

## Review Article

# Sunlight-Initiated Photochemistry: Excited Vibrational States of Atmospheric Chromophores

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Atmospheric chemical reactions are often initiated by ultraviolet (UV) solar radiation since absorption in that wavelength range coincides to typical chemical bond energies. In this review, we present an alternative process by which chemical reactions occur with the excitation of vibrational levels in the ground electronic state by red solar photons. We focus on the O–H vibrational manifold which can be an atmospheric chromophore for driving vibrationally mediated overtone-induced chemical reactions. Experimental and theoretical O–H intensities of several carboxylic acids, alcohols, and peroxides are presented. The importance of combination bands in spectra at chemically relevant energies is examined in the context of atmospheric photochemistry. Candidate systems for overtone-initiated chemistry are provided, and their lowest energy barrier for reaction and the minimum quanta of O–H stretch required for reaction are calculated. We conclude with a discussion of the major pathways available for overtone-induced reactions in the atmosphere.

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## 1. INTRODUCTION

The earth's temperature, climate, and chemistry are determined by the balance of incoming shortwave solar radiation and outgoing longwave infrared (IR). The emission of the sun is modeled as a blackbody at 5800 K, with a maximum photon output in the visible red [1]. Absorption by atmospheric components, notably ozone, limits the ultraviolet radiation reaching the earth's surface to wavelengths greater than 300 nm. In this review, we consider alternative photophysical and photochemical processes driven by solar photons in the visible red and near IR [2].

Traditionally, processes considered in atmospheric photochemistry are those requiring excitation of electronic states by ultraviolet (UV) light as these high energies are of the necessary energy to dissociate covalent bonds [3]. Reactive radicals including hydroxyl radical, OH, the main oxidant of organic and inorganic compounds in the earth's atmosphere can be generated in this way [4, 5]. Chemistry in the stratosphere and troposphere is, therefore, driven by direct photochemical reactions or by photolytically generated OH originating from photolysis of O<sub>3</sub> to give O(<sup>1</sup>D) which reacts with H<sub>2</sub>O and CH<sub>4</sub> to give OH.

In this review, we discuss a sunlight-initiated process which occurs by excitation with red solar photons of vibrational levels of the ground electronic state of atmospheric chromophores [2, 6]. It has recently been shown that these ground electronic state photoreactions can be important in the atmosphere when excited electronic state reactions are precluded by the lack of appropriate electronic states accessible in the solar spectrum [7–16]. Atmospheric conditions, where UV photons are suppressed as is the case at high zenith angle which occurs at dusk, dawn, or the edge of a polar vortex, are also auspicious for such ground state photochemistry [17–32]. Atmospheric chemists describe the rate of formation of photoproducts from atmospheric processing as a first-order rate constant  $J$  ( $J$ -values), where  $J$  is given by a convolution of the photoabsorption cross-section, the wavenumber dependent photochemical quantum yield, and the photon flux of solar radiation [3]. In the present review, the experimental and theoretical methods used to obtain accurate integrated O–H cross-sections for vibrational transitions and the atmospheric impact of ground electronic state chemistry will be discussed.

This overtone-induced chemistry is important in that it contributes to atmospheric aerosol processing. In general,

hydrophilic acids and alcohols promote aerosol nucleation and growth. The overtone-induced chemistry leads to the production of hydrophobic byproducts such as  $\text{CO}_2$ , aldehydes, and ketones, which can evaporate, and therefore process these aerosols. The resulting changes in aerosol size, composition, and surface structure are paramount to understanding radiative transfer and consequently climate.

Our discussion focuses on sunlight-initiated chemistry of significance to secondary organic aerosol (SOA) chemistry and consequently to chemistry relevant to the earth's climate. We propose photochemistry of excited vibrational levels of the ground electronic state as potential contributions to explain the gap between modeled and measured organic concentrations [33–35]. Atmospheric aerosols influence global radiative forcing by back scattering and/or absorption of solar radiation and by enhancement of cloud albedo due to an increased number of cloud droplets [36]. Current aerosol models underestimate SOA mass by up to two orders of magnitude [37–39]. Atmospheric oxidation processes are largely driven by oxidants such as OH and  $\text{O}_3$ . However, direct photolysis processes are also important degradation pathways of potential SOA precursors and contributors. Photolysis processes of a variety of highly oxidized organics might represent an unrecognized chemical pathway in the multiphase (gas/particle/droplet) system that might help to explain the large gap between measured and modeled organic concentrations.

## 2. VIBRATIONALLY EXCITED STATES

The vibrations of polyatomic molecules are often represented as normal modes [40]. In the normal mode picture, the potential energy surface is expanded to the second-order term at the minimum, and the mass-weighted Cartesian force constant matrix is diagonalized to give the normal modes. These normal modes are sets of concerted, collective, and harmonic motions of all the atoms in the molecule with a fixed center of mass. Vibrations are uncoupled, and each type of vibration possesses its own distinct harmonic potential energy well. Spectra in the fundamental region have been assigned successfully using this normal mode picture assuming a linear dipole moment surface in these coordinates [40]. However, this double harmonic approximation (harmonic potential energy surface and linear dipole moment surface) becomes increasingly invalid for treatments of transitions to higher vibrational states [41–43]. In real molecules, the mechanical and electrical anharmonicities (the anharmonic terms of the potential energy surface and the nonlinear terms of the dipole moment surface, resp.) relax the  $\Delta\nu = \pm 1$  vibrational selection rule and allow for the observation of transitions involving multiple quanta in one vibrational mode (i.e., overtone bands) or multiple quanta in two or more differing vibrational modes (i.e., combination bands). However, in most cases, these anharmonicities are relatively small, and, in general, overtone and combination bands are weak and not easily observed.

