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SYMMETRY-ADAPTED TRANSITION STATE THEORY
AND A UNIFIED TREATMENT OF MULTIPLE
TRANSITION STATES

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Abstract

It is shown how a recently discussed symmetry-adapted transition state theory leads to a unified treatment of reactions that involve multiple transition states that are symmetry-related. If the two (or more) transition states are well separated, the present description reduces to the standard prescription based on symmetry numbers, but it also applies more generally to the case that the transition states are close enough to interact dynamically, and even to the limit that they merge into a single transition state.

It has recently been pointed out¹ that any geometrical symmetry that a transition state may possess can have interesting consequences for the dynamics of the related reaction. For the unimolecular dissociation of formaldehyde,

for example, which has a planar transition state (i.e., C_s symmetry), states of A' and A'' symmetry are non-interacting; thus even if the dynamics is sufficiently non-discriminating so as to justify a statistical approximation (e.g., microcanonical transition state theory), one should make the statistical approximation separately for A' and for A'' states. For $J=0$ it was seen¹ that this symmetry-adapted transition state theory predicts a significant degree of mode-specificity for reaction (1) in the energy region of the origin of the $S_0 \rightarrow S_1$ excitation: A' states dissociate, on the average, at a rate ~ 20 times faster than A'' states of essentially the same energy.

The purpose of this paper is to show how symmetry-adapted transition state theory also leads one to see how multiple transition states that are symmetry related should be included in transition state theory, even when they are not sufficiently "isolated" so that the standard symmetry number prescription² is appropriate. In such cases it will also be seen that it is actually better to choose the "transition", or reference configuration, for the reaction as a stationary point on the potential energy surface that has two imaginary vibrational frequencies, rather than a conventional saddle

point on the potential surface that is characterized by a single imaginary frequency.³ To keep the presentation as simple and as clear as possible, it will be carried through explicitly for the formaldehyde reaction (1); it should then be clear how the idea applies more generally.

Consider first symmetry-adapted transition state theory as it applies to reaction (1) with its planar transition state. The irreducible representations A' and A'' correspond to even and odd vibrational states of the out-of-plane vibrational mode, so that the microcanonical rate constants are¹ (for J=0)

$$k_{A'}(E) = [2\pi\hbar\rho_{A'}(E)]^{-1} \sum_{n_1, n_2, n_3, n_4=0}^{\infty} \sum_{n_5=0, 2, 4}^{\infty} P(E - \epsilon_n^{\ddagger}) \quad (2a)$$

$$k_{A''}(E) = [2\pi\hbar\rho_{A''}(E)]^{-1} \sum_{n_1, n_2, n_3, n_4=0}^{\infty} \sum_{n_5=1, 3, 5}^{\infty} P(E - \epsilon_n^{\ddagger}) ; \quad (2b)$$

modes k=1,2,3,4 are the in-plane modes, mode k=5 the out-of-plane mode, $\epsilon_n^{\ddagger}$ the vibrational energy of the transition state [usually approximated harmonically, $\epsilon_n^{\ddagger} = V_{\text{barrier}} + \sum_{k=1}^5 \hbar\omega_k^{\ddagger} (n_k + \frac{1}{2})$], and P is the tunneling probability along the reaction coordinate. The barrier is sufficiently high that at relevant energies the densities of A' and A'' states are essentially the same,

$$\rho_{A'}(E) = \rho_{A''}(E) = \frac{1}{2} \rho(E) \quad , \quad (3)$$

where $\rho(E) = \rho_{A'} + \rho_{A''}$ is the total density of reactant states.

Suppose now that the transition state for reaction (1) were not planar; by symmetry, there would then be two such non-planar transition states. Rather than use either of these non-planar transition states and conventional transition state theory, however, it is better to choose the reference configuration to be planar (i.e., C_s), approximately the average of the two non-planar transition state structures. Within a harmonic approximation the potential in the out-of-plane coordinate, q_5 , is the top of a barrier (i.e., has an imaginary frequency), so that one must describe it better than harmonically; the lowest order such approximation would include a quartic term,

$$V(q_5) = -\frac{1}{2} |\omega_5|^2 q_5^2 + a q_5^4 + \dots, \quad (4)$$

and is seen to have the character of a symmetric double well potential; cf. Figure 1. (The reference configuration can be specified precisely by requiring that it be a stationary point on the potential surface that also has an imaginary frequency for the reaction coordinate; i.e., it is a stationary point characterized by two imaginary frequencies and is thus not a saddle point of the potential surface.) The significant point is that the potential is an even function of q_5 , so that the out-of-plane vibrational levels are still even or odd, i.e., A' and A'' . Thus symmetry-adapted transition state theory applies here just as it does if the two transition states coalesce into one planar transition state, the only difference being that the even (A') and

odd (A'') vibrational energy levels are determined by the double well potential, e.g., Eq. (4), rather than harmonically.

One can easily see how the above description reduces to the usual one in the limit that the two non-planar transition states are very non-planar, i.e., far from each other. In this limit the double well potential in q_5 has a very high barrier, and the vibrational levels become degenerate in pairs (one A' and one A''); cf. Figure 1. The sums over even and odd values of n_5 in Eq. (2) thus become equal, and equal to the sum over harmonic-like vibrational levels of one of the two wells of the symmetric double well potential. Together with Eq. (3), this thus gives

$$k_{A'}(E) = k_{A''}(E) = 2k_1(E) \quad , \quad (5)$$

where $k_1(E)$ is the ordinary transition state theory rate constant for reaction through one of the two non-planar transition states. In this very non-planar limit, therefore, Eq. (5) shows that one loses A'/A'' mode-specificity--i.e., $k_{A'} = k_{A''}$ --and also that the rate is given by the usual prescription:² one calculates the ordinary transition state rate through one of the transition states and multiplies by 2.

Symmetry-adapted transition state theory thus gives the correct result if the two non-planar transition states are very far apart, close together, or even as they merge into one (planar) transition state. Also, the mode-specificity that has been noted in the planar case is not lost discontinuously if the transition state becomes slightly non-planar, but rather diminishes gradually as the

transition state is made progressively non-planar.

Another interesting point of this analysis is that stationary points on a potential energy surface that have more than one imaginary harmonic frequency, which are usually ignored because they are not true transition states (i.e., saddle points),³ may in some cases actually be the most relevant reference configuration by which to characterize the reaction.

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References

1. W. H. Miller, J. Am. Chem. Soc., in press.
2. See, for example, P. Pechukas, in Dynamics of Molecular Collisions Part B (Vol. 2 of Modern Theoretical Chemistry), ed. W. H. Miller, Plenum, N.Y., 1976, p. 285.
3. J. N. Murrell and K. J. Laidler, Trans. Faraday Soc. 64, 371 (1968).

Figure Caption

Sketch of the vibrational potential function for the out-of-plane mode $k=5$ (with vibrational energy levels indicated) for the cases of a planar (a), or non-planar (b), transition state.

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Figure 1

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