

The High-Resolution Spectroscopy of Dissociating Molecules [and Discussion]

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The high-resolution spectroscopy of dissociating molecules

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Results from spectroscopic studies of the vibrational levels of dissociating molecules and from state-selected, state-resolved photofragmentation spectroscopy are presented. The extent of energy flow among the modes of a molecule is explored through the couplings, or lack thereof, revealed by high-resolution spectroscopy. The dynamics of energy flow during bond breaking are revealed by photofragment excitation spectroscopy and by product energy state distributions. These completely resolved data provide sensitive tests of dynamical constraints such as vibrational or rotational adiabaticity and thus of theoretical models for unimolecular reaction dynamics.

0. Introduction

For many years statistical theories have provided useful models for unimolecular reactions (Robinson & Holbrook 1972; Forst 1973). All start from the assumption that vibrational energy is transferred among the modes of a molecule much faster than chemical reaction occurs. A reaction coordinate is defined along the lowest energy path to products and a transition state is identified as a surface orthogonal to the reaction coordinate which gives the minimum value for the reaction rate

$$k(E, J) = W(E, J)/h\rho(E, J), \quad (1)$$

where E and J are the total energy and angular momentum, ρ is the molecular density of states and W is the number of vibrational levels with angular momentum J and energy less than E for modes orthogonal to the reaction coordinate. For reactions close to threshold, W includes a significant contribution from levels with energy greater than E weighted by a tunnelling probability.

1. Reactions with barriers

When there is a high barrier between reactant and products, the transition state is clearly located at the saddle point defined at the energy maximum along the reaction coordinate and (1) is the standard Rice–Ramsperger–Kassel–Marcus

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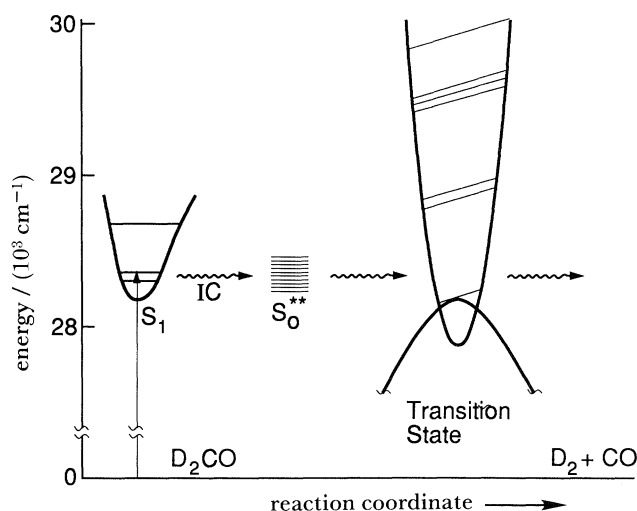


Figure 1. Bond breaking with a high barrier. A single rovibronic level of the first excited singlet state of D_2CO is excited by a pulsed ultraviolet (uv) laser. This level is Stark tuned through resonances with ground singlet state levels using a direct current (DC) electric field. Internal conversion of electronic to vibrational energy is fastest on resonance and thus the spectrum of S_0^{**} levels may be recorded. The linewidth of each level gives its dissociation rate constant. The rate of dissociation is controlled by passage through the transition state; the energy levels for vibrations orthogonal to the reaction coordinate are taken from *ab initio* computations (Scuseria & Schaefer 1989).

(RRKM) theory. The formaldehyde molecule with its barrier some 28000 cm^{-1} above both reactants and products provides an ideal example, figure 1 (Moore & Weisshaar 1983). The properties of the transition state have been calculated *ab initio* (Scuseria & Schaefer 1989) and $W(E, J)$ computed. Stark level crossing spectroscopy has permitted $\rho(E, J)$ and $k(E, J)$ to be determined experimentally for energies just at the reaction threshold (Polik *et al.* 1990*a*). Equation (1), with tunnelling included, is quantitatively accurate for the average rate constant to well within the uncertainty introduced by the 700 cm^{-1} uncertainty in the *ab initio* barrier height.

