

predict each species variation with each rate parameter, along with terms for non-local effects. This procedure tracks chemically sensitive observations, and identifies steps and product ratios requiring further investigation; it can suggest field measurements, and the accuracies required of the kinetics. Key photolysis processes, H atom addition reactions to various hydrocarbon molecules and radicals, and methyl recombination to form ethane are identified. The use of kinetics rate theory approaches such as RRKM theory to provide low pressure and temperature rate constant values for these reactions will be described, noting uncertainties when relevant data are unavailable or limited.

Supported by NASA Planetary Atmospheres and NSF Planetary Astronomy Programs. D.A.N. was sponsored by an NSF Research Experiences for Undergraduates grant.

SA72A MCC: Hall D Sunday 1330h

Microscopic Processes in Solar System Atmospheres II Posters (*joint with A, P*)

Presiding: T G Slanger, SRI International; D L Huestis, SRI International

SA72A-0510 1330h POSTER

Recommended OH Vibrational Energy Transfer Rate Constants Based on Laboratory Studies

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Emission from vibrationally excited OH radicals is used to monitor the condition of the mesopause region and to trace the propagation of gravity waves through the nightglow layer. To extract information from the intensity of the emission, collisional energy transfer rate constants must be known or estimated for the temperature of the emitting layer. In addition to OH emission itself the energy from the reaction of hydrogen atoms with ozone can show up in CO₂, affecting the altitude profile of the infrared emission from this important species.¹

Laboratory studies have attempted to measure these rate constants for over forty years with varying degrees of success. In this work the rate constants for the interaction of vibrationally excited OH with the important atmospheric colliders, O₂, N₂, and O atoms will be assembled and critically evaluated. Where conflicting measurements are available a recommended value will be presented and the justification for excluding specific results outlined. Where no experimental values have been measured, best estimates will be provided based on the behavior of similar chemical systems. Estimates of the temperature dependence will be undertaken based on the limited laboratory data. The reasons and basis for the estimates will be outlined.

This research is supported by the National Science Foundation Aeronomy Program under Grant No. ATM-9909807.

M. Lopez-Puertas, R. H. Picard, M. Garcia-Comas, P. P. Wintersteiner, J. R. Winick, M. G. Mlynczak, C. J. Mertens, J. M. Russell, and L. L. Gordley, *Eos, Trans. AGU, 83(19)*, Spring Meet. Suppl. Abstract SA51A-06, 2002.

SA72A-0511 1330h POSTER

Quantum Mechanical Investigation of the O+H₂ → OH + H Reaction

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The reaction between O(³P) atoms and vibrationally excited H₂ molecules has been suggested as an important source of OH in the mesosphere. The reaction is dominated by tunneling at low temperatures and quantum mechanical calculations are needed for accurate calculation of its rate coefficient. We report quantum mechanical calculations of cross sections and rate coefficients for the O+H₂ → OH + H reaction on chemically accurate potential energy surfaces. We present rotational and vibrational energy distributions of the product OH molecule for different initial vibrational state of the reagent H₂ molecule and O(³P) atom kinetic energies.

SA72A-0512 1330h POSTER

The Role of the Quenching of O₂(1) by Atomic Oxygen on 6.3 μm Atmospheric Radiances and its Impact on the Retrieval of Water Vapour

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The high sensitivity of the new generation of atmospheric IR sounders has made the remote sensing of the upper atmosphere a reality. Emission from the high atmospheric layers is, however, quite often in non-local thermodynamic equilibrium (non-LTE). To retrieve the atmospheric parameters accurately, the excitation mechanisms of the emitting energy levels have to be well known. The emission of water vapor at 6.3 μm is one such example, that is in non-LTE above about 55-60 km. The major sources of uncertainty in this emission come from the vibrational-vibrational energy rate of transfer between H₂O(010) and O₂(1), the yield of O₂(1) from O₃ photolysis and the thermal quenching of O₂(1) by atomic oxygen. The latter has been measured only at high temperatures (1000-3500 K) until recently. Consequently, this posed a large uncertainty in H₂O(010) populations and in its 6.3 μm atmospheric emission. The recent accurate measurements of this rate at room temperature (Kalogerakis et al., 2001) allow us to retrieve H₂O in the mesosphere more accurately. We discuss in this paper the importance of this rate for the water vapor retrieval and its application to the H₂O 6.3 μm measurements currently being taken by the SABER instrument on the TIMED satellite.

