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Atmospheric Photochemistry via Vibrational Overtone Absorption

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I. Introduction

A. Solar Intensities and Atmospheric Chemistry.

The scale, geometry, and environment of planetary atmospheres make them significantly different from conventional chemical reaction vessels: homogeneity and equilibrium cannot be ensured or assumed. On Earth, temperature is a well-defined variable locally in the atmosphere at altitudes less than about 100 km; however, the atmosphere is not in thermodynamic equilibrium. Although there is an approximate heat balance between the incoming solar and outgoing terrestrial radiative fluxes, a thermodynamic disequilibrium is maintained by an entropic imbalance. Absorption by the Earth of the incoming beam of photons from the sun, which may be approximated by a blackbody at about 5800 K, gives rise to an entropy increase of the planet, equal to $\Delta S_{\mathrm{in}} = \delta q_{\mathrm{in}}/5800$. The outgoing longwave IR radiation to space at an approximate blackbody temperature of about 250 K gives a loss of entropy of about $\Delta S_{\mathrm{out}} = \delta q_{\mathrm{out}}/250$. Since δq_{in} and δq_{out} are of comparable magnitude, the Earth's entropy loss is greater than the entropy input, thereby increasing the free energy of the planet above its equilibrium value. The difference is expended on driving, *inter alios*, chemical processes at the surface and in the atmosphere, along with winds, clouds, and the general circulation of the atmosphere. In this review we discuss chemical processes which are driven by solar radiation and so are not in equilibrium.

The fluid mechanical motions, which dominate at millimeter and larger scales (i.e., 9 orders of magnitude in horizontal lengths), result in very large adiabatic heating and cooling rates.[1] However, because of the high collision frequencies in the atmosphere, Boltzmann distributions among molecular internal states and a Maxwell−Boltzmann distribution of molecular speeds are, on average, maintained, ensuring that temperature is well-defined locally. This allows straightforward calculation of reaction kinetics, phase equilibria, partitioning of species among gas, liquid, and solid phases, etc. The presence of exponential factors involving energies and temperatures in the equations describing these processes and the temperature distribution in the middle and lower atmosphere (below about 100 km altitude) suggest that processes with activation energies in

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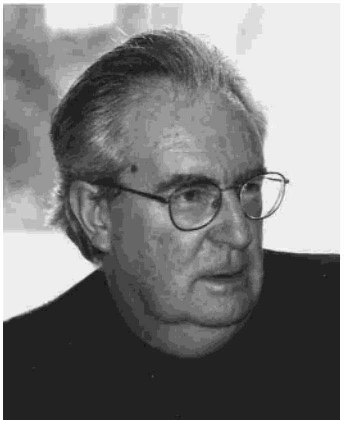

Adrian Tuck obtained his B.Sc.(Tech) degree in Chemistry in 1965 from the Manchester College of Science and Technology of the Victoria University of Manchester and was awarded his Ph.D. degree in Physical Chemistry from Cambridge University in 1969. He was a postdoctoral Fulbright Scholar at UCSD before joining the British Meteorological Office in 1972. In 1986 he joined the NOAA Aeronomy Laboratory in Boulder, where he heads the Meteorological Chemistry Program.

excess of 50 kJ mol^{-1} should occur very slowly, if at all. Given that limitation, clearly any mechanism which promotes excursions from strict local thermodynamic equilibrium conditions may have significant effects on chemistry.[2]

One such mechanism is the absorption by atmospheric molecules of incoming solar radiation. Absorption of a photon deposits a molecule, boosting that molecule's energy content above that determined by the local temperature. This energy may be dissipated by collisions, bringing the molecule back into Boltzmann equilibrium with the surrounding atmosphere, or may be used to effect chemical change, most importantly, bond cleavage. In this manner, solar photons may promote chemical processes which are far too energetically unfavorable to proceed in their absence. Generally, one considers such chemical effects taking place in electronically excited states, but solar photons may promote ground-state chemical processes as well.

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The presence of solar radiation of sufficient energy to drive chemical processes is fundamental to our understanding of atmospheric chemistry. The solar wavelengths considered are typically in the UV spectral region (200−400 nm), since these correspond to "normal" chemical bond energies. Absorption by O_2 in the upper atmosphere and by O_3 in the upper−mid stratosphere gives an altitude and solar zenith angle dependence to the spectrum of radiation available in the atmosphere. Shorter wavelengths are attenuated at higher altitudes and larger zenith angles (i.e., as the sun approaches the horizon), giving rise to differences in the photochemistry depending on altitude, season, and time of day. For example, in the lowest region of the atmosphere, readily photolyzable molecules such as NO_3 and O_3 are important oxidizing reagents at night (in the dark) but lose their relative importance in daytime, due to photolysis and the higher daytime concentrations of OH. At the lowest altitudes, essentially all of the higher energy ultraviolet radiation is attenuated, leaving light of $\lambda > 305$ nm to effect any photochemistry. Photons in the visible region of the solar spectrum ($\lambda > 400$ nm) are very much more abundant than those of higher energies at all altitudes and solar zenith angles. Although visible radiation can have sufficient energy to rupture weaker chemical bonds, it is generally not in the correct wavelength range to excite molecular electronic transitions, and so is not usually considered as a driving force in atmospheric chemistry. Figure 1 illustrates the altitude and zenith angle dependence of the solar radiation reaching the earth.

Through the mid-1990s, observations of the $[HO_x]$ ($OH + HO_2$) at high solar zenith angles differed from values given in model calculations, particularly for the lower stratosphere. During both the 1993 Stratospheric Photochemistry, Aerosols and Dynamics Expedition (SPADE)[3] and the 1997 Photo-

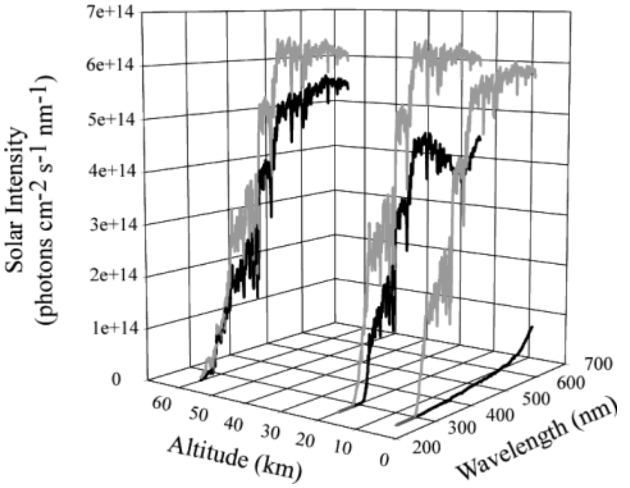

Figure 1. Altitude and solar zenith angle dependence of the solar actinic flux. The black lines show the solar spectrum at a zenith angle of 90° (i.e., at the horizon); the gray lines show the actinic flux at a zenith angle of 0°.

chemistry of Ozone Loss in the Arctic Region In Summer (POLARIS)[4] missions, significant concentrations of HO_x, amounting to almost 20% of the maximum noontime OH concentrations, were measured at high solar zenith angles.

Atmospheric HO_x is primarily produced by the reaction sequence. Models in which OH production

$$O_3 + h\nu\ (\lambda \le 305\ \text{nm}) \rightarrow O(^1D) + O_2\ (^1\Delta)$$

$$O(^1D) + H_2O \rightarrow 2OH$$

is driven entirely by these reactions cannot predict this sudden burst because when the sun is near the horizon, at large solar zenith angles corresponding to dawn, dusk, or the edge of the polar vortex, solar UV light is strongly attenuated due to absorption by ozone along the very long path. However, as shown in Figure 1, visible wavelengths are not significantly attenuated until the sun is at or below the horizon.

In an attempt to account for this effect, we proposed[5] in 1997 that OH-containing species, such as HNO_x (HONO, $HONO_2$, HO_2NO_2), would absorb visible radiation into vibrational overtones of the OH stretch of sufficient energy to cause dissociation to $HO_x + NO_x$. Vibrational overtone transitions to states with 3−6 quanta of OH stretching character take place in the near-infrared to visible region of the spectrum. The absorption strengths of these transitions are sufficiently weak that chemistry initiated by electronic absorptions will always play a dominant role, when it can occur. However, estimates of the potential effects of overtone absorption followed by dissociation suggested that such processes might lead to significant HO_x production in certain circumstances. In molecules without accessible electronic states or in situations where the UV radiation is sufficiently attenuated, the small probabilities associated with overtone-induced chemistry become important. Since the time of our initial proposal, some effort has been spent in several laboratories on making accurate measurements of absorption cross-sections and dissociation quantum yields of atmospheric species likely to be important overtone absorbers. In the following, we outline the physical basis for overtone-driven photodissociation and review the work which has been done to date. We shall see that while overtone-mediated photodissociation has been shown to be a significant process for only a few atmospheric molecules to date, those molecules are important ones, and there is potential for further investigation of this phenomenon.