Level crossing spectroscopy gives values of the dissociation rate constant and the internal conversion matrix element (for electronic–vibrational energy conversion between the excited and ground singlet levels which cross) for each individual vibrational level in the ground electronic state (Polik *et al.* 1990*a*). Since there are roughly 10^2 levels per cm^{-1} , excellent statistics are obtained. In a narrow energy range both rate constant and matrix element fluctuate over a range of some two orders of magnitude. The distributions for these values and for interferences between decays through nearby levels have been found to conform exactly to the distributions predicted for vibrational levels whose wavefunctions correspond to the limit of strong intermode vibrational coupling (Polik *et al.* 1988, 1990*b*). The wavefunctions for a single molecular eigenstate appear to have coefficients which are random numbers when expanded in a basis of eigenfunctions of a separable hamiltonian (no cross terms coupling vibrational modes). The shape of the rate constant distribution gives the number of independent degrees of freedom for passing through the transition state, 3.8 (Polik *et al.* 1990*b*). Each vibrational level contributing to $W(E, J)$ gives an independent path to products. Each of these transition state levels has an independent set of vibrational overlaps (matrix elements) with the molecular

eigenstates. The rate is roughly proportional to the sum of the squares of these overlaps and the distribution of rates becomes narrower as more independent overlaps become important. The *ab initio* prediction for this number of degrees of freedom is 2.0; a 10% decrease in the transition-state frequencies provides agreement with the experimental value.

The assumption of strong vibrational coupling framed in terms of random vibrational wavefunction coefficients provides a statistical theory for both the magnitudes and distributions of rate constants in the fully quantum-state-resolved limit for unimolecular reactions. The number of degrees of freedom characterizing the dissociation rate provides a sensitive test of transition-state properties. For the formaldehyde molecule this theory has been found to be quantitatively useful, but more detailed, *ab initio* work is needed (Polik *et al.* 1990*b*).

2. Reactions without barriers

When a bond breaks to form two free radicals, there is usually no energy barrier above that for separated products. It is much less clear how to identify the transition state and apply (1) when there is no energy maximum along the reaction coordinate leading to products. Several theoretical models have been proposed and are being developed (Robinson & Holbrook 1972; Forst 1973; Quack & Troe 1974, 1975; Pechukas & Light 1965; Wittig *et al.* 1985; Wardlaw & Marcus 1984, 1985; Marcus 1988; Klippenstein & Marcus 1989; Marcus & Klippenstein 1990). State-resolved experiments are beginning to reveal the dynamics of energy flow as an excited molecule moves out along the reaction coordinate (Wittig *et al.* 1985; Brouwer *et al.* 1987; Green *et al.* 1988, 1990; Chen *et al.* 1988; Potter *et al.* 1989). But much remains to be understood about the fundamental dynamics which control these reactions.

Experiments on $\text{NCNO} \rightarrow \text{NC} + \text{NO}$ (Wittig *et al.* 1985) and $\text{H}_2\text{CCO} \rightarrow {}^1\text{CH}_2 + \text{CO}$ (Green *et al.* 1988; Chen *et al.* 1988) show that the rotational and translational degrees of freedom of the products exchange energy freely until their energy levels are identical to those of free products. Rotational distributions are found to be statistical and given accurately by phase space theory. However, the rate of reaction is significantly less than the phase space theory rate just 100 cm^{-1} above the reaction threshold (Green *et al.* 1990; Potter *et al.* 1989; Kim *et al.* 1990). A variational RRKM theory with reasonable potential parameters has successfully predicted rate constants (Klippenstein & Marcus 1989; Potter *et al.* 1989). When the chemical bond is partly formed, the spacing between energy levels increases compared with the free rotor levels of fragments and thus as total energy increases the transition state, point at which $W(E, J)$ is a minimum, moves in along the reaction coordinate, figure 2. Thus at threshold, where only a few product channels are open, both the rate constant and the product energy state distributions are given by the phase space theory asymptotic limit. As the energy increases, $W(E, J)$ increases but less rapidly than the state count for separated fragments; the rate constant is less than that for phase space theory. However, facile energy transfer among rotations and translations as the fragments separate beyond the transition state maintains the product rotational state distribution at the phase space theory limit.

