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Vibrationally Mediated Photodissociation

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We describe a new experimental technique for studying the spectroscopy and photodissociation dynamics of highly vibrationally excited polyatomic molecules. The technique, vibrationally mediated photodissociation, involves one-photon excitation to a high-energy O-H stretching overtone vibration followed by excitation with a second photon (of the same or a different energy) to a dissociative electronic state that produces OH radical fragments. Laser-induced fluorescence of $OH(A^{2}\Sigma^{+}\leftarrow X^{2}\Pi)$ monitors the yield of dissociation products and the OH internal state distribution. We have applied the technique to molecules of the general formula HOX (where X = OH, NO₂ and BuⁱO) and, in this paper, present an overview of the experimental results. Because the OH fragment yield depends on the first photon being resonant with the vibrational overtone state, variation of its wavelength provides an excitation spectrum. Such a spectrum supplies information that is complementary to that obtained from laser photoacoustic spectroscopy. The spectroscopy of the fragment OH radicals reveals details of the photodissociation dynamics, which may be controlled both by the initial vibrational overtone excitation and by the nature of the excited electronic surface from which the parent molecule dissociates.

Studies of the spectroscopy of overtone states of bond-stretching vibrations have attracted considerable interest from experimentalists and theoreticians in recent years, and the understanding and interpretation of the vibrational overtone spectra of polyatomic molecules has advanced considerably. Interpretations are usually based on a local-mode model¹ in which independent Morse oscillators may be coupled harmonically² or anharmonically.³ The quantitative rationalization of vibrational overtone spectra in terms of various couplings of local and normal modes has improved our understanding of vibrational mode mixing and served to link vibrational overtone spectroscopy with the language of classical infrared vibrational spectroscopy. Some of the important coupling schemes that have been proposed are a 'near-universal' C—H stretch/bend Fermi (1:2) resonance,⁴⁻⁶ Fermi resonances involving other low-frequency motions,⁷ linear (1:1) stretch/stretch coupling⁸⁻¹⁰ and vibration-torsion interactions.¹¹ A detailed understanding of the nature and consequences of vibrational mode mixing are important not only for spectroscopy, but also for chemical reaction dynamics,¹² insofar as mode mixing is responsible for intramolecular vibrational energy redistribution (IVR).

The three most popular methods for measuring vibrational overtone spectra are conventional absorption spectroscopy (largely limited to pure liquid samples), thermal lensing spectroscopy, and pulsed and modulated continuous laser photoacoustic spectrocopy. Of these, the last, which measures absorption by monitoring the thermal energy released by the absorbing molecules, has provided most of the data for vapour-phase samples. For a number of years we have measured vibrational overtone spectra of polyatomic molecules excited above their dissociation thresholds by observing either

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Fig. 1. Energy-level diagram for the dissociation of hydrogen peroxide. (a) Vibrationally mediated photodissociation through the $4\nu_{OH}$ vibrational overtone transition. The first photon excites the $4\nu_{OH}$ transition and the second excites the vibrationally excited molecules to a dissociative electronic state. (b) Thermally assisted vibrational overtone induced predissociation through the $5\nu_{OH}$ transition. In this one-photon process, molecules that possess sufficient initial thermal energy dissociate following excitation of the $5\nu_{OH}$ transition. (c) Vibrationally mediated photodissociation through the $5\nu_{OH}$ vibrational overtone transition. The first photon excites the $5\nu_{OH}$ transition and the second promotes the vibrationally excited molecule to a dissociative electronic state. (d) Vibrational overtone induced predissociation through the $6\nu_{OH}$ transition.

product chemiluminescence^{13,14} or laser-induced fluorescence (LIF).^{11,15-18} These techniques have the advantage of being readily extended to the environment of a supersonic expansion.^{14,17,19}