SA72A-0513 1330h POSTER

Temperature Dependence of the Collisional Deactivation Processes in Excited O₂: A Probe to the Relaxation Pathways and Energetics

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Emission from electronically excited O₂ is an important component of the nightglow of the Earth and Venus. Since these emissions occur at altitudes where the temperature is significantly below room temperature, understanding the temperature dependence of collisional removal is crucial to modeling the emission. Recent results have shown an unexpectedly large variation in the removal rates for nearby vibrational levels in the a¹Δ_g, b¹Σ_g⁺, and c¹Σ_u⁻ states. As an example, the b¹Σ_g⁺ (ν = 13) removal rate constant for collisions with O₂ at 150 K is 4 to 60 times larger than that of the neighboring ν = 14 and 12 levels, respectively. Such a large discrepancy can be caused by the presence of a resonant energy transfer pathway. A difference in behavior is also seen in how the magnitude of the rate constant varies with temperature. Knowledge of this behavior helps us to achieve a better understanding of the relaxation pathways and the relevant kinetic parameters in the collisional deactivation of the highly excited levels.

The removal rates for the b¹Σ_g⁺ state ν = 14 and 15 levels by collisions with O₂ were measured to be 2.4 × 10⁻¹² cm³s⁻¹ and found to be almost independent

of temperature over the entire atmospheric range (150-300 K), which points to a deactivation process with little or no energetic barrier. However, the rates for ν = 11 and 12 at 150 K are an order of magnitude slower than those for ν = 13-15. We find that the ν = 12 rate increases by a factor of 5 going from 150 to 240 K, indicative of a relaxation process with an activation barrier of about 350 ± 120 cm⁻¹.

For the c¹Σ_u⁻ state at 155 K, the collisional removal rate constants in O₂ are (2.6 ± 0.3) × 10⁻¹¹ and (7 ± 3) × 10⁻¹¹ cm³s⁻¹ for ν = 10 and 11, respectively. As the temperature is varied between 150 and 300 K, little or no change is observed in the magnitude of these rate constants. In contrast, the rate for ν = 9 increases by more than a factor of 3 in the same temperature range, from 1.5 to 5.4 × 10⁻¹² cm³s⁻¹, perhaps indicating a process with a barrier.

These results will be compared with the collisional removal rates of other O₂ electronic states, namely ⁵Π_g and A³Σ_u⁺, and the lower vibrational levels of the b¹Σ_g⁺ state.

Overall, the magnitude of the collisional removal rate constants and their temperature dependence revealed interesting details of the specific relaxation processes. Experiments are currently underway to determine the involved relaxation pathways and energy transfer mechanisms to help explain the large differences observed from one vibrational level to the next.

This work is supported by the NASA Ionospheric, Thermospheric, and Mesospheric Physics, Supporting Research & Technology, and the Planetary Atmospheres Programs. KVC is grateful for a NSF-REU scholarship under Grant No. PHY-0097861, and ELS thanks the Camille and Henry Dreyfus Foundation for support of a summer internship.

SA72A-0514 1330h POSTER

Theoretical and Experimental Studies of O-CO₂ Collisions

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Infrared emissions near 15 μm from bending-mode vibrationally excited carbon dioxide molecules control the rates of radiative cooling in key altitude regions of the upper atmospheres of Venus, Earth and Mars. The critical limiting process is excitation of CO₂(ν₂) in collisions with atomic oxygen. Laboratory measurements suggest rate coefficients about 3 times smaller than the values preferred by modelers.

Our theoretical investigations have developed improved potential energy surfaces for O + CO₂. A Diatomics-in-Molecules approach combines O-O and O-C repulsion and dispersion interactions, modeled by *ab initio* potential energy curves of the ArO molecule, with electrostatic interactions of the oxygen atom quadrupole moment with fractional charges on the CO₂ molecule, corresponding to its permanent quadrupole and instantaneous dipole moments. Nonadiabatic matrix elements are calculated by integrals over products of bending wavefunctions versus the CO₂ bond angle. Spin-orbit coupling is explicitly included. Results of Landau-Zener calculations will be presented. Calibration with *ab initio* O-CO₂ potential energy surfaces as well as quasiclassical trajectory calculations are underway.

