

LETTERS

Two-Color Vibrationally Mediated Photodissociation of Nitric Acid

Amitabha Sinha, Randall L. Vander Wal, Laurie J. Butler,[†] and F. Fleming Crim*[‡]

Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706 (Received: May 15, 1987)

Two-color vibrationally mediated photodissociation, in which one photon excites an overtone vibration and a second photon of a different wavelength dissociates the highly vibrationally excited molecule prepared by the first photon, is a means of investigating the role of vibrational excitation in photodissociation and of obtaining vibrational overtone excitation spectra. Application of this scheme to nitric acid (HONO₂) involves exciting the third OH stretching overtone vibration ($4\nu_{\text{OH}}$), photodissociating the vibrationally excited molecule with 355-nm light, and detecting the OH fragment using laser-induced fluorescence. These measurements show that most of the OH products are vibrationally unexcited and that about a quarter of the available energy goes into relative translation. The vibrational overtone excitation spectrum has congested P-, Q-, and R-branch rotational structure that forms a 50-cm⁻¹-wide band.

Introduction

The study of molecular photodissociation has recently attracted considerable interest from both experimentalists and theorists.¹ Because photodissociation is a process in which the initial conditions are defined accurately, a thorough study of these "half"-collisions offers excellent insight into more complicated collisional processes. Photofragmentation spectroscopy is also one of the few techniques available for studying dissociative states whose structureless spectra are not amenable to conventional analysis.

One aspect of photodissociation that merits further exploration is the effect of initial vibrational excitation.² Dissociation of vibrationally excited molecules is a means of probing regions of the excited electronic state potential energy surface that are not accessible by excitation from the ground vibrational state. For example, a recent study of hydrogen peroxide showed that the photodissociation of an initially vibrationally energized molecule yields a significantly larger number of vibrationally excited

products than dissociation at comparable or greater energies of molecules initially possessing only thermal energy.³

This Letter presents the first results on the photodissociation of *highly vibrationally excited* molecules using photons of different wavelengths for the vibrational overtone excitation and the photodissociation. In these two-color experiments, one photon excites a vibrational overtone transition and a second photon, of a different

(1) Leone, S. R. *Adv. Chem. Phys.* **1982**, *50*, 255. Shapiro, M.; Bersohn, R. *Annu. Rev. Phys. Chem.* **1982**, *33*, 409. Simons, J. P. *J. Phys. Chem.* **1984**, *88*, 1287. Bersohn, R. *J. Phys. Chem.* **1984**, *88*, 5195. Balint-Kurti, G. G.; Shapiro, M. *Adv. Chem. Phys.* **1985**, *60*, 403. Jackson, W. M. *Adv. Photochem.* **1986**, *13*, 1.

(2) Zittel, P. F.; Darnton, L. A.; Little, D. D. *J. Chem. Phys.* **1983**, *79*, 5991. Zittel, P. F.; Masturzo, D. E. *J. Chem. Phys.* **1986**, *85*, 4362. Kligler, D. J.; Pummer, H.; Bischel, W. K.; Rhodes, C. K. *J. Chem. Phys.* **1978**, *69*, 4652. Bichel, W. K.; Bokor, J.; Dallarosa, J.; Rhodes, C. K. *J. Chem. Phys.* **1979**, *70*, 5593. Zittel, P. F.; Little, D. D. *J. Chem. Phys.* **1979**, *71*, 713. Papernov, S. M.; Shlyapnikov, G. V.; Yanson, M. L. *Sov. Phys.—Dokl. (Engl. Transl.)* **1978**, *23*, 58. Zittel, P. F.; Little, D. D. *J. Chem. Phys.* **1980**, *72*, 5900.

(3) Ticich, T. M.; Döbal, H.-R.; Likar, M. D.; Butler, L. J.; Crim, F. F., submitted for publication in *J. Chem. Phys.*

[†] Present address: Department of Chemistry and James Franck Institute, University of Chicago, Chicago, IL 60637.

[‡] Camille and Henry Dreyfus Teacher-Scholar.