Such measurements rely on the absorption of a single photon that is resonant with the vibrational overtone state to deposit sufficient energy in the molecule to cause decomposition, as illustrated for hydrogen peroxide in fig. 1(d). Alternative excitationdissociation schemes which involve vibrational overtone states that lie below the 0-0 bond dissociation threshold are also possible. Two examples are thermally assisted one-photon dissociation [fig. 1(b)] and vibrationally mediated photodissociation [fig. 1(a) and (c)]. Fig. 1(a) shows a single-colour vibrationally mediated photodissociation scheme that uses one-photon excitation to a vibrational overtone state lying below the 0-0 dissociation threshold (the third O-H stretching overtone, $4\nu_{OH}$, in HOOH)

followed, within the *ca*. 6 ns duration of the laser pulse, by the absorption of a second photon of the same energy. The second photon excites the vibrationally excited molecule to a dissociative electronic state to produce an OH radical fragment that is detected using laser-induced fluorescence. Since the fragmentation requires that the first photon be resonant with a vibrational overtone state, the variation of the yield of OH product with the wavelength of the laser radiation reflects the vibrational overtone-excitation spectrum. The signature of vibrational overtone absorption is molecular dissociation induced by the second photon, in contrast to photoacoustic measurements in which only those molecules that remain intact may contribute to the observed acoustic signal.

The technique is not limited to excitation at a single wavelength, and we have exploited two-colour vibrationally mediated photodissociation, in which the vibrational overtone-excitation and subsequent photodissociation use different laser wavelengths, to study the vibrational overtone spectroscopy and photodissociation dynamics in hydrogen peroxide and nitric acid. The two-colour scheme is, of course, the more general, since it does not require the presence of a dissociative electronic state at twice the energy of the vibrational overtone transition. The second photon not only provides part of the detection scheme by generating the readily observed OH fragment, but also supplies detailed quantum-state-resolved information concerning the photodissociation dynamics of vibrationally excited molecules. Studies of photodissociation provide an important meeting place for *ab initio* quantum theory and experiment,²⁰ and studies of the photodissociation of vibrationally excited molecules can play a key role in correlating theory and experiment, as in the photodissociation of H₂O, for example.²¹

Here we review the experimental approach to the study of vibrationally mediated photodissociation and describe recent results for hydrogen peroxide and nitric acid obtained using both one- and two-colour schemes. In addition, we present new experimental results on t-butyl hydroperoxide (Bu^tOOH) as an interesting contrast with smaller polyatomic molecules.

Experimental

The experimental apparatus is similar to that used in our one-photon vibrational overtone predissociation experiments.^{15,16} In the room-temperature measurements described in this paper, a 6 ns light pulse from a Nd: YAG-laser-pumped dye laser excites a lowpressure (70-500 mTorr) sample of HOOH, HONO₂ or Bu^tOOH in the region of the $4\nu_{\rm OH}$ vibrational overtone transition (740-765 nm). A second photon that is delayed by ca. 5 ns and is of the same energy (HOOH and Bu^tOOH) or of a different energy (HOOH and HONO₂) dissociates the vibrationally excited molecule. Fig. 2 is a generalized potential-energy diagram relevant to these experiments. The photon of wavelength λ_1 excites the vibrational overtone transition, and the dissociation photon of wavelength λ_2 fragments the vibrationally excited molecule by exciting it to a dissociative electronic surface. A counterpropagating 10 ns ultraviolet light pulse from a frequency-doubled nitrogen-laser-pumped dye laser probes the resulting OH fragments by laser-induced fluorescence. A laboratory computer accumulates the gated integrator signal of the fluorescence intensity along with photodiode signals that measure the energy of each laser pulse. The pump laser pulse of 30-35 mJ is focused to a spot ca. 1 mm in diameter. The ultraviolet probe laser energy of a few μ J is focused to a diameter smaller than the pump laser spot only in the experiments with Bu^tOOH.

We perform two types of measurements in these studies. In the first, we monitor a particular OH product vibrational-rotational state while varying the wavelength of the vibrational overtone excitation laser. This yields a vibrational overtone-excitation spectrum for those molecules that dissociate after absorption of the second photon to form an OH product in the observed quantum state. In the second type of measurement we vary the wavelength of the probe laser with the wavelength of the vibrational overtone



Fig. 2. Schematic potential energy surfaces for the two-colour vibrationally mediated photodissociation of HOX. The lower (ground electronic state) surface is bound along both the O-H stretching coordinate (R_{OH}) and the O-X stretching coordinate (R_{OX}), and the upper (excited electronic state surface) is bound only along the O-H 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.

excitation laser fixed in order to obtain the laser-induced fluorescence excitation spectrum, and hence the distribution of the products among their quantum states. The rotational levels are labelled with the quantum number N, which is the total angular momentum except for electron spin of the OH $X^2 \Pi_{3/2}$ product state that we probe with laser-induced fluorescence.

