CENTENNIAL FEATURE ARTICLE

Spectroscopy of Photoreactive Systems: Implications for Atmospheric Chemistry[†]

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This article focuses on the mechanism and molecular dynamics of light-initiated atmospheric reactions. The availability of photons of the correct wavelengths, the response to collisions, and the effect of heterogeneous environments will be considered in this discussion. A new class of light-initiated reactions occurring in the ground electronic state by concerted mechanisms with significant rates are highlighted with examples such as sulfuric acid dehydration and pyruvic acid decarboxylation. The unprecedented mechanism investigated in pyruvic acid initiates reaction by hydrogen atom chattering on very fast time scales. The dynamics suggests significant consequences for this chemistry in photoprocessing acids and alcohols in the atmosphere. An important observation is that water may potentially affect these reactions' energetics, rates, and mechanisms. Examples from our work on light-initiated reactions of atmospheric targets in the gas phase and as affected by water are discussed to point to future areas for physical chemistry research in this field.

Introduction

Unimolecular chemical reactions are initiated by promoting a molecule to chemically relevant energies in electronic and vibrational excited states through absorption of ultraviolet (UV), visible (VIS), or near-infrared (NIR) radiation. The study of light-initiated chemistry relies on the fact that a molecular system is prepared with a relatively narrow distribution of internal energies. This advantage has been recognized and exploited successfully, especially since high-power lasers with high time resolution have become available. Time-resolved measurements of unimolecular reactions are, in principle, able to provide mechanisms and obtain the associated reaction time scale even for extremely complex systems.[1] However, these elegant real-time techniques are limited by the pump and probe wavelength range and the molecular absorption cross sections. Consequently, many interesting and relevant light-initiated reactions in the gas phase as well as in complex environments are not accessible with such direct approaches. Alternatively, as illustrated below with examples from our work on sunlight-driven atmospheric reactions,[2−6] spectroscopic information obtained for reactive systems at chemically relevant energies can provide insight about mechanisms and rates of photochemical reactions. Specifically, we show that absorption spectroscopy can be used to study the early time dynamics of unimolecular reactions. Complementary information can be obtained with time-resolved techniques and by chemical theory to obtain mechanistic and kinetic information for light-initiated chemistry in the ground and in excited electronic states.

The Earth's atmosphere consists of chemically reactive and unreactive molecules sustaining turbulent flow at temperatures in the range of 180 to 320 K and pressures up to 1 atm. The outcome of absorption of solar photons by a molecule can result in emission of radiation, chemical reaction, or evaporation of the molecule from surfaces and aerosols. Much of the absorbed sunlight ends up as translational energy of all air molecules. It is shown below that this process is not as simple as dissipation into a Maxwellian thermal bath. Atmospheric processes are affected by atmospheric conditions, which depend on altitude, latitude, season and time of day, water vapor concentration, and the availability of heterogeneous surfaces and condensed media, usually aqueous aerosols. Consequently, an extensive fundamental database consisting of photochemical mechanisms, energetics, and reaction dynamics is required for predictive models of chemistry and climate which extrapolate to atmospheric circumstances. Atmospheric chemistry is very much influenced by the local environment, the incident solar flux, pressure, temperature, collisional rates, the concentration of trace gases (water, oxidants, etc.), and liquid and solid phases. Winds, clouds, and the general circulation of the atmosphere result in large adiabatic heating and cooling rates; however, below about 100 km, it is assumed that high atmospheric collisional frequencies maintain a Boltzmann distribution of molecular internal states, a Maxwell−Boltzmann distribution of molecular speeds, and, consequently, a well-defined local temperature. The assumption of local thermodynamic equilibrium allows the projection of fundamental molecular parameters obtained in the laboratory to atmospheric processes. These parameters can be used in calculations of reaction kinetics, relaxation rates, phase equilibria, and partitioning of trace gases between gas, liquid, aerosol, and solid phases. The underlying assumptions in this procedure have recently been questioned based on observations of correlation between the molecular-scale production of translationally hot atoms and molecules and the macroscopic fluid mechanics's intermittency of temperature.[7−10] These findings imply departures from the Maxwell−Boltzmann distribution of velocities, with significant consequences for the

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[†] 2008 marked the Centennial of the American Chemical Society's Division of Physical Chemistry. To celebrate and to highlight the field of physical chemistry from both historical and future perspectives, *The J. Phys. Chem.* is publishing a special series of Centennial Feature Articles. These articles are invited contributions from current and former officers and members of the Physical Chemistry Division Executive Committee and from *J. Phys. Chem.* Senior Editors.

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modeling of atmospheric chemistry, especially when one considers the exponential factors involving temperature and energy in equations describing chemical reactions.[11] Departures from local thermodynamic equilibrium require future research with molecular and large-scale methods since they have significant effects on our understanding and the construction of predictive chemical models for the atmosphere. With this caveat, we note that the work presented here addresses fundamental photochemical molecular processes and parameters under atmospherically relevant conditions without solving the problem of extrapolation of these results to planetary scales.

Atmospheric photochemistry is an old discipline primarily concerned with the absorption of solar radiation by an atmospheric chromophore, which consequently acquires sufficient energy to induce transformations of covalent molecular bonds. Atmospheric chemical reactions require sunlight to fuel photochemical transformations either directly or indirectly by photochemical generation of reactive species such as the important oxidizing agents OH, O(^{1}D), O_3, Cl, NO_3, and so forth. These undergo bimolecular reactions with stable organic and inorganic atmospheric constituents. Exponentially decreasing atmospheric pressures with increasing altitude ensure that most molecular components reside mainly at low altitudes and therefore that the stratosphere and the troposphere are the chemically relevant regions. At these lower altitudes, at the characteristic temperatures of 180−320 K, thermal energies fall far below covalent bond dissociation energies; no significant thermochemistry can take place in the atmosphere. From a chemical point of view, the planet's atmosphere is an effective photochemical reactor.

Sunlight fuels all processes at the surface and in the atmosphere of Earth, processes necessary for maintaining life and the habitability of the planet. High-energy and low-entropy incoming beams of solar photons are absorbed by molecular atmospheric components (atmospheric chromophores), promoting deviations from local thermodynamic equilibrium to promote chemical processes not possible at the ambient temperatures characteristic of the middle and lower atmosphere.[12−14] The sun emits radiation which can be approximated by the emission of a blackbody at $T = 5800$ K. The rotation of the planet produces predictable diurnal and seasonal variations in photon flux and wavelengths. Solar radiation of high energy and low entropy, mostly between 300 and 2500 nm, reaches the Earth's atmosphere where it can be absorbed by atmospheric constituents, limiting the wavelength-dependent optical depth. The important absorbers of UV radiation are O_2 and O_3, which filter UV light from the lower atmosphere, providing a UV cutoff at $\lambda > 300$ nm at the surface. The overlap between the decreasing solar flux with decreasing altitude and the decreasing number density of molecular chromophores with increasing altitude gives rise to the formation of stable layers in the atmosphere, notably the stratospheric ozone layer.[12−14] In the IR and near-IR, absorption by water vapor through its rovibronic states with contributions from CO_2, O_3, and other "greenhouse" gases attenuates the high-entropy outgoing terrestrial photon flux, crudely characterizable as emission at a blackbody temperature of 255 K over the whole 4π solid angle. Few significant absorbers exist in the visible, with the notable exception of NO_2, NO_3, forbidden electronic states of O_2, and vibrational overtones of the OH stretching transitions in water.

The variation of photon flux with the altitude and zenith angle are important when considering the role of solar photons in photochemistry. The solar zenith angle, the angle that solar radiation makes to a normal from the surface, affects the illuminated area as well as the wavelength distribution of solar radiation. At large zenith angles characteristic of the sun near the horizon (dusk, dawn, and at the edge of the polar vortex), the intensity of UV radiation at the surface falls with increasing zenith angle much faster than visible radiation; under these circumstances, the UV photons have a long path through the ozone layer and are consequently absorbed at higher altitudes than the longer wavelengths in the red and near-IR. Rayleigh scattering by air molecules is also important in these conditions; the inverse fourth power dependence on wavelength also enhances the importance of solar photons in the red and near-IR. Such variations in the wavelength-dependent photon flux have important chemical consequences. Observations of "anomalous" concentrations of OH at high zenith angles[15] sparked interest in investigations of radical-producing mechanisms which occur with red light. Standard mechanisms model OH radical production by reaction of O(^{1}D) resulting from UV photolysis of ozone with water and methane. The necessary radiation ($310 > \lambda > 260$ nm) was greatly diminished at dusk and dawn under the conditions of the field measurement,[15−18] with the longer wavelengths in this range being relevant in the lower stratosphere. The discrepancy between field measurements and models regarding OH formation led to our studies of vibrational overtone pumping and the proposal that HNO_3, HNO_4, and H_2O_2 can lead to atmospheric radical production.[2,19] This chemistry has recently been investigated with elegant laboratory methods[20−35] leading to important atmospheric consequences.[17,36−38] Inclusions of these ground electronic state photochemical mechanisms along with other visible-light-initiated reactions in model studies were able to explain the observed diurnal profile of OH radicals.[2,17,39] This chemistry also explained the pole to pole distribution of pernitric acid,[40] which without overtone photodissociation included in models had resulted in 50−100% discrepancies between simulations and observations.

