

Review article: Sunlight initiated atmospheric photochemical reactions

V. Vaida[†]

*Department of Chemistry and Biochemistry and CIRES, University of Colorado, Boulder Campus Box 215,
Boulder, Colorado 80309-0215, USA*

ABSTRACT. The Sun is the light source driving atmospheric chemistry. The wavelengths dependent photon flux is controlled by solar emission modulated by absorption of atmospheric gases, aerosols and clouds. The factors determining the characteristics of this light source, its altitude, latitude and zenith angle dependence are discussed to explain the effectiveness of the Sun in driving chemical reactions. Examples of chemical reactions occurring on the excited and the ground electronic state potential energy surfaces of molecules and radicals are used to illustrate the complexity of atmospheric photochemistry. Specifically, the near ultraviolet (UV) photochemistry of chlorine dioxide is used to exemplify electronic state reactions occurring in the atmosphere. The near infrared (IR) photochemistry of nitric and sulfuric acids are discussed to illustrate reactions important in the atmosphere which occur with solar pumping of vibrational overtone transitions in the ground electronic state of these molecules.

1. INTRODUCTION

Sunlight drives the chemistry of the Earth and determines its temperature and climate. Absorption of radiation by molecules leads to transitions to rotational, vibrational and electronic molecular states. The maximum flux of solar radiation is mostly in the ultraviolet (UV), visible (VIS) and near infrared (NIR) with a maximum flux in the visible [1]. Some of the incoming solar radiation which is not absorbed in the atmosphere by gases such as O₂, O₃, CO₂, H₂O or backscattered to space by aerosols and clouds is absorbed by and heats the Earth's surface [2-4]. The radiation absorbed by the Earth is re-radiated and emitted as infrared (IR) radiation [5-7]. The outgoing IR is to some extent absorbed by atmospheric gases ("greenhouse gases") [8], and scattered by aerosols and clouds [9, 10]. The balance of the incoming, high energy solar radiation and the outgoing terrestrial emission, both modulated by the Earth atmosphere, control the temperature and climate of the planet [1, 11, 12]. While interesting chemical issues and molecular processes are involved in radiative transfer [13-16], this review will focus on sunlight initiated chemical reactions in the Earth's atmosphere.

Photochemical reactions generate highly reactive atmospheric free radicals [17, 18]. Free radical reactions have been known to be important in the transformation of atmospheric molecules, notably the oxidation of atmospheric pollutants [19, 20]. The connection between the fields of chemical kinetics of elementary gas-phase reactions, photochemistry and atmospheric science has been known for some time [2, 3, 21], yet only recently has the importance

of condensed phase heterogeneous and multiphase reactions been acknowledged [22-24]. In this review, the discussion will center on gas phase atmospheric photochemistry.

The information necessary to understand atmospheric photochemistry comes from a combination of laboratory measurements of the molecular parameters (spectra and cross sections) and atmospheric field measurements of chromophore concentrations and of photon fluxes. Accurate field measurements of key atmospheric chemical constituents remains a challenge [13, 25-28]. Recent advances in atmospheric measurement techniques including those performed from the ground, and using airplane and satellite platforms have highlighted the need for missing or inaccurate molecular information and provided the impetus for further fundamental work [26, 27, 29-32]. Atmospheric measurements cannot access every variable of interest, therefore measurements have to be integrated with model assessments [33]. Model inputs include fundamental molecular parameters (cross sections and chemical and photochemical reaction rate coefficients) [34, 35] obtained in the laboratory as well as temperature, pressure and concentration measured in the field. Atmospheric modeling studies play a key role in integrating fundamental laboratory cross sections, field observations and the dynamics of the atmosphere [36, 37]. The atmospheric problem is extremely complex yet numerical model results, when compared with measurement, can guide laboratory and field studies.

The discussion in this paper will review the important characteristics of the Sun as a photolytic light source and will exemplify sunlight initiated reactions at high (excited electronic state reactions) and low (ground electronic state reactions) energies. The

[†]E-mail: vaida@colorado.edu

examples presented are primarily atmospheric chromophores studied in our research and illustrate excited electronic state reactivity with the example of chlorine dioxide (ClO) [38–40] and the ground electronic state reactivity with the examples of nitric acid (HNO₃) [41, 42] and of sulfuric acid (H₂SO₄) [41, 43].

2. THE SUN: A PHOTOLYTIC LIGHT SOURCE

Sunlight is the driving force for reactions in the Earth atmosphere. Consequently, it is important to discuss the wavelengths, altitude and latitude dependence of solar radiation. The solar flux outside the earth's atmosphere can be approximated by radiation coming from a black body at 5800 K. The average incoming light intensity per unit area normal to the direction of propagation of sunlight (the solar constant) is 1368 Wm⁻². The effective incoming solar radiation per unit area is 1368 Wm⁻² divided by 4 or 342 Wm⁻². Of this incoming radiation, about 67 Wm⁻² is absorbed by O₃, CO₂, H₂O, O₂ and by aerosols and clouds [44]. The effect of gaseous absorption of incoming solar radiation can be understood by comparing the wavelengths dependent solar flux outside the atmosphere with that at the surface [3, 21]. Absorption of radiation by atmospheric gases is dominated in the NIR by vibrational overtone absorptions by H₂O and CO₂ and in the UV by absorption by O₂ and O₃. These atmospheric absorbers impart a wavelengths dependence to the solar spectrum which is a strong function of altitude.

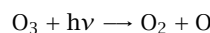
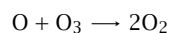
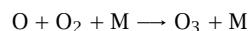
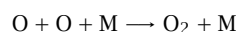
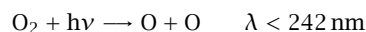
The ozone filtered, wavelengths dependence of actinic radiation is extremely important in promoting chemical reactions [45, 46]. Figure 1 sketches the overlap of the absorption spectrum of CH₃I [47] with the photochemically relevant UV radiation at two different altitudes. The overlap is minimal at ground level but significantly enhanced at high (80 km) altitude. The extremely small overlap between a molecule's UV absorption "tail" and a vanishingly small UV photon flux is a common occurrence in the atmosphere, pointing to the need of understanding both molecular spectra and solar fluxes.