Results and Discussion

Hydrogen Peroxide

Vibrational Overtone Excitation Spectroscopy

Vibrationally mediated photodissociation is a means of obtaining vibrational overtone excitation spectra for bound states in the regions of the $4\nu_{OH}$ [fig. 1(*a*)] and $5\nu_{OH}$ [fig. 1(*c*)] transitions of HOOH.¹⁸ Since dissociation from the $5\nu_{OH}$ overtone level requires only a small amount of additional energy (1100 cm⁻¹), a number of the molecules in the room-temperature sample have sufficient initial vibrational or rotational energy to decompose following absorption of a single photon [fig. 1(*b*)]. Fig. 3 shows vibrationally mediated photodissociation spectra in the $4\nu_{OH}$ and $5\nu_{OH}$ regions, along with the one-photon vibrational predissociation spectrum in the $6\nu_{OH}$ region [*cf.* fig. 1(*d*)]. A spectroscopic model that incorporates the O—H vibration and torsion about the O—O bond¹¹ reproduces the coarse vibrational structure, which is similar in all three spectra.



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Fig. 3. Vibrational overtone excitation spectra for hydrogen peroxide. (a) One-photon vibrational predissociation spectrum in the region of the $6\nu_{OH}$ transition obtained probing the N = 3 rotational state of the OH dissociation fragment. (b) Vibrationally mediated photodissociation spectrum through the region of the $5\nu_{OH}$ transition probing the N = 9 rotational state of the OH dissociation fragment. (c) Vibrationally mediated photodissociation spectrum through the region of the $4\nu_{OH}$ transition obtained probing the N = 3 rotational state of the OH dissociation fragment. The stick spectra are the predictions of the torsional model for the transitions. The right-hand side of the figure is a schematic drawing of a portion of the torsional potential versus the dihedral angle (χ) for different levels of O—H vibrational excitation showing the symmetric and antisymmetric torsional levels and transitions (denoted S and A) between them.

There are three primary vibrational features shown in fig. 3. The figure also gives the torsional potential, some of the possible transitions and the *trans* barrier for different amounts of O-H stretching vibration. The stick spectra are the band positions and intensities predicted by a vibration-torsion interaction model of the transitions.¹¹ The notation used gives the symmetry of the torsional wavefunctions with respect to the *trans* position of the O-H bonds and the quantum numbers of the levels involved in the transition. For example, S_0^1 (A_0^1) describes a transition from the lowest symmetric (antisymmetric) torsional level in the ground state to the first-excited symmetric (antisymmetric) torsional level in the excited O-H stretching vibrational state. The largest feature is predicted by the Birge-Sponer extrapolation from lower vibrational levels, and we assign it as a transition deriving its oscillator strength from n = 4, 5 or 6 quanta

of O-H stretching vibration without torsional excitation $(S_0^0 \text{ and } A_0^0)$. The highestenergy feature is a combination band involving *n* quanta of O-H stretching vibration along with one quantum of torsional excitation $(S_0^1 \text{ and } A_0^1)$. The small feature on the high-energy side of the main band is a hot-band transition that corresponds to a transition from a torsionally excited ground state to a state with *n* quanta of stretching vibration along with a quantum of torsional excitation (primarily S_1^1). The shift in the position of the combination band and hot band relative to the main band with the extent of vibrational excitation reflects an increase of the *trans* torsional barrier by 75 cm⁻¹ for each quantum of O-H stretching vibration excited. Carpenter and Weinhold have recently confirmed this increase in the barrier with increasing O-H vibrational excitation in an *ab initio* calculation.²² Preliminary results indicate that the features and overall contours of the main bands for one- and two-colour vibrationally mediated photodissociation are indistinguishable.

Vibrationally mediated photodissociation is also a means of obtaining spectra of bound states in molecules cooled in a free-jet expansion. We have used this approach to obtain the vibrational overtone excitation spectrum in the region of the $4\nu_{OH}$ transition of HOOH molecules cooled in a supersonic expansion.¹⁷ The spectra have sharp features that are <0.15 cm⁻¹ wide and appear to be predominately Q-branch transitions from the lowest few rotational states. The widths of these transitions to bound states are substantially less than those in the $6\nu_{OH}$ region. These measurements potentially provide a means for assessing the extent of vibrational mode mixing between the O—H stretch motion and the sparse set of background vibrational states present at these energies.