Photochemistry in the atmosphere occurs in environments as different as the gas phase, condensed phases, aerosols, clouds, water near its triple point, and at solid and liquid surfaces. Photochemical reactions, especially when proceeding by multiple reaction pathways, are affected by the environment; their mechanisms and yields are phase-dependent. The chemical challenge in photochemistry is to understand the environment-dependent chemistry using complex and atmospherically realistic systems provided by molecular complexes, aerosols, liquids, solids, and at interfaces. Aqueous environments are especially interesting in this regard, and chemistry in the presence of water may have important atmospheric consequences.[41−43]The need for extending laboratory studies to investigate photochemistry in complex, heterogeneous environments has been recognized, given disagreements between model results and atmospheric observations;[44,45] the work described in what follows addresses the role of water and aqueous environments in atmospheric photochemistry.

The fundamental laboratory studies described aim to understand sunlight-driven reactions in the atmosphere to provide mechanisms and processes not currently included in chemical models. Light-initiated unimolecular reactions are considered with reference to the unimolecular rate constant J (s^{-1}),[46,47] where $d[A]/dt = -J_A[A]$, which is defined as

$$J_A\ (s^{-1}) = \int \Phi_A(\lambda) I(\lambda) \sigma_A(\lambda) d\lambda$$

where $I(\lambda)$ is the intensity of solar radiation. $\Phi_A(\lambda)$, the quantum yield (Q.Y.) for photodissociation, and $\sigma_A(\lambda)$, the molecular absorption cross section at wavelength λ, are fundamental molecular properties which are obtained in the laboratory. In this review, excited and ground electronic state light-initiated reactions will be discussed using their J value to illustrate the atmospheric conditions where they occur and the atmospheric problems which implicate them. The effect of available photons of the correct wavelengths, the response to collisions, and the effect of heterogeneous environments will be considered in this discussion. A new class of light-initiated reactions occurring in the ground electronic state by concerted mechanisms with significant rates are highlighted with examples such as sulfuric acid dehydration[6,48] and pyruvic acid decarboxylation.[3] The unprecedented mechanism investigated in pyruvic acid initiates reaction by hydrogen atom chattering on very fast time scales. The dynamics suggest significant consequences for this chemistry in photoprocessing acids and alcohols in the atmosphere. Acids and alcohols are abundant in the oxidizing Earth's atmosphere, and their chemistry is significant in understanding aerosol nucleation and growth.[49] An important observation is that water may potentially affect these reactions' energetics, rates, and mechanisms. Examples from our work[42,50] on light-initiated reactions of atmospheric targets in the gas phase and as affected by water are discussed to point to future areas for physical chemistry research in this field.

The remainder of this review discusses briefly the experimental approach used to obtain information about the early time molecular dynamics using absorption spectroscopy. A description will be given of the characteristics of the sun as a source of actinic radiation in the atmosphere followed by the characteristic environments where atmospheric chemistry takes place. The discussion continues with examples of photochemical reactions from our work, with emphasis on the recent studies of a new class of reactions proceeding very fast with a concerted mechanism in the ground electronic state by vibrational overtone pumping. These reactions are fundamentally new, and their fast rates imply that organic acids and alcohols could be processed photochemically in the atmosphere.

Methodology

Many light-initiated processes are not sufficiently well understood to be included in atmospheric models.[51,52] The reaction mechanisms, reaction dynamics, and the effect of the environment on photochemistry can be investigated in the laboratory and studied by chemical theory. To gain such information about the potential energy surfaces of reactive molecules, it is desirable to use a multitude of approaches. The work illustrated below using atmospheric examples relies on the advantages and limitations of absorption spectroscopy. Our work employed direct absorption, often in parallel with other spectroscopic methods, to obtain the early time dynamics of reactive systems by measurements of frequencies, cross sections, and natural line widths. Such spectroscopic data are analyzed and interpreted by chemical theory. Reactive electronic states in a number of interesting molecules (polyenes,[53,54] NH_3[55−57]), radicals (OClO,[58,59] CN[60]), and molecular complexes (CH_3I,[61−65] acetone,[66] and $(H_2O)_2$[67]) were successfully investigated in our laboratory by combining spectroscopy with cooling of the sample in supersonic jets. In these experiments, one aims to obtain the spectrum for the bright state with features showing lifetime broadening. The homogeneous contribution to the line width, interpreted as the Fourier transform of an autocorrelation function for the decay of the bright state, is compared with the experimental spectrum where jet cooling reduced inhomogeneous effects. Only a useful upper limit for the reaction rate is obtained by this method since, in addition to broadening due to the fast reaction rate, the homogeneous line width is affected by intramolecular vibrational relaxation or IVR.

Electronic states have sufficiently large cross sections to allow for direct absorption studies in supersonic jets.[68−70] Few absorption experiments using jet-cooled samples of reactive molecules have been successful in the IR or near-IR where vibrational cross sections are several orders of magnitude lower.[71−74] The spectroscopy of jet-cooled samples is especially difficult when overtone transitions are targeted due to the decrease by approximately an order of magnitude with each increasing vibrational quantum[75] of the already weak fundamental vibrational transition intensity. Figure 1 shows the vibrational overtone cross sections for several X−H (X = O and C) vibrations to illustrate the decrease in cross section and point to the relative advantage of OH vibrational overtone transitions.[76] The large anharmonicity and significant dipole moment characteristic of the OH stretch contributes to the intensities for OH stretching overtone vibrations.[75] Figure 2 provides a spectroscopic example with the spectrum of vinylacetic acid. Note in this figure that the C═O and C−H stretching vibrations are the most intense features in the fundamental IR region; yet, only the O−H stretching vibrational overtones have sufficiently large cross sections to be observed in the near-IR. More promising than direct absorption for the study of high-energy vibrational overtones in supersonic jets have been laser-based action spectra of jet-cooled samples.[24,28,30,31] Laser-based methods allow kinetic information to be obtained directly and complement the direct absorption studies.[77,78]

An interesting and relevant example with which we illustrate the use of this experimental approach is the photoreactive chlorine dioxide, OClO, radical. The rovibronic structure in the absorption spectrum in the near-UV (260−480 nm) of the optically active $^2A_2$ electronic excited state of jet-cooled OClO could be obtained in our laboratory and interpreted to generate the excited-state reaction mechanism.[4,79] Supersonic jet cooling of the sample eliminated congestion, reduced inhomogeneous contributions to the spectrum, and allowed analysis of the line width to investigate the OClO chemistry. On the basis of the homogeneous widths of vibronic bands on the optically active $^2A_2$ electronic state, it was concluded that the asymmetric stretch

