LETTERS TO THE EDITOR

COMMUNICATIONS

Direct picosecond time resolution of unimolecular reactions initiated by local mode excitation

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The concept of local mode (LM) states[1] in large molecules raises the possibility of inducing chemical reactions from a well-defined initial state (bond-selective chemistry). The results of linewidth and energy measurements in gases,[2(a)] and low temperature solids,[2(b)] however, indicate that the relaxation times for such high energy ($>15\,000$ cm^{-1}) states can be extremely short, <1 ps. Because of the lack of direct time-resolved measurements, the following fundamental questions have not been unequivocally answered: What are the homogeneous linewidths of LM states and what are the rates of energy relaxation or reaction out of these states? Over the past five years we have made several attempts to observe the picosecond dynamics of LM states. Due to the inherent difficulties associated with making these measurements, such as the very small oscillator strength ($\sigma < 10^{-23}$ cm^2), an extremely sensitive probing technique becomes imperative.

In this Communication, we report our first result of direct picosecond measurements of the $\Delta\nu_{OH} = 5$ LM transition of H_2O_2. In these experiments, a picosecond pulse prepares the OH stretch overtone and a second pulse, delayed in time, monitors the population of the OH radicals produced following the overtone excitation. These time-resolved studies give a direct measure of the unimolecular dissociation rate and provide a lower limit to the rate of energy redistribution from the OH stretch to the O–O reaction coordinate. This information may be used to determine the domain of validity of statistical unimolecular reaction rate theories (e.g., RRKM).

H_2O_2 is a well-defined system in that: (1) the OH stretching overtones provide a means for selectively depositing substantial amounts of energy in the electronic ground state; (2) the molecule undergoes O–O bond fission with an activation energy of 49.6 kcal/mol,[3] accessible by pumping $\nu_{OH} = 5$ or 6; and (3) the OH ($X\,^2\Pi_\Omega$) fragments produced on dissociation can be probed from specific (ν,J,Ω,Λ) quantum states by laser-induced fluorescence (LIF).[4] The pion-

eering work of Crim's group[5] on the $\nu_{OH} = 5$, 6 initiated dissociation of H_2O_2 has produced information regarding OH rotational state distributions[6] and overtone predissociation spectra.[7] The 10 ns time resolution of their experiments precluded any measurements of the rate of product formation.

Our experimental apparatus consists of an amplified, synchronously pumped dye-laser system.[8] The dye-laser fundamental wavelength (pump) is judiciously chosen to be on resonance with the overtone transition such that the second harmonic (probe) is tuned to resonance with particular OH $A\,^2\Sigma{\leftarrow}X\,^2\Pi$ transitions. Since the overtone spectrum is broad and congested we are able to maintain resonance for both pump and probe transitions. LIF from OH is detected at right angles with a PMT which is filtered to remove scattered pump light. A time-to-amplitude converter and multichannel scaler/discriminator are used to count single photon events 130–500 ns after the laser pulses. The maximum count rate is quite low, typically <4 counts/s, compared to the laser repetition rate (20 pps) thus avoiding saturation of the detection scheme.

As can be seen in Fig. 1, the OH product buildup is nonexponential when the probe is tuned to the $Q_1(1) + Q_{21}(1)$ transitions (i.e., $N = 1$ initial OH state). Approximating the transient with a biexponential buildup convoluted with the measured system response function[9] yields the fitted rise times of $\tau_1 = 60 \pm 5$ ps and $\tau_2 = 900 \pm 100$ ps, for parallel relative pump–probe polarization. Similar experiments were performed while probing the $N = 2$ transitions including $Q_1(2)$ giving a single exponential type of behavior where again $\tau_1 = 60 \pm 5$ ps, however, there is no evidence of a slow rising component.

Consideration of the nature of the slow component raises the possibility of OH ground electronic state rotational equilibration. This effect should not be significant for this experiment since the time scale of this redistribution has been measured to be > 500 ns[10] for the pressures used here.
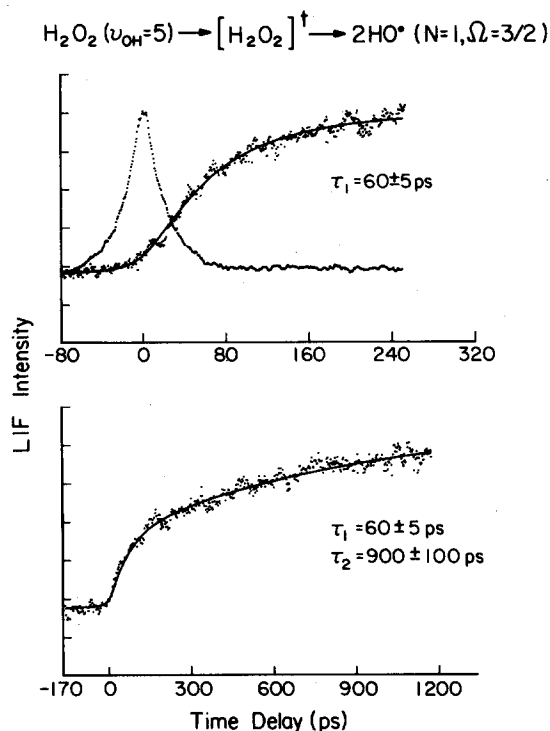
H_2O_2 (v_{OH}=5) $\longrightarrow$ $[H_2O_2]^{\dagger}$ $\longrightarrow$ 2HO• (N=1,Ω=3/2)

τ_1 =60±5 ps

-80   0   80   160   240   320

τ_1 =60±5 ps
τ_2 =900±100 ps

-170   0   300   600   900   1200

Time Delay (ps)