Absorptions of UV solar radiation by oxygen and ozone are important factors in determining the intensity and wavelengths distribution of light available for photochemical reactions at low altitudes, in the troposphere. The ground electronic state of O₂ ($X^3\Sigma_g^-$) is a triplet electronic state so only absorptions to triplet electronic states are spin allowed. Low lying states of O₂ are either symmetry or spin forbidden or both, resulting in weak absorptions in the NIR to the UV [48, 49]. The allowed transition in the UV causes the absorption at 130 nm to 200 nm (Schumann-Runge band) and is the main absorber of solar radiation at these wavelengths in the Earth's atmosphere. The spectral region at wavelengths below 200 nm is known as the vacuum

UV since in laboratory studies air containing O₂ has to be removed from the optical path in this region.

The strong UV absorption of ozone (Hartley band) at 200 nm to 300 nm filters radiation from the solar spectrum shielding the troposphere from high energy, damaging radiation [50]. The low energy edge of this absorption creates the "actinic cut off" in the troposphere at ~ 290 nm. Much weaker bands in the near UV (Huggins bands) and VIS (Chapuis bands) allow radiation in the near UV and visible to reach the Earth's surface [51–54].

The electronic states of both O₂ and O₃ are photo reactive and this light induced chemistry in the upper and middle atmosphere leads to formation of a stratospheric ozone layer, controlling the UV radiation available for chemistry in the troposphere below. S. Chapman in 1930 [55] proposed a set of photochemical reactions leading to the concentration of ozone at 20 to 40 km altitude in the stratosphere.



Atmospheric observations later showed that this photochemical mechanism while qualitatively correct, was predicting too much stratospheric O₃. The ensuing work amended this mechanism with the addition of catalytic ozone loss by atmospheric radicals such as NO_x, HO_x and Cl_x [56–62]. As a result of the extensive photochemical mechanisms of O₂ and O₃, the altitude and concentration of the ozone layer can be predicted with increasing accuracy and modeled to provide a sharp altitude dependent UV cut off of actinic solar radiation.

The concentration of atmospheric absorbers and scatterers of radiation and the path lengths through the atmosphere are important in determining the wavelengths distribution of sun light. These phenomena not only manifest themselves in the altitude dependence but also in the dependence on the angle of the Sun with a fixed point on Earth, which is determined by the time of day, latitude, season, etc. The angle of the sun relative to a fixed point on the surface of the earth defines the solar zenith angle (angle between the direction of the Sun light and the vertical at a given point). A zenith angle of zero (0°) corresponds to the sun overhead (noon) while a high zenith angle (90°) corresponds to the sun on the horizon, as should be the case at dusk, dawn and at the edge of a polar vortex. At high zenith angles the visible light persists to some degree but the UV is suppressed, leaving only low energy visible radiation for photochemical reactions.

This discussion points to special characteristics of the Sun as a photochemical light source providing

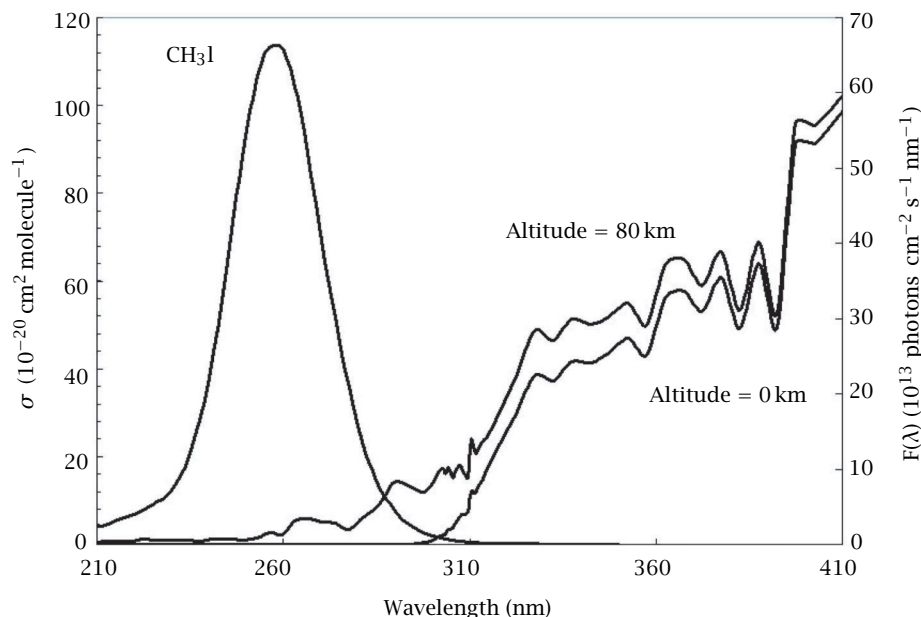


Figure 1. *Overlap of the spectrum of CH₃I [47] (A – X) with the photon flux at low (0 km) and at high (80 km) altitude.*

limited high energy UV radiation with a very sharp UV cut off at $\lambda < 290$ nm and with a strong altitude and solar zenith angle wavelengths dependence. The maximum of the wavelengths distribution of solar radiation is in any case in the visible rather than the ultraviolet, visible wavelengths not filtered to any appreciable degree by atmospheric absorbers.

3. ATMOSPHERIC PHOTOLYSIS RATES

Atmospheric chemists describe the rate of formation of photoproduct B from atmospheric species A as a first-order rate law, with a rate coefficient $J(\text{s}^{-1})$ $d[B]/dt = J[A]$.

The value of J is given by a convolution of the photoabsorption cross section of A, the scaled photochemical quantum yield leading to product B, and the solar photon flux of available atmospheric radiation at the relevant altitude and zenith angle.

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

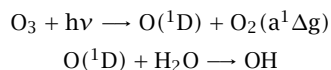
Here, $\sigma(\lambda)$ gives the absorption cross section of A at wavelength λ , $I(\lambda)$ represents the intensity of solar radiation (in photons $\text{cm}^{-2} \text{nm}^{-1} \text{s}^{-1}$) at λ , and $\phi(\lambda)$ gives the wavelength-dependent quantum yield for formation of B via photolysis.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

as well as the altitude and zenith angle dependence of the solar spectrum reaching the Earth. Representative results of calculations of J values along with the necessary values of actinic photon flux as a function of altitude and zenith angle may be found in the text by Finlayson-Pitts and Pitts [3]. Especially at high solar zenith angles, the assumed concentration and vertical distribution of ozone and the assumed number density and scattering properties of aerosols can alter critically both the magnitude of the actinic flux and its wavelength dependence. Model calculations of J values are greatly improved when observations of these quantities are available from satellite or airborne instruments. Better and more accurate measurements of molecular parameters in the laboratory and measurements of atmospheric abundance as a function of altitude and zenith angle are becoming available.

