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PERSPECTIVE

Red-light initiated atmospheric reactions of vibrationally excited molecules

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We present a brief review of long wavelength, red-light initiated chemistry from excited vibrational levels of the ground electronic state of atmospheric trace species. When sunlight driven electronic state reactions are not effective, photochemical processes occurring by vibrational overtone excitation have been found to be important in reactions of oxidized atmospheric compounds (acids, alcohols and peroxides) prevalent in the Earth's atmosphere. This review focuses on the fundamental energetic, mechanistic and dynamical aspects of unimolecular reactions of vibrationally excited atmospheric species. We will discuss the relevance of these red light initiated reactions to address the discrepancies between atmospheric measurements and results of standard atmospheric models.

I. Introduction

Interest in the reactivity of vibrationally excited molecules led to groundbreaking experimental and theoretical research over 25 years ago when laser based methods allowed the preparation of a molecular system with a relatively narrow distribution of internal energies. The fundamental question motivating this research was the possibility that vibrational overtone excitation might result in mode and bond specific unimolecular reactions (*i.e.* isomerization or dissociation of energized molecules).[1–7] These studies explored the effect of intramolecular processes such as intramolecular energy relaxation (IVR) on the reaction dynamics in the hopes that chemistry could be controlled by excitation of specific molecular vibrations. It was recognized that the mechanism and dynamics of reactions initiated by vibrational overtone pumping could be different from thermal reactions of the same molecule, due to the specific nature of the excitation.[8,9] Thermally-induced reactions are inherently different from photochemical processes and have been treated successfully using statistical theories, which assume free flow of energy amongst the internal degrees of freedom of the energized molecule.[9–11] Elegant time resolved and photofragment experiments combined with dynamical theory attempted to test the limits of statistical theories and their requirement that the exchange of energy among the internal modes be infinitely fast compared to the reaction time.[12–15] These studies led to significant insight into chemical reaction dynamics, but only a

few examples of vibrational-induced mode selective unimolecular or bimolecular chemistry have been identified.[2,16–29]

Vibrational excitation is a promising method to search for non-statistical energy flow since energy can be deposited in a vibration that takes the system along a specified reaction coordinate and can, in principle, break one bond over another in a given molecule.[3–6,14,30–35] For the harmonic oscillator, the transition dipole moment is non-zero when $\Delta v = 1$. Vibrational overtone transitions occur in anharmonic potentials from the vibrational ground state to a higher excited state. For these formally forbidden transitions the cross sections are low and decreasing with vibrational quantum number. At low energies, in the mid-IR where fundamental vibrational transitions are observed spectroscopically, the vibration of polyatomic molecules can be treated successfully as sets of concerted and collective motions, *i.e.* the normal modes of the molecule.[36] The normal mode picture is less successful in treating transitions to vibrational levels at higher, chemically relevant energy, in the anharmonic part of the potential energy surface. Energies of at least 30 to 60 kcal mol^{-1} are needed to induce a unimolecular reaction, even in molecules that possess weak covalent bonds. At such energies, high frequency stretching vibrations can be treated as weakly coupled local oscillators.[37–45] Spectra corresponding to excitation of molecules in the near-IR and visible where vibrational overtone transitions are excited are dominated by X–H stretching overtone transitions where X stands for a heavy atom such as C, O, S or N. The cross section of X–H overtone transitions decrease with increasing vibrational quantum number v. Experimental overtone spectra in such systems, while extremely weak, have been successfully treated theoretically using anharmonic oscillator local mode models.[33,34,37–39,41–54] Advances in theoretical methods in this area continue starting from the use of low level *ab initio* and

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density functional calculations scaled empirically with experiment as a predictor of X–H vibrational stretching transitions.[45] More recently, entirely *ab initio* methods with potential energy and dipole moment calculations have become possible using coupled cluster theory.[45] Comparison of theoretical predictions and spectroscopic measurements of X–H vibrational overtone transitions are especially informative since the sensitivity of vibrational overtone spectra to bond properties allows the investigation of subtle effects in molecular structure and configuration.[43,54–57]