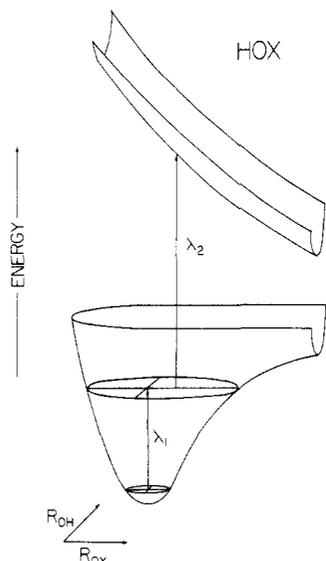


Figure 1. Schematic potential energy surfaces for the two-color vibrationally mediated photodissociation of HOX. The lower (ground electronic state) surface is bound along both the OH stretching coordinate (R_{OH}) and the OX stretching coordinate (R_{OX}), and the upper (excited electronic state surface) is bound only along the OH stretching coordinate. Neither the vibrational overtone excitation photon (λ_1) nor the photolysis photon (λ_2) is sufficiently energetic to reach the electronically excited surface from the equilibrium ground-state geometry.

wavelength, promotes the vibrationally energized molecule to a dissociative electronic state. Figure 1 illustrates this two-step process for the case of HOX, where X is NO_2 in the present experiments. The coordinates for the internal degrees of freedom of X are not included in this simplified picture. The transitions shown in the figure illustrate the ideal situation in a vibrationally mediated photodissociation measurement. Neither photon is sufficiently energetic to dissociate the molecule from the vibrational ground state, and in fact, the energy of the two photons together is less than that required to reach the electronically excited surface from the equilibrium geometry on the ground surface.

We apply this two-color vibrationally mediated photodissociation scheme to nitric acid (HONO_2) by exciting the third overtone of the OH stretching vibration ($4\nu_{OH}$) to deposit the initial energy and using a second photon at $\lambda_2 = 355$ nm to dissociate the molecule. A third photon from another laser monitors the dissociation process by laser-induced fluorescence on the $A^2\Sigma^+ \leftarrow X^2\Pi$ transition of the OH photofragment. This extension of our one-color vibrationally mediated photodissociation technique^{3,4} illustrates the potential generality of using vibrational overtone excitation as a preparative first step for investigating the photodissociation of highly vibrationally excited molecules.

Experimental Approach

The apparatus is a slightly modified version of the one used in our studies of vibrational overtone induced predissociation.⁵ Approximately 30-mJ pulses of 755-nm light from a Nd:YAG laser pumped dye laser (the vibrational overtone excitation laser) and 5–10-mJ pulses of 355-nm light from the third harmonic of the Nd:YAG laser (the photolysis laser) are combined on a dichroic mirror and propagate collinearly into a vacuum chamber containing between 75 and 400 mTorr of room-temperature anhydrous nitric acid. A 50 cm focal length lens reduces the diameter of the vibrational overtone excitation and photolysis laser beams in the observation region to approximately 1 and 3 mm, respectively. Optically delaying the photolysis light, which is generated prior to that for vibrational overtone excitation, ensures the tem-

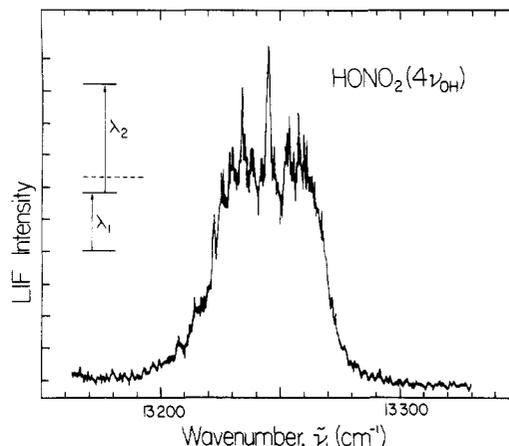


Figure 2. Vibrationally mediated photodissociation excitation spectrum in the region of the $4\nu_{OH}$ vibrational overtone transition of nitric acid. The spectrum is the laser-induced fluorescence signal from the $Q_1(6)$ transition of the OH dissociation product as a function of the vibrational overtone excitation wavenumber. The photolysis laser is fixed at a wavelength of $\lambda_2 = 355$ nm.

poral coincidence of the two pulses. Frequency-doubled light (308 nm) from a nitrogen laser pumped dye laser (the probe laser) counterpropagates relative to the other two laser beams with a typical delay between the probe laser pulse and the photolysis laser pulse of 100 ns. A photomultiplier tube (EMI 9635QB) views the OH fluorescence excited by the probe laser through an $f/1$ optical system, and a gated integrator (SRS) captures the resulting signal. A dichroic edge filter, having a sharp cutoff at 355 nm, and baffles in the side arms leading into the chamber reduce scattered light from the photolysis pulse. We prepare anhydrous nitric acid by bubbling a stream of nitrogen through a mixture containing three parts sulfuric acid and one part nitric acid and collecting the anhydrous nitric acid, which is entrained in the nitrogen flow, in a flask cooled to dry ice temperature. Because nitric acid is very corrosive, the sample introduction system is all glass and Teflon.