In the energy regime of about 30 to 60 kcal/mol, observations have shown that the X–H (X=O, C, N) stretching overtones dominate the ground electronic state vibrational

spectra. These X–H stretching vibrations have been studied and assigned successfully using the local mode model [42–53]. Unlike in the normal mode view, local oscillators are considered to be weakly coupled and each X–H oscillator is treated independently in the local mode description. For example, the dominant absorption in the overtone spectra of the water molecule is better described with a linear combination of two independently oscillating O–H bonds (in the local mode picture) instead of considering a high excitation in either symmetric or asymmetric O–H stretching modes (in the normal mode picture). Albeit weak, these X–H stretching overtones allow for a method of depositing energy into a molecule by the absorption of sunlight, and thus may lead to reaction [54–60]. As mentioned above, sunlight has maximum photon intensity in the visible region, where these overtone transitions are observed. Therefore, in order to assess the importance of overtone-initiated chemistry, it is important to understand the absolute absorption cross-section of these X–H stretching overtones.

In the mid 1980s, Crim et al. reported overtone-initiated unimolecular decomposition for the hydrogen peroxide ( $\text{HOOH}$ ) molecule, where the O–H stretching excitation of  $\Delta\nu_{\text{OH}} = 5$  (+ torsion mode excitation) and 6 resulted in a bond cleavage of the O–O bond ( $\text{De} \sim 50$  kcal/mol) [61–63]. Their wavelength dependent product state distribution showed initial state dependence. Slight differences in the product distribution of OH were seen when the combination band of the O–H stretch overtone and the torsion mode was excited compared to the excitation via pure O–H stretch overtone. Following their work, overtone-induced photodissociation reactions have been investigated in several molecules with the O–O–H bond, such as peroxytrinitric acid ( $\text{O}_2\text{NOOH}$ ) [28, 32], peroxytrinitrous acid ( $\text{ONOOH}$ ) [20, 64–66], methyl hydroperoxide ( $\text{CH}_3\text{OOH}$ ) [27, 67], as well as hydrogen trioxyl radical ( $\text{OOOH}$ ) [68, 69]. Furthermore, systems with weak bonds adjacent to the O–H bond, such as N–O ( $\text{De} \sim 55$  kcal/mol) in nitric acid ( $\text{O}_2\text{NOH}$ ) [70, 71] and O–Cl ( $\text{De} \sim 43$  kcal) in  $\text{ClOH}$  [72–75], have also been investigated as possible candidates to dissociate following O–H stretching overtone excitation.

The O–H bond with its strong polarity usually results in the strongest absorption within the X–H stretching spectra (per X–H bond) for a given quanta of excitation; thus, it is a good absorbing chromophore for the deposition of photon energy into the molecule. For example, the ratio between the average intensities for the O–H bond versus the C–H bond is about 4:1 for  $\Delta\nu = 3$ , 4.5:1 for  $\Delta\nu = 4$ , and 6:1 for  $\Delta\nu = 5$  [23, 76, 77]. Therefore, polyatomic molecules with O–H bonds are candidates for absorbing solar red photons and reacting in the atmosphere [2, 7, 9, 14, 15, 17, 22, 23, 26, 65, 78–81]. Since greater effort is needed to obtain an absolute integrated cross-section in comparison to the peak position, only a few papers report both [82–84]. The weak absorption intensities of these relevant overtones also make it more difficult to obtain absolute values both experimentally and theoretically. In the following work, we compile the available experimental and theoretical integrated cross-sections of the O–H stretching mode for several polyatomic molecules. A comparison on the molecular

dependence as well as an investigation of the accuracy of the calculated values, which are usually obtained using the local mode model, will be presented. In addition, abiding with the possibility that excitation through combination bands may play an important role in the unimolecular reaction dynamics, combination bands in nitric acid are examined as an example. Furthermore, calculated reaction barriers of possible candidates for overtone-initiated reaction will be presented. The possibility of overtone-induced concerted reactions, where the excited O–H bond is strongly coupled to the reaction coordinate, will be discussed [7, 16, 18, 85]. These reactions will be contrasted with previous experimental results of overtone-induced dissociation reaction, where the energy in the excited O–H bond is transferred to rupture a weak adjacent bond [2, 17, 23, 24, 26, 30, 57, 64, 65, 70, 71, 78, 86, 87]. Finally, we will conclude with the discussion of the photochemical rate ( $J$ -values) and important points to note for discussing these overtone-initiated reactions in the atmosphere.