Investigations of the reaction dynamics of vibrationally excited states have accelerated in the last decade,[17,45,58–89] motivated by the possibility that vibrational overtone chemistry initiated by sunlight could help to resolve discrepancies between results of atmospheric measurements and those of atmospheric models. The unimolecular chemistry reviewed here is relevant to excitation by sunlight of vibrational levels in the ground electronic state of atmospheric compounds containing the OH moiety, such as acids, alcohols and peroxides. Such oxidized compounds are prevalent in the Earth's atmosphere and are generated by reactions of stable compounds with reactive species such as OH, HO_2, O_3, NO_3, *etc.* In the past, atmospheric models did not include photochemical reactions of acids and alcohols because the electronic states of these compounds are too high in energy to be accessible by solar UV actinic flux.[90] Inclusion of vibrational overtone chemistry in such models has been significant in the resolution of discrepancies between results of atmospheric measurements and model studies.[77,87,91–94]

II. Atmospheric photochemistry

Solar radiation reaching the uppermost atmosphere can be modeled as the emission of a black body at 5800 K. Molecular oxygen (throughout the atmosphere) and ozone (particularly in the mid-stratosphere, from 25–45 km altitude) are the primary absorbers of the UV component of this radiation, severely diminishing the amount of sunlight with wavelengths below about 290 nm which penetrate to low altitudes. At high solar zenith angles, occurring at dusk and dawn or at the edge of the polar vortex, atmospheric illumination is shifted to long wavelengths compared to that from an overhead sun because of the greatly increased path-length through the atmosphere. The maximum fluxes of solar radiation reaching the troposphere (*i.e.*, below about 15 km altitude) range across the visible spectrum. Thus processes initiated by solar radiation will depend on altitude, latitude, time of day and season. In addition to absorption by molecular species (such as oxygen and ozone), scattering by atmospheric particles further governs the illumination present at any time or place in the atmosphere.

Photochemical reactions are most effectively initiated by radiation in the UV spectral region since absorption at these wavelengths accesses molecular electronic states with sufficient energy for ionization and dissociation to occur. With very few exceptions, notably O_3 and NO_3, atmospheric photochemical reactions initiated *via* electronic excitation require UV light. For example, molecular oxygen, present at $\sim$20 mol% in the atmosphere, has a bond dissociation energy of $\sim$495 kJ mol^{-1},

consequently photons of $\lambda < \sim$242 nm are required for its dissociation. Such radiation is only present in the upper regions of the atmosphere, for the reasons described above.

Light-initiated reactions are treated in models as unimolecular first order kinetic processes with a rate constant J (s^{-1}) given by the convolution over the relevant wavelength range of the molecule's absorption coefficient $\sigma(\lambda)$, its quantum yield for dissociation $\phi(\lambda)$ and the available solar photon flux $I(\lambda)$. The molecule's absorption coefficient will depend on the nature of the process under consideration. The quantum yield is defined for the specific process of interest, *i.e.* dissociation, or formation of a particular product and has a maximum value of 1 (at the concentrations of interest in the atmosphere). Quantum yields and their wavelength dependence are not always known for atmospheric chromophores.[62]

Reactive radical species in the atmosphere result from UV photolysis of stable molecules. *In situ* measurements of the concentrations of important atmospheric radicals such as OH, HO_2, RO_2, NO_3, *etc.* are extremely challenging because of the short lifetimes and therefore low concentrations of these reactive species. For example, the daytime concentration of hydroxyl radical OH is only 10^6 to 10^7 molecules per cm^3. These highly reactive species are predominantly formed in a photochemical process, either directly (*i.e.* dissociation of HOOH into 2 OH radicals) or *via* formation of a reactive intermediate, such as O* (^{1}D), which results from ozone photolysis and may react with water to produce 2 OH radicals. At high solar zenith angles, the solar UV radiation responsible for such photochemical reactions is diminished with a correspondingly reduced photochemical rate constant. Under these circumstances, atmospheric models which include only UV-initiated photochemistry predict lower OH radical concentrations than measurements suggest, requiring alternative chemistry initiated by longer wavelengths radiation.[91,92]

In response to this challenge, photochemistry with long wavelength solar photons has been re-assessed and several mechanisms for radical formation processes have been investigated. For example the chemistry of low-lying electronic states[95] has been re-evaluated. Some electronic states with their maximum absorption lying in the near UV extend weak tails into the visible; excitation by long wavelengths radiation can thus lead to radical formation.[71,85,87] It has recently been pointed out that photochemistry with red light can occur in the presence of a photosensitizer such as chlorophyll,[96] mineral dust,[97] or humic acids.[98] We discuss another mechanism here: molecular excitation *via* absorption of long wavelength solar radiation by vibrational overtone transitions.[89]