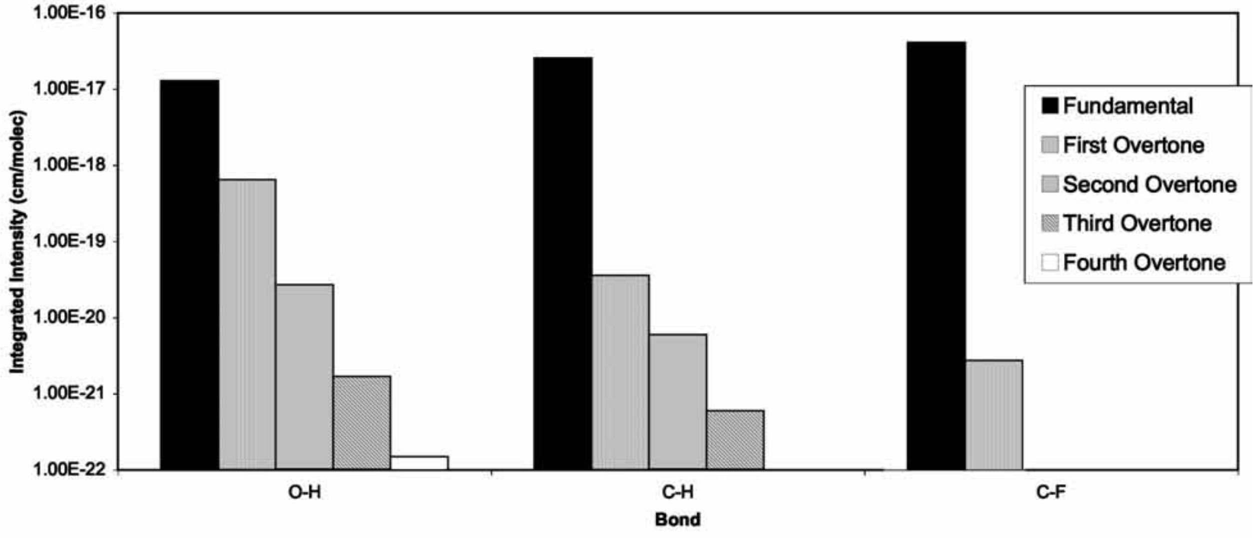

Figure 1. Comparison of the C−H, O−H, and C−F vibrational overtone intensities. Note that the O−H stretching overtone intensities decrease the least with the increasing vibrational quantum number.

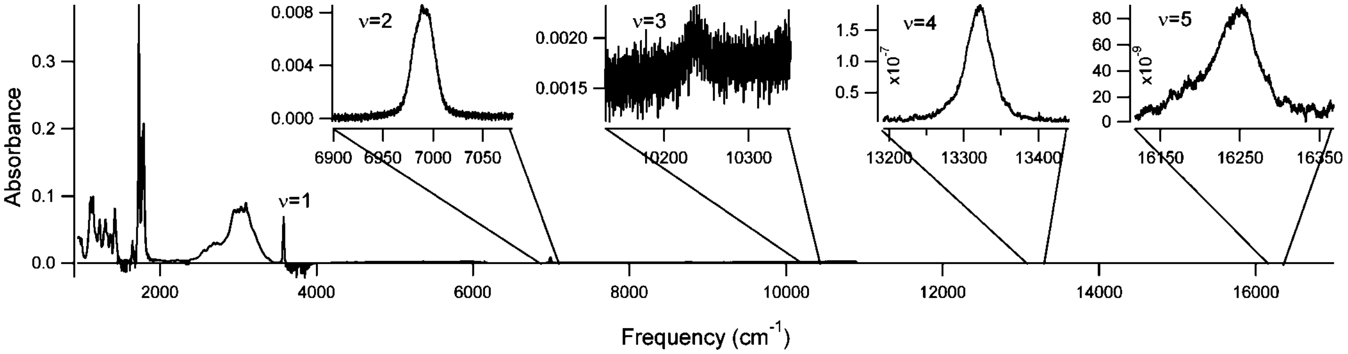

Figure 2. Vibrational spectrum of vinylacetic acid in the 1000−17000 cm^{-1} range at room temperature. The emphasis is on the O−H vibrational transitions $\upsilon = 1-5$. The IR spectra corresponding to $\upsilon_{OH} = 1-3$ were obtained with a Bruker FTIR instrument, while $\upsilon_{OH} = 4$ and 5 were obtained with a CRDS system which allows a much greater effective path length.

and the bending modes are both involved in this reaction. It was found that not only $ClO(^2\Pi) + O(^3P_g)$ but also $Cl(^2P_u) + O_2(^3\Sigma^-{}_g, {}^1\Delta_g)$ could ultimately result from this photochemical reaction.[58,59] Photoreaction occurred on coupled ($^2A_2$ and $^2B_1$) excited electronic potential energy surfaces. To understand the reaction dynamics, it is necessary to eliminate as many of the inhomogeneous factors as possible by cooling to the lowest possible temperatures. However, in atmospheric applications, the relevant temperatures are much higher. In an extension of our work, supersonic jets were used to prepare spectroscopic samples of OClO and of NO_2 at 200 K, conditions appropriate in the lower stratosphere.[80,81] Such spectra give an appropriate database needed to invert atmospheric concentrations from field measurements.

In contrast with fluorescence excitation and multiphoton ionization, direct absorption is a general technique applicable to reactive systems, where the efficient and fast reaction shortens the excited-state lifetime and diminishes the fluorescence and up-pumping needed for ionization when using MPI detection methods. In the case of OClO resonance fluorescence, Raman, multiphoton ionization, and femtosecond spectroscopy provided a complement to direct absorption and guidance for theory in understanding this problem.[82−89] The advantages of using linear broadband sources and Fourier transform spectroscopy have been discussed earlier.[68,70] In our recent work, low molecular vibrational absorption cross sections precluded the use of jet cooling.[90−92] The low vapor pressure and low vibrational overtone absorption cross sections at chemically relevant energies (usually $\upsilon_{OH} = 4$, 5, and 6) necessitated the use of a more sensitive, laser-based cavity ringdown instrument (CRDS).

Atmospheric Photochemical Reactions

The majority of photochemical reactions considered in atmospheric models are reactions on molecular electronic excited states requiring UV and visible light for excitation.[13] UV solar photons have energies equal to most covalent bonds and therefore may cause dissociation. However, UV light is limited in the lower atmosphere because of the wavelength dependence of actinic radiation resulting from absorption by O_2 and O_3 in the overlying upper and middle stratosphere. Atmospheric chemistry is a mature field, yet important light-initiated reactions are unknown or incompletely characterized for inclusion in atmospheric models. Examples of such reactions are those occurring by absorption into weak electronic states; the importance of such reactions has recently been established.[93,94] Weak transitions can contribute to atmospheric photochemistry given the large optical paths involved. Interesting reactions where chemistry involves coupled potential energy surfaces and may proceed by multiple reaction channels giving rise to different products have been investigated.[4,5,79] An example of current interest is the photochemistry of the ClO dimer, which is under study given its importance in polar stratospheric ozone depletion.[95]

Chemical activation through vibrational overtone pumping was explored in search of nonstatistical energy flow.[96−100]

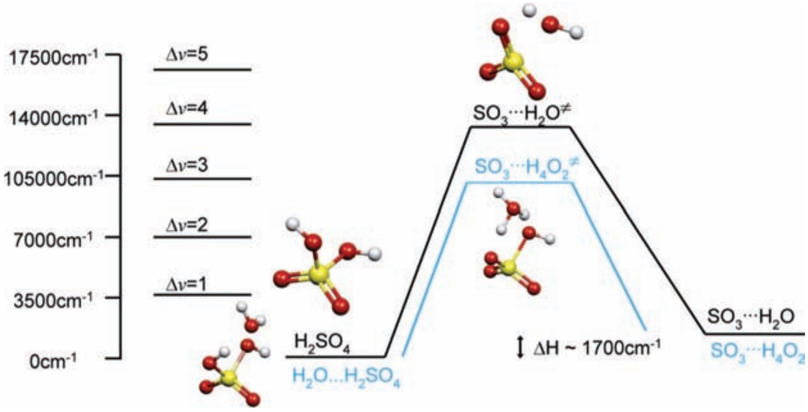

Figure 3. Energy level diagram for the light-initiated dehydration of H_2SO_4 and that of its monohydrate. The excited vibrational levels of the O−H stretch are shown up to the fifth overtone along with the reagent, product, and transition-state energies. Figure courtesy of Dr. Kaito Takahashi.