4. EXCITED ELECTRONIC STATE PHOTOCHEMICAL REACTIONS

Excitation of electronic molecular states at energies corresponding to the ultraviolet, induce chemical reaction by accessing and breaking covalent bonds [63, 64]. The discussion above briefly mentioned the excited electronic state chemistry of O₂ and O₃ and the importance of this photochemistry in atmospheric chemistry and climate. The challenge in the atmosphere, especially at lower altitudes, is the scarce flux of high energy actinic photons of wavelengths below 290 nm, which are absorbed at higher altitudes, in the stratosphere, by O₃ and O₂. Well studied examples of electronic state

chemistry of atmospheric chromophores [2-4] include O_2 , O_3 , NO_2 , chlorofluorocarbons (CFCs), NO_3 and others, important at different altitudes when appropriately energetic photons exist. Reactive radical species formed from these sun light initiated reactions go on to control atmospheric chemistry. For example, UV photolysis of ozone produces electronically excited oxygen atoms which react rapidly with water and methane to form hydroxyl radicals (OH).

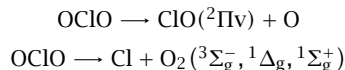


The OH radical, while only found in very low concentrations is the main oxidant expected to "clean" the atmosphere of pollutants.

The remainder of the discussion of photochemistry on excited electronic states will focus on the example of chlorine dioxide (OCIO), studied in several laboratories including our own [38-40] at the University of Colorado. This example illustrates a complex fundamental photochemical problem as the reaction evolves on multiple coupled potential energy surfaces [65] and leads to different product channels at different excitation energies and in different environments [40, 66].

Excitation of the symmetric isomer of chlorine dioxide in the near UV promotes a transition to an electronically excited state (${}^2B_1 \rightarrow {}^2A_2$) with an intense and structured spectrum (see Figure 3). Long vibrational progressions are seen in this electronic spectrum including progressions in ν_1 , the symmetric stretch and combinations with ν_2 the bending mode and even quanta of the asymmetric stretch $2\nu_3$ which are symmetry allowed. This electronic spectrum was obtained at low temperatures and high resolution using supersonic jet expansions and Fourier-Transform UV spectroscopy and analyzed to obtain information both about the excited state structure and its chemical dynamics [38, 39, 67]. In these experiments the natural linewidths suggested that the initially excited state (2A_2) couples to two others (2A_1 and 2B_2). The small coupling elements between these states allowed for a well resolved electronic spectrum which yielded both structural and dynamical information. The spectrum in Figure 2 shows vibrational structure with state lifetimes of 20 ps to 200 fs, independent of rotational level but with a strong dependence on the vibrational state. The photochemistry gleaned from this work showed that in gas phase, the asymmetric stretch is responsible for OCIO dissociation to give ClO and O and also, that combinations of the bending motion with stretching can lead to Cl and O_2 with the possible involvement of the chlorine dioxide asymmetric, reactive isomer ClOO. The energy level diagram summarizing the states involved in the near UV photochemistry of chlorine dioxide is illustrated in Figure 3. Time resolved gas phase studies have been performed to give photochemical reaction rates

for these gas phase processes [68].



The spectroscopic work was validated and expanded by product studies showing all possible products from both pathways with relative quantum yields as a function of excitation energy [69-71]. Excitation of the asymmetric stretch [71] was seen to enhance production of ClO over that of Cl while excitation of bending modes [70] was measured to enhance O_2 production. The experimental work was strongly complemented and expanded by elegant theoretical calculations [65, 72].

The partitioning between all possible product channels is a strong function of the molecule's environment [40, 73-77]. For example, the major gas phase channel leads to ClO production while in condensed phase reaction to Cl and O_2 becomes important and increases as the temperature is lowered. The condensed phase photochemistry of OCIO has been investigated in elegant time resolved and energy resolved studies making this chromophore an effective probe of the environment [66, 73, 74, 78]. The chlorine dioxide chemistry underscores the complexity of the dynamics which arise from reactions on coupled potential energy surfaces and which require sophisticated experimental and theoretical tools.

Chlorine dioxide is generated in the stratosphere primarily by reaction of ClO with BrO which themselves are formed when Cl or Br reacts with O_3 . Its concentration is greatly enhanced by the polluted polar stratosphere when heterogeneous chemistry gives rise to catalytically effective Cl and Br radicals [23, 79, 80]. The near UV spectrum described here has been used in Antarctica as a measure of stratospheric chlorine [81]. The asymmetric isomer, ClOO has been shown to be involved in catalytic ozone loss but the situation is more complex in the case of the symmetric isomer. The dominant gas phase photochemical pathway generates ClO and O which can react with O_2 and regenerate O_3 . This mechanism has no effect on ozone. By contrast, the reaction giving Cl and O_2 , to the extent and at energies where it occurs, results in net catalytic ozone loss [82]. The condensed phase photochemistry leads to ozone depletion. However, measurements of the sticking coefficient of OCIO on ice at stratospheric temperatures gave low values for this parameter making such condensed phase photoreaction unimportant in the stratosphere [83, 84].

5. GROUND ELECTRONIC STATE PHOTOCHEMICAL REACTIONS

The maximum solar flux available is in the visible red, resulting in readily available near IR and visible

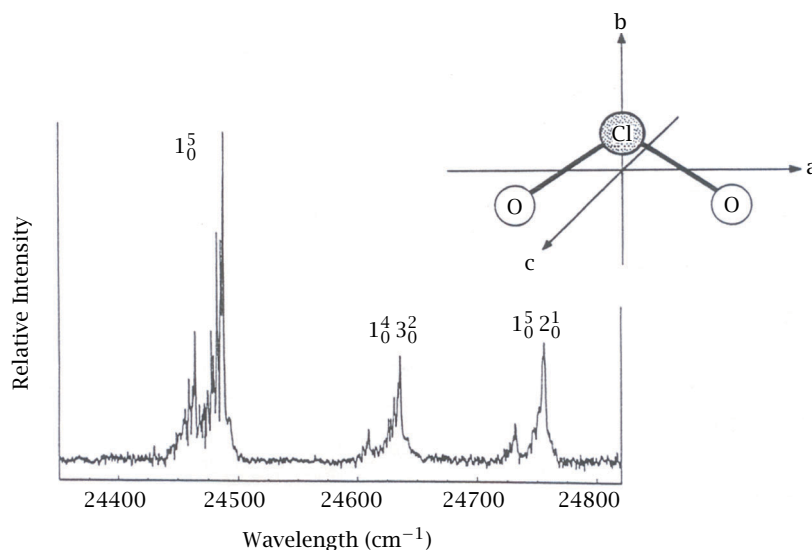


Figure 2. Spectrum of a portion of the jet-cooled OClO near UV transition [39] showing part of a progression in the symmetric stretch (1_0), bend (2_0) and asymmetric stretch (3_0).