### 3. O–H STRETCHING SPECTRA AND THE LOCAL MODE MODEL

Due to the light mass of the hydrogen atom, X–H stretching vibrations have considerably higher frequencies than other vibrational modes. Also, the large difference in the mass between the X (O atom in the present case) atom and H atom allows for this vibrational mode to have relatively small coupling with other modes. In the late sixties, Siebrand and Williams [45], Swofford et al. [88], Henry [42], Burberry et al. [89], and Mortensen et al. [90] observed the following trends in the X–H stretching spectra.

First, the fundamental and overtone transition energies of the X–H stretching spectra were shown to fit to a two-parameter equation:

$$\Delta E_{v_0} = \nu(A - B\nu), \quad (1)$$

where  $\Delta E_{v_0}$  is the transition energy between the ground and  $\nu$ th excited state. This equation, sometimes regarded as Birge-Sponer equation [91], is the solution of a one-dimensional Morse oscillator [92] for diatomic molecules, where the harmonic term is

$$\omega_e = A + B \quad (2)$$

and the anharmonic term is expressed as

$$\chi_e \omega_e = B. \quad (3)$$

Second, Burberry et al. [89] observed the  $\Delta\nu = 3$ –6 aromatic C–H stretching spectra of benzene, toluene, xylene, and trimethyl benzene and reported that while the peak positions did not vary, the absorption intensity showed systematic decrease in relation to the number of aromatic C–H bonds.

These observations lead to the phenomenological “local mode model”, where the vibrational spectra are understood in terms of localized excitation in the X–H bond. For the O–H bond, both experimental and theoretical calculations have

shown that the peak positions can be given by a harmonic frequency of

$$\omega_e \cong 3700 - 3900 \text{ cm}^{-1} \quad (4)$$

and an anharmonic frequency of

$$\chi_e \omega_e \cong 70 - 90 \text{ cm}^{-1}. \quad (5)$$

Therefore, to exceed the reaction barriers of 30–60 kcal/mol discussed in the present review, overtone excitations of  $\Delta\nu_{\text{OH}} = 3$ –6, which reside in the visible to near IR-region, need to be considered. Although we will not tabulate the actual values here, recent high-level calculations give peak positions with errors of less than few percent [51, 77, 93].

### 4. INTENSITIES OF THE O–H STRETCHING MODE

First, we present a brief summary of the experimental and theoretical methods used to obtain absolute integrated cross-sections before discussing the results that have been collected.

A combination of methods is usually needed to obtain experimental intensities for all  $\Delta\nu_{\text{OH}} = 1$ –5 transitions. Use of Fourier transform infrared spectroscopy (FTS) easily provides data for the fundamental and near-IR regions including  $\Delta\nu_{\text{OH}} = 1, 2$ , and 3, while methods such as cavity ring-down (CRD) [94–98] or photoacoustic (PA) [99–105] spectroscopy grants access to higher overtones into the visible region of the spectrum such as  $\Delta\nu_{\text{OH}} = 4, 5$ . Each method has its advantages and disadvantages. Fourier transform spectroscopy, for example, has high wavenumber resolution as well as the Jacquinot advantage, enabling higher throughput of radiation [106]. Unlike conventional or laser spectrometry where one must scan the full wavenumber range, FTS information on all frequencies simultaneously impinge upon the detector and the entire spectrum of the species is recorded at once. In contrast to laser spectroscopy such as CRD and PA, FTS may be  $\sim 10^6$  less sensitive due to its low-photon flux and the difficulty of measuring a small difference between the light intensity with and without an absorber present. Increased sensitivity, necessary for the detection of higher overtones due to their diminishing intensity, is the main advantage of CRD and PA spectroscopy [24, 94, 95, 97, 98, 101–105, 107]. The use of highly reflective mirrors employed in the CRD setup in our lab, for example [8, 10, 18, 108], increases the pathlength of the experiment to orders of kilometers, thereby increasing the sensitivity by at least a factor of 14000 in comparison to FTS experiments. However, CRD spectroscopy is limited in wavenumber range by the laser dye and by the mirrors that can be used. PA spectroscopy provides comparable sensitivity to CRD spectroscopy and is also limited in range by the laser dye. It provides the advantage of using small sample volume due to its ability to detect at parts per trillion levels.

A challenge often encountered in determining experimental cross-sections, regardless of spectroscopic method (FTS, CRD, or PA), is obtaining an accurate number density. This value is usually obtained using the available vapor pressure data and the ideal gas law. The accuracy of vapor

pressure measurements is low for compounds which readily form hydrogen-bonded clusters or hydrates. However, vapor pressures inside the sample chamber can readily fluctuate such that equilibrium in the chamber may be achieved on a different timescale by which point some sample can potentially be lost to the atmosphere, and temperature effects may cause the sample to degrade by thermal reaction. Often times, only relative intensities are reported in the literature due to difficulties met in determining an absolute cross-section.