Renewed interest in such light-initiated processes was motivated by the possibility that photochemical reactions through excited vibrational levels could be important in atmospheric photochemistry.[2] Vibrations of polyatomic molecules are often represented as sets of concerted, collective motions of atoms in the molecule (normal modes).[101] This approach is successful in explaining molecular spectra in the fundamental region but becomes increasingly inconvenient in treating transitions to higher vibrational states,[102−104] especially for X−H (X = C, O, S, N) chromophores. In real anharmonic molecules, an alternative "local mode" approach has been used and applied to explain spectra of X−H (X = O, C, N, S) vibrations.[103−109] Here, local oscillators are considered to be weakly coupled and treated independently. Local-mode pictures have been successful in explaining vibrational spectra to relatively high energies of about 30−60 kcal/mol. Absorption to these vibrational overtone states remains several orders of magnitude less intense than transitions to electronic levels; however, given the large optical paths in the atmosphere, they were recently shown to be effective in driving atmospheric chemical reactions.[2,6,17,19,21,22,25,27,30,40,75,76,93,110−115] Our work has targeted O−H stretching vibrational overtone transitions[2] because they are better suited for spectroscopic investigation given the high frequencies and larger cross sections of O−H stretching vibrations compared with C−H, S−H, and N−H vibrational transitions.[116,117] In the Earth's oxidizing atmosphere, alcohols and acids abound, generated by the oxidation of biogenic and anthropogenic organic and inorganic compounds. The photochemistry of acids and alcohols is not currently included in atmospheric models because their electronic states are too high in energy to be excited by UV solar radiation. Here, we demonstrate the possibility of red-light-initiated chemistry for these compounds. In the atmosphere, the flux of UV photons decreases with decreasing altitude, while the flux of visible photons is approximately constant, with altitude making the photochemistry with visible radiation both possible and likely.

Following the pioneering work of Crim and co-workers on hydrogen peroxide overtone initiated photochemistry,[99,118−123] the overtone-initiated reactions of molecules possessing weak O−OH, N−OH, ONOOH, and Cl−OH bonds have been successfully investigated.[22,26−30,77,113,124−137] In these reactions, absorption by the OH vibrational overtone deposits energy in the OH bond, which subsequently transfers energy to the weak and labile adjacent bond. Overtone-induced reactions of this type have recently received renewed attention due to their success in explaining OH radical formation in the atmosphere at high zenith angles where the UV photon flux is suppressed.[2,17,19,112] Modern techniques applied to systems of interest in the atmosphere led to significant fundamental discoveries. For example, evidence for the nonstatistical behavior in $HOCH_2OOH$ dissociation to OH and $HOCH_2O$ was recently published; the reaction occurs with a slower rate via excitation of the alcohol OH than via excitation of the peroxide OH stretch.[138] Overtone-initiated unimolecular chemistry of this type is similar with electronic state reactions but targets molecules with very weak covalent bonds.

The remainder of this review presents a new class of photochemical reactions with potentially significant atmospheric consequences. Like the overtone reactions discussed above, these unimolecular dissociations occur by OH vibrational overtone excitation near the threshold set by the transition-state energy. Unlike the photochemical processes discussed above, these reactions proceed through a concerted mechanism requiring two bonds to be broken or rearranged in the target molecule. Surprisingly, despite the complex mechanism, these reactions proceed with a very fast rate, as illustrated below with the light-initiated chemistry of sulfuric[48] and pyruvic[3] acids. Alcohols and acids are involved in atmospheric aerosol processing, nucleation, and growth, phenomena of interest because of their effect on climate.[44,45,51,139−141]

The dehydration of sulfuric acid illustrates light-initiated unimolecular reactions occurring by vibrational excitation.[6,48,90,92,142−144] Red light is expected to promote decomposition of H_2SO_4 under atmospheric conditions,[2,6,76,144] as illustrated with the energy level diagram in Figure 3. The electronic states of sulfuric acid are sufficiently high in energy that below 70 km, reaction occurs by OH vibrational overtone excitation,[128] as illustrated in Figure 4 where the electronically excited and vibrational overtone absorption cross sections are overlapped with the wavelength-dependent photon flux at 60 km. Note that no overlap between radiation and the excited electronic state absorption spectrum exists at these and lower altitudes. H_2SO_4 is a very important trace species in the Earth's atmosphere given its role in atmospheric aerosol formation.[142,145−149] Atmospheric aerosols affect the Earth's climate by scattering incoming solar radiation. Sulfate aerosols form at lower altitude and evaporate upon ascent toward the warmer stratopause. Unexplained large concentrations of small cloud condensation nuclei at the top of the aerosol layer in polar spring and in midlatitude air of recent polar origin were observed in field studies.[150,151] Attempts to explain these observations concluded that sunlight-triggered decomposition of H_2SO_4 at high altitude must occur.[143,152,153] UV photolysis was proposed[143,154] but later shown to be ineffective given the very high energy of the H_2SO_4 electronic

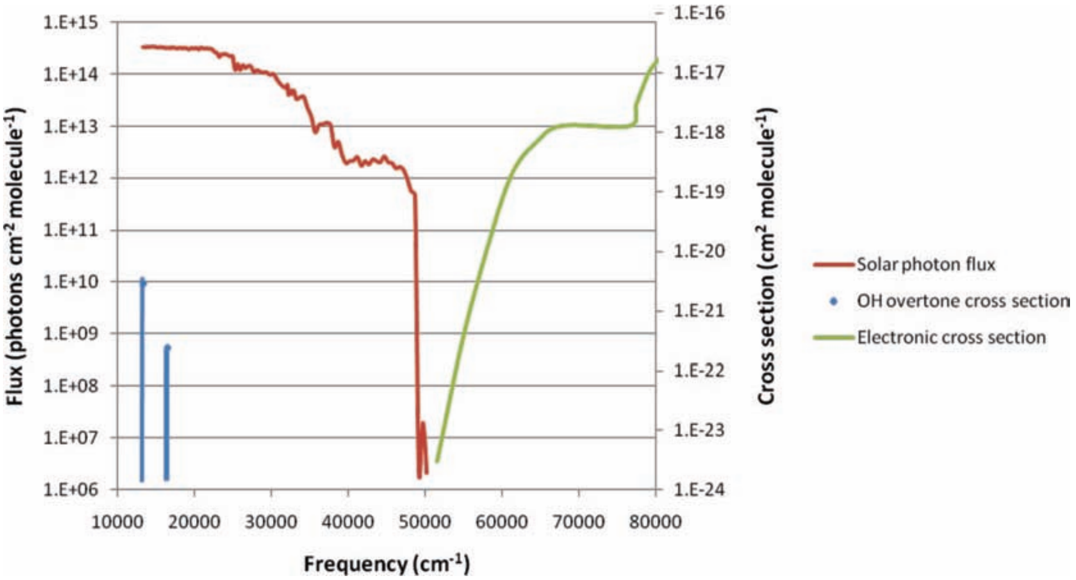

Figure 4. The H_2SO_4 electronic and vibrational absorption cross sections are shown along with the solar photon flux at 60 km.[275] The integrated O−H vibrational cross sections are from Feierabend et al.[90] The calculated electronic cross section is from Lane et al.[128]

states;[92,155,156] the lowest energy singlet transition is calculated to occur at 8.42 eV with an oscillator strength of 0.01.[128]

The mechanism shown to be operative in H_2SO_4 photochemistry in the laboratory and in the atmosphere involves photoreaction by excitation of the OH vibrational overtone transitions in the ground electronic state. This concerted reaction occurs at energies well below the bond dissociation energy of the S−O bond, the weakest in this molecule. Fundamental spectroscopic and theoretical studies aimed at describing the detailed chemical dynamics of H_2SO_4 dehydration were performed, exploring conditions relevant in the atmosphere.[144] The overtone-induced dynamics following excitation of $v_{\mathrm{OH}} = 6$ was described by Miller and Gerber.[48] Photoreaction is initiated by hydrogen atom hopping between equivalent oxygen atoms and occurs on a picosecond time scale. The vibrational overtone cross sections, the reaction mechanism, and the reaction dynamics obtained by experiment and theory were extrapolated to conditions in the upper stratosphere and the mesosphere by considering the competition between the OH vibrational overtone reactions with collisional deactivation by N_2 and O_2. Figure 5 (after Miller et al.[144]) presents the Q.Y. for dehydration of the sulfuric acid $v_{\mathrm{OH}} = 4$, 5, and 6 as a function of altitude to illustrate this point. The result provided a lower limit for the *J* value of H_2SO_4 as a function of altitude; the *J* values obtained were sufficiently large to explain field measurements of SO_2 vertical profiles[157] and the Junge aerosol layer. The light-initiated chemistry of H_2SO_4 has to be taken into account in any geoengineering schemes proposed to alleviate the climate effect of greenhouse gas emissions using sulfate[158] since the same processes that determine the existence and distribution of the natural background Junge sulfate layer will also act on any artificially injected sulfurous layer.