The experimental approach is based on 248-nm photodissociation of ozone, followed by energy transfer of O(¹D) to CO₂(ν₂), whose time evolution is followed by resonance-enhanced multiphoton ionization (REMPI). Preliminary work on the CO₂ REMPI spectrum will be presented.

Supported by the NASA Planetary Atmospheres Program.

SA72A-0515 1330h POSTER

Diurnal Variations of Energetic O(3P) and O(1D) Atoms in the Thermosphere and Mesosphere

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Diurnal variations of energy distributions of hotO(3P) and O(1D) atoms in the thermosphere and the upper mesosphere are investigated. The rate of atmospheric heating by hot oxygen atoms and non-equilibrium rates of atmospheric chemical reactions involving O(3P) and O(1D) atoms are calculated using non-thermal distributions of oxygen atoms. The non-Maxwellian energy distributions of the ground state and metastable oxygen atoms are determined by solutions of the coupled kinetic equations describing the energy relaxation of the fast O atoms in elastic and quenching collisions with the ambient gas. Quenching collisions of metastable oxygen atoms with N₂, O₂ and O are secondary sources of energetic O(3P) atoms. Relative fractions of metastable atoms in non-thermal distributions are calculated and compared with results of previous modeling.

SA72A-0516 1330h POSTER

The Response of the Martian Thermosphere/Ionosphere to Enhanced Fluxes of Soft X Rays

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We investigate the response of the thermosphere/ionosphere of Mars to enhanced fluxes of solar soft x rays, as have been measured by the SNOE satellite and the SEE instrument on TIMED. We model the Martian upper atmosphere for both high and low solar activities, with fluxes from both Hinteregger and Tobiska. We find that the lower peak in the electron density profile is increased, especially at high solar activity. The odd nitrogen densities in the lower thermosphere are enhanced, but the NO densities remain relatively constant. Only the N densities are significantly larger. Thus larger fluxes of solar soft x rays cannot account for the large NO densities measured by Viking 1 below 140 km, but can account for the often prominent peak seen below the main ionospheric peak by the MGS radio occultation measurements.

SA72A-0517 1330h POSTER

Sources of 5.3 μm emission from NO observed by SABER

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The SABER (Sounding of the Atmosphere by Broadband Emission Radiometry) instrument aboard the TIMED (Thermosphere, Ionosphere, Mesosphere, Energetics and Dynamics) satellite has made spectacular observations of emission from NO around 5.3 μm under diverse geophysical conditions. This fundamental vibration-rotation band emission from vibrationally excited NO in the terrestrial thermosphere may be produced by the inelastic collisions of the ground state NO with O, and also by the highly rotationally and vibrationally excited NO resulting from the reaction of N(⁴S) and N(²D) atoms with O₂. While the 5.3 μm emission resulting from the inelastic process is always there, that due to chemiluminescent processes may be very strong or may be entirely absent depending upon the geophysical conditions. In this talk we quantitatively calculate the source of 5.3 μm emission transmitted by the SABER filter as function of altitude for a few geophysical parameters. We also give the contributions of these sources as a function of tangent height to compare our calculations with the SABER observations so that these impressive observations may of greater use to the scientific community.

SA72A-0518 1330h POSTER

Oxygen Molecular Spectroscopy: The Impact of Astronomical Sky Spectra

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Astronomical sky spectra obtained at the W. M. Keck Observatory on Mauna Kea have greatly increased our knowledge of the spectroscopy of the O₂ molecule. In the past, high-resolution studies on O₂ have been largely limited to absorption measurements from the ground state, and those electronic states and vibrational levels that can not be accessed in that way have essentially not been studied. We will review the new nightglow data in this presentation. Included are the following cases, where measurements are made with an instrumental resolution of about 40,000:

- 1) O₂(X³Σ_g⁻), v = 0-15, J = 0-25 (much higher for v = 0,1)
- 2) O₂(a¹Δ_g), v = 1-10, J = 2-25
- 3) O₂(b¹Σ_g⁺), v = 0-15, J = 0-25 (much higher for v = 0,1)
- 4) O₂(A³Δ_u, [Ω=3]), v = 2-10, J = 2-25