As the total energy is increased through the threshold for vibrational excitation of products, the yield of vibrational excitation is found to be in excess of the phase space theory value and to increase with energy in proportion to the number of open channels corresponding to the specific vibrational level (Green *et al.* 1990). This is

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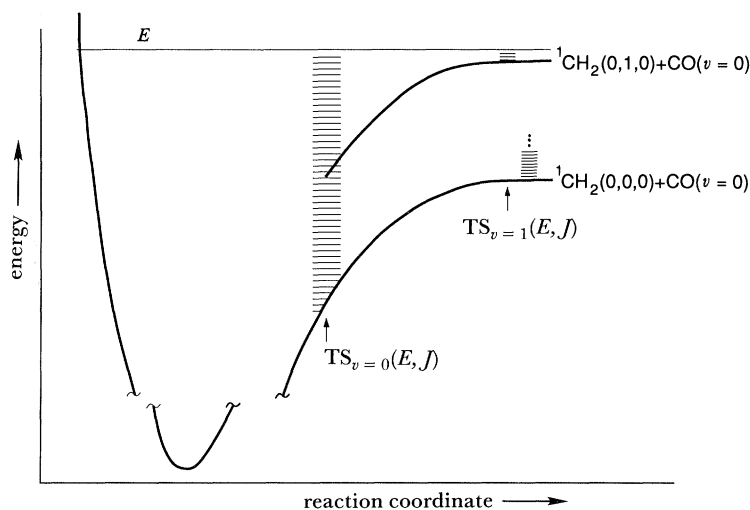


Figure 2. Bond breaking in the absence of a barrier. As fragments approach each other along the reaction coordinate the potential is always attractive. As the chemical bond begins to form, translational and rotational degrees of freedom of the reactants become vibrations and energy levels become more widely spaced. Thus as total energy increases the transition state (point where $W(E, J)$ is a minimum) moves in along the reaction coordinate. The variational RRKM model in which product vibrations become adiabatic at the transition state for $v = 0$ is shown (Klippenstein & Marcus 1989; Marcus & Klippenstein 1990; Chen *et al.* 1988). Each vibrationally adiabatic curve then has its own transition state which moves in from infinity along the reaction coordinate as energy is increased above the threshold for that particular product excitation.

understood in the variational RRKM theory in terms of the product vibrations becoming adiabatic as the molecule moves through the transition state for ground vibrational state products (Marcus 1988; Klippenstein & Marcus 1989; Marcus & Klippenstein 1990). The rate of forming vibrationally excited products is controlled by a separate transition state for motion on the vibrationally adiabatic curve leading to excited products, figure 2 (Klippenstein & Marcus 1989; Green *et al.* 1990; R. A. Marcus, this symposium). The yield of vibrationally excited products as a function of energy has been accurately predicted by the variational RRKM theory for H_2CCO (Klippenstein & Marcus 1989; Green *et al.* 1990).

A complete understanding of dissociations without barriers requires an understanding of how each vibrational degree of freedom becomes adiabatic as the molecule moves out along the reaction coordinate. Stiff and soft degrees of freedom must behave qualitatively differently with respect to decoupling before and after the transition state. More measurements of rates and product vibrational distributions will be required. Extensive potential energy surfaces with anharmonic vibrational constants determined all along the reaction coordinate are needed to put models to quantitative test against experimental results. It must be anticipated that different types of molecules will behave in qualitatively different ways.