B. Overtones and Local Modes in OH-Containing Molecules

The vibrations of polyatomic molecules are often represented as "normal modes", that is, sets of concerted, collective harmonic motions of all the atoms in the molecule, with the molecular center-of-mass remaining fixed in space.[6] For example, in water there are two types of stretching motion: an in-phase extension of both O−H bonds (symmetric stretch) and an out-of-phase (antisymmetric stretch) extension of both bonds (i.e., one bond lengthens while the other contracts), as well as a bending vibration in which the two H atoms approach one another, decreasing the HOH angle of the molecule. In this picture the normal modes of vibration are harmonic and uncoupled from one another. Each type of vibration possesses its own manifold of energy levels; a molecule may exist in an internal state such that one or several of these types of vibration may be active.

Although this is a useful picture at low excitation energies, it becomes increasingly invalid as the internal energy of a molecule increases. It cannot, for example, describe bond cleavage in molecules excited above a bond dissociation limit. Couplings between the different types of vibration can increase greatly with internal energy, allowing vibrational energy to "flow" from one type of motion to another. This anharmonicity of real molecules means that the absorption selection rules appropriate for harmonic motion ($\Delta v = \pm 1$ only) are not strictly valid, and high-lying vibrational levels may, in principle, be excited directly via light absorption. Though allowed, this vibrational overtone absorption is very weak for most types of vibrational motion, and so is not easily observed.

In polyatomic molecules containing O−H, C−H, and N−H groups, the small mass of the hydrogen atom gives rise to X−H stretching frequencies which are considerably higher than other vibrational modes. Quantum states with multiple quanta of vibration in these modes become increasingly decoupled from the remaining vibrations of the molecule as the excitation energy increases. This feature has led to a successful treatment of highly vibrationally excited molecules containing X−H oscillators based on the "local mode" approximation, in which each X−H bond is treated as an independent anharmonic oscillator.[7−10] Although still weak—typically 4−6 orders of magnitude less intense than electronic transitions in the same (near-IR and visible) spectral region—direct excitation from the ground vibrational level to several excited levels ("overtone transitions") may be observed for these molecules.

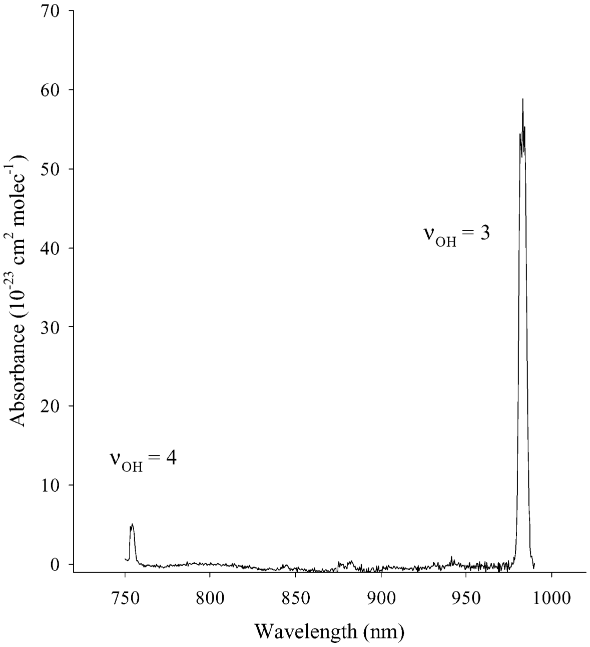

Figure 2. Absorption spectrum of nitric acid in the visible−near-infrared region. Overtone transitions to vibrational states with 3 ($\nu_{OH} = 3$) and 4 ($\nu_{OH} = 4$) quanta in the OH stretching local modes are indicated. See ref 11 for a full discussion of the spectrum.

As an example, Figure 2 displays a portion of the HNO_3 absorption spectrum in the visible wavelength region.[11] Transitions from the ground vibrational level to vibrational states containing three (labeled "$\nu_{OH} = 3$") and four ("$\nu_{OH} = 4$") quanta of OH stretching are shown. As mentioned above, the absorption cross sections are small and decrease by almost an order of magnitude from $v = 3$ to 4. This decrease is a general phenomenon: typically the absorption intensity to any excited vibrational level is roughly 10 times smaller than that to its predecessor. A small number of other combination bands are also observed, but these are extremely weak. Such relatively "clean" spectra are typical of X−H overtone spectra, especially when the molecule contains only one type of X−H oscillator, such as HONO,[12,13] H_2O_2,[14,15] and HNO_4.[15−17]

C. Calculation of Atmospheric Photolysis Rates

The rate of formation of product B from the photolysis of atmospheric species A is expressed as a first-order rate law, with rate coefficient J

$$d[B]/dt = J[A]$$

The value of J is given by a convolution of the absorption spectrum of A, scaled by the quantum yield of formation of B, with the spectrum of available atmospheric radiation

$$J = \int \{\sigma(\lambda)\phi(\lambda)I(\lambda)\}d\lambda$$

where $\sigma(\lambda)$ gives the absorption cross section of A at wavelength λ, $I(\lambda)$ represents the intensity of solar radiation (in photons cm^{-2} nm^{-1} s^{-1}) at λ, $\phi(\lambda)$ gives the wavelength-dependent quantum yield for formation of B via photolysis, and the integration is carried out over the absorption spectrum of the molecule. Calculation of atmospheric photolytic dissociation rates therefore requires good knowledge of the molecular quantities as a function of temperature and pressure (to obtain the altitude dependence) as well as the altitude and zenith angle dependence of the solar spectrum reaching earth.

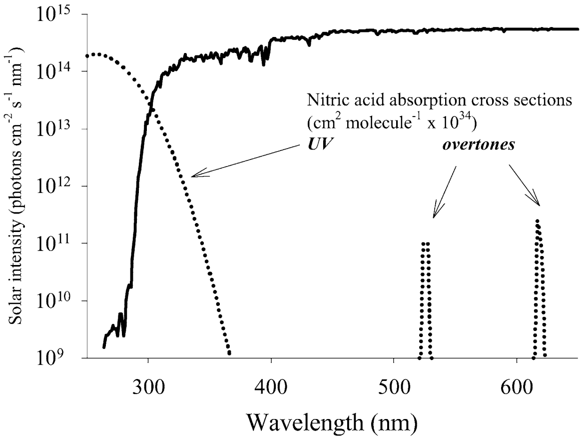

Figure 3. Illustration of the calculation of a J value for nitric acid photodissociation. The solid trace shows the solar actinic flux, and the dotted lines display the nitric acid absorption spectrum in the UV and visible spectral regions (with an assumed dissociation quantum yield of unity in the ultraviolet region). The J value is determined by integrating the areas of overlap between the two traces. The contribution of the overtones is approximately 5% of the total.

Figure 3 illustrates the calculation of the J value for nitric acid photodissociation in the near-ultraviolet and visible regions of the solar spectrum. The wavelength dependence of the product of the nitric acid absorption cross-section and dissociation quantum yield is shown as the dotted line. These parameters are obtained by experiment, as described below. On the same axes, the actinic flux at 90° zenith angle and 15 km are also plotted as a function of wavelength. The convolution of these two wavelength-dependent quantities over the entire absorption spectrum gives the J value.

The actinic flux used in the calculation of J is a result of atmospheric radiative transfer calculations and so depends to some extent on the input to those calculations. Representative results of such calculations may be found in the text by Finlayson-Pitts and Pitts.[18] Especially at high solar zenith angles, the assumed concentration and vertical distribution of ozone and the assumed number density and scattering properties of aerosols can alter both the magnitude of the actinic flux and its wavelength dependence. In favorable cases, observations of these quantities may be available from satellite or airborne instruments.