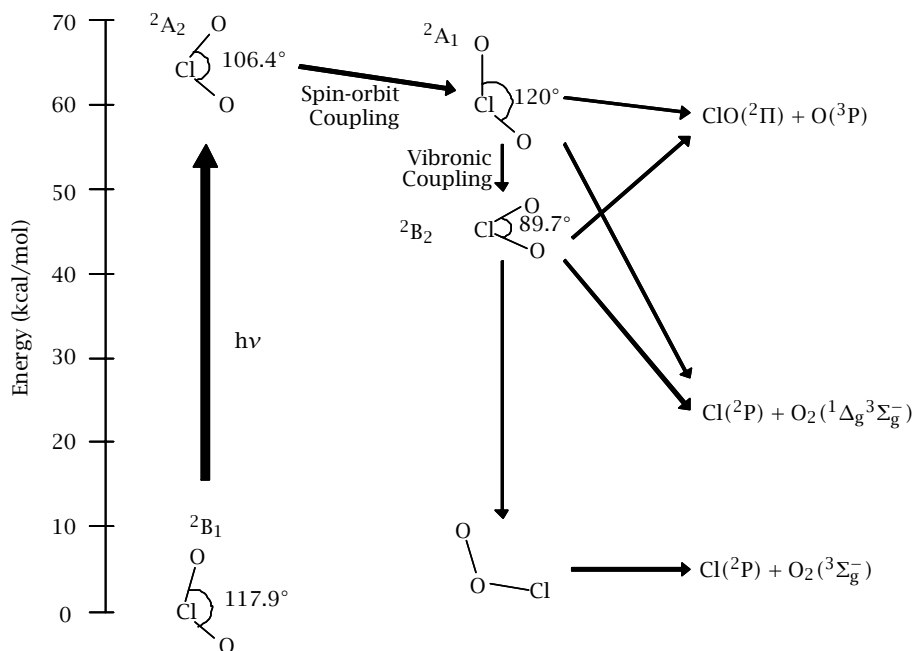


Figure 3. Energy level diagram of chlorine dioxide electronic states and isomers involved in near UV photochemistry.

radiation ($\lambda > 400$ nm). However, excitation energies corresponding to these wavelengths are below the bond dissociation energy of most covalent bonds. Very few atmospheric chromophores are able to undergo electronic state reactions, notable exceptions being O_3 and NO_3 . The present discussion will focus on chemistry in the near IR and visible ($\nu \sim 4,000 \text{ cm}^{-1}$ to $20,000 \text{ cm}^{-1}$) initiated by solar radiation through absorption of en-

ergy by vibrational overtone transitions of atmospheric chromophores [41].

Vibrational transitions have much lower cross sections than electronic states by several orders of magnitude [85, 86]. The idealized model for a molecule of a harmonic oscillator would carry no intensity in vibrational overtone transitions. However, real molecules are best described by anharmonic potentials, situation

where the $\Delta v \pm 1$ selection rule is not strictly obeyed. Consequently, in such real molecules, one can access relatively high overtones with some intensity [85, 87]. Furthermore, if the molecule contains high frequency HX (X = C, O or N) oscillators, significant excitation energies can be deposited in the ground electronic state [42, 88–93]. The examples studied by our group [41–43, 94–96] and described below are atmospheric chromophores containing OH (HNO₃ and H₂SO₄ along with organic acids and alcohols) where excitation is performed via the OH stretching vibration [41, 43, 97]. The example of HNO₃ and H₂SO₄ will be outlined.

As mentioned above, electronic cross sections are much larger than vibrational overtone cross sections. Consequently, ground electronic state photochemistry can only be important when the excited electronic state cannot be accessed by solar radiation. It is well known that vibrational excitation to high energy may initiate chemical reactions [90] with elegant studies of the specific excitation of high energy vibrational levels of H-X stretching having been performed [86–90]. This circumstance is chemically important when the molecule has a low energy threshold for reaction and the UV electronic states are inaccessible at the altitude and at the zenith angle where photochemistry is important. Figure 4 illustrates the small overlap of the electronic spectrum of HNO₃ with solar flux at two different zenith angles. The overlap is small in both cases, with the high zenith angle case illustrating the very limited probability for electronic state reaction. This is the case for all HNO_x atmospheric photochemistry [98–100].

Photochemistry relevant in the atmosphere and induced by solar pumping of OH stretching vibrational overtones has recently been described with the example of HNO₃ and HNO₄. The energetics of HNO₃ allow energy to be deposited in the molecule by overtone pumping of the thermally populated rotational states of $v = 5$ level (16165 cm^{-1}) and higher energy overtones and combinations [101–103]. The energy thus deposited in the molecule is sufficient for dissociation since the zero degree bond dissociation energy, D_0 of the HO-NO₂ bond lies at 16740 cm^{-1} . Following excitation of the localized OH stretching vibration, rapid intramolecular energy redistribution (IVR) takes place enabled by kinetic and potential couplings amongst the internal motions of the molecule. IVR redistributes energy from the OH stretch to the O-N bond which breaks to give NO₂ and OH with a strong temperature dependence.

Pernitric acid HNO₄ can dissociate with a low bond dissociation energy to form HOO and NO₂. Recent measurements of the overtone intensities produced larger than previously estimated integrated absorption cross sections for $v = 2$ (9.5 ± 1.9) $\times 10^{-19}\text{ cm}^2\text{molecule}^{-1}$, $v = 3$ (3.8 ± 1.1) $\times 10^{-20}\text{ cm}^2\text{molecule}^{-1}$ and $v = 4$ (3.0 ± 1.8) $\times 10^{-21}\text{ cm}^2\text{molecule}^{-1}$ and high quantum yield for dissociation with a strong temperature dependence

[41, 94, 104, 105]. In the example of HNO₄, the total overtone contribution to the dissociation rate is 10^{-5} s^{-1} about the same at low zenith angles as the UV photolysis rate [106, 107].

Alternative reaction pathways may exist in both cases with HNO₃ isomerization to HOONO and dissociation of HNO₄ to HONO and O₂(¹Δ) being strong possibilities [108]. Theoretical and experimental work in progress in several groups are investigating this vibrational overtone chemistry on the ground electronic potential energy surface [109].