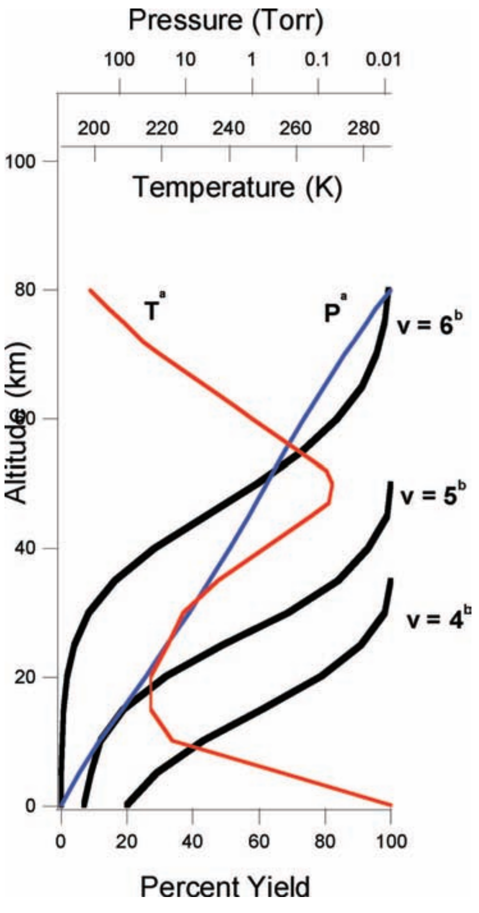

Figure 5. The quantum yield (Q.Y.) for dehydration of H_2SO_4 for $v_{\mathrm{OH}} = 4$, 5, and 6 as a function of altitude.[144] For reference, the atmospheric pressure and temperature is plotted as a function of altitude.

In a recent illustration of light-initiated chemistry, a combination of experiment and theory was used to study the dynamics of OH vibrational overtone excited, ground electronic state chemistry of pyruvic acid.[3] Red-light-initiated decarboxylation was observed in an experiment where the rate of CO_2 production could be monitored spectroscopically. This unimolecular decarboxylation reaction requires transfer of the atom between the oxygen atoms and the C−C bond fission. The energetics and the reaction pathways for pyruvic acid are depicted in Figure 6 (after Takahashi et al.[3]). Two conformers are populated at ambient temperature. The more stable conformer Tc, involves a strong intramolecular hydrogen bond between the hydroxyl hydrogen and the ketonic oxygen atoms, while in the less stable conformer Tt, the hydroxyl hydrogen points away from the ketonic oxygen. Only the stable, hydrogen-bonded conformer is chemically relevant, and its vibrational levels are depicted in

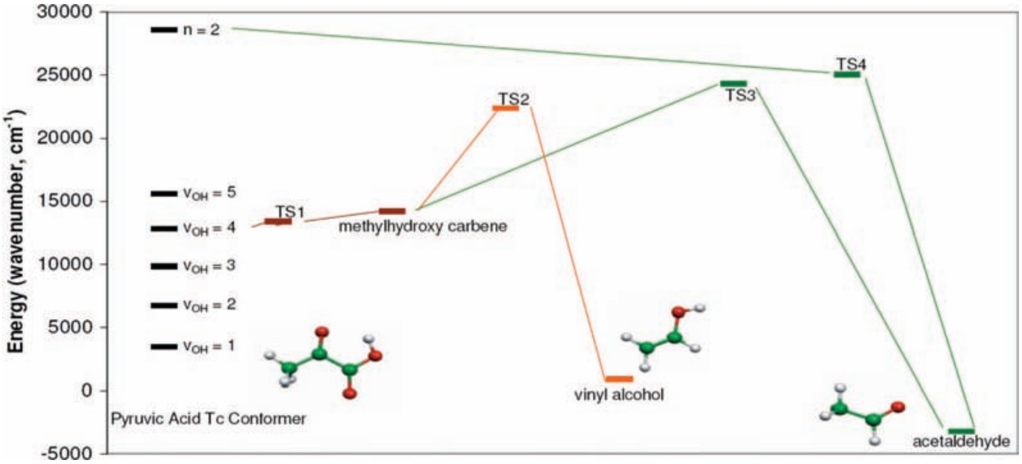

Figure 6. Energy level diagram for the light-initiated decarboxylation of pyruvic acid.[3] The energy of the O−H vibrational overtones $\upsilon_{OH} = 1-5$ of the pyruvic acid stable conformer Tc are shown along with the transition-state energies TS1, TS2, and TS3 and the energies of products methoxylhydroxy carbene, vinyl alcohol, and acetaldehyde.

Figure 6. The computed transition-state energies are given in Figure 6 along with the energies of the final products expected. Of interest in the OH overtone chemistry is the lowest transition state TS1, 13400 cm^{-1} above the pyruvic acid ground state. TS1 is nearly isoenergetic with the methylhydroxy carbene and CO_2 that it generates photochemically. The excited electronic state reaction and the thermochemistry of pyruvic acid, which occurs at 800−1000 K, generate predominantly acetaldehyde with a higher transition state TS2. In contrast with the electronic state reaction, which has access to TS2, decarboxylation by overtone pumping generates at threshold a cold methyhydroxy carbene with insufficient energy to reach either TS2 or TS3. The methylhydroxy carbene generated by vibrational overtone pumping of pyruvic acid has the energy to participate in subsequent chemistry currently under investigation. This subsequent chemistry would not of course be available to thermally excited reactants.

Spectra of the OH vibrational overtone transitions in this molecule were obtained for $\upsilon_{OH} = 1-5$ of the two conformers of pyruvic acid to obtain dynamical information.[3] These conformers are separated by 2 kcal/mol, corresponding to different orientations of the OH group; the stable conformer Tc has a strong intramolecular hydrogen bond which turns out to be very important in the reaction dynamics. The low vapor pressure of pyruvic acid and the low overtone cross sections did not allow the sample to be cooled in supersonic jets; these laboratory experiments were performed at room temperature. Nevertheless, interesting dynamical information could be extracted from the spectra. The time scale for reaction of the hydrogen-bonded conformer proved to not be too slow to be masked by inhomogeneous contributions to the line widths and not too fast to preclude detection. The "just right" early time dynamics resulted in broadening of the $\upsilon_{OH} = 4$ and 5 transitions of the stable, hydrogen-bonded conformer. No comparable chemistry was observed for the unstable Tt conformer, as illustrated with the line width comparison of the O−H vibrational overtones of the Tc and Tt conformers in Figure 7; the bandwidths remain well defined in Tt but broaden significantly in $\upsilon_{OH} = 4$ and 5 of Tc. The line positions and intensities of pyruvic acid were obtained using a three-mode quantum mechanical model for the vibrational states. The line widths were calculated by a direct dynamical calculation where the potential was computed "on-the-fly" and all degrees of freedom were included. Theory finds that the experimental line widths observed for the internally hydrogen-bonded conformer are due to the onset of hydrogen atom "chattering" between the two oxygen atoms.[3] Thus, after overtone excitation, the hydrogen atom rapidly exchanges back and forth between donor and acceptor oxygen atoms. In contrast with quantum mechanical hydrogen atom "tunneling", chattering is a classically allowed process that occurs only above any exchange barrier. As a consequence, the chattering motion proceeds on a time scale set by the vibrational frequency. The tunneling time, on the other hand, may be orders of magnitude slower since the penetration