FIG. 1. Time-resolved buildup of OH ($N = 1$, $\Omega = 3/2$) fragments of H_2O_2 dissociation initiated by $v_{OH} = 5$ excitation ($\bar{v}_{pump} = 16\,242\,cm^{-1}$). In the lower plot the points are the experimental data and the solid curve is a best-fit biexponential rise convoluted with the cross correlation function of the pulses (≈ 13 ps, $\approx$ transform limited). The upper plot is an expanded scale scan of the early-time portion of the buildup along with a fit of a rising exponential convoluted with the cross correlation function. Also shown on the same scale is the cross correlation function of the pump and probe pulses measured using difference frequency generation (Ref. 9). Typical pulse energies at the sample (70% H_2O_2, 0.23 Torr, flowing gas system) were ≈ 150 μJ for the pump and < 0.25 μJ for the probe pulse.

Moreover, since the rotational distribution for dissociation from $v_{OH} = 5$ is known to be cold,[10] the low N states probed in this study would be depleted rather than populated by such a process. It should be noted that the pump-field intensity dependence of the LIF signal is linear and therefore consistent with a one photon excitation of the $v_{OH} = 5$ transition.[10] Thus, we conclude that the observed transient behavior of the OH product is due to a truly unimolecular process which is initiated by overtone excitation.

To compare these results to statistical unimolecular dissociation rates, RRKM (direct state count) calculations have been performed for various configurations of the transition state and including anharmonic corrections and angular momentum conservation. The calculations give rise times of ≈ 400 ps at the reaction barrier and ≈ 60 ps 2000 cm^{-1} above the barrier. These rise times are remarkably close to the values of the limiting slow and fast components measured for the $N = 1$ OH product state. In order to determine if the thermal distribution of reactant states above the reaction barrier energy could be responsible for the observed nonexponential behavior an energy averaged simulation of the transient was performed using microcanonical RRKM

rates. It is found that the smooth vibration–rotation distribution and the very discrete vibration-only distribution give similar nonexponential transient behavior which qualitatively show an apparent biexponential dependence.[11] It is also possible that this behavior is due to a divided vibrational phase space.

Further experimental work extending the domain of the studies discussed above should provide information on the angular momentum dependence of the microcanonical rates[12] and restrictions of the vibrational phase space in the redistribution.[13] At this time we are unable to conclude whether the different behavior observed while probing the OH $N = 2$ state is due to the slight variation of the pump excitation energy or due to the different final state probed. Experiments with independently tunable pump and probe lasers are in progress in order to separate these possible effects.

In conclusion, the build-up rate of the fast component measured in this work gives a homogeneous linewidth contribution to the $v_{OH} = 5$ transition of H_2O_2 of ≈ 0.09 cm^{-1} in contrast to the apparent ~ 200 cm^{-1} linewidth. Furthermore, our measurements indicate that the energy redistribution time from the OH stretch to the O–O reaction coordinate is < 60 ps for the cases studied.

a) Contribution number 7326.

[1] For recent reviews see: M. S. Child and L. Halonen, Adv. Chem. Phys. **57**, 1 (1984); B. R. Henry, *Vibrational Spectra and Structure*, edited by J. R. Durig (Elsevier, New York, 1981), Vol. 10; M. L. Sage and J. Jortner, Adv. Chem. Phys. **47**, 293 (1981); H. L. Fang and R. L. Swofford, *Advances in Laser Spectroscopy*, edited by B. A. Garetz and J. R. Lombardi (Hayden and Sons, London, 1982), Vol. 1, p. 1.

[2] (a) K. V. Reddy, D. F. Heller, and M. J. Berry, J. Chem. Phys. **76**, 2814 (1982); (b) J. W. Perry and A. H. Zewail, *ibid.* **80**, 5333 (1984), and references therein.

[3] H. Okabe, *Photochemistry of Small Molecules* (Wiley, New York, 1978).

[4] G. H. Dieke and H. M. Crosswhite, J. Quant. Spectrosc. Radiat. Transfer **2**, 97 (1962); W. L. Dimpfl and J. L. Kinsey, *ibid.* **21**, 223 (1979).

[5] F. F. Crim, Annu. Rev. Phys. Chem. **35**, 657 (1984).

[6] T. R. Rizzo, C. C. Hayden, and F. F. Crim, J. Chem. Phys. **81**, 4501 (1984).

[7] H. R. Dubal and F. F. Crim, J. Chem. Phys. **83**, 3863 (1985).

[8] J. W. Perry, N. F. Scherer, and A. H. Zewail, Chem. Phys. Lett. **103**, 1 (1983). In the current work, the pulses were broadened to reduce the bandwidth (using an etalon) to effectively excite the *narrow* transitions of OH.

[9] N. F. Scherer, J. W. Perry, F. E. Doany, and A. H. Zewail, J. Phys. Chem. **89**, 894 (1985).

[10] T. R. Rizzo, Ph. D. thesis, University of Wisconsin, Madison, 1983.

[11] W. L. Hase, Chem. Phys. Lett. **116**, 312 (1985).

[12] For recent discussions, see for example, D. M. Wardlaw and R. A. Marcus, Chem. Phys. Lett. **110**, 230 (1984); J. Chem. Phys. **83**, 3462 (1985), and references therein.

[13] T. Uzer, J. T. Hynes, and W. P. Reinhardt, Chem. Phys. Lett. **117**, 600 (1985); B. G. Sumpter and D. L. Thompson, J. Chem. Phys. **82**, 4557 (1985).