For the theoretical calculation of the peak positions and integrated cross-sections, one must first obtain the potential energy surface (PES) and the dipole moment surface (DMS) from quantum chemistry ab initio calculations. With this PES, the vibrational eigenvalues and eigenfunctions are calculated by solving the vibrational Schrödinger equation. Local and normal mode pictures result in different coordinate systems, thereby giving different equation forms for the vibrational Schrödinger equation. The peak position or transition energy is obtained from the difference between the respective initial and final state energies. The integrated cross-section is obtained by [109]

$$S^{\text{calc}} = \frac{8\pi^3}{3hc} |\langle \Psi_f | \vec{\mu} | \Psi_i \rangle|^2 \tilde{\nu} \\ = 4.16 \times 10^{-19} |\langle \Psi_f | \vec{\mu} | \Psi_i \rangle|^2 \tilde{\nu} \text{ (cm molecule}^{-1}\text{)}, \quad (6)$$

where  $\tilde{\nu}$  is the transition energy in  $\text{cm}^{-1}$ , and  $|\langle \Psi_f | \vec{\mu} | \Psi_i \rangle|^2$  is the square of the absolute magnitude of the transition moment in debye squared. The transition moment is obtained by the integration of the aforementioned DMS using the initial and final state eigenfunctions. It should be noted that there are numerous quantum chemistry methods that can be used to calculate the PES and DMS ranging from the relatively “cheap” wave function method of Hartree Fock [110, 111] and density functional theory methods [112], such as B3LYP [113, 114], to the “expensive” wave function methods, such as QCISD(T) [115–117], CCSD(T) [116, 118–120], and MRSDCI [121]. In using these methods to obtain the PES/DMS needed to calculate highly excited vibrational states, one needs to calculate geometries that are displaced from the equilibrium geometry. At these geometries, such as elongated X–H bond lengths, multireference methods are necessary to accurately describe the electronic state, and instability may occur with the use of single reference methods.

Many different methods have been used to solve the vibrational Schrödinger equation, and one of the usual methods is the variational method where one diagonalizes the Hamiltonian matrix using a given basis set [122–124]. Quack [51] used harmonic oscillator basis sets to obtain the eigenfunctions for the CH stretching overtone of  $\text{CX}_3\text{H}$ . Methods such as vibrational self-consistent field [125] and their higher level expansions VCI [126] and VCCSD [127] have also been used for the calculation of OH stretching overtone transitions of nitric acid [128]. Furthermore, several methods solve the time-dependent Schrödinger equation and obtain the spectra from the Fourier transform of the autocorrelation

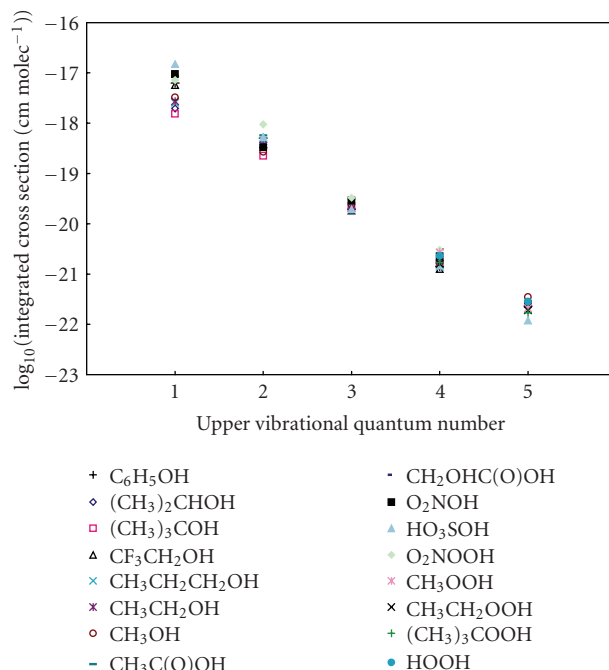


FIGURE 1: Compilation of experimental integrated cross-sections of O–H stretching overtones.

function of the wavepacket [129]. For the calculation of X–H stretching modes, Henry et al. developed the harmonic coupled anharmonic oscillator model, where the PES of the X–H stretching motion is approximated as a Morse potential and Taylor’s expansion fitting of the ab initio dipole moments are used to obtain the DMS as a function of bond coordinates [90, 130]. Initially, experimental peak positions were used to obtain the needed parameters for the Morse oscillators, but in recent calculations these parameters are obtained from the fitting of ab initio energies. Recently, some of us used the local mode model and calculated the intensities of the O–H stretching spectra for several simple acids and alcohols using the grid variational method with the finite difference approximation [131]. In this calculation, the PES and DMS were obtained from the highly accurate numerical interpolation of the energy and dipole moment calculated by B3LYP/6-311++G(3df,3pd) [113, 114, 132–136].

A summary of the O–H stretching intensities for various alcohols, carboxylic acids, and peroxides is presented in Figures 1 and 2 which illustrate the trend in O–H stretching integrated cross-sections as a function of upper quantum number [8, 18, 20, 24, 28, 67, 76, 78, 82–84, 102, 137–140]. Typically, intensities of the O–H stretches are comparable for most organic compounds. Figure 1 summarizes the experimental results from a variety of sources, [8, 18, 24, 78, 83, 102, 137, 141] including work from our group, while Figure 2 compiles theoretically derived integrated cross-sections [77, 131]. It should be noted that these figures list molecules in which both experimental and theoretical values are available. Furthermore, as mentioned above, many different quantum chemistry methods are available for the calculation of the PES and DMS, and the same applies