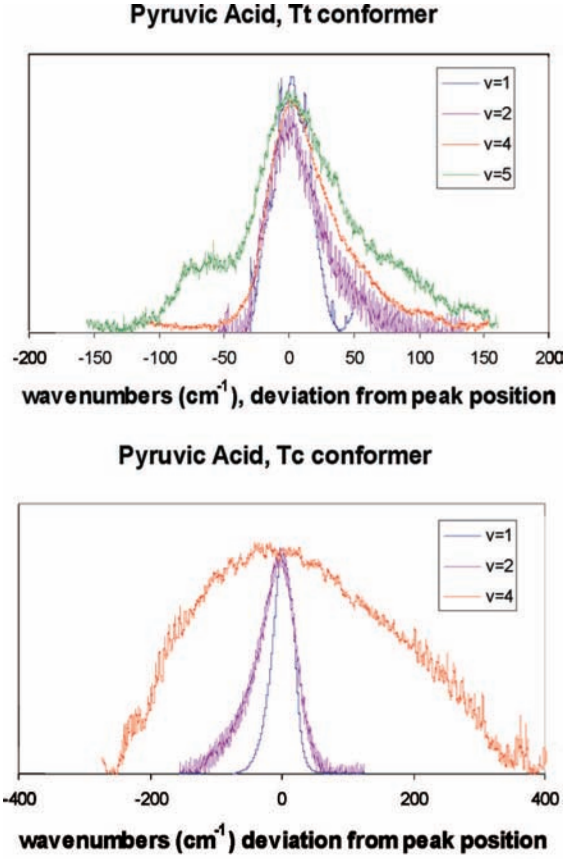

Figure 7. Line width comparison for the pyruvic acid stable Tc and unstable Tt conformers. Each vibrational transition was adjusted to a peak intensity of 1 and a peak frequency of 0. Data from Takahashi et al.[3]

integral through the barrier can be quite small.[159] This is the first step in decarboxylation of pyruvic acid, which subsequently involved breaking of the C−C bond. This vibrationally induced reaction is initiated by excitation of the $v_{OH} = 4$ and 5 of the hydrogen-bonded conformer. The chromophore is strongly coupled to the reaction coordinate, inducing chemistry "directly" at a rate far greater than that predicted by statistical theory. At the energy of these high overtones, the rate of energy flow out of the OH stretch is high, estimated to be approximately 10^{11} sec^{-1}, far greater than that predicted by RRKM theory. The dynamics of this reaction are greatly influenced by hydrogen bonding, which enables hydrogen atom chattering between oxygen atoms.[3] Light atom chattering was theoretically predicted in other light−atom exchange reactions[160−167] but had not been observed experimentally until our work.[3] Theoretical simulations of the intramolecular dynamics of vibrational overtone excited reactions have been performed in a number of cases[120,168−173] in an attempt to use theory and experiment to understand the competition of IVR with reaction.[168,174−176] In the overtone-induced reaction of HOOH, excitation results in energy flow to the weak O−O bond. In HOOH, the experimental line widths were dominated by inhomogeneous effects, which precluded obtaining dynamical information from the spectra. The homogeneous line widths in this case were dominated by the stretch−bend IVR. In pyruvic acid, the homogeneous line widths obtained spectroscopically reflect the reaction initiated by hydrogen atom chattering between the two oxygen atoms in the molecule.[3]

Significant consequences of this reaction mechanism and its associated dynamics result for pyruvic acid in the atmosphere. Thermochemistry requires 800−1000 K and is of no importance in the atmosphere. Vibrational overtone pumping produces high-energy methylhydroxy carbene at ambient temperatures, a reactive species available for subsequent chemistry with other radicals, hydrocarbons, and water. Pyruvic acid is an abundant atmospheric acid generated by the oxidation of biogenically produced organic compounds. Like many organic acids in the atmosphere, pyruvic acid plays an important role in secondary organic aerosol formation.[52] This chemistry is of importance given the potential effect of atmospheric aerosols on the Earth's climate.[177]

Photochemistry in Aqueous Environments

At the temperatures and pressures characteristic of the Earth's atmosphere, water in all of its phases plays an important role in climate and in chemistry. Water is the main absorber of solar radiation in the IR and near-IR and contributes to absorption in the visible. A characteristic of water is its ability to form hydrogen-bonded complexes with other water molecules $(H_2O)_n$, as well as to form weakly bonded complexes with different atmospheric constituents. The bond strengths in such hydrates[178−181] can vary from less than 1 kcal/mol for $O_2 \cdot H_2O$ and $N_2 \cdot H_2O$ to approximately 5 kcal/mol for $(H_2O)_2$ and more than 10 kcal/mol for $HNO_3 \cdot H_2O$ and $H_2SO_4 \cdot H_2O$. Intermolecular interactions responsible for complex formation induce spectral shifts which may enhance or diminish absorption of solar radiation. The mid-IR features corresponding to intramolecular vibrations in $(H_2O)_2$ may be of importance in the atmosphere since they absorb in the "water window" region at frequencies where there are no vibrational transitions in monomeric water. The effect on climate of the O−H vibrational overtone transitions in water clusters has been proposed and investigated, yet the fundamental database needed to model the consequences of absorption by water clusters is insufficient, especially at ambient temperatures.[182−191] Much of the spectroscopic information and many of the theoretical calculations performed to model these spectra are obtained at low temperature and are inadequate in treating the anharmonic part of the shallow $(H_2O)_n$ potential. Recently, laboratory experiments have been successful in identifying water cluster overtone features in the near-IR at ambient temperatures,[192,193] yet observation by field measurements remains elusive.[194,195] It has been suggested that water clusters contribute to the "water vapor continuum".[192,196,197] The water cluster overtone spectra are expected to be diffuse, a characteristic which enhances their effect in radiative transfer but also complicates detection in the atmosphere.[198] In a global warming scenario, absorption due to water complexes becomes more important since their abundance increases nonlinearly with the vapor pressure of H_2O.[198]

Hydrates readily form in the Earth's atmosphere.[189,196,198−203] While observational evidence is scarce, there is a growing consensus that such complexes form and are important.[204] Using fundamental parameters such as structures and the spectra of water complexes, their atmospheric abundance and importance can be evaluated.[186,189,193,195,196,203,205−212] Intermolecular interactions such as those responsible for generation of molecular complexes alter the properties of constituent monomers by shifting and broadening their spectra and modifying their reactivity.[213,214] Atmospheric molecules are found at the water−air interface and in the condensed phase in a variety of terrestrial and atmospheric environments,[43] notably in atmospheric aerosols. The atmospheric chemistry of hydrated complexes in and on aerosols is especially important. Aerosols are ubiquitous in the atmosphere, where they influence climate by scattering and absorbing solar and thermal radiation.[13,215] Spectral shifts due to intermolecular interactions are important in photochemistry since they modify the wavelength dependence of the chromophore's absorption cross section. For example, a red shift is expected in the Hartley band of ozone upon hydration, leading to the suggestion, not yet tested observationally, that photolysis of $O_3 \cdot H_2O$ may lead to O−H formation at lower frequencies than those absorbed by O_3 in the gas phase.[50] The sharp UV cut off in the wavelengths of solar radiation at altitudes below the ozone layer enhances the spectroscopic effect of intermolecular interactions.

Additionally, intermolecular interactions responsible for complexation and condensation can affect the mechanism of a chemical reaction. Light-initiated unimolecular reactions proceeding through multiple reaction channels are particularly susceptible to the molecule's environment. The environment-dependent photochemistry of OClO has become a classic case study of solvent effects on chemical reactions.[5,89,216−219] The OClO photochemistry varies significantly with the environment; in the gas phase, a small wavelength-dependent quantum yield of <0.004 is observed, while in the condensed phase, Cl and O_2 are the dominant products. The relevance of the OClO photochemistry on ice to ozone depletion was investigated[220] given that the ozone depleting channel leading to $Cl(^2P_u) + O_2(^3\Sigma^-{}_g, {}^1\Delta_g)$ is the dominant process on ice.[221,222] However, at stratospheric temperatures and pressures, the equilibrium concentration of OClO on ice is insufficient for this chemistry to be a significant ozone sink.[5,223]

The suggestion that water modifies the rates of bimolecular and of unimolecular light-initiated reactions led to investigation of their energetics and mechanisms. The possibility of water acting as a catalyst in both unimolecular and bimolecular reactions has been proposed.[43,196,224−226] In the example of sulfuric acid, hydration reduces the barrier to reaction by more than 25 kcal/mol,[227,228] as illustrated in Figure 3. From an energetic point of view, a reaction