Interest in this chemistry arose from atmospheric measurements of anomalously high OH production at high zenith angle (dusk, dawn and at the edge of the polar vortex) [95, 110–112]. At the time of the measurements, atmospheric models accounted for OH production solely by UV photolysis of ozone giving O(¹D) and further reaction of this highly reactive oxygen atom with H₂O and CH₄ to give OH. The problem was that the UV radiation necessary for this chemistry was not available at high zenith angles. Field measurements observed a spike of OH at dusk, dawn and at the edge of the polar vortex correlated with visible radiation but occurring with highly diminished UV. Solar pumping of OH vibrational overtones of HNO₃, HNO₄, and H₂O₂ could account for some of this effect [95, 106]. As a result of recent laboratory studies, it is now known that HNO₃ overtone pumping at high zenith angles contributes 10 to 20% to the J value while this process in HNO₄ contributes 20% of the maximum J value (which occurs at noon at a zenith angle of zero) [41]. Results of recent field measurements such as the 1997 POLARIS mission can be brought into agreement with model results of HO_x production when the recent laboratory cross sections for HNO_x ground electronic state photolysis are included.

Sulfuric acid, H₂SO₄, is of significance in the atmosphere as a nucleating agent for aerosols and clouds at all altitudes, influencing greatly the Earth's temperature, climate and chemistry [113, 114]. Photochemistry of H₂SO₄ had been postulated by atmospheric models [115, 116] to explain the formation of the springtime aerosol layer [117–119] and the vertical SO₂ concentration profiles [120]. The estimated UV cross sections used by atmospheric models were unrealistic analogues to the cross section of HCl and were recently proven to be erroneous. Sulfuric acid's electronic states have as yet not been observed, but are calculated to be extremely high in energy [96, 121, 122], outside the solar spectrum and therefore not important in the atmosphere. Solar pumping of the ground electronic state vibrational overtones of the OH stretch is possible [96]. However, this process, unlike the example of HNO_x, does not provide sufficient energy to break the S-O bond as the high bond dissociation energy would require at least the 9th overtone to be excited. The cross section for such high overtones is negligible. Interestingly, at

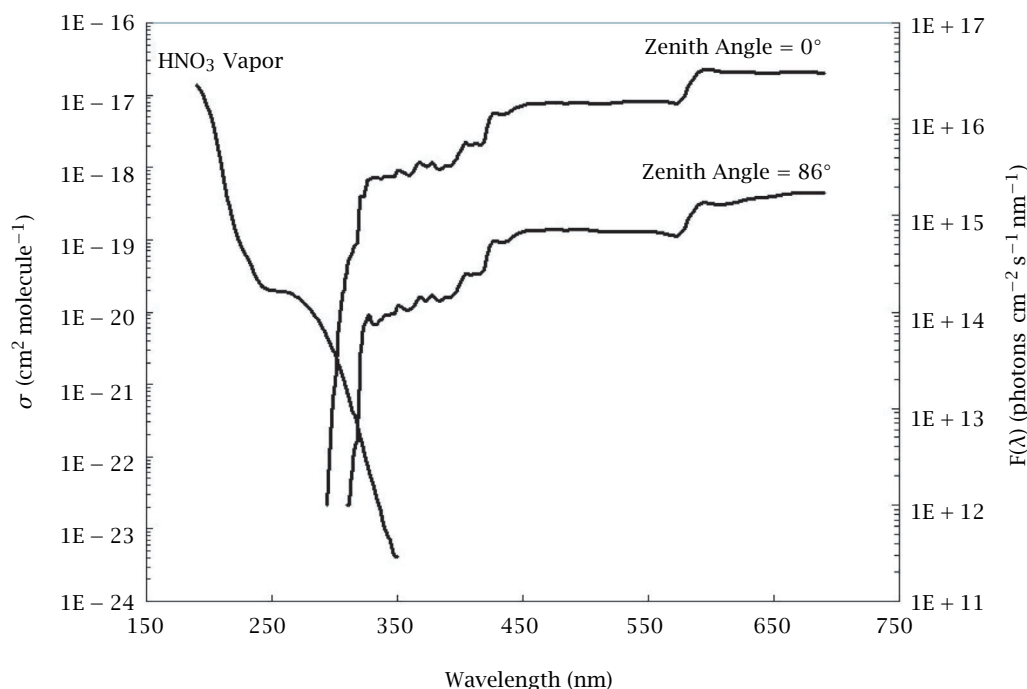
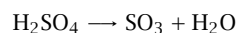


Figure 4. Low energy “tail” of the electronic spectrum of HNO_3 (left) superimposed with the solar flux at a high (sun near horizon) and low (sun overhead) zenith angle.

low energy requiring only excitation of the 4th and 5th overtone in H_2SO_4 one can access the threshold for the concerted dehydration reaction [43]:



This reaction is greatly aided (catalyzed) by the presence of additional molecules of water. The reverse reaction has been studied by both experiment [123–125] and theory [126–128] and the important role of H_2O in promoting H_2SO_4 formation had been discussed [126, 127]. The ground state photochemistry of H_2SO_4 gives an estimate for the J value of $3 \times 10^{-8} \text{ s}^{-1}$, sufficient to explain the atmospheric spring sulfate layer [117, 119] and the vertical SO_2 concentration profile [43, 120].

There are several further examples of photochemistry by solar pumping of vibrational overtones which could lead to ground electronic state photoreaction and play a role in atmospheric chemistry [129–133]. A notable example is the decarboxylation of some organic acids [41, 134, 135]. These reactions, like the example of H_2SO_4 above occur by a concerted mechanism efficiently catalyzed by water. Organic acids have photoreactive excited electronic states at wavelengths filtered by stratospheric ozone, consequently in the lower atmosphere ground electronic state reactions rather than excited electronic state chemistry is important.

6. CONCLUSIONS

The driving force for reactions in the atmosphere is provided by the Sun. Solar radiation can be described as equivalent to the emission of a blackbody at 5800 K, filtered by absorptions by atmospheric gases, aerosols and clouds. The result is a strong altitude, latitude and zenith angle dependence of the available radiation.

Most photochemical reactions require UV light as the energy of UV photons is sufficient to break covalent bonds. In the atmosphere, many important photochemical reactions occur in excited electronic states, especially at high altitude, above the ozone layer. Important examples of electronic state reactions in the atmosphere are the high altitude photolysis of O_2 , O_3 , chlorofluorocarbons, etc. In this paper, the example of OCIO [40, 129] with photoreaction involving several coupled potential energy surfaces is described to illustrate the complexity of atmospheric photoreactions.