3. Quasi-stable vibrational motion at high energies

The postulate that intramolecular vibrational energy transfer is rapid and complete on the timescale of dissociation has often been tested and rarely found wanting (Oref & Rabinovitz 1979). At energies sufficient for breaking a chemical

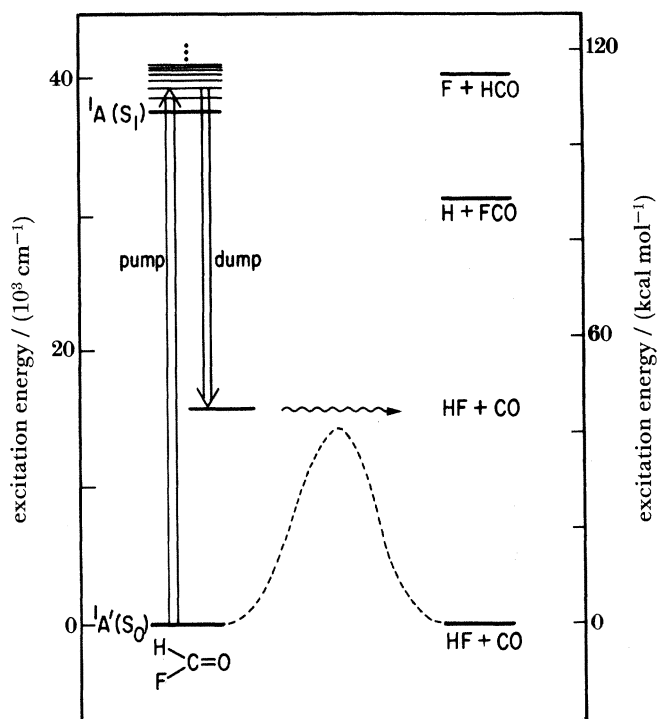


Figure 3. Stimulated emission pumping (SEP) spectroscopy of HFCO. A tunable UV laser pumps a single rovibronic level in S_1 and a visible laser stimulates emission from that level down to high vibrational levels of S_0 . Depletion of fluorescence from S_1 is observed when the dumping laser is on resonance.

bond, vibrational anharmonicities are usually large and reaction rates independent of the initial mode of vibrational excitation of the molecule. By contrast, at the small energies required to dissociate a van der Waals complex, rate constants are a strong function of the initial quantum numbers and not just the total energy and angular momentum (Nesbitt 1988).

The reaction $\text{HFCO} \rightarrow \text{HF} + \text{CO}$ has a tuning near 14000 cm^{-1} , figure 3. At this modest total energy it is not clear that intramolecular vibrational mixing should be complete. Stimulated emission pumping experiments have been undertaken to explore the vibrational level structure spectroscopically and to study dynamics for individual molecular eigenstates. Spectra have been observed from 14000 cm^{-1} to 23000 cm^{-1} of vibrational energy in the ground electronic state. Some examples are shown in figures 4 and 5 and in Choi & Moore (1989), Choi *et al.* (1990) and Moore *et al.* (1990). These spectra show some rather striking features. In nearly all cases the oscillator strength associated with the Franck–Condon favoured transitions to levels of CO stretching ν_2 and out-of-plane bending ν_6 is concentrated within a range of 1 cm^{-1} . At a given total energy, the widths increase as energy is shifted from ν_6 to ν_2 . When the total energy is increased by adding quanta of ν_6 , the linewidths decrease. Normally, intermode coupling increases with total energy. For some levels with as much as 6000 cm^{-1} energy in excess of the dissociation threshold all of the oscillator strength is concentrated on a single molecular eigenstate.