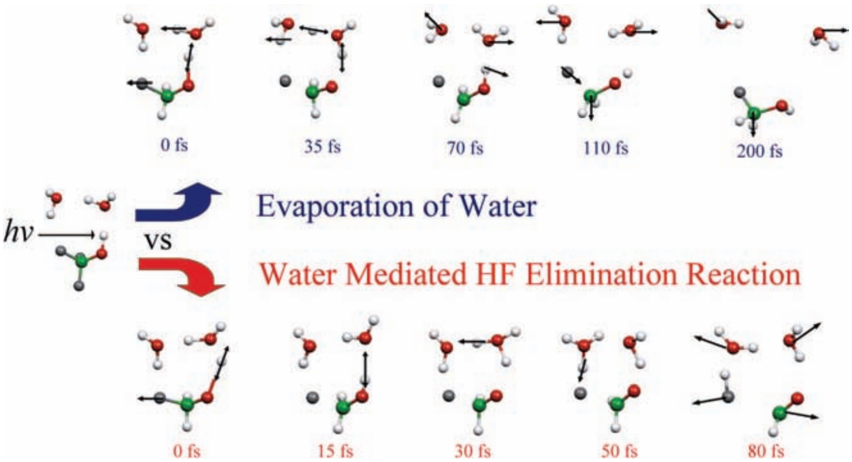

Figure 8. Competition of the O−H overtone-induced reaction and evaporation in the $H_2CF(OH)$ dehydrate.[42]

is now possible by excitation of a lower overtone with the advantage of a larger cross section for absorption. The formation of a doubly hydrogen bonded six-member ring was the proposed cause for the stabilization of the transition state through energy delocalization.[228] On the basis of density functional theory (DFT) calculations, a similar mechanism was proposed by Staikova et al. for the water-catalyzed decarboxylation in malonic acid.[111,224] The stabilization of the transition state upon hydration has been established in a number of reactive systems, but much less information is available about the effect of hydration on the reaction dynamics. It has only been appreciated recently that water may greatly affect the reaction dynamics and that the dynamical effect cannot be deduced from structural and energetic arguments.[42] The feasibility of light-initiated reactions depends critically on the time scale for the reaction; in solution, at an interface, or in a high relative humidity environment, the Q.Y. of the reaction will be insignificant unless the reaction proceeds fast, via a direct mechanism. In the atmosphere, only at very high altitudes where pressures are low and collisional frequencies are low, as was the case in the example of H_2SO_4 (see Figure 5), photodissociation can compete with vibrational deactivation.[144] However, most of the chemistry in the atmosphere occurs at lower altitudes, in gas and condensed phases. Any simple analysis of reaction dynamics based on transition-state or RRKM theory[229] is inappropriate under circumstances when direct and fast dynamics are possible.

Hydrates provide an interesting system for the study of unimolecular reactions. Upon hydration, a competition between reaction and dissipation is set up. This competition is illustrated in Figure 8 (after Takahashi et al.[42]) for hydrates of $H_2CF(OH)$. Here, as in all other systems of this type, the reaction has a barrier of ∼20−30 kcal/mol, while dissipation in the form of evaporation of water has a lower barrier of about 5 kcal/mol. In such situations, use of statistical theories such as RRKM predict that dissipation, the lower energy process, rather than reaction will occur. The need to understand the dynamics in these reactions is obvious, and we give some recent results below. Hydrated complexes of $SO_3 \cdot H_2O$[227,228] and $H_2SO_4 \cdot H_2O$[48,230] have been investigated. Kinetic evidence finds that hydration promotes formation of H_2SO_4 from SO_3 and H_2O.[231,232] For the reverse process, the overtone-induced dehydration of $H_2SO_4 \cdot H_2O$, the dynamics were investigated theoretically.[48] In the hydrate, photon absorption resulted only in evaporation of the cluster, and reaction was suppressed. However, in the simple prototype system of HF elimination from $H_2CF(OH)$, the reaction was water catalyzed.[42] The full dimensional light-initiated unimolecular reaction dynamics of hydrated complexes of this molecule were investigated[42] to find that hydrogen bonding leads to the formation of rings which effectively catalyze the hydrogen atom transfer reaction. The reaction occurs on a very short time scale, about 60 fs. On this time scale, the rapid dynamics precludes energy randomization in the cluster. In this vibrational overtone-induced reaction, competition with IVR favors reaction. The reaction mechanism and fast reaction rate suggest that the dynamics of reactions in clusters such as this example can provide insight into reactions at interfaces or in the condensed phase.

Discussion

Illumination of the planet by solar photons of sufficient energy to drive chemical reactions leads to absorption of these photons by atmospheric chromophores, which are consequently energized above the local temperature. If excitation energies are sufficient to overcome reaction barriers, bond cleavage or rearrangement may occur. The examples considered here include sunlight-initiated excited and ground electronic state reactions in atmospherically relevant circumstances.

Radical generation by dissociation of excited electronic states is limited at low altitude to wavelengths greater than 290−300 nm since solar radiation of shorter wavelengths is absorbed by stratospheric oxygen and ozone. Atmospheric measurements of radical species (e.g., OH, HO_2, RO_2, NO_3, etc.) are extremely difficult because of the low atmospheric concentration of these reactive species. Recent advances in measurement techniques and the simultaneous use of complementary methods in field studies yielded concentration and diurnal profiles for such reactive species both in the stratosphere[15] and the troposphere.[233,234] Comparison of the observed concentrations of atmospheric trace gases with model results pointed to interesting effects such as dusk and dawn measurements of high hydrocarbon and sulfur compound concentrations.[235−244] These observations are consistent with the strong attenuation of short-wavelength radiation, which occurs at dusk and dawn due to scattering and absorption of UV radiation by ozone over the longer path lengths for radiation with the sun near horizon. Consequently, UV-photon-initiated electronic state reaction yields are diminished for some important atmospheric photochemical reactions. For example, UV photolysis of ozone generates $O(^1D)$, which efficiently reacts with H_2O and CH_4 to give OH. At high zenith angle, the OH radical concentrations are expected to be small. Under the same high zenith angle conditions, in the troposphere, other oxidants such as NO_3 are photolyzed with visible radiation (420−630nm), and NO_2 photoreacts at 300−400nm to give NO, resulting in an "oxidant deficit" at dusk and dawn. Sunlight-initiated reactions, which occur by excitation of vibrational levels of the ground electronic state, provide alternatives to excited electronic state chemistry. In the atmosphere, such possibilities were suggested by the discrepancy in the wavelength dependence of radical concentrations between measurements and model results.[15,17,23−28,36−38,132,138,234,245,246] Vibrational overtone-initiated reactions require red solar photons and gain importance when UV-initiated processes are inefficient.[2] Discrepancies of modeled and measured OH and HO_2 concentrations at dusk and dawn in the lower stratosphere led to our investigation of a photochemical mechanism promoted by visible-light excitation of vibrational overtone transitions in the ground electronic state of HNO_3, HNO_4, and H_2O_2. This work[2,19,126,247] was recently expanded with insightful experimental and theoretical studies addressing the reaction mechanisms and J values of HONO, $HONO_2$, HOONO, $HOONO_3$, and so forth.[30−35]

The feasibility of atmospheric chemical reactions depends on the reaction time scale. In a dense gas or in a condensed-phase environment, the Q.Y. for reaction will be diminished unless the reaction proceeds promptly. For a slow, 10^{-9} s (1 ns), time scale process, the photon energy is dissipated by molecular collisions, primarily with N_2 and O_2. Dissipation preempts reaction in a slow process. The altitude dependence of the atmospheric pressure, and therefore that of collisional frequencies, causes an attenuated quantum yield at lower altitude where the pressure and resulting collision frequencies are higher. Atmospheric chemical reactions occur on the time scale controlled by a "clock" provided by collisions through the competition of photochemical reaction rates with rates of the collisional deactivation of energized species. This competition leads to the altitude dependence for atmospheric photochemistry, with a much higher probability for reaction in the stratosphere and mesosphere than at lower altitudes in the troposphere.

The light-initiated dehydration of sulfuric acid illustrates the effect of collisional deactivation on the excited vibrational levels. In a recent theoretical study, the Q.Y. for reaction,[144] which is explicitly in the expression for the atmospheric unimolecular rate constant J, was investigated and corrected from the previous assumption of Q.Y. = 1. This work led to corrected J values to be used in atmospheric modeling. Only a few instances exist[144] where the correct Q.Y. for reaction is known, and in evaluating the potential importance of a photochemical reaction, Q.Y. = 1 is often assumed for a maximum rate constant to be obtained. The study of H_2SO_4 yielded reaction dynamics and rates following OH vibrational overtone excitation of H_2SO_4 which were compared at relevant altitudes with the time scales for both collisional deactivation and vibrational fluorescence. The latter is a very long-lived process of little significance under most atmospheric circumstances. Collisional deactivation was treated under the strong collision limit and compared with reaction rates. Figure 5 presents the Q.Y. for H_2SO_4 dehydration following excitation of the OH vibrational overtones $v_{OH} = 4$, 5, and 6. The dynamics following excitation of $v_{OH} = 6$ was calculated to be very fast, 1.1×10^{-9} s. Accordingly, the effect of collisional deactivation is small even at low altitudes. The dynamics for $v_{OH} = 4$ and 5 were assumed to occur with a much slower RRKM rate because the fast process was found to be inefficient for the lower energy vibrational overtones. Collisional deactivation is much more important for $v_{OH} = 4$ and 5, as illustrated in Figure 5. Vibrational overtone cross sections decrease significantly with increasing energy (see Figure 1); therefore, the J value of H_2SO_4 is dominated by $v_{OH} = 4$ with a few percent contribution from $v = 5$. Taking the corrected Q.Y. into consideration, J values are recalculated and found to be reduced at low altitude over the previous Q.Y. = 1 scenario. Light-initiated sulfuric acid dehydration is important at high altitude in the stratosphere and mesosphere. For this reaction, the corrected J values are sufficiently large to account for the observed SO_2 vertical profiles and the polar stratospheric sulfate aerosol layer at those altitudes.