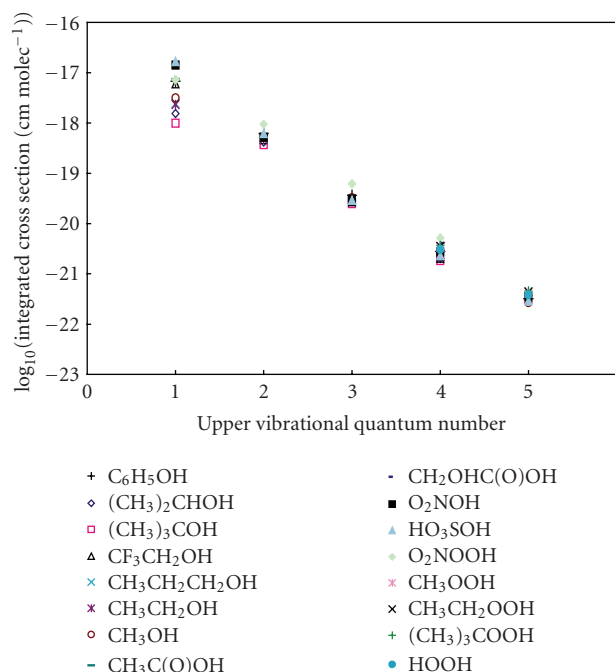


FIGURE 2: Compilation of theoretical O–H stretching integrated cross-sections.

for solving the vibrational problem. In order to keep the comparison consistent in terms of calculation method, the results given in Figure 2 are given by the grid variational method using the PES and DMS calculated by the B3LYP/6-311++G(3df,3pd) method. In addition, due to the limits in the experimental methodology mentioned above, for most molecules we were unable to collect literature values for all  $\Delta\nu_{\text{OH}} = 1$ –5 transitions.

Both Figures 1 and 2 illustrate that the O–H stretch preserves its intensity even though it decreases with each overtone. The “order-of-magnitude” rule [61], which states that the intensities of O–H stretching vibrational transitions successively decrease in magnitude by approximately a factor of 10, is illustrated in both figures by a linear decrease in log scale. This trend has also been observed in C–H and N–H stretching transitions. In general, the “order-of-magnitude” rule works best for higher energy overtones, and one sees great variance when comparing the fundamental and first overtone intensities. For example, Figure 1 reveals that the drop in intensity for sulfuric acid from the  $\Delta\nu_{\text{OH}} = 1$  to the  $\Delta\nu_{\text{OH}} = 2$  transition is 28 [137], while that for propanol is 4.7 [82]. Previously, we have shown that for propionic and pentafluoropropionic acid, this factor drops by about 14 [9, 79] and 18 for longer chained perfluorocarboxylic acids [15].

As shown in Figure 1, intensities for the  $\Delta\nu_{\text{OH}} = 1$  vary over an order of magnitude, from  $1.54 \times 10^{-18}$  cm molec $^{-1}$  for tert-butanol [82] to  $1.49 \times 10^{-17}$  cm molec $^{-1}$  (per O–H stretch) for sulfuric acid [137]. Upon observation of several simple acids and alcohols, Lange et al. [82] have discussed the correlation of the fundamental O–H stretching intensities with the electron withdrawing ability of the substituent bound to the O–H group. Theoretical work on the same set

of molecules also showed the same trend that the stronger the electron withdrawing ability of the substituent, the greater the fundamental intensity [77]. Lange et al. [82] also found that molecules with more electron withdrawing substituents have a larger decrease in successive O–H overtone intensities relative to the fundamental O–H stretch. As can be seen from Figures 1 and 2, overtone intensities show much smaller variance between molecules than fundamental intensities, and this trend seen by Lange et al. [82] is probably the result of variance in the fundamental intensity. For the C–H stretching vibration, Burberry et al. [89] have mentioned the “universal intensity concept” [142], in which the  $\Delta\nu_{\text{CH}} = 3, 4, 5$ , and 6 transition absorption intensities per C–H oscillator become nearly equal regardless of type of molecule. A similar trend is seen for the O–H bond, where overtone intensity loses its molecular dependence, but it should be noted that in peroxide molecules (ROO–H), the theoretical results show stronger overtone intensity compared to the acids and alcohols (R–OH) [77]. Experimental results do not show clear trends as discussed and more study is needed to obtain a full understanding of the factors that determine overtone intensities.

As mentioned above, the intensity trend seen in the fundamental region is different from that seen in the overtones region. As seen in Figures 1 and 2, the O–H cross-section of sulfuric acid has the largest intensity at  $\Delta\nu_{\text{OH}} = 1$  compared with the compounds investigated here, but decreases with increasing vibrational quanta more rapidly until possessing the smallest value at  $\Delta\nu_{\text{OH}} = 5$ . We believe this behavior is a result of the onset of dehydration reaction and Section 6 addresses this in detail.