III. Vibrational overtone initiated atmospheric photochemical reactions: energies, mechanisms and reaction dynamics

The overall atmospheric importance of reactions initiated by vibrational overtone excitation is limited by the low cross

section of vibrational overtone transitions; these formally forbidden transitions have cross sections typically 3 to 6 orders of magnitude lower at chemically relevant energies than electronic transitions at the same total energy. Quantifying their contributions therefore requires accurate measurements of very small absorption cross sections. In addition, at or near energetic barriers for chemical reactions, vibrational overtone transitions with their already inherent low absorption strengths will experience an increase in line width due to lifetime shortening,[77] making their spectroscopic quantitation even more challenging. Thus the unambiguous detection of vibrational overtone transitions at chemically relevant energies remains an intrinsically difficult proposition. New cavity-enhanced techniques have made possible the spectroscopic identification and investigation of such weak vibrational overtone transitions.[55,69–71,81,86,99–104] Most commonly used are cavity ring down methods and photoacoustic spectroscopy as these methods have the sensitivity for the spectroscopic characterization of vibrational overtone transitions.

The intensities of vibrational local mode transitions depend upon both the anharmonicity in the local mode oscillator and the derivative of the dipole moment function along the local mode coordinate.[44] The dependence of vibrational overtone intensities on the molecular potential and dipole moment as a function of internal coordinates has been investigated theoretically and compared with experimental vibrational overtone spectra.[42,45,49,53,54,105–113]

Significant differences exist in the intensity of the X–H stretching vibrational transitions of different heavy atoms X. Absolute oscillator strengths for C–H and O–H stretching overtone vibrations have been investigated using harmonically (HCAO) and anharmonically (ACAO) coupled anharmonic oscillator local mode models.[15,42,45,46,55,114–117] Fewer studies have been done on N–H and S–H transitions.[46,118–121] In Fig. 1 we present a comparison of vibrational frequencies and intensities for typical O–H, C–H and S–H oscillators. The fundamental oscillator strengths follows in the order S–H (10^{-7}), C–H (10^{-7} to 10^{-6}) < O–H (10^{-6}).[42] Recent work found that the S–H stretching vibration intensity drops by about a factor of 30 while C–H and O–H intensities drop by a factor of about 20 to 10 in

going from $\nu = 1$ to $\nu = 2$.[46,121] It is worth noting that the fundamental vibrational frequency and therefore the overtone vibrational frequencies are in the order S–H < C–H < O–H. This is an important observation from the chemical point of view, because in order to access a given reaction barrier, fewer quanta of the O–H stretch, with frequency about 3600 cm^{-1} and anharmonicity of approximately 85 cm^{-1} are required to reach a given reaction barrier.[48,77,78,112,122–126] It follows that excitation of OH stretching vibrational overtones is uniquely suited to initiate reaction.[77,89,127] Intensities of OH vibrational overtone transitions are affected further by intra and intermolecular hydrogen bonding.[77,112,113,127–131] The examples discussed below involve excitation of the OH stretching overtone vibrations of atmospherically abundant chromophores such as alcohols, acids and peroxides.

(a) Cleavage of weak bonds by vibrational overtone excitation

Reactions initiated by vibrational overtone excitation take place on the ground electronic state surface, following transfer of energy out of the initially excited vibration. As with thermal reactions, one may imagine a "simple" mechanism, in which the excitation energy (or some fraction thereof) migrates to an adjacent weak bond, causing that bond to cleave. For example, in the well-studied case of hydrogen peroxide, H_2O_2,[132–135] an overtone of the OH stretch was excited at energies exceeding the O–O bond dissociation energy. Reaction occurs by energy flow from the initially excited OH stretch local mode to the weak O–O bond to give the OH radical. Dynamical information was obtained from the photofragment spectra, however the experimental line-width of the overtone absorption was dominated by inhomogeneous effects,[133,134] which precluded a direct spectroscopic determination of the dynamics of the excited HOOH prior to dissociation.[132] Theoretical simulations of the dynamics following overtone excitation found that the homogeneous line-widths were dominated by migration of the energy (intramolecular vibrational redistribution, IVR) from the OH stretch to combinations of lower-energy stretching and HOO bending modes.[132,136] Similar reaction mechanisms have been used to explain the dynamics observed following vibrational overtone pumping in peroxides[17,67,81,133,135,137–140] and hydroxyperoxides,[17,68,141,142] with mode selective behavior having been observed in some overtone induced dissociation of hydroperoxides.[16,17]