While UV light is filtered in the mesosphere and stratosphere by O_2 and O_3 , visible and near IR radiation is available even at low altitude. Examples of ground electronic state reactions occurring by solar pumping of OH stretching vibrational overtones have been discussed above and shown to be important in the atmosphere in circumstances where UV photochemistry is inefficient. This was the case presented for the OH

stretching pumped reactions of inorganic and organic acids [41, 43] important in the atmosphere.

This review focused on gas phase photochemical reactions induced in the atmosphere by solar radiation. Interesting possibilities for both excited and ground state photochemistry in complex environments (molecular and radical complexes, condensed phases, at interfaces) have been proposed [40, 129-133] and are currently under investigation. Heterogeneous reactions are known to be important in the atmosphere yet few examples of heterogeneous photochemical reactions have been studied. In the atmosphere water and aqueous environments are important. Consequently the chemistry of hydrates, water catalyzed reactions, reactions in aqueous solutions, snow and ice and at water interfaces are targeted for future study.

ACKNOWLEDGMENT

VV would like to acknowledge support from the NSF and fellowships from the Radcliffe Institute for Advanced Study and the John Simon Guggenheim Memorial Foundation. The illustrations presented here were contributed by Teresa Williams whose help is gratefully acknowledged.

REFERENCES

- [1] R. Goody, *Principles of Atmospheric Physics and Chemistry*, Oxford University Press, Oxford, 1995.
- [2] G. P. Brasseur, J. J. Orlando, and G. S. Tyndall, *Atmospheric chemistry and global change*, Topics in environmental chemistry (B. J. W., ed.), Oxford University Press, New York, Oxford, 1999.
- [3] B. J. Finlayson-Pitts and J. N. Pitts, *Chemistry of the upper and lower atmosphere*, Academic Press, San Diego, San Francisco, New York, Boston, London, Sydney, Tokio, 1999.
- [4] R. P. Wayne, *Chemistry of Atmospheres*, Clarendon Press, Oxford, second ed., 1991.
- [5] J. N. Howard, J. I. F. King, and P. R. Gast, *Handbook of Geophysics*, Macmillan, New York, 1960.
- [6] R. A. Hanel *et al.*, *J. Geophys. Res.* **77** (1972), 2629-2641.
- [7] W.-C. Wang, M. P. Dudek, and X.-Z. Liang, *Future climates of the world: A modeling perspective* (A. Henderson-Sellers, ed.), Elsevier, Amsterdam/New York, 1995, vol. 16.
- [8] H. Rohde, *Science* **248** (1990), 1217.
- [9] V. Ramanathan, *Proc. Kon. Ned. Akad. Wetensch.* **98** (1995), 361-383.
- [10] K. N. Liou, *Radiation and cloud processes in the atmosphere*, Oxford University Press, Oxford, 1995.
- [11] J. T. Kiehl and K. E. Trenberth, *Bull. Am. Meteorol. Soc.* **78** (1997), 197-208.
- [12] IPCC, (1994).
- [13] K. S. Groves and A. F. Tuck, *Quart. J. R. Met. Soc.* **106** (1980), 125-140.
- [14] V. Ramanathan *et al.*, *Rev. Geophys.* **25** (1987), 1441-1482.
- [15] V. Ramanathan, *The changing atmosphere* (F. S. Rowland and I. S. I. Isaksen, eds.), Wiley, New York, 1988.
- [16] S. R. Weart, *Phys. Today* **50** (1997), 34-40.
- [17] J. G. Calvert and J. N. Pitts, *Photochemistry*, Wiley, New York, 1966.
- [18] R. P. Wayne, *Principles and applications of photochemistry*, Oxford University Press, Oxford, 1988.
- [19] M. J. Pilling and P. W. Seakins, *Reaction kinetics*, Oxford University Press, New York, 1995.
- [20] M. J. Molina, L. T. Molina, and D. M. Golden, *J. Phys. Chem.* **100** (1996), 12888-12896.
- [21] G. Brasseur and S. Solomon, *Aeronomy of the Middle Atmosphere*, D. Reidel Publishing Company, Dordrecht, second ed., 1986.
- [22] M. J. Molina, *Atmos. Environ.* **25A** (1991), 2535-2537.
- [23] S. Solomon, *Nature* **347** (1990), 347-354.
- [24] M. A. Tolbert, M. J. Rossi, and D. M. Golden, *Geophys. Res. Lett.* **15** (1988), 847-850.
- [25] G. L. Stephens, *Remote sensing in the lower atmosphere*, Oxford University Press, Oxford, 1994.
- [26] A. F. Tuck *et al.*, *Quart. J. R. Met. Soc.* **123** (1997), 1-69.
- [27] D. L. Albrightton, F. C. Fehsenfeld, and A. F. Tuck, *Science* **250** (1990), 75-81.
- [28] D. E. Heard and M. J. Pilling, *Chem. Rev.* **103** (2003), 5163-5198.
- [29] A. F. Tuck, R. T. Watson, and O. B. Toon, *J. Geophys. Res.* **94** (1989), 11170-11737.
- [30] A. F. Tuck, R. T. Watson, E. P. Condon, J. J. Margitan, and O. B. Toon, *J. Geophys. Res.* **94** (1989), 11181-11222.
- [31] P. O. Wennberg *et al.*, *Rev. Sci. Instr.* **65** (1994), 1858-1878.
- [32] S. C. Wofsy, R. C. Cohen, and A. L. Schmeltekopf, *Geophys. Res. Lett.* **21** (1994), 2535-2538.
- [33] G. P. Brasseur, F. Lefevre, and A. K. Smith, *Perspectives in Environmental Chemistry* (D. L. Macalady, ed.), Oxford University Press, New York, 1998.
- [34] M. J. Molina, L. T. Molina, and C. E. Kolb, *Annu. Rev. Phys. Chem.* **47** (1996), 327.
- [35] W. B. DeMore *et al.*, *Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling: Evaluation Number 9*, JPL Publication 90-1, NASA, 1990.
- [36] A. F. Tuck, *Phil. Trans. R. Soc. A* **290** (1979), 477-494.
- [37] J. A. Pyle and C. F. Roger, *Nature* **287** (1980), 711.
- [38] E. C. Richard and V. Vaida, *J. Chem. Phys.* **94** (1991), 163-171.