D. Dissociation of Vibrationally Excited Molecules

There is a good understanding of how a high degree of vibrational excitation may initiate unimolecular reactions.[19] Multiphoton dissociation (MPD) experiments have typically used infrared lasers as excitation sources to excite molecules to energies above the dissociation limit, without the involvement of rota-

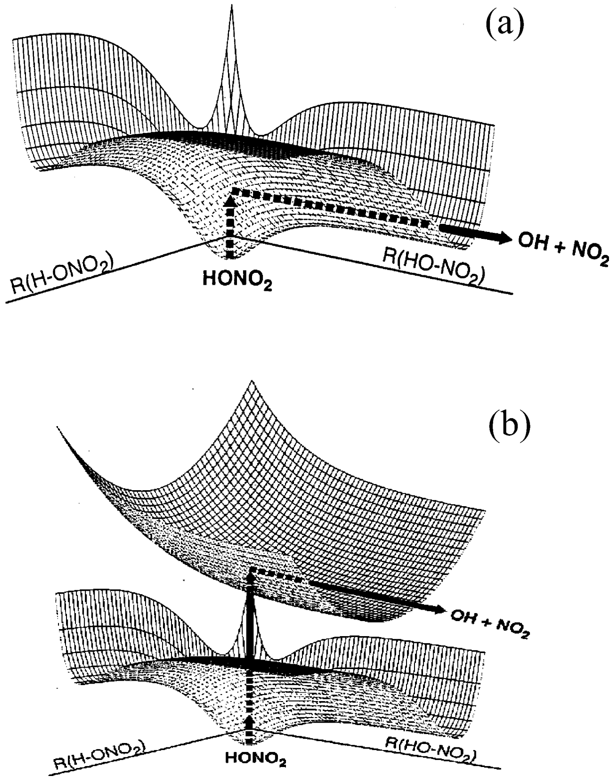

Figure 4. Schematic illustrations of the overtone-induced processes discussed here. (a) The direct overtone-induced dissociation of nitric acid is shown. Here, an overtone of the O−H stretch is excited and dissociation results from energy flow out of this mode into the $HO-NO_2$ coordinate. (b) Vibrationally mediated photodissociation. In this case, an overtone is excited which lies below the dissociation energy. This is shown as the short arrow. Dissociation is achieved by absorption of a second photon, elevating the nitric acid molecule to an excited electronic state.

tional and translational degrees of freedom. In these experiments, absorption following the first or second photon is nonspecific; for molecules with a reasonable density of states, a quasi-continuum of ro-vibrational states may be accessed. More recent work, especially from the groups of Crim[20−22] and Rizzo,[23] has performed the excitation more specifically, by populating high vibrational levels in X−H stretching modes via direct overtone absorption. If the vibrational level accessed in this way lies above the dissociation limit, dissociation is observed.

For example, in nitric acid, transitions to $v = 5$ and higher of the O−H stretch provide the molecule with sufficient energy to rupture the $HO-NO_2$ bond.[24] This energy is initially localized in the O−H stretching vibration, creating a highly nonthermal distribution within the excited molecule. Rapid intramolecular vibrational redistribution (IVR), a consequence of the anharmonic coupling between the H−O stretching motion and the other vibrations of the nitric acid molecule, gives rise to migration of energy out of the OH stretch.[25] Because of potential and kinetic couplings among the internal motions of the molecule, this energy will eventually become distributed statistically into the “bath” of internal quantum states, which is the nitric acid molecule, providing sufficient thermal energy for the O−N bond to break.[24] Figure 4a displays a schematic representation of this process. In the figure, it is clear that whereas motion in the $H-ONO_2$ coordinate is bound, following excitation there is sufficient internal energy for the molecule to dissociate along the $HO-NO_2$ coordinate. Since the anharmonic couplings depend on the density of available states near the initially excited level, the rate of dissociation is expected to increase sharply at energies above the energetic threshold for dissociation.

At energies near the dissociation threshold, molecular rotational and torsional degrees of freedom are effective at coupling the H−X and other molecular modes[26] as well as providing any extra energy required for dissociation. In nitric acid, the 0 K dissociation energy (D_0) of the $HO-NO_2$ bond lies at 16 740 cm^{-1};[27] so the lowest vibrational overtone transition which causes dissociation in this molecule is that to the $v = 5$ level, centered at 16 165 cm^{-1}.[14,24,28] Although this lies somewhat lower in energy than the 0 K dissociation threshold, bond rupture does occur following excitation of this overtone from thermally populated rotational states.[24] There is therefore a temperature dependence to the dissociation quantum yield, related to the internal energy of the molecule prior to the overtone excitation. This effect is seen as well in the overtone-initiated dissociation of HNO_4.[16] The energetic threshold for dissociation to $HO_2 + NO_2$ products lies somewhat above the rotationless $v = 2$ level of the O−H stretch.[16] Excitation of this state (and other close lying combination bands) yields products with a strongly temperature-dependent quantum yield. Exciting higher-lying vibrational transitions gives dissociation with unit quantum yield at all temperatures studied.

For small (3 or 4 atom) molecules the situation described above can be more complex. Because smaller molecules have lower densities of states, the rate of dissociation can depend strongly on the specific rotational state populated by the overtone transition[12,26,29] because of the rotational dependence of the specific couplings involved in the IVR process. This can give rise to dissociation rates which are lower than those calculated using RRKM theory for small molecules.[30] For larger molecules (5 atoms and above), this seems not to be the case, however.[31]

II. Methods for Obtaining the Important Parameters in *J*

As noted in section I.C, to incorporate the effects of overtone excitation into atmospheric chemistry models, the absolute absorption cross-sections and quantum yields of overtone-induced chemistry must be known as a function of wavelength. To provide quantitative *J* values, the temperature and pressure dependence of these parameters should also be known. Such measurements are readily available in the literature for large absorption cross-section electronic transitions of atmospheric species.[27] Until recently, there has been little published on the absolute absorption intensities of atmospherically relevant overtone transitions. As noted above, these are quite weak and therefore difficult to measure accurately, especially the higher overtones which are more reactive and may lie close to the high wavelength "tail" of much stronger electronic absorption transitions. Both experimental measurements and quantum calculations have been used to determine $\sigma(\lambda)$.

A. Experimental Methods

Experimental measurements of absolute overtone intensities pose a challenge. The very weak absorption strengths would suggest that sensitive fluorescence- or ionization-based spectroscopic methods should be employed. However, multiquantum (i.e., $\Delta v > 1$) fluorescence from vibrational overtones is extremely unlikely, just as it is in absorption; the most probable fluorescence occurs in the infrared region corresponding to $\Delta v = -1$ transitions. Lifetimes for infrared fluorescence are typically in the 10^{-3} s regime and so will not compete with any chemistry (i.e., dissociation), which occurs on a time scale of $10^{-12}-10^{-9}$ s. Selective multiphoton ionization from the initially excited level (and no others) is very difficult to achieve experimentally and has not been applied to the measurement of overtone intensities.

Absorption spectroscopic methods are much less sensitive than fluorescence or ionization because of the high background signal associated with the light source but are more universal. Short excited-state lifetimes are manifested in broadened, diffuse spectra, often with little or no rotational structure. Vibrational overtones below the dissociation limit remain sharp, while intensity redistribution into diffuse bands occurs once the dissociation limit is reached or exceeded. The most straightforward absorption technique is direct absorption spectroscopy, in which the attenuation of the intensity of a stable light source is measured as a function of wavelength. The measured absorbance, A, is plotted as a function of absorber concentration, n, (and, ideally, path length, L) to yield the integrated absorption coefficient, σ, for the overtone band, via Beer's Law

$$A = \ln(\mathrm{I}/\mathrm{I}_0) = -\sigma \mathrm{nL}$$

For weak transitions such as overtones, a potential artifact may be introduced at higher sample concentrations: the molecules in the sample may undergo self-association, forming dimers, trimers, etc.[32] For this reason it is always preferable, when possible, to perform direct absorbance measurements using several different path lengths. When such measurements are not possible, spurious effects due to complexation may be identified and corrected by performing a series of temperature-dependent measurements. Since the equilibrium concentrations of complexes show an exponential dependence on $1/T$ (via the van't Hoff relationship), absorption features assignable to complexes show strongly nonlinear temperature and pressure dependences. Direct absorption methods have been used to determine absolute absorption cross-sections for several O−H overtone transitions in H_2O_2,[15] HNO_3,[11,15] HNO_4,[15,17] as well as organic acids[33,34] and alcohols.[33,35] Figure 2 displays such a direct absorption spectrum.

A more sensitive variation on direct absorption uses tunable pulsed or chopped light sources, coupled with opto-acoustic detection. Here, the energy of the absorbed radiation is dissipated to a bath gas by collisions and the resulting transient temperature increase is measured as an acoustic signal in phase with the excitation source. Opto-acoustic detection provides a very sensitive method for the study of nonradiative states. Like direct absorption, this technique is not handicapped by short reactive excited-state lifetimes and provides a more sensitive, zero background alternative to that method. Signal is generated in phase with the excitation modulation frequency when energy is dissipated, whether due to simple absorption or absorption followed by dissociation. The limited availability of tunable laser sources in the near-IR region of the spectrum provides a constraint on the accessible wavelength range for this technique. Recent work from the group of B. R. Henry[36] illustrates the method.