The dissociation of the N–O bond in HNO_x compounds following OH stretch overtone excitation has yielded interesting and atmospherically relevant results.[12,14,19,58–61,64,66,69,72,76,78,83,86,87,89,93,94,143–149] There are several similar examples of vibrational overtone driven dissociation reactions of significance in the atmosphere. Such red light reaction affects atmospheric ozone formation by releasing the NO_2 sequestered in HNO_x.[93,94,147] The O–N bond in such species ruptures as a result of excitation of the $\Delta\nu = 3–6$ (depending on the molecule) overtone transitions of the O–H stretching vibration. Excitation of the $\nu_{OH} > 5$ of the O–H stretching mode in nitric acid energizes the molecule above the dissociation limit to OH + NO_2. In the isolated molecule at low pressure where collisional deactivation is unfavorable, IVR from the initially excited state will deposit energy along
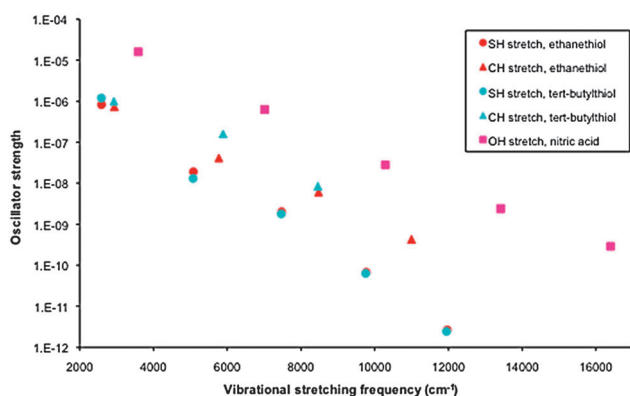

Fig. 1 Comparative frequencies and cross section of vibrational overtone transitions of HX (X = S, C or O) stretching transitions.
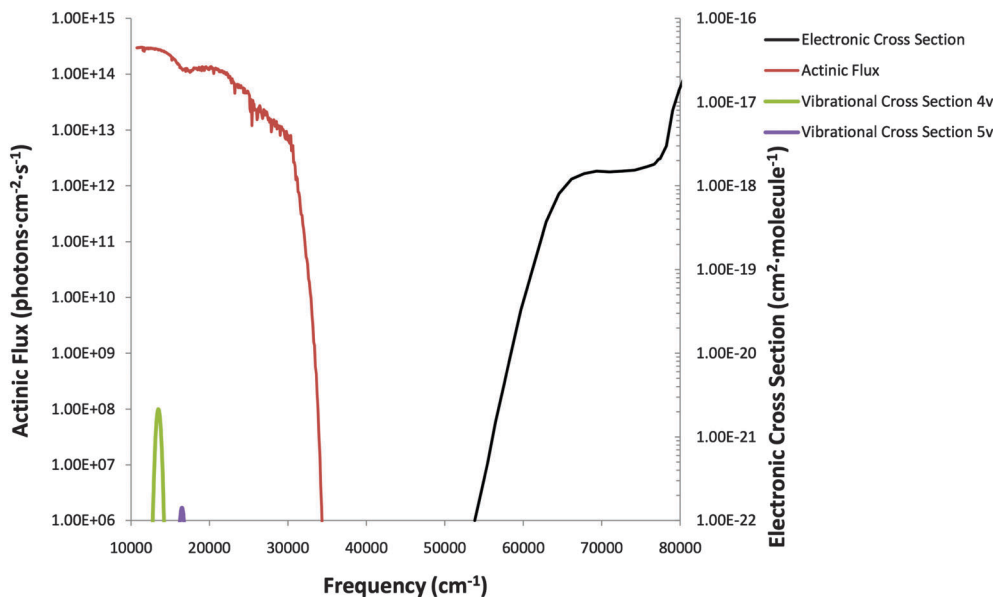
Fig. 2 Actinic flux reaching the Earth's atmosphere (red) superimposed on the electronic and vibrational ($v = 4$ and $v = 5$) absorption spectra in H_2SO_4.