Energy dissipation by collisions, primarily with N_2 and O_2, is an important factor in atmospheric chemistry. The altitude dependence of reaction is expected and observed for all but the fastest reactions. Reactions initiated by UV excitation of dissociative excited electronic states proceed with a large excess of energy and are therefore less affected by collisional deactivation. Competition between reaction and collisional deactivation is significant for chemistry initiated by vibrational overtone pumping since these reactions proceed with little excess energy over the threshold. The recent discovery of direct and fast dynamics for concerted reactions such a pyruvic acid decarboxylation is significant in this respect.[3] In pyruvic acid, OH vibrational overtone excitation leads to hydrogen atom chattering in approximately 150 fs. In the troposphere, this and related processes (decarboxylation and decarbonylation of organic acids and the dehydration of alcohols) are likely to be competitive with other atmospheric processing mechanisms, primarily excited electronic state photoreaction and oxidation by OH.

It is worth mentioning that collisional deactivation precludes significant vibrationally mediated reactions in the atmosphere, even at high altitude. Vibrational overtone-mediated reaction involves pumping of vibrational overtones followed by subsequent excitation of the vibrationally excited states to a dissociative electronic state where reaction occurs. This mechanism has been used successfully in laboratory studies of excited vibrational levels.[27,31,119,138,174] In the laboratory, laser dissociation of an excited vibrational level was followed by analysis of the OH photoproduct. Such action spectra had the sensitivity to investigate in detail reactive vibrationally excited states. However, solar photon fluxes in the atmosphere are relatively low compared to a laser. The vibrationally mediated dissociation of water was investigated by theory[248] to explore the possibility of this process as a source of OH radicals in the mesosphere where high-energy UV radiation is available. The importance of this process remained uncertain, but the recent measurements of the water vapor vibrational relaxation rates by N_2 and O_2 are too fast to allow excited vibrationally mediated water photochemistry to contribute significantly to mesospheric OH radical generation.[249] The importance of collisional deactivation has been considered in the atmospheric and physical chemistry literature in the analysis of bimolecular reactions of vibrationally excited species.[250−253] Here, we underscore the fact that unimolecular light-initiated chemistry must occur on short time scales to compete successfully with dissipation. Understanding quantitatively the reaction dynamics of atmospheric photochemical reactions is important as are studies of reaction mechanisms, energetics, and absorption cross sections.

Heterogeneous reaction environments are recognized as important in the atmosphere.[254] Especially important are aqueous media (liquid and ice) and water−air interfaces such as occur at the surface of the sea and of atmospheric aerosols.[43] Water−air interfaces offer rich, interesting, and relatively unexplored chemical environments in the contemporary[43,255] and prebiotic[256] Earth. The presence of photoactive compounds at the air−sea interface where surface-active biogenically produced fatty acids, alcohols, amines, and so forth are enriched has been documented,[257,258] yet little is known about light-initiated processes in these environments. Recent studies found evidence for the heterogeneous reactive loss of gas-phase NO_2 and O_3 under illumination at surfaces containing photoactive compounds such as chlorophyll and humic acids.[259−263] Enhanced uptake is correlated with the visible spectrum of the photoactive compound; these light-initiated processes are implicated in the chemistry of the marine boundary layer.

Atmospheric aerosols play an important role in global climate and air quality, yet outstanding fundamental chemical questions preclude their accurate treatment in atmospheric models.[13,177,215,264] It has been recognized that the air−particle interface is crucial in the aerosols' ability to act as cloud condensation nuclei. Recent field measurements found that aerosols have a substantial organic content[45,265−267] and confirm the suggestion that organic species partition to the surface[268−270] where they are continualy oxidized by reaction with OH, O_3, NO_3, and so forth. As a result of atmospheric processing (aging), the photochemical properties of aerosols are modified.[255] Enhancement of the J values is expected under these circumstances since hydrocarbons, acids, and alcohols are oxidized to aldehydes, ketones, and peroxides with larger photoabsorption and photodissociation cross sections. The realization that atmospheric processing of organics in and on aerosols can modify the particles' surface properties has generated interest in the surface photochemistry of organic molecules. Insightful experiments are being performed to investigate the photodissociation of organic films produced by ozonolysis in an attempt to model processes occurring on secondary organic aerosols.[271−273] In the context of this discussion, it should be mentioned that photochemical studies in aqueous environments, with the notable exceptions given above, are unavailable and missing from atmospheric models.[51]

Conclusions

Atmospheric measurement techniques continue to improve, giving new information which underscores the need to consider processes not anticipated to contribute to atmospheric chemistry. In response to the discrepancies between observations and model results, light-initiated reactions have been investigated.[2,17,19] Physical chemistry affects atmospheric science, and conversely, the problems of the atmosphere inevitably point to fundamental processes and mechanisms that are not understood. The relevance of fundamental research on atmospheric problems and, conversely, the effect of atmospheric problems on fundamental research are illustrated in this review, with examples from our recent studies of concerted light-initiated reactions through excitation of OH vibrational overtone transitions of alcohols and acids.[2,3,6] In recent examples from our laboratory and others of ground electronic state reactions energized by vibrational overtone pumping, reaction proceeds with direct dynamics[3] (i.e nonstatistical) and shows evidence of mode-selective behavior.[138] These reactions bring new insight to the study of unimolecular reaction dynamics. As illustrated with the example of pyruvic acid,[3] decarboxylation is initiated by hydrogen atom chattering, which is a very fast process. Photochemical reactions are initiated over a narrow distribution of internal energies and, unlike thermal reactions, do not require collisional activation. In the atmosphere, however, the feasibility of reaction depends critically on the rate of reaction. If the reaction is slow, occurring on nanosecond time scales, the system dissipates the photon energy through collisions with N_2 and O_2. If, however, a reaction occurs by a direct mechanism on femtosecond time scales, as illustrated for pyruvic acid, reaction can be important in a dense gas or even in solution. For such reactions, the traditional analysis based on transition-state theory or RRKM cannot be used; instead, theoretical approaches able to address direct dynamics have to be developed to model fast reactions. A consequence of the reaction dynamics is that the photochemistry in the ground electronic state discussed here opens the possibility, not yet considered in chemical models of the atmosphere, that photochemical processing of acids and alcohols in the atmosphere may occur with red sunlight.

The fundamental database contributed to by laboratory studies and theoretical chemistry can, in principle, be extrapolated to the atmosphere provided that the specific conditions of illumination, pressure, temperature, and the inhomogeneous environment are explicitly considered. The extrapolation from the molecular to the planetary scale relies at present on the assumption that local thermodynamic equilibrium holds. Recent high-quality airborne observations of ozone, temperature, and the spectral actinic photon flux for ozone in the arctic lower stratosphere led to connections between the rate of production of translationally hot atoms and molecules as a result of ozone photolysis and the intermittency of temperature.[7−10,274]These findings imply departures from Maxwell−Boltzmann distributions of molecular velocities, with potentially important consequences for atmospheric chemistry, radiative line shapes, and turbulence in the atmosphere.[11] The implication is that the energy distribution over molecular states in the atmosphere will need to be evaluated properly via nonequilibrium statistical mechanics in order to have a fundamental understanding and formulation of atmospheric temperature. Molecular dynamics simulations may have an important role to play in connecting the scaling behavior at the smallest scales with that at the observable scales. Correct representation of molecular behavior in the atmosphere, which is far from equilibrium, will be particularly important for getting accurately formulated models of climate with predictive power.[11] This state of affairs places a new importance on the kinds of kinetic and nonequilibrium photochemistry described in this paper, particularly for the distribution of energy, originally from the sun, over the whole range of air molecules. There are fundamental problems in both experimental and theoretical chemistry that await attack.

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