Photodissociation Dynamics

The dynamics of the vibrationally mediated photodissociation through the highly vibrationally excited intermediate state are quite different from those in the direct ultraviolet photodissociation at $248^{23,24}$ and 266 nm.^{25} A characteristic feature of the single-photon ultraviolet photodissociation of hydrogen peroxide is the absence of vibrationally excited products. Since the thermodynamic O—O bond dissociation threshold for HOOH is 17 400 cm⁻¹, excitation between 248 and 355 nm deposits energy in the range 23 000-11 000 cm⁻¹ in excess of that needed to break the O—O bond. However, dissociation in this range produces no vibrationally excited OH fragments,²³⁻²⁵ and Gericke *et al.*²⁵ have established an upper limit of 2% of the OH fragments being vibrationally excited in the 266 nm photolysis experiments. The absence of product vibrational excitation is consistent with an impulsive release of energy following electronic excitation, although such a picture does not quantitatively predict the details of the rotational energy release.^{24,25}

The OH product-state distributions from vibrationally mediated photodissociation are strikingly different from the ultraviolet photolysis results. In the one-colour experiment, $11 \pm 2\%$ of the OH fragments are vibrationally excited, even though the available energy (excess energy above threshold including the initial thermal energy) is only 9600 cm⁻¹. This fraction increases to over 15% in the two-colour measurements, where the available energy is 15 000 cm⁻¹. Table 1 summarizes the energetics and results for both two-photon vibrationally mediated and direct one-photon photodissociation of hydrogen peroxide. Apparently, the vibrationally mediated photodissociation process channels excess energy into product vibration more efficiently than the direct photodissociation. Table 2, which collects the results for all three molecules studied here, shows that more of the OH fragments are vibrationally excited for the vibrationally mediated photodissociation of HOOH than for HONO₃ or t-butyl hydroperoxide.

The distribution of the OH products among their rotational states also reflects the difference in the dissociation dynamics. Fig. 4 shows the distribution of the OH fragments among their rotational states for the lowest (v''=0) and first excited (v''=1) vibrational

excitation wavelength λ_1/nm	dissociation wavelength λ_2/nm	total added energy/cm ⁻¹	fraction of OH in $v'' = 1$		
vibrationally mediated photodissociation					
750	750	26 700	0.11		
750	532	32 100	0.15-0.20		
direct photodissociation					
355	-	28 200	-a, b		
266		37 600	a, c		
248		40 300	—a, d, e		

Table 1. Vibrational Excitation in the Photodissociation of HOOH

^{*a*} No vibrationally excited OH detected. ^{*b*} Ref. (18). ^{*c*} Ref. (25). ^{*d*} Ref. (23). ^{*e*} Ref. (24).

Table 2. Average energy disposal in the vibrationally mediated photodissociation of hydrogen peroxide, nitric acid and t-butyl hydroperoxide^a

	ΗΟΟΗς	HONO ₂ ^d	Bu ^t OOH ^e
E_{avail}^{b}	9 600	25 000	14 020
$E_{\rm T}(\rm OH)$	6 850 (0.71)	3 130 (0.13)	960 (0.07)
$E_{\rm R}({\rm OH})$	2 000 (0.21)	1 000 (0.04)	420 (0.03)
$E_{\rm V}({\rm OH})$	760 (0.08)	200 (0.01)	$0 (0.00)^{f}$
$E_{int}(\mathbf{X})$		19 500 (0.78)	12 420 (0.89)

^a The numbers in parentheses are the fraction of the energy available that appears in the designated degree of freedom. All energies are given in units of cm⁻¹. ^b $E_{avail} = h\nu + E_{thermal} - \Delta H_0^{\circ}$ where the thermal energy is the initial rotational energy of $\frac{3}{2}kT$ (T = 300 K) and ΔH_0° is the thermodynamic dissociation threshold energy. For t-butyl hydroperoxide $E_{thermal}$ also includes the average vibrational energy of a thermal distribution of harmonic oscillators calculated using the frequencies and degeneracies given in ref. (32*a*). ^c Onecolour dissociation with $\lambda_1 = \lambda_2 = 750$ nm. ^d Two-colour dissociation with $\lambda_1 = 755$ nm and $\lambda_2 = 355$ nm. ^e One-colour dissociation with $\lambda_1 = \lambda_2 =$ 752 nm. ^f No vibrationally excited OH fragments could be detected. An upper limit for the fraction of vibrationally excited OH products formed, based on the sensitivity of the experiment, is 0.04.