the weak N–O bond, which ruptures as a result of this process.[19,72,74,76,82,84,86,94,150,151] Of greater atmospheric significance is the case of peroxynitric acid (HO_2NO_2, or PNA) where the dissociation limit is achieved at energies a little below that of $\nu_{OH} = 3$ of the O–H stretch[72,74,83,86,147,152] and therefore with a reasonably large absorption cross section. Elegant laboratory experiments have measured wavelength-dependent HO_2 formation from HO_2NO_2, finding a temperature dependent HO_2 forming process following excitation of the $\nu_{OH} = 2$ level and a temperature invariant HO_2 formation following excitation of $\nu_{OH} = 3$, chemistry possible in the atmosphere by absorption of near-IR solar radiation.[91]

The simple mechanism of energy flow from the OH to the weak bond in reacting molecules presented above appears to be somewhat more complicated in HONO and $HONO_2$, where dynamical simulations have been performed.[64,66,80] Gerber *et al.* find that following excitation of the OH vibrational overtone, not only IVR to the N–O bond but an additional fast process takes place by intramolecular hopping of hydrogen atoms.[64] A hydrogen carrying a negative partial charge is found in the transition state for this process in $HONO_2$.

(b) Concerted chemical reactions

Some polyatomic molecules, specifically conformers which contain an intramolecular hydrogen bond, undergo concerted unimolecular reactions with a very different overtone-driven mechanism. Overtone initiated photochemical reactions of a number of organic[73,89,113,130,153] and inorganic[154] acids and alcohols proceed by a concerted mechanism at energies well below the bond dissociation energy of the weakest bond in the molecule. Overtone induced chemistry of sulfuric acid, H_2SO_4,[154,155] and organic acids[73,113,130,156] provide illustrative examples for the vibrational overtone chemistry proceeding by such a concerted mechanism.

Sulfuric acid, formed in the atmosphere *via* oxidation of SO_2, is one of the main constituents of atmospheric aerosols, of interest because of the large and as yet not completely understood effect these aerosols have on the planet's climate.[157] Discrepancies between measured and modeled SO_2 stratospheric concentrations,[158] as well as the observed formation of a springtime aerosol layer in the polar stratosphere[159] motivated modeling studies, which concluded that sun-light initiated chemistry of H_2SO_4 must occur at high altitude.[160–162] However, both laboratory studies and theoretical calculations later established that the low-lying electronic states of this molecule do not contribute significantly to dissociation at any altitude:[154,155,163–165] electronic absorption by H_2SO_4 is very high in energy, well above the atmospheric ozone cutoff. Below 70 km altitude photodissociation of H_2SO_4 is initiated by absorption of red light by OH vibrational overtones, specifically by $\nu_{OH} = 4$ and 5,[77,102,166,167] leading to H_2O and SO_3 products. This reaction is a concerted process occurring with excitation of approximately 45 kcal mol^{-1}, well below the bond dissociation energy of the weakest bond in the molecule, the S–O bond. The overlap of solar radiation in the stratosphere and mesosphere with the UV and overtone spectra of H_2SO_4 is shown in Fig. 2 to illustrate that only overtone excitation is possible for photo-initiation of reaction.

The possibility of vibrational overtone initiated dehydration of sulfuric acid $H_2SO_4 + h\nu \rightarrow SO_3 + H_2O$ in the ground electronic state was investigated using spectroscopic and theoretical methods.[63,65,77,89,145,154,155,168–170] Spectroscopy established that the frequency and intensity of the OH vibrational overtone transitions are at and near the energy limit calculated theoretically for this reaction. Dynamical simulations of the dehydration reaction find two mechanisms to be operative: a fast picoseconds-timescale process initiated by hydrogen atom hopping, and a second mechanism assumed to occur on
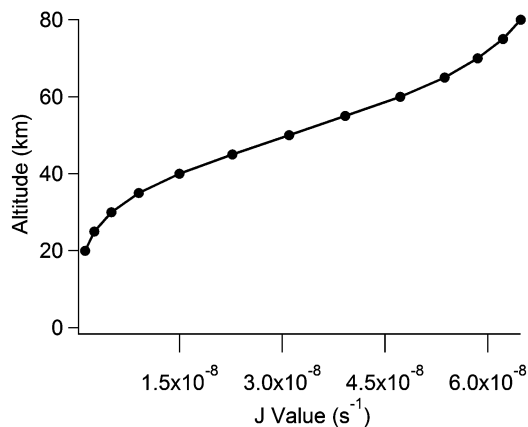
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Fig. 3 Altitude dependent "J" values (s^{-1}) for the red-light initiated dehydration of H_2SO_4. The altitude dependence of the solar photon flux as well as the altitude dependent collisional deactivation rates of reactive OH stretching vibrations of H_2SO_4 are taken into account in calculating these J values.[62]

