁸ Formaldehyde and its transition state, however, are almost prolate rotors, with approximate energy levels characterized more appropriately by K_a (cf. Eq. (2.2)). In terms of K_a the doubly degenerate levels for $K_a > 0$ (i.e., $|K_a|$ and $-|K_a|$ have the same energy) give rise each to one A' state and one A'' state; $K_a = 0$ levels are non-degenerate and are A' (A'') if J is even (odd).⁸ The composite symmetry of the ro-vibrational states is obtained by using the multiplication rule of C_s symmetry: $A' \otimes A' = A'$, $A'' \otimes A'' = A'$, $A' \otimes A'' = A''$.

The symmetry-adapted microcanonical transition state theory rate constants are given by¹

$$k_\lambda(E, J) = N_\lambda(E, J) / [2\pi\hbar\rho_\lambda(E, J)] \quad , \quad (2.3)$$

for $\lambda = A'$ or A'' , where E is the total energy, and N_λ and ρ_λ involve sums over states of composite symmetry λ . Following the discussion in the previous paragraph, it is not hard to see that these sums over states are

$$N_{\lambda}(E, J) = \sum_{\tilde{n}=0}^{\infty} \sum_{K_a=-J}^J \frac{1}{2} [1 \pm (-1)^{J+n_5}] \delta_{K_a, 0} P(E - V_0 - E_{\tilde{n}, J, K_a}^{\dagger}) \quad (2.4a)$$

$$\rho_{\lambda}(E, J) = \sum_{\tilde{n}=0}^{\infty} \sum_{K_a=-J}^J \frac{1}{2} [1 \pm (-1)^{J+n_5}] \delta_{K_a, 0} \delta(E - E_{\tilde{n}, J, K_a}) \quad (2.4b)$$

where the "+" and "-" signs are for $\lambda=A'$ and A'' , respectively, P is the usual⁶ one-dimensional tunneling probability as a function of translational energy in the reaction coordinate, δ is the Dirac delta function, and $E_{\tilde{n}, J, K_a}$ is an energy level of the reactant molecule that is given by an expression similar to Eq. (2.1) (except here $\tilde{n} = n_1, n_2, n_3, n_4, n_5, n_6$, with n_5 still being the out-of-plane vibrational quantum number). The "symmetry factor" $\frac{1}{2} [1 \pm (-1)^{J+n_5}] \delta_{K_a, 0}$ in Eq. (2.4) is a concise statement of the fact that the state with quantum numbers $(\tilde{n}, J, K_a)$ is, on the average, 50% A' and 50% A'' for $K_a \neq 0$, and for $K_a = 0$ it is A' (A'') if $J+n_5$ is even (odd).

The generalization of Eq. (2.4) to arbitrary symmetries is that the "symmetry factor" becomes a factor $P_{\lambda}(\tilde{n}, J, K)$ which is the fraction that the state $(\tilde{n}, J, K)$ is in the irreducible representation λ . In the present example of C_s symmetry it is quite simple to deduce these factors, but for higher symmetries one would need to utilize more of the full apparatus of group theory.⁹ Since

$$\sum_{\lambda} P_{\lambda}(\tilde{n}, J, K) = 1$$

for all states $(\tilde{n}, J, K)$, it is easy to see that the average micro-canonical rate constant,

$$k(E, J) \equiv \sum_{\lambda} \rho_{\lambda}(E, J) k_{\lambda}(E, J) / \sum_{\lambda} \rho_{\lambda}(E, J) \quad , \quad (2.5)$$

is given by the standard microcanonical transition state expression without regard for symmetry (i.e., Eq. (2.4) without any symmetry factors).