Cavity ring-down laser absorption spectroscopy (CR-LAS) has proven over the last 15 years to be one of the most sensitive spectroscopic absorption techniques available. Typically, a pulsed dye laser is focused into a cavity containing two mirrors of high reflectivity ($\geq$99.9%). The light is reflected inside the cavity many times, thus achieving extremely long—on the order of kilometers—path lengths. A tiny fraction of the light is not reflected at the rear mirror but is transmitted and its intensity detected. As the light pulse traverses the cavity, a fraction may be absorbed with each pass by any absorbing species present. Since the amount of light absorbed depends on the path length, through Beer's law, each round trip of a light pulse through the cell gives rise to an attenuation of its intensity, measured by the detector. The time constant for the resulting exponential decrease in the detected intensity (the cavity "ring-down" time) depends on the cavity design and also the absorption strength of any species present in the cell. Measurements of the ring-down time as a function of wavelength can thus be used to determine absorption intensities. The absorption intensity measurements of higher overtones of H_2O_2 and HNO_3 by Brown et al.[14] show the strong potential of this method. Figure 5 illustrates a spectrum of the transition to $\nu_{OH} = 5$ in nitric acid, measured by those authors. The high signal-to-noise ratios obtainable, even for very weak absorptions, are obvious from this figure, especially in comparison to Figure 2.

For states that dissociate to products which may be detected quantitatively, calibrated action spectra may be used to obtain the product of the absorption cross-section and the dissociation quantum yield. In this technique, the excitation source (generally a tunable laser) is scanned over the overtone transition and the product is detected, using LIF, MPI, or other sensitive detection methods. The product signal measured is compared to a reference signal, which is generated using compounds having well-known absorbances and quantum yields. Wennberg and coworkers[16] used this approach to determine the combined absorption cross-section and dissociation quantum yield for absorption to $v = 2$ of the OH stretch

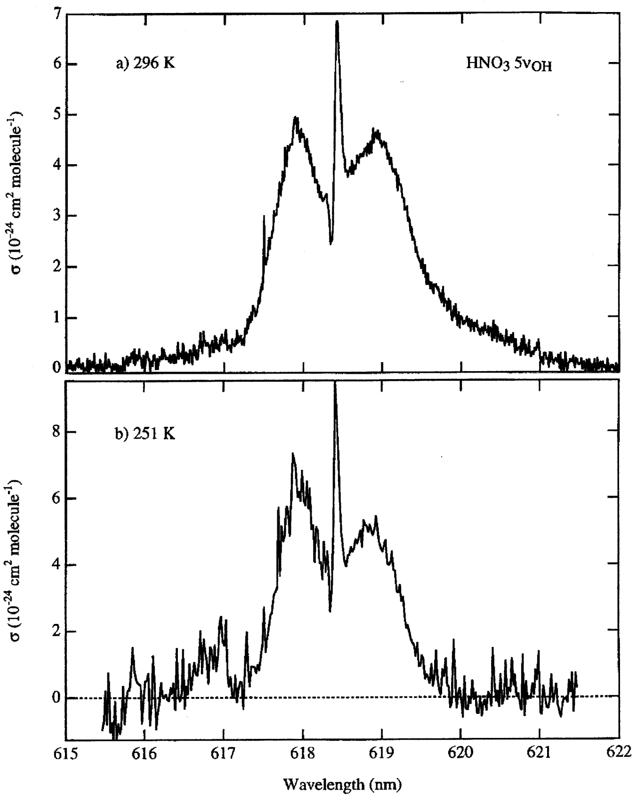

Figure 5. $\nu_{OH} = 5$ absorption spectrum of nitric acid, measured by cavity ring-down spectroscopy. Note the high S/N ratio, despite the very small cross-section for absorption. (Reprinted with permission from ref 14. Copyright 2000 American Chemical Society.)

in pernitric acid. Because this type of experiment gives a signal proportional to the product of the absorption cross-section and the dissociation quantum yield, it provides all the required elements for calculation of the *J* value for dissociation.

B. Theoretical Methods

Overtone intensities may be calculated using ab initio quantum chemical methods.[37] The quantity of interest is the oscillator strength, $f_{g\rightarrow e}$, of a vibrational overtone transition from $|g>$ to $|e>$. This is given by[38,39]

$$f_{g\rightarrow e} = 4.70165 \times 10^{-7}\,[\mathrm{cm\ D^{-2}}]\nu_{eg}[\mu_{eg}]^2$$

where ν_{eg} gives the transition frequency in $\mathrm{cm^{-1}}$ and μ_{eg} represents the transition dipole moment matrix element, $<e|\mu|g>$ in Debye. The oscillator strength can be shown to be related to the integrated absorption cross-section, $\sigma(\nu)$, by[40]

$$f = 1.1296 \times 10^{12} \int \sigma(\lambda)d\lambda$$

The transition dipole matrix elements are calculated using the eigenfunctions of an assumed form of the potential energy function (generally a Morse function), which describes the local mode stretch. The function is fitted to energies calculated along the stretching coordinate using ab initio methods. The dipole moment function is an expansion in the local mode stretching coordinate, *q*, expanded about the equilibrium position

$$\mu(q) = \Sigma \mu_i\, q^i$$

where the coefficients μ_i are obtained by incrementing *q* and calculating the dipole moment at each position using ab initio quantum calculations. In the context of the present work, such approaches have proved to be quite successful at calculating accurate absorption cross-sections for O−H overtone transitions in HNO_3,[11] HNO_4,[17] and H_2SO_4.[41]

III. Case Studies of Overtone Chemistry of Atmospheric Species

A. Pernitric Acid, HO_2NO_2

Pernitric acid is formed in the atmosphere predominantly through the recombination of HOO and NO_2. Although it is a minor component of the total atmospheric nitrogen oxide family (with typical maximum atmospheric mixing ratios of hundreds of pptv), it gains significance as an important reservoir species for both HO_x and NO_x in the atmosphere. It undergoes reaction with OH and can dissociate both via ultraviolet photolysis and thermally, since the HOO−NO_2 bond energy is only about 21 kcal mol^{-1}.[42]

1. Experimental and Theoretical Measurements of Overtone Intensities

When overtone-initiated photodissociation was first proposed, we suggested that the dissociation of pernitric acid, forming HOO + NO_2, should play a significant role in HO_x and NO_x recycling due to its low bond strength.[5] At that time, it was believed that dissociation could occur following excitation of the $v = 3$ level of the OH stretch. In the absence of measured overtone intensities, we estimated the absorption cross-sections to be 10^{-22} cm^2 for the transition to $v = 3$, decreasing by an order of magnitude with each successive *v* level. Under that assumption, the estimated *J* value for overtone-driven photodissociation was a significant fraction of the UV photolysis rate throughout the atmosphere; we suggested that overtone-driven photolysis should dominate the photochemistry of pernitric acid at high solar zenith angles.

Following that initial hypothesis, much work has been done to obtain more quantitative estimates of the *J* value. Fono et al.[17] used a combination of solution-phase spectroscopy and ab initio calculations to estimate the integrated intensities for the transitions to $v = 3$ and 4 of the OH overtones. These suggested that the cross-sections were 3−5 times larger than the estimates used by Donaldson et al.[5] The first gas-phase measurements of pernitric acid overtone intensities were reported by Zhang et al.,[15] who used a long path length, direct absorption apparatus. Their measurements confirmed the estimates given by Fono et al.[17] with integrated absorption cross-sections of $(3.8 \pm 1.1) \times 10^{-20}$ cm^2 molecule^{-1} cm^{-1} for $v = 3$ and $(3.0 \pm 1.8) \times 10^{-21}$ cm^2 molecule^{-1} cm^{-1} to the $v = 4$ level. Those measurements were

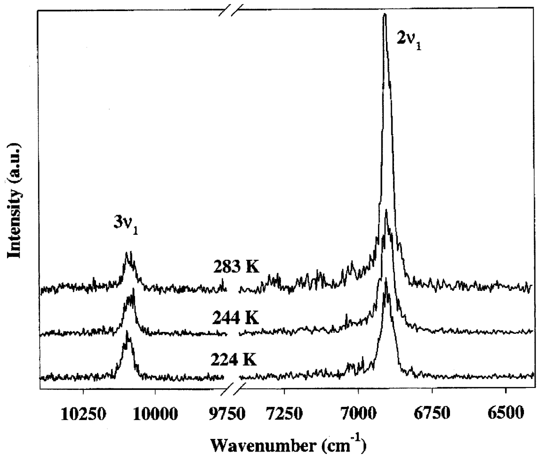

Figure 6. Action spectra of pernitric acid in the region of the $\nu_{OH} = 2$ and $\nu_{OH} = 3$ overtone transitions. The relative intensities in the spectra indicate the relative concentrations of HO_2 resulting from absorption by pernitric acid; they are normalized to the intensity in the $\nu_{OH} = 3$ band. Note the strong temperature dependence of the dissociation quantum yields in the $\nu_{OH} = 2$ band. (Reprinted with permission from ref 16. Copyright 2002 American Chemical Society.)

extended by Roehl et al.,[16] who measured the integrated absorption cross-sections for transitions to the $v = 2$ OH stretching level ($(9.5 \pm 1.9) \times 10^{-19}$ cm^2 molecule^{-1} cm^{-1}) as well as those to combination bands which are close in energy to that level. In addition to the cross-section measurements, those authors also determined the photodissociation quantum yields for excitation of the lower energy bands, assuming the quantum yield for dissociation of the $v = 3$ band to be unity. These measurements showed that dissociation does indeed occur from the lower-lying levels with a temperature-dependent quantum yield, suggesting the participation of rotational excitation in the dissociation process. Figure 6 displays the excitation spectra observed by Roehl et al.[16] at three different temperatures. This figure illustrates very nicely that dissociation may occur in the ground electronic state following nonthermal excitation.