Fig. 4 Comparison of the fundamental $v_{OH} = 1$ and overtone $v_{OH} = 4$ transitions in the unreactive (no intramolecular hydrogen bond) and reactive (intramolecular hydrogen bond) conformers of pyruvic acid.

slower, statistical time scales.[63] The fast process occurs by intramolecular proton transfer with a characteristic time scale of about 9 ps and was observed in 5% of the trajectories.[63] Based on these mechanisms and rates, the dehydration of sulfuric acid was examined under atmospheric conditions to evaluate the quantum yield and subsequently the J value for dehydration.[62] Fig. 3 presents the J value for the red-light initiated dehydration of H_2SO_4 as a function of attitude. The J value varies with altitude because of the variation in the solar photon flux as well as the collisional quenching of the reactive vibrational levels.[62] For H_2SO_4 the rate for the vibrational overtone induced dehydration reaction was compared with collisional deactivation and vibrational fluorescence rates. In the upper stratosphere and the mesosphere this reaction is effective and its rate is sufficient to explain atmospheric observations of the SO_2 vertical profile and the formation of large concentrations of cloud condensation nuclei at the top of the aerosol layer in polar spring or in midlatitude air of recent polar origin.[171] The dehydration of H_2SO_4 by vibrational overtone excitation, when included in models, explains quantatively the observed SO_2 vertical profiles on Earth[171] and qualitatively the SO_2 inversion in the middle atmosphere of Venus.[172,173]

Similar mechanisms for decarboxylation reactions initiated by OH vibrational overtone excitation have been proposed to occur in organic acids and their reaction mechanisms and rates have recently been investigated by theoretical and spectroscopic methods.[73,113,130] Organic acids, diacids and ketoacids are important in the atmosphere where they are found in significant concentrations in atmospheric aerosols.[174,175]

The early time dynamics of vibrationally excited pyruvic and glyoxylic acids was studied by a combination of "on-the-fly" dynamics simulations and cavity ringdown spectroscopy. The combined studies concluded that decarboxylation should occur on sub picosecond time scales in these ketoacids.[113,130] A strong correlation between structure and reactivity was observed: conformers that posses intramolecular hydrogen bonded structures react on excitation of the third and fourth
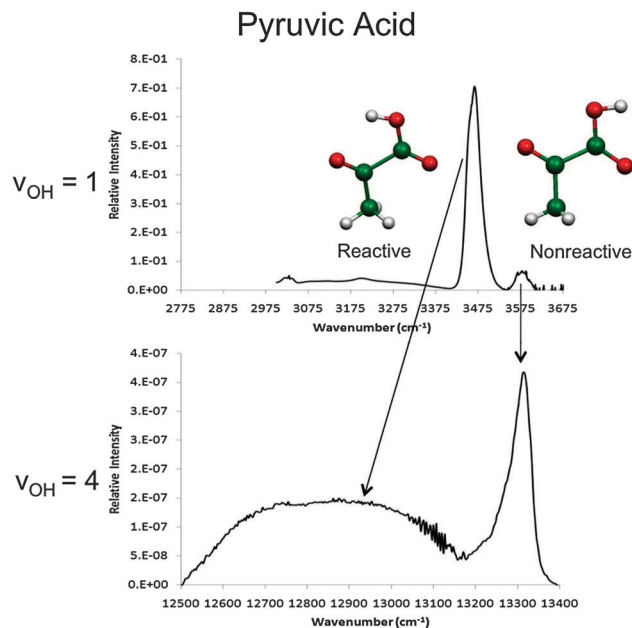
OH overtone while nearly isoenergetic conformers of *trans* geometry do not react by a fast process.[156,176] The reactive and unreactive conformers of pyruvic acid are shown in Fig. 4 along with the vibrational spectrum of the OH stretch of these conformers. In vinylacidic acid with no intramolecular hydrogen bond and in glycolic acid which contains an intramolecular hydrogen bond no significant broadening has been observed implying that fast reaction is not occurring at these energies.[124,125,177] Overtone spectra of both reactive and unreactive conformers of pyruvic and glyoxylic acids have been obtained as illustrated for pyruvic acid $v_{OH} = 4$ in Fig. 4. Although a band is observed for the unreactive conformer, for the reactive conformer, which contains an intramolecular hydrogen bond, no absorption is seen at energies corresponding to the transition state for decarboxylation.[156,176] Trajectory calculations have shown that hydrogen atom chattering gives rise to the broad feature in both glyoxylic and pyruvic acids, illustrated in Fig. 5 with a snapshot of the trajectories following excitation of $v_{OH} = 4$ of pyruvic acid.[113] Intramolecular hydrogen bonding places the hydrogen atom between two "heavy" oxygens, orienting the system for fast decarboxylation.[113,130] Overtone reactions of these organic acids are sufficiently rapid to avoid dissipation by gas phase collisions or even by energy transfer in aerosol phase.