Since theoretical values are used when experimental limitations (low vapor pressure, no laser in the absorption range, and so on) make it impossible to obtain the integrated cross-sections experimentally, it is important to gauge the accuracy of these calculations. Methods such as mean absolute percentage error and logarithmic deviation have been used to evaluate the accuracy of the calculated versus the experimental values since they span many orders of magnitude [122]. In the present paper, we compare the accuracy by using the mean absolute percentage error:

$$\text{MAPE} = \frac{1}{N_{\text{data}}} \sum_{i=1}^{N_{\text{data}}} \left| \frac{A_i^{\text{calc}} - A_i^{\text{exp}}}{A_i^{\text{exp}}} \right|. \quad (7)$$

Using all the available experimental values shown in Figure 1, we obtain an error of 45%, signifying that the calculated results are within a factor of 2 of the experimental values. It should be noted that if we only use the fundamental intensities, the error is a much smaller value of 15%, signifying that the experimental values are reproduced with high accuracy. The use of a more sophisticated and time-consuming quantum chemistry methods to obtain the PES and DMF, as well as a more detailed treatment in the vibrational calculation (such as consideration of coupling to other vibrational modes) will probably lead to a slightly better agreement with experiment, but it is expected that at the present moment the error limit for the calculated integrated cross-sections for overtone transitions

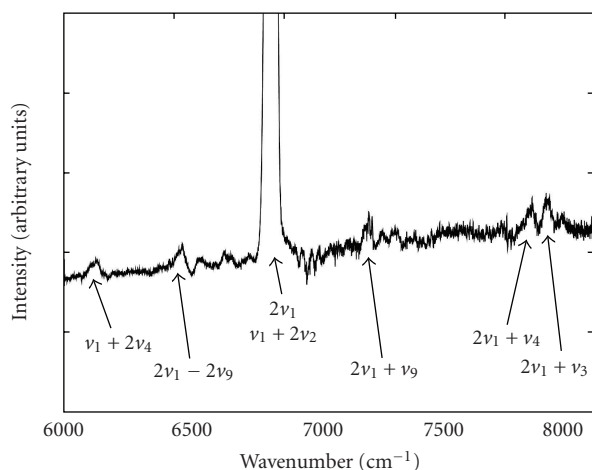


FIGURE 3: Illustration of combination bands observed for  $\text{HNO}_3$  in the NIR. Assignments taken from Feierabend et al. [128, 143].

is about 30%. In systems where the relative intensities of the overtones with respect to the fundamental transition may be obtained experimentally, a hybrid method of using the theoretical fundamental intensity and the experimental relative intensities may be used to obtain an absolute cross-section for the overtones. As mentioned above for the fundamental transition, the theoretical values can reproduce experimental values with high accuracy.

## 5. SIGNIFICANCE OF COMBINATION BANDS

As mentioned in the introduction, product distributions of the photoinduced dissociation of  $\text{HOOH}$  showed initial state dependence [61–63]. It is expected that near the dissociation threshold, the dissociating product may show mode dependence on the band used to excite it. Therefore, Homitsky et al. [102] performed detailed analysis on the O–H stretch and torsional excitation on the overtone and combination bands of methylhydroperoxide. The observation of combination bands suggests mode coupling [144] and many combination bands involving the O–H stretching overtones of  $\text{HNO}_3$  are shown as an example in Figure 3. Feierabend et al. [128, 143] showed that the O–H stretching overtones are not the only important absorbers in the near-IR (NIR) and visible regions; the appearance of combination bands involving the O–H stretch is also prevalent in the higher energy regions. These have fairly large absorption intensities for combination bands, although in general the local mode model often neglects mode mixing. The following mode assignments are made as shown in Figure 3:  $2\nu_1$  = first O–H stretching overtone,  $\nu_2$  =  $\text{NO}_2$  asymmetric stretch,  $\nu_3$  =  $\text{NO}_2$  symmetric stretch,  $\nu_4$  = H–ON bend, and  $\nu_9$  = O–H torsion. A hot band of the O–H torsional mode in combination with the first O–H stretching overtone was attributed to the band centered at approximately  $6500\text{ cm}^{-1}$ . The work of Havey et al. [145] showed that molecules which contain many low-frequency torsional modes may have significant hot band contributions. These hot band contributions can

add to the total intensity of the O–H stretching overtones region. A surprising result of the  $\text{HNO}_3$  work revealed that the intensities of the combination bands do not drop off in the O–H stretching overtone region.

Interestingly, the absorption intensities of these types of combination bands scale roughly the same as the intensities of the overtones. For example, the intensity of overtones is about the same as that of combination bands;  $I[n\nu_{\text{OH}}/(n+1)\nu_{\text{OH}}] \sim I[\nu_x + \nu_{\text{OH}}/\nu_x + (n+1)\nu_{\text{OH}}]$ , where  $\nu_x$  is an arbitrary mode with fundamental absorption intensity. The fact that these combination modes are observed with significant absorption intensities in the NIR suggests a few key ideas. First, these combination modes should not be ruled out and regarded as bright states for overtone-induced photodissociation, especially if the vibrational mode involved is closely coupled to the reaction coordinate. Next, more local mode simulations have begun treating the coupling of the O–H stretch with other modes [43, 80, 138, 146, 147]. These types of treatments are expected to be more accurate due to the qualitative evidence for mode coupling/mixing in the observed spectra. Finally, while the combination modes cannot provide any direct quantitative measurement of mode coupling, their frequencies and intensities can serve as a test for theoretical calculations. This will allow for the assessment of the accuracy in the theoretical methods, providing information on the method to be used for calculating the spectra of molecules in which experimental determination is not possible.