At 240 K, Roehl et al.[16] measured a quantum yield of 0.14 for photolysis of the $\nu_{OH} = 2$ level and thus infer a J value of about 6.4×10^{-6} s^{-1}, about 5 times greater than the J value for $v = 3$ photolysis at that temperature. Summing all the overtone contributions to the dissociation rate gives a rate of about 10^{-5} s^{-1}, equivalent to the daytime, low zenith angle, midday ultraviolet photodissociation rate.

2. Field and Model Studies

The suggestion that overtone-initiated dissociation might play a role in the atmosphere was first suggested in an attempt to account for field measurements. During the 1993 Stratospheric Photochemistry, Aerosols and Dynamics Expedition (SPADE), measurements of HO_x concentrations were higher than those expected from known atmospheric chemistry.[3] In addition, the temporal evolution of the HO_x concentration was quite surprising, indicating a rapid onset of these radicals at daybreak, amounting to close to 20% of the maximum amount (occurring at noon). Models did not predict this sudden burst of OH because near dawn the intensity of solar UV radiation is very close to zero. The same discrepancy between measured and modeled [HO_x], particularly at sunrise, was also observed in the 1997 Photochemistry of Ozone Loss in the Arctic Region In Summer (POLARIS) mission.[4] Inclusion of heterogeneous chemistry in the atmospheric chemistry models did not resolve these discrepancies. Wennberg et al.[4] showed that in order to reproduce the experimental measurements, there must exist a photochemical process which yields HO_x occurring at wavelengths between 650 and 1250 nm.

Since overtone-driven processes are almost independent of solar zenith angle, whereas UV dissociation has a strong zenith angle dependence, overtone-induced processes held promise to play a role in HO_x-producing photochemistry. The first calculations which included overtone absorption and dissociation of HO_2NO_2 considered absorption to $v = 3$ and higher of the OH stretching mode only, since the dissociation threshold was then thought to lie somewhat below this level.[4,43] Those calculations[4] also included HOBr triplet state photochemistry and were able to reproduce the solar zenith angle dependence of the appearance of HO_x but underestimated the magnitude by about a factor of 2 at dawn and somewhat more at dusk.

More recent work has included photodissociation from the $v = 2$ OH stretch and other nearby combination bands using photodissociation cross-sections measured by Roehl et al.[16] Because the cross-sections for absorption into these lower vibrational levels are more than an order of magnitude larger than those to $v = 3$, the calculated HO_x production rate increases significantly when they are included. A calculation with these lower vibrational levels included was done by Salawitch et al.[44] That work shows that near-IR photochemistry of HO_2NO_2 plays an important role in atmospheric chemistry, especially in the high latitude springtime. Including overtone photochemistry in stratospheric models brings measured and modeled HO_2NO_2 concentrations and their altitude dependence into very close agreement.[44,45] The temporal profiles of HO_x production are also better reproduced, as shown in Figure 7, reprinted from ref 44, although some discrepancies remain.

3. Alternate Dissociation Pathways

As well as a simple bond cleavage, a molecular rearrangement–dissociation channel may be accessed by molecules with sufficient vibrational excitation. Ab initio calculations of the HO_2NO_2 potential energy surfaces suggest that a hydrogen-atom migration, followed by dissociation to HONO + O_2 ($^1\Delta$), could contribute significantly to the total dissociation yield of overtone-excited pernitric acid.[42] A rearrangement reaction on the singlet potential surface is calculated to occur via a five-membered ring transition-state structure, lying about 31 kcal/mol above the ground state. Inspection of the reaction pathway suggests that OH stretching motion is likely to facilitate achieving this structure; the energetics indicate that excitation of $\nu_{OH} \geq 3$ will provide sufficient energy to overcome the calculated dissocia-

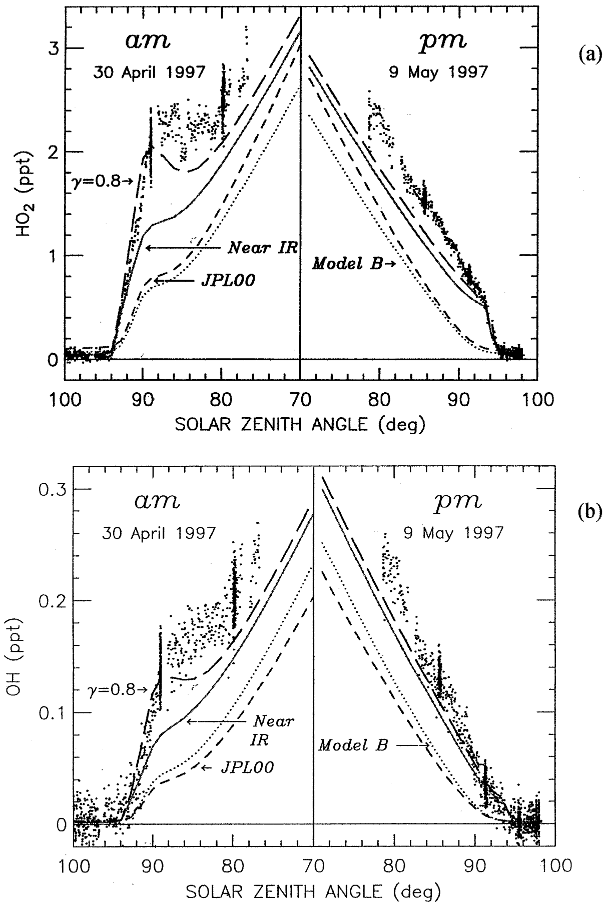

Figure 7. Comparison of observations of HO_2 (a) and OH (b) concentrations observed in the lower stratosphere with those predicted using different models for the HO_x chemistry. The best agreement requires inclusion of near-IR photolysis as well as bromine nitrate hydrolysis. (Reprinted with permission from ref 44. Copyright 2002 American Geophysical Union.)

tion barrier. This process might be occurring in competition with the OH and HO_2 formation channels, following excitation of the $\nu_{OH} = 3$ or 4 overtones of pernitric acid. At the time of writing, this channel has not been confirmed.

The reaction which produces ground-state products, HONO + $O_2(^3\Sigma)$, is about 5 kcal/mol exoergic but is spin-forbidden. This reaction could proceed if the reacting HO_2NO_2 molecule undergoes a singlet–triplet surface crossing. Staikova et al.[42] suggested that this crossing must lie at energies above the HO_2 + NO_2 dissociation channel and so might be accessible following higher overtone excitation of ground-state pernitric acid.

B. Other HO_x–NO_x Species: HNO_3, HONO, and H_2O_2

Like pernitric acid, these molecules are atmospherically significant because they act as reservoirs for HO_x and NO_x species and so can have a large influence on ozone concentrations.

In the paper in which we first proposed overtone-initiated HO_x production,[5] we used estimated overtone absorption intensities for nitric acid. On the basis of these values, we calculated that the J value for dissociation of this molecule increased by some 5–10% at high solar zenith angles when overtone-initiated dissociation from the $v = 5$ and 6 levels of the OH stretch were included. The overtone absorption cross-sections have since been measured using direct absorption[11,15] and cavity ring-down techniques[14] and calculated [11] using the ab initio methods outlined above. The resulting four sets of intensities, reported by three research groups, show very good agreement and are approximately 2 times the values used in ref 5. Substitution of the measured absorption cross-sections into the J-value calculations increases the enhancement of this quantity due to overtone-initiated dissociation by about a factor of 2.[14] However, since this enhancement is only appreciable at high solar zenith angles, where the J value for ultraviolet photodissociation of nitric acid is not large, overtone-driven dissociation of nitric acid does not play an important role in atmospheric HO_x production, at least in the stratosphere. It could, however, be important in polar regions, where high solar zenith angles are persistent in the absence of UV radiation.