levels. Because the amount of energy added is similar, the most direct comparison that can be made is between the one-colour vibrationally mediated photodissociation and the ultraviolet dissociation at 355 nm. As shown in fig. 4, the direct dissociation produces fewer highly rotationally excited molecules, and hence a smaller fraction of the energy is disposed into rotation. A more energetic rotational distribution for vibrationally mediated photodissociation might reflect a greater extent of bending or torsional excitation that leads to product rotation or could arise from the participation of another electronically excited surface in the dissociation. Future experiments that explore the angular distribution of the OH photofragment may clarify this point. Measuring the Doppler width of the OH transitions in the LIF excitation spectrum completes the picture of the energy disposal in HOOH. As we also infer from the vibrational and rotational state measurements, the Doppler widths show that most of the excess energy is deposited into relative translational of the two OH fragments (table 2).



Fig. 4. Rotational product state distribution of the OH from the vibrationally mediated photodissociation of hydrogen peroxide through the region of the $4\nu_{OH}$ transition ($\lambda = 750$ nm). (a) Distribution for the products in v'' = 1. (b) Distribution for the products in v'' = 0 (solid points). The solid lines are the distributions obtained in the 248 nm single-photon photolysis [(a) ref. (23); (b) ref. (24)] and in the 266 nm photolysis [(c) ref. (25)]. The broken line is the distribution obtained in the single photon photolysis at 355 nm [ref. (18)]. The vertical arrows in both (a) and (b) indicate the highest state that is accessible for the nominal excess energy if both fragments are created with the same amount of rotational energy.

Nitric Acid

We have used the two-colour vibrationally mediated photodissociation scheme to study the vibrational overtone-excitation spectroscopy and photodissociation dynamics of nitric acid (HONO₂).²⁶ The approach is analogous to that illustrated in fig. 2, and involves excitation of the third O—H stretch overtone ($4\nu_{OH}$), which has a band centre at 755 nm, followed by 355 nm excitation of the vibrationally excited molecule to a dissociative electronic state that produces OH fragments. Although the details of the excited-state potential-energy surface are not accurately known for nitric acid, calculations find that the electronic excitation is primarily localized on the NO₂ chromophore.²⁷ The low-frequency vibrations and low-lying electronic states of the NO₂ fragment potentially alter the photodissociation dynamics of nitric acid compared to those of hydrogen peroxide.





Fig. 5. 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 Q₁(4) transition of the OH dissociation product. The photolysis laser is fixed at a wavelength $\lambda_2 = 355$ nm and the spectrum is normalized to the product of the excitation pulse energy and photolysis pulse energy and also to the probe laser pulse energy.

Vibrational Overtone Excitation Spectroscopy

The vibrational overtone excitation spectrum of HONO₂ in the region of $4\nu_{OH}$ is shown in fig. 5. This spectrum comes from monitoring fluorescence excited from the Q₁(4) rotational line of the OH($A^{2}\Sigma^{+}$, $v' = 0 \leftarrow X^{2}\Pi$, v'' = 0) transition while scanning the wavelength of the vibrational overtone excitation laser and fixing the wavelength of the photodissociation laser at 355 nm. Measurements of the dependence of the OH LIF intensity on the power levels of both the vibrational overtone excitation and photodissociation lasers confirmed that we are observing a two-photon (1+1) vibrationally mediated photodissociation process. The spectrum has an inhomogeneous width of 50 cm⁻¹ that primarily arises from rotational congestion in the room temperature sample. The distinct P-, Q- and R-branch structure suggests a hybrid band involving *a*- and *b*-type transitions, and preliminary spectral simulations confirm this analysis. Measurements of this band system in a supersonic expansion should provide the data necessary for an assessment of the extent of vibrational mode mixing between the O—H stretch and background vibrational states.

Photodissociation Dynamics

The thermodynamic threshold energy for production of ground-state OH and NO₂ fragments from nitric acid is 16 700 cm⁻¹ (200 kJ mol⁻¹). The two-colour excitation, with $\lambda_1 = 755$ nm and $\lambda_2 = 355$ nm; thus provides the molecule with *ca*. 25 000 cm⁻¹ of excess energy to be partitioned among the internal degrees of freedom and relative translation of the fragments. Although the amount of available energy is substantial, we find that only 5% of the OH fragments are formed in v'' = 1. We also observe a small amount of background 355 nm photodissociation that we estimate to be *ca*. 20% of that obtained in the two-colour vibrationally mediated photodissociation experiments. This one-photon 355 nm photodissociation, which probably involves hot-band excitation, enables us to estimate a photodissociation cross-section for vibrationally excited HONO₂ of 10^{-19} cm².²⁶



quantum number, N

Fig. 6. Rotational product state distribution of the OH from the vibrationally mediated photodissociation of nitric acid through the region of the $4\nu_{OH}$ transition for the Q_1 branch of the OH v'' = 0 dissociation product.

