

On the Question of Mode-Specificity in Unimolecular Reaction Dynamics

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Unimolecular decomposition following state-specific laser excitation is considered. If the transition state for the unimolecular reaction possesses any geometrical symmetry, then it is shown that this can lead to mode-specificity in the decay rates (i.e., different states with essentially the same total energy and angular momentum react at significantly different rates). This is illustrated for a model problem of two coupled oscillators (the Henon–Heiles potential) and also for the unimolecular dissociation of formaldehyde, $\text{H}_2\text{CO} \rightarrow \text{H}_2 + \text{CO}$, which has a planar transition state. Dynamical calculations indicate that there may also be a significant degree of mode-specificity for the formaldehyde reaction beyond that due to symmetry.

1. INTRODUCTION

With the continuing development of laser technology it is becoming increasingly possible to excite molecules in very specific ways.¹ For the unimolecular dissociation of formaldehyde,



for example, which will be one of the examples considered below, one can imagine exciting individual ro-vibrational states that are predominantly C–H stretching motion, CO stretching, out-of-plane bending vibration, etc. The interesting question is then whether various characteristics of the reaction—i.e., its rate, the product state distribution, etc.—depend on which quantum state, or mode is excited, or only on the total energy of excitation. If a reaction is mode-specific, then mode-specific laser excitation would give one much greater

control of the chemical system, with obvious important practical consequences. If, on the other hand, the reaction is not mode-specific—i.e., depends only on the total excitation energy—then exciting it mode-specifically accomplishes nothing.

Whether or not a particular reaction behaves mode-specifically is clearly related to intramolecular vibrational relaxation (IVR): If the initially excited vibrational state in some sense randomizes itself before the reaction occurs, then one thinks intuitively that the system will not behave mode-specifically. IVR has been discussed a great deal² in recent years in terms of the intramolecular classical mechanics of various model molecular systems, and much attention has been focused on the distinction between quasi-periodic, i.e., separable like classical dynamics, and chaotic, or ergodic-like classical dynamics.³ One is inclined to think intuitively that quasi-periodic classical dynamics, which is prevalent at low energies, would give rise to mode-specific chemistry, while chaotic dynamics, which sets in at higher energies, would lead only to statistical behavior. As seen below, however, things are more subtle than this. One obvious limitation to a correlation of quasi-periodic/chaotic character of the classical mechanics and the degree of mode-specificity in chemical reaction rates, is that the quasi-periodic/chaotic characterization has no time scale in it. That is, the standard procedure^{2,3} is to generate a Poincare surface of section and characterize it as quasi-periodic or chaotic, but there is nothing in this analysis that has anything to do with *how long* it might take the chaotic behavior to appear. It seems clear, however, that mode-specificity in a chemical reaction should depend on the *rate* that chaotic behavior develops compared to the rate of the reaction.

Section 2 first discusses these issues with regard to a simple model of two coupled vibrational modes, the so-called Henon–Heiles system. Although of no particular physical significance, this system has been studied extensively with regard to the quasi-periodic/chaotic character of its classical dynamics, and since it is a unimolecularly decaying system, it is interesting to see if mode-specificity in the unimolecular rate constants can be understood in terms of the character of the classical mechanics. The system also shows some interesting effects due to the symmetry of the potential energy surface.

Symmetry is also found to play an important role in determining the extent of mode-specificity in the unimolecular dissociation of

formaldehyde, reaction (1.1). This is discussed in Section 3, and the chief conclusion is that in the tunneling region which is important for this reaction there should be at least a factor of ~ 20 difference between unimolecular decay rates of states with the same total energy (and total angular momentum $J = 0$) but of different symmetry. Section 4 concludes.

2. EXAMPLE: THE HENON-HEILES POTENTIAL

The Henon-Heiles⁴ system consist of two degenerate harmonic oscillators coupled by a cubic interaction. In reduced units the potential function is

$$V(x, y) = \frac{1}{2}x^2 + \frac{1}{2}y^2 - \frac{1}{3}x^3 + xy^2 \quad (2.1a)$$

or in polar coordinates one sees its C_{3v} symmetry more explicitly,

$$V(r, \theta) = \frac{1}{2}r^2 - \frac{1}{3}r^3 \cos(3\theta) \quad (2.1b)$$

There are thus three equivalent saddle points, or transition states, leading to dissociated products. In these reduced units the potential energy of the saddle point, i.e., the barrier height is $V_0 = \frac{1}{6} \approx 0.17$.