IV. Discussion

Significant differences exist between unimolecular reaction dynamics initiated by near-IR or visible light through vibrational overtone excitation and reactions initiated at high temperatures or by UV radiation for the same molecular species. In comparing the ground and excited electronic state photochemistry of a molecule one must consider the large difference between molecular
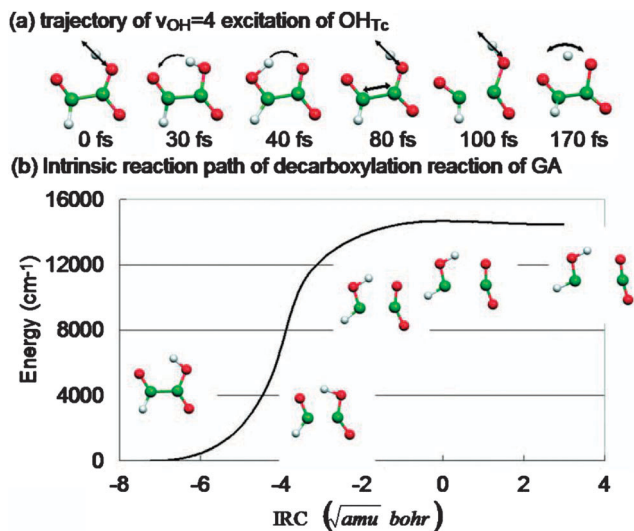
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Fig. 5 (a) Snap shot of the trajectories showing hydrogen atom chattering for the $v_{OH} = 4$ transitions for glyoxylic acid and (b) energy as a function of the intrinsic reaction coordinate (IRC) of the carbene forming reaction of glyoxylic acid. Reprinted with permission from ref. 113. Copyright 2010, AIP Publishing LLC.

absorption cross sections for electronic states compared with that of the much weaker vibrational overtone transitions. However, in the Earth's atmosphere, radiation from the Sun reaching the troposphere is limited to wavelengths greater than 290 nm. Vibrational overtone initiated chemistry is only important when no electronic transitions can be excited by the available sunlight, as is the case for most acids and alcohols, or when the Sun is near the horizon, at dusk, dawn and at the edge of the polar vortex. Chemistry initiated by electronic excitation may occur in an excited state or on the ground electronic state surface, following internal conversion. In these situations, significant energy in excess of the reaction barrier is available and deposited in the primary photoproducts. By contrast, the rapidly decreasing vibrational overtone intensities with increasing excitation energy (see Fig. 1) ensure that vibrational overtone excitation generates the primary radical products at threshold. Both UV excitation and high temperatures needed to drive the thermal reaction produce the radical with excess energy able to react unimolecularly to form stable products.[113,130] Radical species formed by overtone excitation are poised to undergo bimolecular reactions generating more effectively oligomers and hydrates which could contribute to aerosol nucleation and building of the aerosol mass.