- [39] E. C. Richard and V. Vaida, *J. Chem. Phys.* **153** (1991).
- [40] V. Vaida and J. D. Simon, *Science* **268** (1995), 1443-1448.
- [41] D. J. Donaldson, A. F. Tuck, and V. Vaida, *Chem. Rev.* **103** (2003), 4717-4729.
- [42] D. J. Donaldson, G. J. Frost, K. H. Rosenlof, A. F. Tuck, and V. Vaida, *Geophysical Research Letters* **24** (1997), 2651-2654.
- [43] V. Vaida, D. J. Donaldson, H. G. Kjaergaard, and P. E. Hintze, *Science* **299** (2003), 1566-1568.
- [44] J. Lean, *Rev. Geophys.* **29** (1991), 505-535.
- [45] S. Mandronich, *J. Geophys. Res.* **92** (1987), 9740-9752.
- [46] S. Mandronich, *Environmental UV photobiology* (A. R. Young, ed.), Plenum, New York, 1993.
- [47] G. C. G. Waschewsky, R. Horansky, and V. Vaida, *J. Phys. Chem.* **100** (1996), 11559-11565.
- [48] T. G. Slanger and P. C. Cosby, *J. Phys. Chem.* **92** (1988), 267-282.
- [49] T. G. Slanger and R. A. Copeland, *Chem. Rev.* **103** (2003), 4731-4766.
- [50] J. B. Burkholder and R. K. Talukdar, *Geophys. Res. Lett.* **21** (1994), 581-584.
- [51] L. T. Molina and M. J. Molina, *J. Geophys. Res.* **91** (1986), 14501-14508.
- [52] J. Malicet *et al.*, *J. Atmos. Chem.* **21** (1995), 263-273.
- [53] W. B. DeMore *et al.*, *Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling: Evaluation Number 12*, JPL Publication 97-4, NASA, 1997.
- [54] Y. Matsumi and M. Kawasaki, *Chem. Rev.* **103** (2003), 4767-4782.
- [55] S. Chapman, *Mems. R. Met. Soc.* **3** (1930), 103-125.
- [56] P. J. Crutzen, *Quart. J. R. Met. Soc.* **96** (1970), 320-325.
- [57] J. Hampson, Canadian Armaments Research and Development Establishment Technical note 1738 (1964).
- [58] J. Hampson, Canadian Armaments Research and Development Establishment Technical note 1738 (1966).
- [59] H. S. Johnston, *Science* **173** (1971), 517-522.
- [60] M. J. Molina and F. S. Rowland, *Nature* **249** (1974), 810-814.
- [61] D. R. Bates and M. Nicolet, *Publ. Astron. Soc. Pacific* **62** (1950), 106.
- [62] R. S. Stolarski and R. J. Cicerone, *Can. J. Chem.* **52** (1974), 1610.
- [63] H. Okabe, *Photochemistry of Small Molecules*, Wiley, New York, 1978.
- [64] N. J. Turro, *Modern Molecular Photochemistry*, Benjamin/Cummings, Menlo Park, 1978.
- [65] K. A. Peterson, *J. Chem. Phys.* **109** (1998), 8864-8875.
- [66] P. J. Reid, *J. Phys. Chem.* **106** (2002), 1473-1482.
- [67] E. C. Richard, C. T. Wickham-Jones, and V. Vaida, *J. Phys. Chem.* **93** (1989), 6346.
- [68] T. Baumert, J. L. Herek, and A. H. Zewail, *J. Chem. Phys.* **99** (1993), 4430.
- [69] E. Ruhl, A. Jefferson, and V. Vaida, *J. Phys. Chem.* **94** (1990), 2990.
- [70] H. F. Davis and Y. T. Lee, *J. Chem. Phys.* **105** (1996), 8142-8163.
- [71] E. Bishenden and D. J. Donaldson, *J. Chem. Phys.* **105** (1993), 3129.
- [72] K. A. Peterson and H.-J. Werner, *J. Chem. Phys.* **105** (1996), 9823.
- [73] P. J. Reid, *Acc. Chem. Res.* **34** (2001), 691-696.
- [74] C. J. Pursell, J. Conyers, P. Alapat, and R. Parveen, *J. Phys. Chem.* **99** (1995), 10433-10437.
- [75] R. C. Dunn, B. N. Flanders, V. Vaida, and J. D. Simon, *Spectrochimica Acta Part a-Molecular and Biomolecular Spectroscopy* **48** (1992), 1293-1301.
- [76] I. Chorny, J. Vieceli, and I. Benjamin, *J. Chem. Phys.* **116** (2002), 8930.
- [77] C. J. Kreher, R. T. Carter, and J. R. Huber, *J. Chem. Phys.* **110** (1999), 3309.
- [78] Y. J. Chang and J. D. Simon, *J. Phys. Chem.* **100** (1996), 6406-6411.
- [79] S. Solomon, R. R. Garcia, F. S. Rowland, and D. J. Wuebbles, *Nature* **321** (1986), 755-758.
- [80] S. Solomon, *Rev. Geophys.* **26** (1988), 131-148.
- [81] S. Solomon, R. W. Sanders, M. A. Carroll, and A. L. Schmeltekopf, *J. Geophys. Res.* **94** (1989), 11393.
- [82] V. Vaida, S. Solomon, E. C. Richard, E. Ruhl, and A. Jefferson, *Nature* **342** (1989), 405.
- [83] L. A. Brown, V. Vaida, D. R. Hanson, J. D. Graham, and J. T. Roberts, *J. Phys. Chem.* **100** (1996), 3121-3125.
- [84] J. D. Graham, J. T. Roberts, L. A. Brown, and V. Vaida, *J. Phys. Chem.* **100** (1996), 3115-3120.
- [85] B. R. Henry and H. G. Kjaergaard, *Can. J. Chem.* **80** (2002), 1635-1642.
- [86] J. H. Gutow, D. Klenerman, and R. N. Zare, *J. Phys. Chem.* **92** (1988), 172-177.
- [87] L. J. Butler, T. M. Ticich, M. D. Likar, and F. F. Crim, *J. Chem. Phys.* **85** (1986), 2331-2332.
- [88] F. F. Crim, *Annu. Rev. Phys. Chem.* **35** (1984), 657-691.
- [89] F. F. Crim, *Molecular photodissociation dynamics* (M. N. R. Asfold and J. E. Baggott, eds.), Royal Society of Chemistry, London, 1987.
- [90] F. F. Crim, *J. Phys. Chem.* **100** (1996), 12725-12734.
- [91] S. K. Witonsky *et al.*, *J. Chem. Phys.* **115** (2001), 3134-3143.
- [92] S. C. Homitsky, S. M. Dragulin, L. M. Hynes, and S. Hsieh, *J. Phys. Chem. A* **108** (2004), 9492-9499.
- [93] K. R. Lange, N. P. Wells, K. S. Plegge, and J. A. Phillips, *J. Phys. Chem. A* **105** (2001), 3481-3486.