Quantum mechanically, of course, this system has no bound states, only metastable states, which decay unimolecularly by tunneling through the barriers. Waite and Miller⁵ have calculated the energies and lifetimes (the inverse of the unimolecular decay rate) of the individual metastable quantum states of the system, and Figure 1 shows a sample of their results. Because of the C_{3v} symmetry of the system, the calculation is carried out separately for states of A_1 symmetry (solid circles in Figure 1), A_2 symmetry (open squares), and E symmetry (open circles). The solid line in Figure 1 is the result given by standard statistical theory, i.e., microcanonical transition state theory,⁶

$$k(E) = 3 \sum_{n=0}^{\infty} P[E - V_0 - (n + \frac{1}{2})\hbar\omega^\ddagger] / [2\pi\hbar\rho(E)] \quad (2.2)$$

Here P is the one-dimensional tunneling probability as a function of the energy along the reaction coordinate, $\omega^\ddagger = \sqrt{3}$ is the frequency of the "activated complex", $\rho(E)$ the density of reactant states, and the factor of 3 is due to the three equivalent transition states.

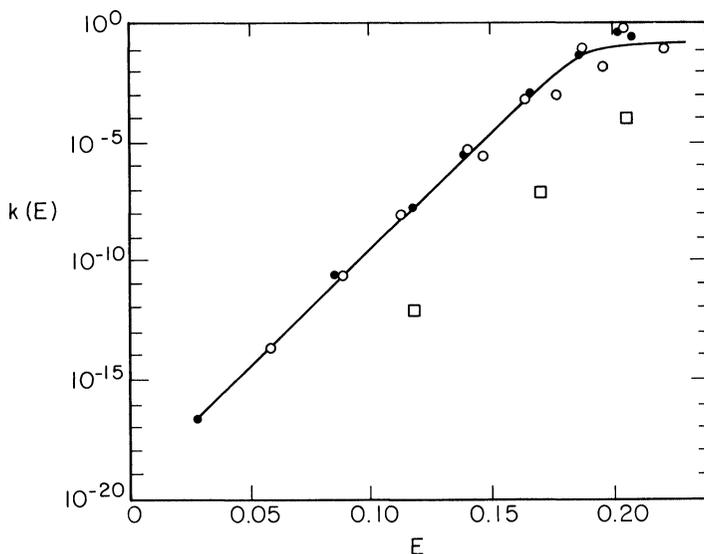


FIGURE 1 State-specific unimolecular rate constants ($k = -(2/\hbar) \times$ imaginary part of the complex eigenvalue) versus energy (real part of the complex eigenvalue) for metastable states on the Henon-Heiles potential. Solid points, squares, and open circles denote states of A_1 , A_2 , and E symmetry, respectively.

The first thing that one observes in Figure 1 is that the statistical approximation to the rate constants (i.e., Eq. 2.2) is quite good for the A_1 and E states, even in the low energy region below ~ 0.11 where the classical mechanics is essentially completely quasi-periodic. On closer inspection one does see some mode-specificity in the A_1 and E states, i.e., some dispersion about the average curve, but this is more pronounced at *higher* rather than lower energies. To the extent that there is any trend at all, therefore, it is opposite to what one would predict on the basis of the quasi-periodic/chaotic character of the classical mechanics. The appearance of some degree of mode-specificity at high energies is perhaps understandable in that even if the various degrees of freedom are strongly coupled, states with most of the energy in the reaction coordinate will decay essentially instantaneously (i.e., within one vibrational period) while those with most of the energy in inactive modes will require at least a few vibrations for the energy to flow into the reaction coordinate.

The next most striking result seen in Figure 1 is that the A_2 states (the open squares) decay significantly slower than the A_1 and E states. This is easily understood, however, when one realizes that the wavefunctions of A_2 symmetry have nodal lines along the reaction coordinates through each saddle point. (The angular functions of A_2 symmetry are $\sin(3l\theta)$, $l = \text{an integer}$.) In terms of transition state theory, therefore, the vibrational quantum number of the "activated complex," the mode perpendicular to the reaction coordinate, must be odd; i.e., for A_2 states Eq. (2.2) is modified so that the sum is only over odd values of n . In the tunneling region this has the effect of raising the activation energy for the A_2 states by the amount $\hbar\omega^\ddagger$, which in the present reduced units is ~ 0.05 , and one sees that the rates for the A_2 states do indeed lie on a line that is shifted in energy from the A_1, E curve by about 0.05.

For this model problem, therefore, the most significant degree of mode-specificity is that which is symmetry-induced. An important aspect of the symmetry effect, however, is that it is not the *global* symmetry of the potential surface that is relevant to the mode-specificity, but a *reduced* symmetry. Thus A_1 and E states do not display mode-specificity, only the A_2 states do. As will be discussed in the next section, it is the symmetry of the transition state (which is the same as the symmetry maintained along the reaction path) that is relevant to the reaction dynamics. In the present example, the global symmetry is C_{3v} , but the symmetry of a given transition state is only C_s , i.e., reflection in the plane that bisects the saddle point. Since the correlation between C_{3v} and C_s symmetry is $A_1 \rightarrow A'$, $A_2 \rightarrow A''$, $E \rightarrow A' + A''$, and since it is the A' states of the transition state (even n in Eq. (2.2)) that react much faster than the A'' states (odd n in Eq. (2.2)), the result is as observed, namely that A_1 and E states decay at essentially the same rate, and much faster than A_2 states.