The direct overtone-induced dissociation of nitrous acid, HONO, has not, to our knowledge, been reported. Overtone spectra have been measured by several groups, often in the context of studies of vibrationally mediated dissociation.[12,13] Very recently, the absolute intensity of the $\nu_{OH} = 3$ band of *trans*-nitrous acid has been measured[46] to be about an order of magnitude smaller than the corresponding transitions in HNO_3, HNO_4, or H_2O_2. The energetics of HONO dissociation are similar to those of HNO_3, so excitation of $v \geq 5$ is required to effect dissociation. However, the atmospheric photochemistry of HONO is dominated by a structured electronic spectrum in the near-ultraviolet region of the spectrum. The absorption intensity to this state is some 5–6 orders of magnitude larger than the expected $v = 6$ overtone intensity,[18] so overtone-induced dissociation of HONO is not expected to be important in the atmosphere.

Hydrogen peroxide, H_2O_2, is another atmospherically important species which may undergo direct overtone photodissociation. In this case, excitation to energies at or above the $\nu_{OH} = 5$ level are required for O–O bond cleavage to occur. Recent studies by Brown et al.[14] and by Zhang et al.[15] provided absolute absorption cross-sections for the transitions $\nu_{OH} = 3–5$ in this molecule. Incorporation of the overtone contribution to the J value for photolysis increases the OH production rate from H_2O_2 by about 2% at very high solar zenith angles.[14]

C. Sulfuric Acid, H_2SO_4

Another inorganic acid of great atmospheric importance is sulfuric acid, which acts as a nucleating agent for aerosol and cloud formation at all altitudes. An enhancement in springtime stratospheric particle concentrations has been observed in air of recent Arctic and Antarctic origin.[47–49] New particle formation is observed in the stratospheric vortex in the "old" air which has descended from higher altitudes during the long polar night. This has been attributed to high-altitude photolysis of H_2SO_4, producing SO_3, which photolyzes to SO_2, followed by descent of that compound and reformation of sulfuric acid at lower altitudes.[50] To give reasonable agreement with observations, this mechanism requires an absorption cross-section of 10^{-21} cm^{-2} between 179 and 226 nm and a dissociation quantum yield of unity.[51] Hintze et al. recently showed that there is no appreciable absorption cross-section for H_2SO_4 throughout the ultraviolet region of the spectrum (down to 140 nm),[41] making this mechanism impossible.

Sulfur trioxide may be released photolytically from sulfuric acid if excitation of the OH vibrational overtones of H_2SO_4 promotes the known thermal dehydration reaction[52]

$$H_2SO_4 \rightarrow SO_3 + H_2O$$

Morokuma and Mugurama[53] performed ab initio calculations on the reverse process and determined that there is an energetic barrier of approximately 25 kcal mol^{-1} for the exothermic bimolecular reaction. The minimum energy required for the dehydration reaction is predicted to be about 40 kcal mol^{-1}, corresponding to excitation of $v = 4$ or 5 of the O−H stretch.

The frequencies and oscillator strengths of the OH stretching local modes in sulfuric acid have been investigated using a combination of direct absorption measurements and ab initio calculations.[41,52] As in the similar work on nitric[11] and pernitric acids,[17] the calculated frequencies and intensities for H_2SO_4 agreed to within better than 10% with the measured values. Using the calculated overtone absorption cross-sections and an assumed unity quantum yield for dehydration, we estimated[52] the J value for dehydration via overtone pumping to be approximately 3×10^{-8} s^{-1}. At altitudes below 30 km, this value is greater than or equal to that for UV photolysis calculated using erroneously large cross-sections and so is sufficient to explain the observations of the sulfate layer.

D. Other Molecules

The possibility of overtone-driven rearrangement followed by dissociation exists for other atmospheric molecules as well. For example, organic peroxides, ROOH, could rearrange to RH + O_2 following overtone excitation of the OH bond. Dicarboxylic acids are known to decarboxylate thermally[54] and via infrared MPD,[55,56] with activation energies similar to those expected for lower overtone transitions. If lower overtone excitation effects decarboxylation in these compounds, the resulting lifetimes could be on the order of days, and this mechanism might compete with rainout for their removal. Reynard and Donaldson[34] recently proposed, based on a combination of ab initio calculation of important features of the potential energy surface and measurements of OH overtone intensities, that perfluoroacetic acid (CF_3COOH) could dissociate to HF + CO_2 + CF_2 following excitation of $v = 5$ or 6 of the OH stretch. The estimated J value for this process is several orders of magnitude larger than the J value for ultraviolet photolysis in the troposphere. Other organic acids and peroxides might behave in a similar manner.

IV. Other Fates of Overtone-Excited Molecules

In the foregoing we discussed instances in which the overtone excitation delivers sufficient energy to a molecule for dissociation to occur rapidly following IVR. In addition to dissociation, two chemically interesting fates are possible for overtone-excited molecules at energies below a dissociation limit: the molecule might absorb a second photon, exciting it to a reactive electronic state, or it might undergo bimolecular reaction with some appropriate collision partner. Since in either case the excited molecule must maintain its excitation for some time, both of these potentially interesting fates are in competition with collisional deactivation by the surrounding air. This makes both of these fates unlikely, except in special circumstances.

A. Absorption of a Second Photon

This mechanism for overtone-enhanced photodissociation involves absorption of two photons: the first excites a vibrational overtone transition, and the second promotes the overtone-excited molecule to a dissociative electronic state.[21,57] Figure 4b illustrates this process schematically. This procedure has been used by several authors to study the influence of vibrational excitation on dissociation dynamics (vibrationally mediated photodissociation, VMP). To illustrate the atmospheric possibilities, we detail the case of water here.

The dissociation of water vapor into H + OH involves very high energies, corresponding to an excitation wavelength near 240 nm. Unlike the cases considered above, rupture of the initially excited O−H bond is required for molecular dissociation rather than excitation of the OH overtone followed by IVR to a much weaker bond and its subsequent dissociation. The high dissociation energy for the OH bond in H_2O requires a very high overtone to reach the energy required for bond fission. The near-dissociation anharmonic part of the potential energy surface of water is not described accurately in the literature; nevertheless, we do not expect direct overtone pumping to be an important dissociation mechanism for water since the absorption intensity for the high overtone required is expected to be extremely small.

The mechanism for VMP of water involves excitation from $v = 0$ to excited vibrational levels ($\nu^* > 0$) on the ground electronic state, $H_2O^*(X, \nu^* > 0)$, followed by further excitation to the electronic state $A(^1A_1)$, where dissociation to H + OH is prompt (subpicosecond time scale). The dissociative electronic state can be accessed from the vibrationless ground state at wavelengths $\lambda < 185$ nm. By adding energy in the form of vibrational excitation to the water, the wavelengths required to access the A state become progressively longer. Depending on the level of excitation of $H_2O^*(X, \nu^* > 0)$, this up-pumping step can occur at relatively low energies, using wavelengths readily available in the solar spectrum.

Absorption of the second photon competes with vibrational deactivation in the ground electronic state to form $H_2O(X, \nu' < \nu^*)$ by collisions with other species present, notably N_2 and O_2. This reaction scheme is summarized in the sequence R1–R3 below

$$H_2O(X, \nu = 0) + h\nu_1 \rightarrow H_2O^*(X, \nu^* > 0) \qquad (R1)$$

$$H_2O^*(X, \nu^* > 0) + M \rightarrow H_2O(X, \nu' < \nu^*) + M \quad (R2)$$

$$H_2O^*(X, \nu^* > 0) + h\nu_2 \rightarrow H_2O(A) \rightarrow H + OH \quad (R3)$$

where $h\nu_1$ and $h\nu_2$ represent two different photon energies.

The rate of photodissociation via VMP is given by a J value for up-pumping from the overtone excited level, multiplied by the concentration of vibrationally excited species. At steady state, the latter quantity is given by

$$[H_2O^{\nu}] = \frac{J_{H_2O\nu}[H_2O] + \sum k_i^{\nu+1\rightarrow\nu}[M_i][H_2O^{\nu+1}] + A_{\nu}^{\nu+1}[H_2O^{\nu+1}]}{\sum k_i^{\nu\rightarrow\nu-1}[M_i] + A_{\nu-1}^{\nu} + J^*}$$

where

$$J_{H_2O\nu} = \int_{spectrum} \sigma(\lambda) I(\lambda) d\lambda$$

is the rate of absorption from $\nu = 0$ to ν, at wavelength λ, with solar intensity $I(\lambda)$, J^* is the rate of up-pumping, the A's represent the Einstein A factors for spontaneous emission, and the terms in k_i represent the collisional deactivation rate for excited water with all other species present (M_i).

The excitation step R3 is in direct competition with the collisional quenching of H_2O^* back to the ground state (R2). A thorough analysis of this mechanism is given in Goss et al.,[58] who calculated J^* theoretically and used the formalism of Troe[59] to estimate the deactivation rate coefficients. The requisite state-to-state deactivation rate coefficients are not all known; however, given reasonable guesses for energy transfer probabilities, R2 dominates over R3. Goss et al. conclude that VMP of water is probably not an important process in the atmosphere.[58] This is most likely a general result, at least in the lower and middle atmosphere of Earth. However, in an atmosphere with low number density but high attenuation of ultraviolet and higher energy radiation, such two-photon absorptions could give rise to radical formation.

