COMMENTS

Comment on "State-specific unimolecular reaction of NO_2 just above the dissociation threshold" [J. Chem. Phys. 99, 254 (1993)]

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The recent paper by Miyawaki *et al.*[1] on photoinduced NO_2 unimolecular decomposition just above D_0 presents high quality spectroscopic data that can be interpreted in terms of a detailed reaction mechanism, including energy dependent rates, $k(E)$. Likewise, we have presented the results of time domain measurements of $k(E)$,[2] which are in qualitative agreement with theoretical estimates made by using variational RRKM theory with an *ab initio* potential energy surface.[3] Triatomic systems are attractive for such detailed studies because the small number of degrees of freedom enables fine details to be revealed which are at the core of transition state theories. However, systems having sparse level spacings and offering high degrees of parent and product state resolution can provide data that challenge one's interpretive skills. For example, Miyawaki *et al.* noted significant differences between their results and ours. In this comment, we point out that these stated differences are not experimental, but in how the data are interpreted. Moreover, when viewed within the framework of unimolecular theory in the regime of sparse level denisities and overlapping decay widths,[4,5] there are no inconsistencies of the kind suggested.[1] In fact, consistency *extends* to reconciling the nonuniform NO rotational distributions and the level correlations between the transition state and products that have been observed from threshold to thousands of cm^{-1} above threshold.[6,7]

Unimolecular reactions that can be modeled with PST just above threshold have now been examined in detail for several small molecular systems such as NCNO,[8] CH_2CO,[9] and NO_2. As the energy above reaction threshold, $E^\dagger$, increases, the transition state has been shown to move to smaller interfragment distances, as revealed clearly in variational RRKM theory, which has been applied successfully to these systems.[3,10,11] Specifically, as $E^\dagger$ increases, the free rotor states of PST evolve toward bending levels and the differences between PST and variational RRKM theory increase. Therefore, though PST-like behavior makes sense for NO_2 just above D_0, variational RRKM theory is more appropriate for calculating $k(E)$ and rationalizing product state distributions at $E^\dagger \sim 100$'s of cm^{-1}.[3] One of the most obvious consequences of tightening of the transition state is the change in the steplike behavior of $k(E)$. Namely, the rotor spacings between the $k(E)$ increments just over the threshold give way at larger $E^\dagger$ to bigger steps, corresponding to bending motions at the transition state. Thus, our observation of structure in $k(E)$ a few hundred cm^{-1} above D_0 does not contradict the loose transition state spectral features observed by Miyawaki *et al.* for $E^\dagger \leqslant 13$ cm^{-1}. Our observed energy increments, as well as the

product state distributions reported by several authors[1,6,7] are consistent with a tightening of the transition state, in support of the variational RRKM model.

Above D_0, the resonances observed in the yield spectra reflect the couplings that take place to the dissociation continuum through the transition state. When stated in terms of decaying "molecular eigenstates,"[12] we say that their decay widths overlap, with the relative phases and amplitudes defining the interferences which are present at the transition state and are reflected in product excitations. Due to these interferences, spectral features can appear broader or narrower than the corresponding Lorentzian widths of isolated, noninteracting levels.[4] Though the resonance lineshapes are not generally Lorentzian and spectral congestion is a problem, *average* widths can still provide an estimate of the threshold rates, for example, at $E^\dagger \leqslant 5$ cm^{-1}. However, when the $J_{NO} = 1.5$ channel opens, congestion becomes worse, and at higher energies rates inferred from line shapes should be used only for qualitative guidance.

In NO_2 the level density for a given J_{total} is sparse enough for some levels to be essentially isolated for $E^\dagger \leqslant 5$ cm^{-1}. However, the widths of such isolated levels are known to fluctuate significantly about a mean value.[13] Were all decaying levels isolated, $W/h\rho$ would describe an average of the individual rates weighted by the strenghts of the resonances.[14] With interferences, this result is only obtained for the case of random phases of a large number of participating "molecular eigenstates." Bias in the phase relationships will increase the rate somewhat relative to the case of isolated resonances.

A consequence of the above is that the smallest observed rate reported in Ref. 1 (8.5×10^9 s^{-1}) cannot be assigned to the transition state threshold rate, $k_{th} = W/h\rho$. A measure of the threshold rate that can be attributed to $W/h\rho$ is obtained by averaging the widths observed in the first 5 cm^{-1} above D_0, yielding $\sim 3 \times 10^{10}$ s^{-1}. Extrapolation to $E^\dagger$ values of hundreds of cm^{-1} yields rates which are close to those observed (see below). At these energies we do not anticipate that PST and variational RRKM theory yield markedly different rates.

Counting the number of open channels in the threshold region by using PST is sensible. However, in applying PST to the $O(^3P_j) + NO(^2\Pi_\Omega)$ system, electronic angular momenta (including spin) must be perused carefully. The assumption that j and Ω take on all possible relative orientations at large interfragment distances implies a mixing of different molecular electronic surfaces. A few cm^{-1} above threshold the transition state is expected to be very

loose, so this assumption is appealing, resulting in the number of $J_{NO}=0.5$ open channels being equal to 4 and 8 for $J_{NO_2}=0.5$ and 1.5, respectively. However, this requires not only that all projections of J_{total} onto a body fixed axis are included, but also that the NO and O electronic angular momenta are allowed to take on all relative orientations. This constitutes an upper bound to the number of accessible states and may prove questionable for a reaction proceeding on a potential surface that correlates with the lowest product fine structure levels. Graff and Wagner have shown for the similar $O(^3P_j)+OH(^2\Pi_\Omega)$ case that the orientations of ^3P_j relative to $^2\Pi_\Omega$ can differ significantly in their long range attractiveness,[15] suggesting that the unimolecular reaction may be confined to specific orientations of j in the body frame. For example, assuming a single orientation of j relative to Ω and taking $k_{th}=3\times10^{10}$ s^{-1}, PST predicts $k=2\times10^{11}$ s^{-1} at $E^\dagger=100$ cm^{-1}, which is close to the measured rate.

Miyawaki et al. argue that the structure observed in $k(E)$ at $E^\dagger>100$ cm^{-1} may be rationalized as due to the opening of channels for the fragment fine structure levels. We deem this unlikely. The $^3P_1$ and $^3P_0$ populations have been shown to be minor at the energies of interest,[16] and similarly the $^2\Pi_{3/2}$ population is believed to be small near its energetic threshold.[6] In fact, $^2\Pi_{3/2}$ has been shown to account for only 25% of the population at excess energies throughout the range 392–3038 cm^{-1}.[7(b)]

Finally, we point out that although the majority of experimental results are in accord with variational RRKM theory some details require further enquiry. For example, our measurements of the reaction rate at $E^\dagger>100$ cm^{-1} do not indicate a steep rise followed by a pronounced flattening in $k(E)$. It will be interesting to extend these measurements to higher energies and to see if the lack of flattening at $E^\dagger\sim100$ cm^{-1} is due to peculiarities in $\rho(E)$.[17]

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[12] The term "molecular eigenstate" refers to a level broadened by coupling to the continuum. Since it decays, it is not a true eigenstate.

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