3. EXAMPLE: UNIMOLECULAR ASSOCIATION OF FORMALDEHYDE

The unimolecular dissociation of formaldehyde, reaction (1.1), has taken on the role of a benchmark⁷ for photochemistry and reaction dynamics in small polyatomic molecules. Our present interest is focused on the question of mode-specificity in reaction (1.1). Even

for total angular momentum $J = 0$, though, the six vibrational degrees of freedom of formaldehyde make direct quantum calculations of the type of Waite and Miller⁵ for the state specific unimolecular decay rates prohibitive.

Without making any dynamical calculations, however, one can draw some conclusions based on symmetry. As with the example in the previous section, it is not the global symmetry of the potential surface (which is C_{2v}) that is relevant, but rather the symmetry of the transition state, which is planar (i.e., C_s) for reaction (1.1). Thus using the reaction path Hamiltonian⁸ model to describe the reaction dynamics, one can show⁹ that planar symmetry of the transition state, which is also the symmetry conserved along the reaction path (the minimum energy path through the transition state from reactants to products), leads to selection rules that are essentially the same as those dictated by group theory; i.e., there is no coupling between A' and A'' states. For total angular momentum $J = 0$, this simplifies to the statement that even and odd vibrational states of the out-of-plane vibration are uncoupled. Even within a statistical approximation, i.e., microcanonical transition state theory, one should therefore take account of this selection rule and apply it separately to each irreducible representation.

Stated most generally (as least for $J = 0$), this "symmetry-adapted transition state theory" gives the microcanonical rate constant for irreducible representation λ as

$$k_\lambda(E) = N_\lambda(E) / [2\pi\hbar\rho_\lambda(E)] \quad (3.1)$$

where N_λ and ρ_λ are the cumulative reaction probability and density of reactant states, respectively, for irreducible representation λ . Specifically, within the usual harmonic approximation for the vibrational energy level, one has

$$N_\lambda(E) = \sum_{\mathbf{n}} \mathcal{P}_\lambda(\mathbf{n}) P[E - V_0 - \hbar\omega^\ddagger \cdot (\mathbf{n} + \frac{1}{2})] \quad (3.2a)$$

$$\rho_\lambda(E) = \sum_{\mathbf{n}} \mathcal{P}_\lambda(\mathbf{n}) \delta[E - \hbar\omega \cdot (\mathbf{n} + \frac{1}{2})] \quad (3.2b)$$

where ω^\ddagger and ω are the frequencies of the transition state and the reactant molecule, respectively, P the one dimensional tunneling probability, and the factor $\mathcal{P}_\lambda(\mathbf{n})$ is the fraction of the state with

quantum numbers \mathbf{n} that has symmetry λ . For the formaldehyde reaction these "symmetry factors" are quite trivial to deduce: if modes 1, 2, 3, 4 of the transition state are the in-plane modes and mode 5 the out-of-plane mode, then $\mathcal{P}_\lambda(\mathbf{n})$ is 1 (0) for n_5 even (odd) for $\lambda = A'$, and vice-versa for $\lambda = A''$.

Figure 2 shows these symmetry adapted transition state theory rate constants for reaction (1.1) for $J = 0$. The energy region of interest experimentally⁷ for the unimolecular decay of formaldehyde from the $S_0 \rightarrow S_1$ laser excitation is ~ 3 – 5 kcal/mol below the classical threshold (which is the energy origin in the figure), and one sees that here there is a factor of ~ 20 between the A' and A'' rate constants at the same total energy. On the basis of symmetry alone, therefore, one predicts a significant degree of mode specificity in the tunneling region. Similar to the situation in Section 2, one can understand the origin of this quite simply: in the tunneling region the lowest state of each symmetry dominates the sum over states in N_λ , and for A' symmetry this is the ground state $n_1 = n_2 = \dots, n_5 = 0$, while for A'' symmetry one has $n_5 = 1$; the activation energy for A'' symmetry is thus increased by the amount $\hbar\omega_5^\ddagger$.