## 6. CANDIDATES SYSTEMS OF OVERTONE-INITIATED CHEMISTRY

Previous studies [7] have revealed that overtone-induced photolysis of sulfuric acid is the source of  $\text{SO}_2$  in the stratosphere and mesosphere [12, 13]. UV photolysis of sulfuric acid was ruled out [13, 137] because the electronic excitation lies well above the energies available from the sun in the earth's atmosphere. Sulfuric acid only absorbs in the IR and the near-IR regions, where the O–H stretching vibration plays a dominant role in its atmospheric chemistry. These studies on overtone-induced photolysis of sulfuric acid have predicted that the photochemical reaction is a concerted dehydration reaction, where the product is  $\text{H}_2\text{O}$  and  $\text{SO}_3$  rather than a bond cleavage reaction where the product would be OH and  $\text{SO}_3\text{H}$ . This concerted reaction only requires  $\sim 32\text{--}40\text{ kcal/mol}$ , so, consequently, excitation of  $\Delta\nu_{\text{OH}} = 4$  and higher overtones provides sufficient energy to drive the reaction and generate  $\text{SO}_3$  and  $\text{H}_2\text{O}$ . The strong S–O (about 80 to 90 kcal/mol) [148] bond requires significantly more energy for direct bond cleavage that cannot be provided from overtone chemistry because of the low cross-sections expected for the 9th overtone required to reach this threshold. Figure 3 shows the calculated energy barrier, including the minimum and the transition state structures for the dehydration reaction of sulfuric acid  $\text{H}_2\text{SO}_4 \rightarrow \text{SO}_3 + \text{H}_2\text{O}$ . It should be noted that the occurrences of reactions may cause the absorption spectrum to broaden, thereby making it difficult to obtain an accurate cross-section due to the low signal-to-noise.

TABLE 1: Organic acids and barriers for their chemistry.

Compound	Chemical formula	Lowest energy barrier for reaction (kcal/mol)	Reaction products	OH quanta exceeding barrier	Reference
Sulfuric acid	H <sub>2</sub> SO <sub>4</sub>	32–40	SO <sub>3</sub> , H <sub>2</sub> O	$\nu_{\text{OH}} = 4$	[7, 149, 150]
Nitric acid	HNO <sub>3</sub>	47.7	NO <sub>2</sub> , OH	$\nu_{\text{OH}} = 5$	[57]
Pernitric acid	HO <sub>2</sub> NO <sub>2</sub>	21.2	HO <sub>2</sub> , NO <sub>2</sub>	$\nu_{\text{OH}} = 3$	[30]
Formic acid	HCOOH	41.5 <sup>(a)</sup> , 63.0 <sup>(b)</sup>	CO, H <sub>2</sub> O	$\nu_{\text{OH}} = 5, 7$	[151] <sup>(a)</sup> , [152] <sup>(b)</sup>
Glycolic acid	OHCH <sub>2</sub> COOH	50.9	H <sub>2</sub> CO, CO, H <sub>2</sub> O	$\nu_{\text{OH}} = 6$	[153]
Lactic acid	OHCHCH <sub>3</sub> COOH	47.4	HCOCH <sub>3</sub> , CO, H <sub>2</sub> O	$\nu_{\text{OH}} = 5$	[153]
Malonic acid	HOOCCH <sub>2</sub> COOH	27.6	H <sub>2</sub> CC(OH) <sub>2</sub> , CO <sub>2</sub>	$\nu_{\text{OH}} = 3$	[16]
Acetic acid	CH <sub>3</sub> COOH	67.01 <sup>(c)</sup> , 71.5 <sup>(d)</sup>	CH <sub>4</sub> , CO <sub>2</sub>	$\nu_{\text{OH}} = 7, 8$	[154] <sup>(c)</sup> , [155] <sup>(d)</sup>
Trifluoroacetic acid	CF <sub>3</sub> COOH	50.3	CF <sub>2</sub> CO <sub>2</sub> , HF	$\nu_{\text{OH}} = 6$	[14]

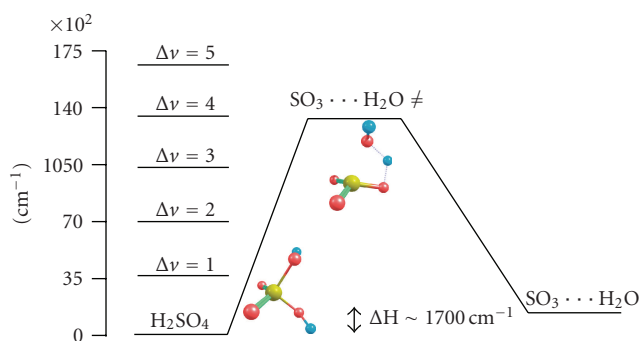


FIGURE 4: Calculated energy barrier for sulfuric acid dehydration.