B. Bimolecular Reactions

Another possible fate of overtone-excited molecules is bimolecular reaction. The effects of vibrational excitation of reagents on the kinetics and dynamics of gas-phase reactions have been extensively studied, at least for small systems.[60–62] Depending on the specific system, reaction rate coefficients can be enhanced by many orders of magnitude when the bond being broken contains one or several quanta in vibration. In the atmosphere, collisional reaction necessarily competes with collisional deactivation, as described above. It is straightforward to show that reaction between two trace species, one of them overtone excited, is highly unlikely, even if vibrational deactivation is slow, due to the overwhelming amount of N_2 and O_2 bath gas present. However, it is conceivable that reaction could occur between an overtone-excited reagent and O_2. Staikova et al.[42] considered this possibility for the reaction of $O_2(^3\Sigma)$ + HONO(ν).

The abstraction of hydrogen from HONO by ground-state oxygen molecules is calculated to have an activation barrier of 28.4 kcal mol^{-1}. The $\nu_{OH} = 3$ absorption in HONO is centered around 975 nm, corresponding to an energy of about 29 kcal mol^{-1}. It is possible, then, that ground-state O_2 could abstract hydrogen from HONO excited to $\nu_{OH} \geq 3$. Endoergic hydrogen-transfer reactions of this type, with "late" barriers (i.e., in which the transition state resembles the products), are often aided by vibrational excitation, with rate coefficients increasing by many orders of magnitude.

Staikova et al.[42] estimated the steady-state concentration of HONO ($\nu_{OH} = 3$) and also its reaction rate with O_2 to compare the resulting "extra" HO_x production rate with that due to HONO photolysis in the near-ultraviolet region. They assumed the absorption coefficient for the transition to $\nu_{OH} = 3$ in HONO to be similar to that in nitric acid and that every collision of excited HONO with O_2 gives rise to reaction. These assumptions gave an upper limit of the HO_2 production rate by this mechanism of approximately 10^4 molecule cm^{-3} s^{-1}, for a HONO mixing ratio of 1 ppbv in the lower troposphere, several orders of magnitude smaller than the OH production rate by near UV photolysis of HONO under those conditions.[18] Given that the absorption cross-section for the transition to HONO ($\nu_{OH} = 3$) is actually about 10 times smaller[46] than that used by Staikova et al.,[42] the reaction of vibrationally excited HONO is not important in the atmosphere. This may not be a general result, however, since similar hydrogen-transfer reactions, forming HO_2, could be significant in the absence of available photolysis pathways.

V. Conclusions and outlook for the Future

It should be clear from the above that there is a strong degree of interaction among workers performing field measurements, modelers, and those making laboratory measurements of J values. Comparisons between field measurements and numerical model calculations of atmospheric chemistry often throw up discrepancies, spurring further laboratory work. The results of laboratory studies are incorporated into atmospheric models, improving (one hopes!) their agreement with field measurements. For example, the dawn "burst" of OH observed by an instrument on the ER-2 aircraft in the lower stratosphere[3] was inexplicable by then-current models.[63] Donaldson et al.[5] proposed on the basis of theory and modeling that photodissociation of pernitric acid via the second and third overtones could be the explanation. Laboratory investigation initially suggested but a small role for this process,[15] but further work[16] revealed that the first overtone had a significant quantum yield at 1.4 μm wavelength. This transformed the significance of the overtone mechanism, making near-IR photodissociation of pernitric acid a major factor in the HO_x–NO_x coupling throughout the lower stratosphere and into the upper and middle troposphere,[64] even at relatively low solar zenith angles.[44] The same process may play a role in the chemistry of nitric and pernitric acids in the Antarctic boundary layer and in the interstitial air of the snowpack.[65] Slusher et al.[65] estimated a lifetime of 17 h for pernitric acid there, a figure which should drop to 3−4 h when photodissociation[16] from $\nu_{OH} = 2$ is included in their calculation. Similar discrepancies between modeled and measured aerosol concentrations in the middle stratosphere have led to the proposal, based on laboratory J-value determinations, that sulfuric acid may undergo overtone-induced dehydration. This very recent suggestion has yet to be incorporated into models, but simple calculations indicate that this mechanism could be important. We should be alert for other atmospheric molecules which could replay the pernitric and sulfuric acid overtone stories.

In the 5 years since it was first suggested that overtone excitations of OH local mode vibrations could be chemically important in the atmosphere, much work has been done. It is now clear that pernitric acid is an important source of atmospheric HO_x at high solar zenith angles via direct solar excitation of the lower overtones of the OH vibration. Overtone-driven dissociation seems also to be an important loss process for this molecule in the free troposphere and may be so in the Antarctic boundary layer and snowpack. HONO might be a product of these low-energy photodissociation events, although this has not been established experimentally. The overtone-induced dehydration of sulfuric acid in the middle to upper stratosphere could also be an important process in forming the Junge layer, particularly in its enhancement in the polar springtime vortex. This suggestion awaits experimental verification. We conjecture that overtone-induced decarboxylation of tropospheric diacids and the abstraction of hydrogen in overtone-excited molecules by O_2 will probably be shown to be important in some instances.

The common thread in the overtone-induced chemical reactions considered to date is that they gain importance when other more probable types of chemistry are somehow prevented. The absorption intensities to OH local mode overtones are sufficiently weak that chemistry initiated by electronic absorptions will always play a dominant role, when it can occur. In molecules without accessible electronic states (i.e., H_2SO_4) or in situations where the UV radiation is sufficiently attenuated (i.e., HO_2NO_2), the small J values associated with overtone-induced chemistry become important. As our understanding of atmospheric chemistry and physics becomes increasingly more sophisticated, other such low-probability processes will undoubtedly be uncovered.