Results and Discussion

The thermodynamic threshold energy for production of ground-state OH and NO_2 fragments from nitric acid is $16\,700\text{ cm}^{-1}$ (200 kJ mol^{-1}), and thus, exciting the third overtone of the OH stretching vibration ($4\nu_{OH}$) at $13\,250\text{ cm}^{-1}$ provides insufficient energy to dissociate the molecule.⁶ However, additional energy provided by the second photon from the photolysis laser dissociates the molecule by excitation to a repulsive excited electronic state, as illustrated in Figure 1. Scanning the vibrational overtone excitation laser wavelength (λ_1) while monitoring a particular quantum state of the OH fragment maps out the vibrational overtone excitation spectrum of bound levels from which the second photon (λ_2) dissociates the molecule to form a fragment in the interrogated quantum state. The vibrational overtone excitation spectrum of the $4\nu_{OH}$ transition shown in Figure 2 comes from fixing the probe laser on the $Q_1(6)$ rotational transition of the OH (0,0) band and monitoring the total laser-induced fluorescence signal as a function of the vibrational overtone excitation laser frequency. The spectrum has an inhomogeneous width of 50 cm^{-1} that comes mainly from rotational congestion in the room-temperature sample. The distinct P-, Q-, and R-branch structure⁷ suggests a hybrid band involving both a- and b-type transitions. The observed signal depends linearly on the energies of both the

(4) Butler, L. J.; Ticich, T. M.; Likar, M. D.; Crim, F. F. *J. Chem. Phys.* **1986**, *85*, 2331.

(5) (a) McGinley, E. S.; Crim, F. F. *J. Chem. Phys.* **1986**, *85*, 5741. (b) Ticich, T. M.; Rizzo, T. R.; Dúbal, H.-R.; Crim, F. F. *J. Chem. Phys.* **1986**, *84*, 1508.

(6) Okabe, H. *Photochemistry of Small Molecules*; Wiley: New York, 1978.

(7) Cohn, H.; Ingold, C. K.; Poole, H. G. *J. Chem. Soc.* **1952**, 4272. Herzberg, G. *Molecular Structure and Molecular Spectra. II. Infrared and Raman Spectra of Polyatomic Molecules*; Van Nostrand Reinhold: New York, 1945; p 469.

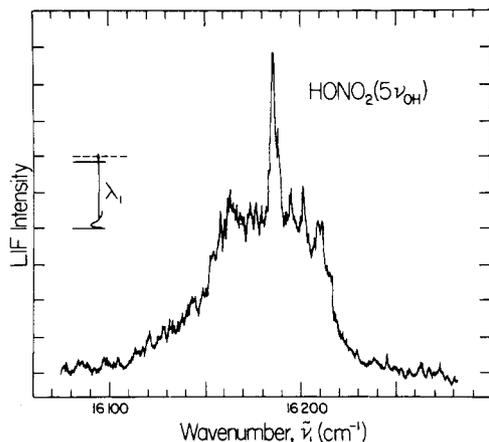


Figure 3. Vibrational predissociation excitation spectrum in the region of the $5\nu_{\text{OH}}$ vibrational overtone transition of nitric acid. The spectrum is the laser-induced fluorescence signal from the $Q_1(6)$ transition of the OH dissociation product as a function of the vibrational overtone excitation wavenumber. The energy added by the photon is less than the HO-NO₂ bond strength, but initial thermal excitation permits the decomposition.

vibrational overtone excitation and photolysis lasers, as expected for a two-photon process.