Similar to sulfuric acid, other atmospherically relevant compounds, specifically oxidized organic species such as acids and alcohols, are capable of undergoing concerted reaction by overtone pumping of the O–H bond [2, 7, 14, 16, 18, 30, 108]. Table 1 shows several organic acids, their lowest energy barrier for reaction, the reaction products, and the minimum quanta of O–H stretch required for the chemistry to occur [7, 14, 16, 30, 57, 149–155]. The values for the energy barrier do not include the zero point energy corrections, therefore they are possibly higher than the actual reaction thresholds.

In general, if there is a lack of competing processes (such as collisional deactivation), the energy provided by overtone pumping is sufficient to drive the reaction to completion [12, 156, 157]. For example, in nitric and pernitric acid, theoretical calculations and experimental data have shown that visible wavelength excitation of O–H overtone vibrations contain sufficient energy to cleave the O–O and N–O bonds [26, 158]. Similarly, the work of Staikova et al. [16] showed that for malonic acid excitation of  $\Delta\nu_{\text{OH}} \geq 3$  has the ability to decarboxylate the acid, although experimental validation of the reaction is not yet available [159]. In the case where a water molecule is available and forms a complex with the acid, it lowers the energy for reaction by one quantum of an O–H stretch [7, 16, 160]. Briefly, the presence of the water molecule forms an eight-membered hydrogen-bonded cyclic ring with the chromophore and relaxes the strain on the transition state as compared to the pure acid which forms

a six-membered hydrogen-bonded cyclic ring on its own. In doing so, the transition state energy for decarboxylation of malonic acid is lowered from 25.6 to 17.6 kcal/mol [16]. The energetic difference is equal to one quantum of an O–H stretching vibrational overtone and in theory, excitation to  $\Delta\nu_{\text{OH}} = 2$  can promote the reaction when a water molecule is present. Several other systems such as sulfuric acid, fluoromethanol, and perfluoromethanol have shown similar decrease in barrier heights with hydrate complex formation [160]. Abundance of water in the atmosphere point to the high possibility of the existence of hydrated complexes indicating the likelihood of water catalyzed overtone reaction being a factor in atmospheric chemistry. These hydrated clusters may serve as a model to mimic the environment that these acids are in/on the surface of aerosols. More detailed experimental investigations of these overtone-initiated concerted reactions are needed to fully assess their importance in the atmosphere.

## 7. CONCLUSIONS

Solar radiation provides sufficient energy to drive chemical reactions in the atmosphere and determines the earth's climate and temperature. Typically, the UV region of the solar spectrum (200–400 nm) is considered for chemical reactions since electronic transitions occur in this region and absorption in that wavelength range corresponds to normal chemical bond energies [3]. At high solar zenith angles, UV light is suppressed and low-energy visible radiation becomes important [2, 26]. Therefore, absorption of radiation in the near-IR and visible regions, which are usually dominated by X–H stretching vibrational overtones, play a significant role in determining the atmospheric chemistry and fate of certain organic compounds [7, 14, 16, 161].

Atmospheric chemistry via O–H overtone pumping can be driven by three mechanisms. In the first case, an O–H stretch (or any other strongly absorbing local mode oscillator) is excited into a vibrational overtone followed by intramolecular vibrational energy redistribution (IVR) which transfers sufficient energy into a weaker bond in the molecule to cause dissociation [2, 22, 26, 30]. Even though the O–H stretch itself is excited, it is ultimately a different weaker bond in the molecule that is broken. This is the

case for compounds such as nitric acid [57], pernitric acid [17, 32], and hydrogen peroxide [61–63] which all have relatively weak bonds. A second scenario involves exciting the O–H overtone state which is strongly coupled to the reaction coordinate [2]. Strong coupling of the excited state with the reaction coordinate allows for the concerted excitation of low-frequency modes (heavy atom motion) causing the photoexcited O–H bond to break at energies significantly lower than the bond dissociation energy at its equilibrium geometry. The mechanism is best described as a concerted reaction. In sulfuric acid, for example, excitation well above  $\nu_{\text{OH}} = 6$  induces the hydrogen of the O–H bond to migrate to a different location in the molecule followed by dissociation [11]. This occurs on the timescale of picoseconds, while the process of IVR requires a significantly longer time on the order of nanoseconds [12]. Malonic acid is another example in which case the reaction is also concerted [16]. Lastly, the third process is a mechanism entailing solar radiation in sequential two-photon absorption [162]. The first photon excites a vibrational overtone into an intermediate state, while the second photon promotes the system to a repulsive dissociative first excited electronic state.

In the atmosphere, the excited species are under conditions, where deactivation can occur through collisions with water and other “cold” molecules ( $\text{N}_2$ ,  $\text{O}_2$ , etc.). Therefore, the quantum yield will be defined by how fast the reaction proceeds in comparison to the deactivation time defined by collisions to these “cold” surrounding bath molecules [11, 12, 160, 163]. In discussing the time scales of overtone-induced unimolecular reaction, a key aspect to consider is whether the reaction proceeds directly or statistically. It would be expected that concerted reactions which have the excited O–H bond strongly coupled to the reaction coordinate will likely occur more directly than bond dissociation, although this will be left for future studies. Detailed study of the reaction dynamics following overtone excitation is needed in order to calculate the quantum yield and accurate  $J$ -values for overtone-induced reactions which appear to be possible and probable in the atmosphere.

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