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VII. References

(1) Murphy, D. M.; Gary, B. L. *J. Atmos. Sci.* **1995**, *52*, 1753
(2) Murphy, D. M.; Ravishankara, A. R. *Geophys. Res. Lett.* **1994**, *21*, 2471.
(3) Wennberg, P. O.; Cohen, R. C.; Stimpfle, R. M.; Koplow, J. P.; Anderson, J. G.; Salawitch, J. R.; Fahey, D. W.; Woodbridge, E. L.; Keim, E. R.; Gao, R. S.; Webster, C. R.; May, R. D.; Toohey, D. W.; Avallone, L. M.; Proffitt, M. H.; Loewenstein, M.; Podolske, J. R.; Chan, K. R.; Wofsy, S. C. *Science* **1994**, *266*, 398.
(4) Wennberg, P. O.; Salawitch, R. J.; Donaldson, D. J.; Hanisco, T. F.; Lanzendorf, E. J.; Perkins, K. K.; Lloyd, S. A.; Vaida, V.; Gao, R. S.; Hintsa, E. J.; Cohen, R. C.; Swartz, W. H.; Kusterer, T. L.; Anderson, D. E. *Geophys. Res. Lett.*. **1999**, *26*, 1373.
(5) Donaldson, D. J.; Frost, G. J.; Rosenlof, K. H.; Tuck, A. F.; Vaida, V. *Geophys. Res. Lett.* **1997**, *24*, 2651.
(6) Wilson, E. B., Jr.; Decius, J. C.; Cross, P. C. *Molecular Vibrations: The theory of infrared and Raman vibrational spectra*; McGraw-Hill: New York, 1955.
(7) Henry, B. R. *Acc. Chem. Res.* **1977**, *10*, 207.
(8) Child, M. S. *Acc. Chem. Res.* **1985**, *18*, 45
(9) Henry, B. R. *Acc. Chem. Res.* **1987**, *20*, 429.
(10) Henry, B. R.; Kjaergaard, H. G. *Can. J. Chem.* **2002**, *80*, 1635.
(11) Donaldson, D. J.; Orlando, J.; Tyndall, G.; Proos, R. J.; Henry, B. R.; Vaida, V. *J. Phys. Chem. A* **1998**, *102*, 5171.
(12) Reiche, F.; Abel, B.; Beck, R. D.; Rizzo, T. R. *J. Chem. Phys.* **2000**, *112*, 8885.
(13) Holland, S. M.; Strickland, R. J.; Ashfold, M. N. R.; Newnham, D. A.; Mills, I. M. *J. Chem. Soc., Faraday Trans.* **1991**, *87*, 3461.
(14) Brown, S. S.; Wilson, R. W.; Ravishankara, A. R. *J. Phys. Chem. A* **2000**, *104*, 4976.
(15) Zhang, H.; Roehl, C. M.; Sander, S. P.; Wennberg, P. O. *J. Geophys. Res.* **2000**, *105*, 14593.
(16) Roehl, C. M.; Nizkorodov, S. A.; Zhang, H.; Blake, G. A.; Wennberg, P. O. *J. Phys. Chem. A* **2002**, *106*, 3766.
(17) Fono, L.; Donaldson, D. J.; Proos, R. J.; Henry, B. R. *Chem. Phys. Lett.* **1999**, *311*, 131.
(18) Finlayson-Pitts, B. J.; Pitts, J. N., Jr. *Chemistry of the Upper and Lower Atmosphere*; Academic Press: San Diego, CA, 2000.
(19) See, for example: Levine, R. D.; Bernstein, R. B. *Molecular Reaction Dynamics and Chemical Reactivity*; Oxford University Press: Oxford, 1987.
(20) Crim, F. F. *J. Phys. Chem.* **1995**, *100*, 12725.
(21) Crim, F. F. In *Molecular Photodissociation Dynamics*; Ashfold, M. N. R., Baggott, J. E., Eds.; Royal Society of Chemistry: London, 1987.
(22) Crim, F. F. *Annu. Rev. Phys. Chem.* **1984**, *35*, 657.
(23) Callegari, A.; Rizzo, T. R. *Chem. Soc. Rev.* **2001**, *30*, 214.
(24) Sinha, A.; Vander Wal, R. L.; Crim, F. F. *J. Chem. Phys.* **1990**, *92*, 401.
(25) Fleming, P. R.; Li, M.; Rizzo, T. R. *J. Chem. Phys.* **1991**, *94*, 2425.
(26) Kuhn, B.; Rizzo, T. R. *J. Chem. Phys.* **2000**, *112*, 7461.
(27) DeMore, W. B.; Howard, C. J.; Sander, S. P.; Ravishankara, A. R.; Golden, D. M.; Kolb, C. E.; Hampson, R. F.; Molina, M. J.; Kurylo, M. J. *Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling*; JPL Publication, 1997, 97-4.
(28) Sinha, A.; Vander Wal, R. L.; Crim, F. F. *J. Chem. Phys.* **1989**, *91*, 2929.
(29) Barnes, R. J.; Sinha, A. *J. Chem. Phys.* **1997**, *107*, 3730.
(30) Song, K.; Sun, L.; Hase, W. L.; Grebenshchikov, S. Yu.; Schinke, R. *J. Phys. Chem. A* **2002**, *106*, 8339.
(31) Baklanov, A. V.; Aldener, M.; Lindgren, B.; Sassenberg, U. *J. Chem. Phys.* **2000**, *112*, 6649.
(32) Waschewsky, G. C. G.; Horansky, R.; Vaida, V. *J. Phys. Chem.* **1996**, *100*, 11559.
(33) Lange, K. R.; Wells, N. P.; Plegge, K. S.; Phillips, J. A. *J. Phys. Chem. A* **2001**, *105*, *3481*.
(34) Reynard, L. M.; Donaldson, D. J. *J. Phys. Chem. A* **2002**, *106*, 8651.
(35) Phillips, J. A.; Orlando, J. J.; Tyndall, G. S.; Vaida, V. *Chem. Phys. Lett.* **1998**, *296*, 377.
(36) Petryk, M. W. P.; Henry, B. R. *Can. J. Chem.* **2001**, *79*, 279.
(37) Kjaergaard, H. G.; Daub, C. D.; Henry, B. R. *Mol. Phys.* **1997**, *90*, 201.
(38) Kjaergaard, H. G.; Yu, H.; Schattka, B. J.; Henry, B. R.; Tarr, A. W. *J. Chem. Phys.* **1990**, *93*, 6239. Kjaergaard, H. G.; Henry, B. R. *J. Phys. Chem.* **1995**, *99*, 899.
(39) Atkins, P. W. *Molecular Quantum Mechanics*, 2nd ed.; Oxford University Press: Oxford, 1983.

(40) Kauzmann, W. *Quantum Chemistry*; Academic Press: New York, 1957.
(41) Hintze, P. E.; Kjaergaard, H. G.; Vaida, V.; Burkholder, J. B. *J. Phys. Chem. A* **2003**, *107*, 1112.
(42) Staikova, M.; Donaldson, D. J.; Francisco, J. S. *J. Phys. Chem. A* **2002**, *106*, 3023.
(43) Donaldson, D. J.; Tuck, A. F.; Vaida, V. *Phys. Chem. Earth* **2000**, *25C*, 223.
(44) Salawitch, R. J.; Wennberg, P. O.; Toon, G. C.; Sen, B.; Blavier, J. F. *Geophys. Res. Lett.* **2002**, *29* (16), 10.1029/2002GL015006.
(45) Evans, J. T.; Chipperfield, M. P.; Oelhaf, H.; Stowasser, M.; Wetzel, G. *Geophys. Res. Lett.* **2003**, *30* (5), 10.1029/2002GL016470.
(46) Witonsky, S. K.; Canagaratna, M. R.; Coy, S. L.; Steinfeld, J. I.; Field, R. W.; Kachanov, A. A. *J. Chem. Phys.* **2001**, *115*, 3134.
(47) Rosen, J. M.; Hofmann, D. J. *J. Geophys. Res.* **1983**, *88*, 3725.
(48) Hofmann, D. J.; Rosen, J. M. *Geophys. Res. Lett.* **1985**, *12*, 13.
(49) Wilson, J. C.; Loewenstein, M.; Fahey, D. W.; Gary, B.; Smith, S. D.; Kelly, K. K.; Ferry, G. V.; Chan, K. R. *J. Geophys. Res.* **1989**, *94*, 16437.
(50) Rinsland, C. P.; Gunson, M. R.; Ko, M. K. W.; Weisenstein, D. W.; Zander, R.; Abrams, M. C.; Goldman, A.; Sze, N. D.; Yue, G. K. *Geophys. Res. Lett.* **1995**, *22*, 1109.
(51) Mills, M. J.; Toon, O. B.; Solomon, S. *Geophys. Res. Lett.* **1999**, *26*, 1133.
(52) Vaida, V.; Kjaergaard, H. G.; Hintze, P. E.; Donaldson, D. J. *Science* **2003**, *299*, 1566.
(53) Morokuma, K.; Muguruma, C. *J. Am. Chem. Soc.* **1994**, *116*, 10316.
(54) Clark, L. W. In *The chemistry of carboxylic acids and esters*; Patai, S., Ed.; Interscience: New York, 1969.
(55) Longfellow, C. A.; Lee, Y. T. *J. Phys. Chem.* **1995**, *99*, 15532.
(56) Buechele, J. L.; Weitz, E.; Lewis, F. D. *Chem. Phys. Lett.* **1981**, *77*, 280.
(57) Bar, I.; Rosenwaks, S. *Int. Rev. Phys. Chem.* **2001**, *20*, 711.
(58) Goss, L. M.; Vaida, V.; Brault, J. W.; Skodje, R. T. *J. Phys. Chem. A* **2001**, *105*, 70.
(59) Troe, J. *J. Chem. Phys.* **1977**, *66*, 4745.
(60) Polanyi, J. C. *Acc. Chem. Res.* **1972**, *5*, 161.
(61) Smith, I. W. M. In *Bimolecular Collisions*; Ashfold, M. N. R., Baggott, J. E., Eds.; Royal Society of Chemistry: London, 1989.
(62) Crim, F. F. *Acc. Chem. Res.* **1999**, *32*, 877.
(63) Salawitch, R. J.; Wofsy, S. C.; Wennberg, P. O.; Cohen, R. C.; Anderson, J. G.; Fahey, D. W.; Gao, R. S.; Keim, E. R.; Woodbridge, E. L.; Stimpfle, R. M.; Koplow, J. P.; Kohn, D. W.; Webster, C. R.; May, R. D.; Pfister, L.; Gottlieb, E. W.; Michelsen, H. A.; Yue, G. K.; Prather, M. J.; Wilson, J. C.; Brock, C. A.; Jonsson, H. H.; Dye, J. E.; Baumgargner, D.; Proffitt, M. H.; Loewenstein, M.; Podolske, J. R.; Elkins, J. W.; Dutton, G. S.; Hintsa, E. J.; Dessler, A. E.; Weinstock, E. M.; Kelly, K. K.; Boering, K. A.; Daube, B. C.; Chan, K. R.; Bowen, S. W. *Geophys. Res. Lett.* **1994**, *21*, 2551.
(64) Murphy, J. M.; Cohen, R. C. Personal communication, 2002.
(65) Slusher, D. L.; Huey, L. G.; Tanner, D. J.; Chen, G.; Davis, D. D.; Buhr, M.; Nowak, J. B.; Eisle, F. L.; Kosciuch, E.; Mauldin, R. L.; Lefer, B. L.; Shetter, R. E.; Dibb, J. E. *Geophys. Res. Lett.* **2002**, *29* (21), 10.1029/2002GL015703.

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