Unimolecular reactions have traditionally been treated using statistical approaches such as Rice–Ramsperger–Kassel–Marcus (RRKM) theory,[10] which assumes that even when the initial excitation is non-random, strong intramolecular coupling leads to statistical redistribution of the excitation energy amongst vibrational modes on a time scale faster than unimolecular reaction rates. Excitation of a molecular system by vibrational overtone pumping could deposit energy directly and effectively in the reaction coordinate and result in mode and bond specific reaction. This possibility provided the impetus for the elegant experimental and theoretical studies of more than two decades ago, yet only a few examples of mode specific chemistry have since been documented.[17,20–25]

The chemistry of oxidized atmospheric compounds provide examples of very fast reactions initiated through the excitation of the OH stretch.[77,113,127,129,130] Acids and alcohols are not expected to undergo light initiated reactions in the atmosphere since their electronic states are at very high energies, outside the solar spectrum. In sulfuric, pyruvic and glyoxylic acids reactions occur with a concerted mechanism where two bonds are broken to form the observed products. Concerted reactions have a long history in organic and biological chemistry where they are of interest in predictions of the stereochemistry of reaction products.[178,179] Dynamical approaches have been used to investigate the difference between concerted and non-concerted (stepwise) processes and find the distinction elusive.[180–182] In the examples recently studied of overtone induced dehydration of H_2SO_4[154] and the decarboxylation of pyruvic[130] and glyoxylic acids,[113] the H–O stretch initiated reaction is predicted to happen between 40 and 50 kcal mol^{-1}, less than half the bond energy of the weakest bond in these molecules. A significant "energy of concert" was observed in these examples. In pyruvic, glyoxylic, peroxyformic and peroxyacetic acids reaction is initiated by excitation of the 3rd and 4th OH stretching overtone, initiated by hydrogen atom chattering between the two oxygen atoms to drive the overall formation of a reactive intermediate on sub-picosecond timescales.[88,113,130,183] Fast unimolecular reactions like those described above may lead to high-energy products in the real environment by competing with energy dissipation over other small barriers processes. Understanding the dynamics of the competition between these processes is necessary for predictions of the chemical outcome of light initiated reactions under real environmental conditions.

V. Conclusions

The Earth's atmosphere is an effective photochemical reactor where sunlight drives chemical reactions directly or indirectly by generating reactive radical species, which are further involved in oxidative chemistry. Numerical models of photochemistry include processes initiated by UV excitation of atmospheric chromophores. However, the maximum solar flux reaching the Earth is in the visible red; the availability of UV photons is limited in the stratosphere and even more so, in the troposphere where most reactive species reside. Examples discussed here document the possibility of sun-light initiated reactions through excitation of vibrational levels of the ground electronic state with emphasis on problems where such chemistry explains discrepancies between atmospheric field measurements and results of numerical models. Atmospheric models including red-light vibrational overtone chemistry have been successful in explaining the release of NO_2 from HNO_x.[91,147] The vibrational overtone chemistry of H_2SO_4 quantitatively explained the SO_2 vertical profiles on Earth as well as the observed springtime aerosol layer in the polar stratosphere.[171,184] Vibrational overtone induced reactions are most effective when excitation occurs through the OH stretch which exhibits larger absorption cross-sections and vibrational frequencies than other X–H chromophores. Such processes allow for the possibility of light initiated reactions of alcohols and acids whose electronic states

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are too high in energy to be excited by UV solar photons in the Earth's atmosphere. The variation in the wavelengths distribution of solar photons with altitude and solar zenith angle enhances the importance of red light in promoting reactions at low altitude with the sun near horizon.

The examples discussed above point to interesting fundamental issues related to vibrational overtone initiated chemistry of atmospheric species. These reactions occur near the energetic threshold for reaction because of the significant decrease of overtone intensity with vibrational quantum number. In contrast, reactions of electronically excited states tend to deposit large energy excess into the molecule. As shown with the examples of sulfuric, pyruvic and glyoxylic acids near threshold reactions proceed efficiently by direct dynamics.[113,130] The dynamics of vibrational overtone initiated reactions are crucially important in establishing their atmospheric fate since reaction competes with dissipation in the natural environment. Atmospheric reactions occur in complex environments and in the presence of water, which can form hydrogen-bonded complexes with oxidized species.[127] The role of water in chemistry has been investigated for some vibrational overtone initiated reactions.[16,63,66,73,80,185–195] Theoretical simulations of overtone initiated processes in molecular clusters suggest that water can act as a catalyst, mediate or suppress reaction depending on the competition between reaction and dissipation.[73,77,78,129,196] Light initiated chemistry in gas-phase clusters as well as at surfaces, at water–air interfaces and in/on atmospheric aerosols is an area where further fundamental theoretical and experimental studies, especially with emphasis on the reaction dynamics are needed towards understanding environmental processes.[89,197–200]

Acknowledgements

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