The OH fragments should arise only from the simultaneous action of both the vibrational overtone excitation and photolysis lasers in the ideal vibrationally mediated photodissociation scheme illustrated in Figure 1. However, we find that the photolysis laser alone produces a small ($\sim 20\%$) OH background signal that apparently arises from hot band absorption in the room-temperature nitric acid. This background signal allows us to estimate the cross section for photodissociation of nitric acid from the level prepared by vibrational overtone excitation. Using the extrapolated absorption cross section of nitric acid at 355 nm (1×10^{-24} cm²)⁸ and a rough estimate of the fraction of molecules excited by the vibrational overtone excitation laser ($f \sim 3 \times 10^{-5}$),⁹ we calculate a photodissociation cross section of 1×10^{-19} cm² for the vibrationally excited molecule, HONO₂($4\nu_{\text{OH}}$). A point of comparison is the $\sigma(240) = 2.6 \times 10^{-20}$ cm² photodissociation cross section for HONO₂ at 240 nm, a wavelength that corresponds to the sum of the frequencies of the two lasers.

Photodissociation with $\lambda_2 = 355$ nm following excitation of the third OH stretching overtone transition ($4\nu_{\text{OH}}$) of nitric acid provides $\sim 25\,000$ cm⁻¹ of energy to the fragments. These first measurements indicate that most of the OH fragments are formed in $v = 0$ but with a moderate amount of translational excitation. The Doppler widths of ~ 0.5 cm⁻¹ for the OH transitions in the

laser-induced fluorescence excitation spectra correspond to approximately a quarter of the available energy appearing in relative translation of the fragments. Although the measurement of rotational state distributions is presently incomplete, we have observed significant population in states as high as $N = 6$ and, hence, expect higher rotational states to be populated.

We have also attempted to observe vibrationally mediated photodissociation in the $5\nu_{\text{OH}}$ region, but the signal from a competing process, thermally assisted vibrational predissociation, overwhelms that from the two-photon photodissociation. The energy deposited by exciting the $5\nu_{\text{OH}}$ transition ($\sim 16\,200$ cm⁻¹) in conjunction with the thermal energy initially present in the molecule is sufficient to initiate unimolecular decomposition of nitric acid on the ground electronic surface, as we have observed in the same energy range for hydrogen peroxide.^{5b} Figure 3 shows the overtone excitation spectrum for the $5\nu_{\text{OH}}$ transition obtained by fixing the probe laser on the $Q_1(6)$ transition of the OH (0,0) band and monitoring the total laser-induced fluorescence as a function of the vibrational overtone excitation frequency. In contrast to the two-photon dissociation observed for the $4\nu_{\text{OH}}$ transition, this process depends solely on the vibrational overtone excitation laser. Its linear dependence on the pulse energy confirms the one-photon nature of the transition. Because of the importance of hydroxyl radicals in atmospheric chemistry, several kinetic studies have investigated the three-body recombination of OH with NO₂ to form HONO₂.¹⁰ Our observation of unimolecular decomposition initiated by vibrational overtone excitation indicates that we can obtain detailed kinetic data for comparison with the analysis of the reverse three-body recombination.

The experiments on nitric acid described here illustrate how vibrationally mediated photodissociation can potentially reveal information about both high vibrational levels of the ground electronic state and regions of the excited electronic surface not accessible by direct one-photon absorption. We are currently using the technique to make detailed measurements on the internal state distribution of the OH photofragment in order to unravel the dynamics of the two-photon dissociation process. Future plans include investigating the complementary single-photon ultraviolet photodissociation,¹¹ studying the vibrationally mediated photodissociation of nitric acid cooled in a supersonic expansion, and investigating its vibrational overtone induced unimolecular decomposition.

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(10) Anastasi, C.; Smith, I. W. M. *J. Chem. Soc., Faraday Trans. 2* **1978**, *74*, 1056. Anderson, J. G.; Margitan, J. J.; Kaufman, F. *J. Chem. Phys.* **1974**, *60*, 3310. Burkholder, J. B.; Hammer, P. D.; Howard, C. J. *J. Phys. Chem.* **1987**, *91*, 2136.

(11) There is one reported observation of the products of the photodissociation at a wavelength of 193 nm (Jacobs, A.; Kleinermaans, K.; Kuge, H.; Wolfrum, J. *J. Chem. Phys.* **1983**, *79*, 3162) but apparently none at longer wavelengths.

(8) Extrapolated from the data given in: Johnston, H.; Graham, R. *J. Phys. Chem.* **1973**, *77*, 62.

(9) Crim, F. F. *Annu. Rev. Phys. Chem.* **1984**, *35*, 657.