Calculations similar to earlier ones⁶ have been carried out for reaction (1.1) using Eq. (2.4), but one can understand the essential results by considering a simple approximation. In the tunneling region the ground vibrational state $\tilde{n} = 0$ of the transition state makes the dominant contribution to N_{λ} , and the rotational energy is sufficiently small for low J that it can be set to zero; thus

$$N_{\lambda}(E, J) \approx [J + \frac{1}{2} (1 \pm (-1)^J)] P(E - V_0 - E_{0,0,0}) \quad (2.6a)$$

The energy relative to the reactive molecule is so high (~ 80 kcal/mole), however, that the densities of A' and A'' states are essentially equal,

$$\rho_{A'}(E, J) \approx \rho_{A''}(E, J) \quad . \quad (2.6b)$$

For $J > 0$, Eq. (2.6) gives

$$\frac{k_{A'}(E,J)}{k_{A''}(E,J)} = \left\{ \begin{array}{ll} 1 + 1/J & , \quad J \text{ even} \\ (1 + 1/J)^{-1} & , \quad J \text{ odd} \end{array} \right\} , \quad (2.7)$$

and this is accurate to a few percent up to $J=5$. Compared to a ratio of ~ 20 for $J=0$, Eq. (2.7) shows that the "mode-specific ratio" is 0.5, 1.5, 0.75, and 1.25 for $J=1, 2, 3$, and 4. For larger J one can use the fact that in the tunneling region P is approximately exponential,

$$P(E_r) \approx \alpha e^{\gamma E_{tr}} ; \quad (2.8)$$

it is then not hard to show that the ratio in Eq. (2.7) becomes

$$\frac{k_{A'}(E,J)}{k_{A''}(E,J)} \approx 1 + \left[\sum_{K_a=1}^J \exp\left\{-\gamma\left[A^\ddagger - \frac{1}{2}(B^\ddagger + C^\ddagger)\right]K_a^2\right\} \right]^{-1} \quad (2.9)$$

for J even, and the reciprocal of this for J odd. The exponential parameter γ and the rotation constants of the transition state give

$$\gamma\left[A^\ddagger - \frac{1}{2}(B^\ddagger + C^\ddagger)\right] \approx 0.0248 .$$

One can easily see that Eq. (2.7) is regained from Eq. (2.9) if J is small. For large J , however, the ratio $k_{A'}/k_{A''}$ does not approach 1, as Eq. (2.7) would suggest, but actually reaches a constant value

of ~ 1.18 for J even and $\sim (1.18)^{-1} = 0.85$ for J odd.

The chief reason for this diminished mode-specificity for $J > 0$ is, of course, that A' and A'' states both have a contribution from the ground vibrational state $\tilde{n} = \tilde{0}$ of the transition state (cf. Eq. (2.6a)). For $J=0$, on the other hand, the ground vibrational state is pure A' ; the lowest A'' state has $n_5=1$ and thus a significantly smaller value for $N_{A''}$.

III. Concluding Remarks.

It has been shown how symmetry-adapted transition state theory can be generalized to deal with non-zero total angular momentum: one simply considers the overall symmetry of the ro-vibrational states. For the dissociation of formaldehyde, reaction (1.1), the degree of mode-specificity between A' and A'' states--i.e., the difference of the ratio $k_{A'}/k_{A''}$ from unity--diminishes as J increases, but does not disappear completely even in the limit $J \rightarrow \infty$.

In concluding, it should be emphasized again that $k_{\lambda}(E, J)$ is the average rate constant for states of symmetry λ , energy E , and total angular momentum J , and also that the degree of mode-specificity imposed by symmetry is the minimum that can exist; i.e., there is always the possibility that there may be additional mode-specificity if all the states within a given symmetry are not sufficiently strongly coupled. If, for example, coriolis coupling between vibrational and rotational states is extremely weak, which might be true for small J , then the A'/A'' symmetry of vibrational and rotational states would be conserved separately, not just the composite ro-vibrational symmetry. In the tunneling region of reaction (1.1), for example, there would then be the factor of ~ 20 between rate constants for states whose vibrational symmetries are A' and A'' . Symmetry alone, of course, cannot answer the question of whether or not there exist weak coupling, i.e., weak selection rules, between states within a given irreducible representation; for this one needs a Hamiltonian and dynamics.

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