The lowest-energy one-photon photodissociation studies of HONO₂ for which product state distributions are available for comparison are those of Jacobs *et al.*²⁸ using 193 nm excitation. They find no vibrationally excited OH product but, because of differences in detection sensitivity, it is impossible to draw firm conclusions from this comparison. The rotational-state distribution of fragment OH($X^2\Pi$, v''=0) resulting from vibrationally mediated photodissociation, shown in fig. 6, is not substantially different from that found in the 193 nm photodissociation of HONO₂.²⁸ Photodissociation at 193 nm does result in slightly more rotational excitation, in keeping with the increased amount of energy available to be disposed among the product quantum states. The apparent break at N = 9 in the distribution shown in fig. 6 hints at the possible presence of two electronic surfaces that lead to different patterns of energy disposal into fragment rotation.

Further insight into the dissociation dynamics comes from the ratio of the populations in the lambda doublet states of the OH fragments. For the rotational levels corresponding to N = 8, 9 and 10, we find the ratio of the populations of the π^+ and π^- states, as measured by the P-branch and Q-branch transitions, respectively, to be $P(\pi^+)/P(\pi^-) =$ 2.1 ± 0.3 . This is quite close to the value found in the 193 nm photolysis.²⁸ The importance of the lambda doubling ratio arises from the correlation in high rotational levels of the Π^+ state with an orientation in which the orbital containing the unpaired electron (coming from the broken bond) is located in the plane of rotation of the OH fragment. This suggests that nitric acid, which is planar in its equilibrium geometry, remains so during both the 193 nm photolysis and the vibrationally mediated photodissociation. Thus we infer that the state initially prepared by vibrational overtone excitation must not contain appreciable amounts of torsional or other out-of-plane excitation.

The disposal of available energy in the vibrationally mediated photodissociation of $HONO_2$ shows an interesting pattern that points to the role of the low-lying electronic states of the NO₂ fragment. Table 2 summarizes the results for nitric acid and compares them to those of hydrogen peroxide and t-butyl hydroperoxide. From energy conservation it appears that internal excitation of the NO₂ carries away the largest fraction (0.78) of the excess energy. The presence of low-lying electronic states of NO₂²⁹ make it improbable that this fraction, which amounts to over 19 000 cm⁻¹, goes soley into vibration and rotation of the NO₂ fragment. We suspect that a significant fraction of the NO₂ fragments are formed electronically excited. This is in contrast to the situation for single-photon photodissociation, which produces no electronically excited NO₂ at wavelengths above 220 nm.^{30,31} It is likely that excitation from the highly vibrationally excited intermediate state reaches regions of the electronically excited surfaces that are not accessible by one photon absorption at comparable total energies. This is yet another example of the change in dissociation dynamics affected by two-step dissociation through a vibrationally excited intermediate state.

t-Butyl Hydroperoxide

Vibrationally mediated photodissociation of the much larger t-butyl hydroperoxide (Bu'OOH) molecule allows interesting comparisons to be made with smaller polyatomic molecules. Experiments involving the direct one-photon excitation of the $5\nu_{OH}$ and $6\nu_{OH}$ transitions, both of which are above the threshold for O—O bond fission, have revealed anomalous kinetic behaviour in the subsequent steady-state fragmentation kinetics,³² with one possible interpretation being that the dissociation contains contributions from a non-statistical (mode-selective) channel. As with hydrogen peroxide, we have performed time-resolved one-photon photofragmentation experiments with Bu'OOH excited to the $5\nu_{OH}^{33}$ and $6\nu_{OH}^{34}$ regions and have found largely statistical behaviour with, at $6\nu_{OH}$, complications due to direct one-photon excitation to a dissociative electronic state.^{33,35}

Despite the obvious differences, Bu'OOH and HOOH both contain the OOH group, suggesting that vibrationally mediated photodissociation through the $4\nu_{OH}$ transition, which is below the threshold to O—O bond dissociation for both molecules, also should be possible with the larger molecule. We can easily obtain laser photoacoustic spectra of Bu'OOH, unlike the case for HOOH, and directly compare them to vibrational overtone-excitation-dissociation spectra. Furthermore, experimental information on the 248 nm one-photon direct photodissociation dynamics of vibrationally unexcited Bu'OOH is becoming available.^{36,37}