- [94] D. J. Donaldson, A. F. Tuck, and V. Vaida, *Phys. Chem. Earth*. **25** (2000), 223-227.
- [95] P. O. Wennberg *et al.*, *Geophys. Res. Lett.* **26** (1999), 1373-1376.
- [96] P. E. Hintze, H. G. Kjaergaard, V. Vaida, and J. B. Burkholder, *J. Phys. Chem. A* **107** (2003), 1112-1118.
- [97] K. J. Feierabend, D. K. Havey, and V. Vaida, *Spectrochimica Acta A* **60** (2004), 2775-2781.
- [98] J. Matthews, R. Sharma, and A. Sinha, *J. Phys. Chem. A* **108** (2004), 8134-8139.
- [99] G. Knight, A. R. Ravishankara, and J. B. Burkholder, *Phys. Chem. Chem. Phys.* **4** (2002), 1432-1437.
- [100] C. M. Roehl *et al.*, *J. Phys. Chem. A* **105** (2001), 1592-1598.
- [101] D. J. Donaldson *et al.*, *Journal of Physical Chemistry A* **102** (1998), 5171-5174.
- [102] H. Zhang, C. M. Roehl, S. P. Sander, and P. O. Wennberg, *J. Geophys. Res. Atm.* **105** (2000), 14593-14598.
- [103] S. S. Brown, R. W. Wilson, and A. R. Ravishankara, *J. Phys. Chem. A* **104** (2000), 4976-4983.
- [104] C. M. Roehl, S. A. Nizgorodov, H. Zhang, G. A. Black, and P. O. Wennberg, *J. Phys. Chem. A* **106** (2002), 3766-3772.
- [105] M. Staikova, D. J. Donaldson, and J. S. Francisco, *J. Phys. Chem. A* **106** (2002), 3023-3028.
- [106] R. J. Salawitch, P. O. Wennberg, G. C. Toon, B. Sen, and J. F. Blavier, *Geophys. Res. Lett.* **29** (2002), 1762.
- [107] J. T. Evans, M. P. Chipperfield, H. Oelhaf, M. Stowasser, and G. Wetzel, *Geophys. Res. Lett.* **30** (2003), 1223.
- [108] M. Staikova, D. J. Donaldson, and J. S. Francisco, *J. Phys. Chem. A* **106** (2002), 3023.
- [109] J. Matthews, A. Sinha, and J. S. Francisco, *J. Chem. Phys.* **120** (2004), 10543-10553.
- [110] R. C. Cohen and J. R. Murphy, *Chem. Rev.* **103** (2003), 4985-4998.
- [111] J. R. Murphy *et al.*, *Atm. Chem. Phys.* **4** (2004), 377-384.
- [112] P. O. Wennberg, *Science* **266** (1994), 398-404.
- [113] C. A. Brock, P. Hamill, J. C. Wilson, H. H. Jonsson, and K. R. Chan, *Science* **270** (1995), 1650-1653.
- [114] S.-H. Lee *et al.*, *Science* **301** (2003), 1886-1889.
- [115] M. J. Mills, O. B. Toon, and S. Solomon, *Geophys. Res. Lett.* **26** (1999), 1133-1136.
- [116] J. X. Zhao, O. B. Toon, and R. P. Turco, *J. Geophys. Res.* **100** (1995), 5215-5227.
- [117] J. M. Rosen and D. J. Hofmann, *J. Geophys. Res.* **88** (1983), 3725-3731.
- [118] J. C. Wilson *et al.*, *Geophys. Res. Lett.* **17** (1990), 361-364.
- [119] D. J. Hofmann, *Geophys. Res. Lett.* **17** (1990), 357-360.
- [120] C. P. Rinsland *et al.*, *Geophys. Res. Lett.* **22** (1995), 1109-1112.
- [121] S. J. Wrenn, L. J. Butler, G. A. Rowland, C. J. H. Knox, and L. F. Phillips, *J. Photochem. Photobiol. A. Chem.* **129** (1999), 101-104.
- [122] T. W. Robinson, D. P. Schofield, and H. G. Kjaergaard, *J. Chem. Phys.* **118** (2003), 7226-7232.
- [123] T. Reiner and F. Arnold, *Geophys. Res. Lett.* **20** (1993), 2659-2662.
- [124] C. E. Kolb *et al.*, *J. Am. Chem. Soc.* **116** (1994), 10314-10315.
- [125] E. R. Lovejoy, D. R. Hanson, and L. G. Huey, *J. Phys. Chem.* **100** (1996).
- [126] L. L. Larson, M. Kuno, and F.-M. Tao, *J. Chem. Phys.* **112** (2000), 8830.
- [127] K. Morokuma and C. Muguruma, *J. Am. Chem. Soc.* **116** (1994), 10316-10317.
- [128] M. R. Hoffmann and P. Schleyer, *J. Am. Chem. Soc.* **116** (1994), 4947-4952.
- [129] V. Vaida, D. J. Donaldson, S. J. Strickler, S. L. Stephens, and J. W. Birks, *J. Phys. Chem.* **93** (1989), 506-508.
- [130] V. Vaida, G. J. Frost, L. A. Brown, R. Naaman, and Y. Hurwitz, *Ber. Bunsenges Phys. Chem.* **99** (1995), 371.
- [131] G. J. Frost and V. Vaida, *J. Geophys. Res.* **100** (1995), 18803.
- [132] L. Brown and V. Vaida, *J. Phys. Chem.* **100** (1996), 7849-7853.
- [133] V. Vaida, H. G. Kjaergaard, and K. J. Feierabend, *Int. Rev. Phys. Chem.* **22** (2003), 203-219.
- [134] M. Staikova and D. J. Donaldson, *Phys. Chem. Earth* **26** (2001), 473-478.
- [135] M. Staikova, M. Oh, and D. J. Donaldson, *J. Phys. Chem. A* **109** (2005), 597-602.



Hindawi

Submit your manuscripts at
<http://www.hindawi.com>