The observed narrowing or vibrational decoupling with increasing energy in a

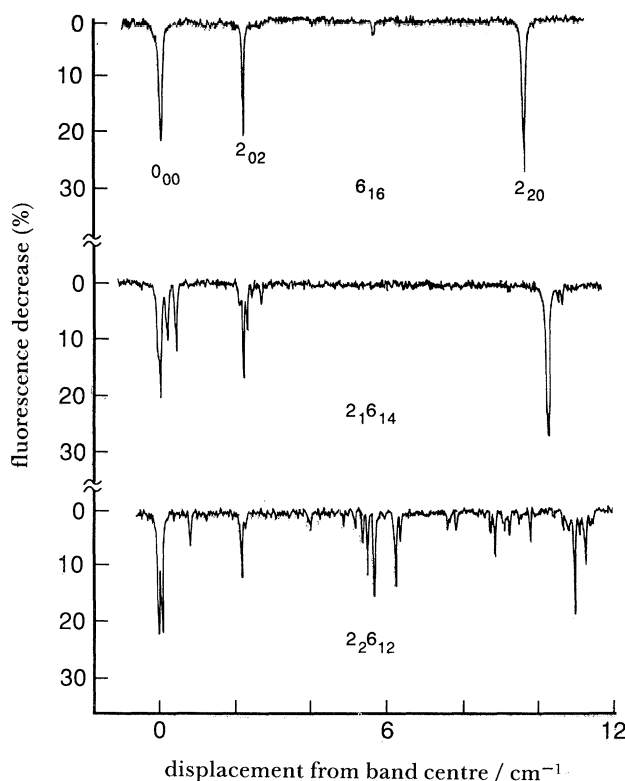


Figure 4. SEP spectra of HFCO for levels near 15300 cm^{-1} . As energy is moved from the out-of-plane bend ν_6 into the CO stretch ν_2 , the extent of vibrational mixing increases. The rotational level assignments are indicated on the top spectrum. $E_v = 15486\text{ cm}^{-1}$ (top), 15347 cm^{-1} (middle) and 15207 cm^{-1} (bottom).

single mode has been anticipated theoretically based on calculated quasi-stable vibrational motions for two dimensional model potentials (Hose *et al.* 1984; Stechel & Heller 1984; Shapiro & Child 1982). Some of these quasi-stable states are found to have all of their vibrational energy in a single mode and to be well localized in coordinate space (Hose *et al.* 1984). Unimolecular reaction rates of these states are expected to be significantly different from those predicted by statistical theories which assume complete redistribution of the initial vibrational energy over all modes before reaction.

It is by no means clear how general this phenomenon of quasi-stable 'extreme motion' (Hose *et al.* 1984) states is. The absorptions for high overtones of hydrogen stretching vibrations are concentrated into bands less than 100 cm^{-1} in width. Do these high overtones ever exhibit quasi-stable extreme motion states like those observed in HFCO? In which modes and for which molecules do quasi-stable extreme motion states exist? Many more spectra of high vibrational states are required to understand the dynamics and generality of quasi-stable extreme motion states.

The combined application of many new experimental and theoretical tools of high accuracy and resolution is rapidly improving our fundamental understanding of highly excited molecules and their reaction dynamics. A completely new level of understanding and possibly control is coming within reach.

Phil. Trans. R. Soc. Lond. A (1990)

High-resolution spectroscopy

303

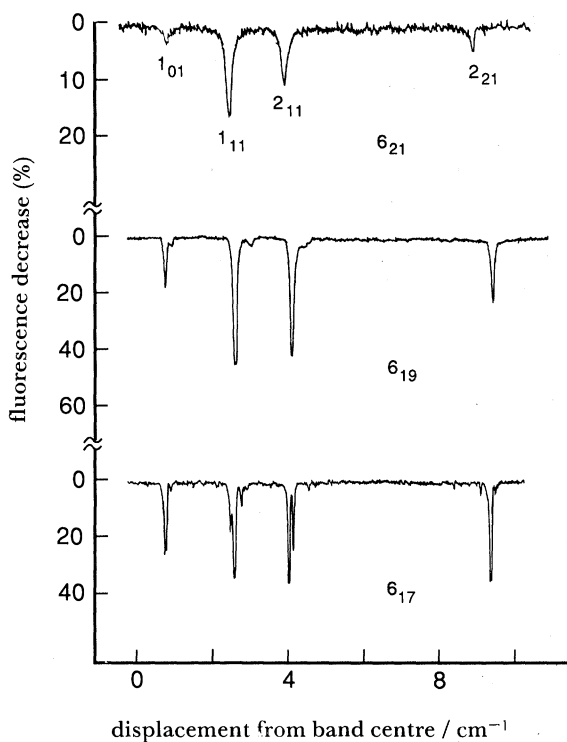


Figure 5. As total energy is increased by adding quanta to the out-of-plane bend, vibrational mixing decreases. At 20000 cm^{-1} , 6000 cm^{-1} above the dissociation limit, line broadening due to dissociation can be observed. $E_v = 20021\text{ cm}^{-1}$ (top), 18224 cm^{-1} (middle) and 16405 cm^{-1} (bottom).