Vibrational Overtone Spectroscopy

Fig. 7(*a*) shows the pulsed laser photoacoustic spectrum of a 8 Torr sample of Bu¹OOH in the region of the $4\nu_{OH}$ transition. The main band, centred at 13 298 cm⁻¹, is characteristic of the O—H stretching vibration overtone transitions of this molecule and is similar in appearance to bands that have been assigned as $5\nu_{OH}$ and $6\nu_{OH}$ transitions in previously reported photoacoustic spectra.³² Thus, we identify the main band in fig. 7(*a*) as the $4\nu_{OH}$ transition. The *ca.* 29 cm⁻¹ width (f.w.h.m.) of the band is likely to arise primarily from unresolved rotational structure. The shape of the band suggests the presence of unresolved P-, Q- and R-branch features.

We assign the second most intense feature, centred at 13 520 cm⁻¹, as a combination band involving both O–H stretching and O–O torsional motions, in analogy with the vibrational overtone spectroscopy of HOOH. An analysis similar to that presented for HOOH, involving the adiabatic separation of O–H stretch and O–O torsional motions,¹¹ should thus be possible for Bu'OOH. There are also several weaker features in the spectrum shown in fig. 7(*a*). The shoulder to higher energy of the main band,



Fig. 7. The photoacoustic and vibrationally mediated photodissociation spectra of t-butyl hydroperoxide excited to the region of the $4\nu_{OH}$ transition. In the photoacoustic spectrum (a), the absorption of t-butyl alcohol ($4\nu_{OH}$), which is present as a 5% impurity, is indicated by the arrow, and sharp features to higher energy are assumed to be water transitions. The photoacoustic spectrum is normalized to the pulse energy of the excitation laser. The vibrationally mediated spectra (b) and (c) are taken probing N = 3 and N = 9 of the v'' = 0 state of the OH fragment, respectively. These spectra are normalized to the square of the pulse energy of the excitation laser and to the pulse energy of the probe laser.

centred at ca. 13 350 cm⁻¹, is probably a hot-band transition in which Bu^tOOH thermally excited to the lowest excited torsional level in the ground vibrational state makes a transition to a level having four quanta of O—H stretching motion and one quantum of torsional motion, again in analogy to the situation for HOOH. The shoulder to higher energy of the combination band, indicated by an arrow at ca. 13 532 cm⁻¹ corresponds to the $4\nu_{OH}$ transition of t-butyl alcohol (Bu^tOH), which is present as an impurity in the sample of Bu^tOOH and is a product of the decomposition of Bu^tOOH on the surface of the photoacoustic cell. Recording the photoacoustic spectrum of a pure sample of Bu^tOH in this region confirms this assignment. In addition, the shoulder grows in intensity in spectra of samples of Bu^tOOH that decompose for several days in the photoacoustic cell. The sharp features observed at even higher energy from the combination band are apparently water-vapour transitions.

The vibrational overtone spectroscopy of Bu^tOOH in this region seems to be completely dominated by transitions involving the O-H stretching motion. The data in fig. 7(a) provide no substantive evidence for the presence of C-H overtone transitions despite the prediction by a local-mode model of a complicated band system associated with the $5\nu_{CH}$ manifold. Laser photoacoustic spectra of t-butyl chloride confirm that the $5\nu_{CH}$ bands are indeed present, but, with a sample pressure and detection sensitivity identical to those for the spectrum in fig. 7(a), they are extremely weak. The close similarities between the spectroscopies of Bu'OOH and HOOH lend support to the notion that O-H vibrational overtone levels in the former are not mixed significantly with vibrational motions of the t-butyl group, which provides the bulk of the vibrational state density at these excitation energies. Fig. 7 illustrates the close similarity between the photoacoustic absorption and vibrationally mediated photodissociation spectra. The photodissociation spectra reproduce all of the features assigned as belonging to the $4\nu_{\rm OH}$ vibration-torsion manifold. The shoulder to higher energy of the combination band and the sharp transitions seen in the photoacoustic spectrum are absent in the vibrationally mediated photodissociation spectrum since they are vibrational overtone transitions of Bu^tOH and H₂O, which are present as impurities and which produce no detectable fragments in the photodissociation scheme.