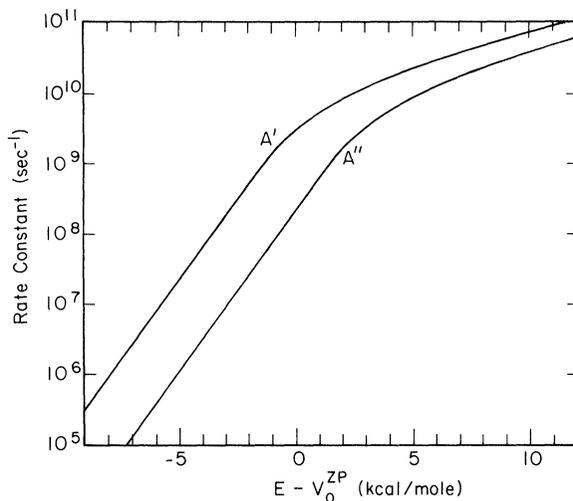


FIGURE 2 Microcanonical rate constant for the reaction $\text{H}_2\text{CO} \rightarrow \text{H}_2 + \text{CO}$ (for $J = 0$) for the symmetries A' and A'' , as a function of total energy E relative to V_0^{ZP} (the barrier height plus zero point energy of the transition state).

The symmetry analysis can be generalized to non-zero total angular momentum;¹⁰ one simply utilizes the composite symmetry of the ro-vibrational states to identify non-interacting states. For reaction (1.1) the degree of symmetry induced mode-specificity decreases as J increases, but does not disappear completely even in the limit $J \rightarrow \infty$.

Finally, Waite *et al.*¹¹ have carried out dynamical calculations for a two-mode approximation for formaldehyde—the reaction coordinate and the out-of-plane bend—to determine the energies and lifetimes of the eigenmetastable states, i.e., the same kind of calculations described in Section 2. Figure 3 shows the results. The solid (open) squares and circles are for states that are even (odd) in the out-of-plane bend, and the circles (squares) are for states that are even (odd) in the reaction coordinate; i.e., the overall symmetry of the potential surface is C_{2v} , and the four symmetries A_1 , A_2 , B_1 and B_2 , are all computed separately. As one sees, however, the only symmetry-induced mode-specificity is that between states that are even (A') and odd (A'') in the out-of-plane vibration; i.e., the solid points lie, on the average, above the open points, by the factor of ~ 20 . In addition

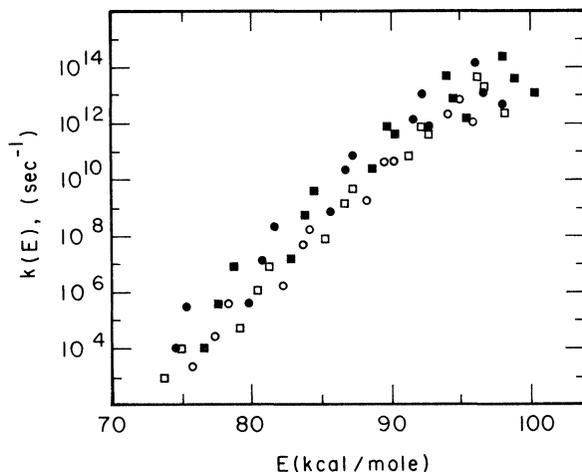


FIGURE 3 State-specific unimolecular rate constants for the two-mode model of the reaction $\text{H}_2\text{CO} \rightarrow \text{H}_2 + \text{CO}$. Each point corresponds to a complex eigenvalue $E_n - i\Gamma_n/2$; the energy of the metastable state is E_n and its unimolecular decay rate $k_n = \Gamma_n/\hbar$. The solid (open) points and squares are for states that are even (odd) in the out-of-plane vibration, and the circles (squares) are for states that are even (odd) in the reaction coordinate.

to this symmetry-induced mode specificity, however, one sees that there is a significant degree of mode specificity within the A' and A'' manifolds of the states themselves. This can only be ascertained, of course, by dynamical calculations such as these.

4. CONCLUDING REMARKS

The general ideas that these studies have illustrated is that any geometrical symmetry that the transition for a reaction possesses will lead to selection rules in the dynamics of the reaction. Thus even if one employs a statistical approximation (i.e., micro-canonical transition state theory), then at the most rigorous level one should use a symmetry-adepted transition state theory and compute the micro-canonical rate constants for each irreducible representation of the symmetry group. This can give rise to symmetry-induced mode-specificity in the reaction.

In conclusion it should be emphasized that the symmetry adapted microcanonical transition state theory rate constants $k_\lambda(E)$ (cf. Eq. 3.1) are the *average* rates for energy E and symmetry λ ; i.e., there is always the possibility that actual dynamical calculations will give rates that have some dispersion about this average value, as do the results in Figure 3. The degree of mode-specificity required by symmetry is therefore the *minimum* amount that can exist, but to discover whether any further exists requires more detailed dynamical treatments.

ACKNOWLEDGEMENTS

This work has been supported in part by the Division of Chemical Sciences, Office of Basic Energy Sciences, US Department of Energy under Contract W-7405-Eng-48. All calculations were carried out on a Harris H800 minicomputer funded by a National Science Foundation grant CHE-79-20181.

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