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Phil. Trans. R. Soc. Lond. A (1990)

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Discussion

M. QUACK (*Physical Chemistry Laboratory, ETH Zürich, Switzerland*). I should like to add some brief comments on the experiments of the Moore group on ketene dissociation and their interpretation in terms of statistical models for lifetimes and product state distributions. For lifetimes one may use any of the statistical models, whereas originally RRKM theory did not predict energy distributions in products as pointed out by R. A. Marcus a number of years ago. More recently theories rather similar (but not identical) to the adiabatic channel model for product state distributions have been called RRKM theory, but I shall not address the question of nomenclature, rather the logical interpretation of the ketene experiments.

The first finding is the close agreement of measured product state distributions with predictions from phase space theory. This has been taken as evidence against the validity of the adiabatic channel model by the Moore group in some places in the literature. Such a conclusion is logically impossible, as phase space theory can be obtained as a limiting case of the adiabatic channel model by simple approximations (setting $\alpha = \infty$, corresponding to an isotropic potential and approximating centrifugal energy by the two-particle expression (see Quack 1979; Quack & Troe 1981)). If there is thus agreement of experiment with phase space theory this implies agreement with a limiting situation in the adiabatic channel model, which is the inclusive theory (the reverse is not true, in general). Thus the claimed disagreement of experiment with the adiabatic channel model on the basis of product state distributions is a logically inconsistent conclusion and totally unjustified.

The second finding concerns specific dissociation-rate constants, which are measured to be about a factor of two smaller than would seem to result from a calculation in the 'loose complex' phase space theory or similarly the adiabatic channel model in that limit. The interpretation of this result is ambiguous for several reasons. In principle, it contradicts the simple one parameter adiabatic channel model, because if $k(E, J)$ defines a parameter $\alpha < \infty$ then the product state distribution corresponding to $\alpha = \infty$ (phase space theory) should be impossible. In reality, this reasoning is a bit too simple and I shall summarize here several possible interpretations of the combined experimental results on $k(E, J)$ and product state distributions.

1. The discrepancy may be only apparent and disappear, if quantitative calculations are done. It may well be that $\alpha < \infty$ applies, but that the resulting product energy distribution is too similar to a phase space theory result to be distinguished from it within experimental error, quantitatively.

2. The product energy distribution depends upon the number of open adiabatic channels, $W(E, J)$, whereas the specific rate constants $k(E, J)$ depend upon the density of states $\rho(E, J)$ as well:

$$k(E, J) = \gamma W(E, J) / h \rho(E, J).$$

If the estimate of $\rho(E, J)$ were off by a factor of two, this would resolve the discrepancy (there are many reasons for an error in ρ , which I shall not discuss in detail here).

3. As I have proposed before, in the adiabatic channel model one may include transitions between channels of the separating fragments (in the complex region such transitions are assumed anyway). An extreme, perfectly *ad hoc* assumption would be that the transitions provide a quasi-equilibrium among channels up to a point, which

corresponds, approximately, to the distribution defined by phase space theory. This would resolve the discrepancy in a somewhat arbitrary manner (it seems that the interpretation favoured by Moore and co-workers invokes such an assumption). A much better way to include transitions would be approximate scattering theory for the separating fragments (but avoiding the difficult calculation for the complex). Such a model has been discussed by Quack & Troe (1981) but has not yet been applied to ketene. The results would depend upon the potential.