Important questions concerning the extent of O-H and C-H vibrational mode mixing in this molecule remain unanswered. Initial C-H overtone excitation might be expected to be less efficient as compared to O-H overtone excitation in promoting further photon absorption and subsequent dissociation, but the weakness of the C-Hovertone transitions in this region means that we cannot address this question properly. In addition, our ignorance concerning details of the dissociative electronic state prevents our drawing conclusions regarding the extent of O-H stretch and O-O stretch mixing, as may be possible for HOOH. One-photon ultraviolet (355 nm) photolysis experiments, which can help to reveal more details of the nature of the upper electronic surface in this energy region, are in progress.

Photodissociation Dynamics

We have determined the product $OH(X^{2}\Pi, v''=0)$ rotational state distribution resulting from vibrationally mediated photodissociation at 13 298 cm⁻¹, corresponding to the maximum of the main band in the $4\nu_{OH}$ region of Bu'OOH. Fig. 8 shows this distribution in the form of a plot of relative population *versus* the quantum number N. The products have less rotational energy than those obtained from the corresponding process in HOOH (*cf.* fig. 4). From the 0.4 cm⁻¹ (f.w.h.m.) widths of individual rotational lines in the OH fluorescence excitation spectrum, we conclude that less energy is released into translation for Bu'OOH than for HOOH and HONO₂, as reported in table 2. We find no evidence for the formation of $OH(X^{2}\Pi, v''=1)$. This again contrasts with the results for HOOH and HONO₂ in which *ca.* 11% and *ca.* 5% of the OH fragments are formed vibrationally excited in the vibrationally mediated photodissociation process, respectively. Simons and coworkers³⁷ observe production of OH fragments exclusively in v''=0 in the one-photon 248 nm direct photolysis of Bu'OOH.

The total energy deposited in the parent molecule in these experiments is roughly $26\,600\,\mathrm{cm^{-1}}$, which exceeds the threshold for O–O bond fission $(170\,\mathrm{kJ\,mol^{-1}}$ or $14\,270\,\mathrm{cm^{-1}})^{32a}$ by $12\,300\,\mathrm{cm^{-1}}$. This excess energy is partitioned among the translational, rotational and vibrational degrees of freedom of the Bu^tO and OH photogfragments, and the results described above show that very little of this excess energy is retained in the OH fragment. This is consistent with the t-butyl group in Bu^tOOH providing an energy 'sink' that retains much of the excess energy in the numerous internal quantum states of the Bu^tO fragments.



Fig. 8. Rotational product state distribution of the v'' = 0 OH fragment from the vibrationally mediated photodissociation of t-butyl hydroperoxide through the region of the $4\nu_{OH}$ transition.

We conclude by noting that these observations do not necessarily contradict the suggestion that in the one-photon direct photofragmentation of Bu'OOH through $5\nu_{OH}$ and $6\nu_{OH}$ part of the dissociation occurs from vibrationally excited Bu'OOH in which the excitation energy is distributed non-statistically.³² Our experiments probe the nature of the vibrationally excited molecule on a nanosecond timescale, whereas the timescale for proposed nonstatistical dissociation is a few ps.³² Vibrationally mediated photodissociation experiments that address the question of whether or not the initially excited vibrational state evolves on a picosecond timescale require a picosecond pulsed laser source.

Summary

Vibrationally mediated photodissociation is a useful experimental technique for studying both the spectroscopy of bound vibrational overtone states and the photodissociation dynamics of highly vibrationally excited polyatomic molecules. In its two-colour variant, the vibrationally mediated photodissociation technique appears to be generally applicable to molecules possessing a dissociative or predissociative electronic surface in the ultraviolet region and one or more X—H 'chromophores' (X = C, N, O *etc.*) whose vibrational overtone levels may be excited. As we have demonstrated with hydrogen peroxide, the vibrationally mediated photodissociation technique allows us to obtain vibrational overtone-excitation spectra in supersonic jets. The resulting spectral simplification is essential for an assessment of the role of vibrational mode mixing. By photodissociating the vibrationally excited molecule and examining the energy disposal in the fragments, we probe the intramolecular dynamics of the vibrationally excited states we have prepared, and thus make a link with theoretical dynamics calculations. We have already gathered detailed information on the photodissociation dynamics of vibrationally excited HOOH, HONO₂ and Bu'OOH. For the smaller polyatomic molecules, it should be possible to obtain good *ab initio* potential-energy surfaces for use in modelling the experimental results.

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