4. A further possibility is to take $\gamma < 1$ in the expression for $k(E, J)$. In the simplest treatment the transmission coefficient γ is set equal to its maximum value 1. However, a careful derivation of the statistical expression for $k(E, J)$ does not justify this approximation and the general result is, indeed, $\gamma \leq 1$, as we have stressed in many places (reviewed by Quack & Troe 1981). The reason why $\gamma \approx 1$ is usually assumed is the difficulty of an accurate calculation, except at threshold, where γ rapidly rises from zero to one, but at high energy it will decrease to smaller values in a way that is not easy to foresee without calculation.

I should mention that the above discussion is by no means particular to ketene. Indeed the test case H_3^+ for the statistical theory has been investigated and reviewed along these lines (Quack 1979; Quack & Troe 1981). As discussed there for the isotopomer $H^+ + D_2 \rightarrow HD + D^+$, Gerlich *et al.* have presented experimental results for product state distributions more than a decade ago and have interpreted these in terms of a 'modified phase space theory', in which transmission coefficients were calculated with classical trajectories, including also 'inelastic' transitions between channels outside the region of the complex. An analysis of the *ab initio* potential (Csizmadia *et al.* 1969) by Quack (1979) indicates a highly isotropic potential favouring the phase space theory limit. There are no accurate experiments on picosecond lifetimes of the Feshbach type compound states available yet for H_3^+ and its isotopomers and thus the experimental situation is not completely known. Accurate adiabatic channel calculations along the lines discussed above are possible, when accurate potentials are known.

W. H. GREEN AND C. B. MOORE. A useful physical model must simultaneously provide a basis for the following observations:

- (i) each product quantum state is produced at its energetic threshold (Green *et al.* 1988; Chen *et al.* 1988; Green *et al.* 1990);
- (ii) near the threshold for each product vibrational state its formation rate is controlled by a 'loose transition state' (Green *et al.* 1990);
- (iii) product rotational state distributions correspond closely to phase space theory (PST) (Kim *et al.* 1990);
- (iv) vibrationally excited product states are formed in excess of populations predicted by PST (Green *et al.* 1990);
- (v) as total energy increases from threshold, the absolute rate constant for dissociation decreases from the PST value by about a factor of three in the first 500 cm^{-1} (Kim *et al.* 1990; Potter *et al.* 1989).

In the statistical adiabatic channel model (SACM) one constructs non-crossing adiabatic potential curves for each product channel (Quack & Troe 1974, 1975). If none of these curves exhibits a maximum above the asymptotic limit, then SACM and PST give identical channel counts, rate constants and product state distributions. SACM gives rate constants less than PST only when states with asymptotic energies less than the total energy, E , have barriers above E on the adiabatic curve. These

barriers result from the increased level spacing as fragments bond together and free rotations become hindered. They increase with increasing product energy. However, the data show that every product state, which is permitted by conservation of total angular momentum and energy, is formed. Experimentally, the reactive flux is not limited by adiabatic channel barriers; there are no barriers. For SACM it seems logically inconsistent to have rate constants less than PST and product quantum state thresholds identical to PST.

The preceding comment suggests four sources of ambiguity in this reasoning. In response we note the following.

1. The rate constant falls rapidly below the PST value as the energy increases from 100 to 500 cm^{-1} above threshold. In this energy range there are many PHOFEX and product state distribution spectra. These spectra would be drastically different if half of the channels were cut off by adiabatic barriers.

2. It is unlikely that the ratio of the real density of states for ketene to the calculated density increases by a factor of two between 30 100 cm^{-1} and 30 600 cm^{-1} .

3. It is proposed that adiabaticity is maintained in the region along the reaction coordinate where the adiabatic channel potentials go through their maxima but that non-adiabatic coupling is strong on both the reactant and product sides of this region. It seems more plausible to consider non-adiabatic coupling significant throughout and adopt the variational RRKM model.

4. It is proposed that the transmission coefficient instead of (in addition to ?) the adiabatic channel barriers are responsible for rates being less than in phase space theory. This suggested improvement to PST must await quantitative calculations.

In discussions of the ketene data we have tended to emphasize quantitatively predictive models and may have implicitly wielded Occam's razor to cut off a viable model.

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