We also find it possible to carry out spectroscopy on the b-X 0-0 band from the ground, the atmosphere being relatively transparent to high-J lines originating in the ionosphere. In addition, a new O₂ emission system has been discovered, the c¹Σ_u⁻ - b¹Σ_g⁺ bands. There has been a synergistic effect of the existence of such data on laboratory studies, where information is now available for both the a¹Δ_g and b¹Σ_g⁺ states in the v = 10-25 range, not only in terms of spectroscopy, but also for removal rate coefficients and reaction pathways.¹

We are grateful to the various astronomers who have shared their Keck sky spectra with us. This study has been supported by the NSF Aeronomy program.

¹K S Kalogerakis, A Totth, P C Cosby, T G Slanger, and R A Copeland, Laboratory studies of the production of highly vibrationally excited O₂(a¹Δ_g and b¹Σ_g⁺) from O₂(A³Σ_u⁺) relaxation, Eos Trans. AGU 81, F944 (2000).

SA72A-0519 1330h POSTER

The Far-Ultraviolet Emission From SO₂ by Electron Impact

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The auroral FUV observations of IO by the Space Telescope Imaging Spectrograph (STIS) on board the Hubble Space Telescope (HST) revealed strong emission features of atomic sulfur and atomic oxygen. For the purpose of interpreting these observations laboratory studies of electron-impact UV emission spectrum of S and O bearing species become necessary. Electron-impact UV emission spectrum of SO₂ has been studied from 1250 - 1490 Å at high resolution (0.1 Å) using 100 and 30eV electrons. The laboratory spectrum emitted by dissociatively excited atomic sulfur from SO₂ has been compared with HST STIS observations for IO and also with the model spectrum of electron excitation of atomic Sulfur. FUV emission cross sections have been established for fine structure spectral lines of neutral and ionic O and S produced by collision of 100 and 30eV electrons with SO₂ molecules.

SA72A-0520 1330h POSTER

VUV Photoabsorption Cross Section Measurements of Carbon Dioxide in Support of Analyses of Planetary Atmospheres

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We report preliminary measurements of carbon dioxide photoabsorption cross sections in the 106 to

120 nm region. CO₂ is the principal constituent of the atmospheres of Mars and Venus. Its dissociation by ultraviolet solar radiation initiates the production of non-thermal atoms that may escape these atmospheres, and leads, through further photochemistry, to ultraviolet and visible airglow features. The analyses of recent high-quality VUV observations of emission features in the Martian atmosphere and the modeling of non-thermal escape mechanisms from the Martian and Venusian atmospheres are limited by poorly and incompletely characterized CO₂ VUV photoabsorption cross sections.

We recently tested the feasibility of a new measurement program for CO₂ absorption cross sections in the 91 to 120 nm region at 295 K and 195 K. Our preliminary results for the 106 to 120 nm region derive from that feasibility study. Our measurements, at a resolution of 0.05 nm, were carried out on the 3-meter normal-incidence vacuum monochromator on the BL-20A beam line at the Photon Factory synchrotron facility in Tsukuba, Japan. Two points are evident from the preliminary spectra: (a) there is significant spectral structure in the CO₂ absorption cross section that is not resolved in earlier lower-resolution work, and (b) there is clear evidence of systematic underestimation of peak absorption cross sections for the strongest CO₂ features in the existing literature - a consequence of inadequate instrumental resolution.

SA72B MCC: Hall D Sunday 1330h

Ionosphere-Thermosphere Modeling Posters (joint with SM)

Presiding: H F Parish, University of California, Los Angeles; A G Burns, National Center for Atmospheric Research

SA72B-0521 1330h POSTER

Nonlinear Energy Transfer from Linear Right-hand polarized Instabilities to Left-handed waves

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It is shown that an ion-beam plasma electromagnetic right-hand polarized instability can be stabilized at the expense of nonlinear growth of left-hand polarized waves. In other words, due to nonlinear effects, left-hand polarized Alfvén or ion-cyclotron waves can grow even when the system is left-hand polarized linearly stable. This phenomenon constitutes a nonlinear dissipation mechanism for right-hand polarized instabilities.

SA72B-0522 1330h POSTER

Structuring of full plasma patches in the high latitude with realistic drives-continued.

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The robustness of plasma patches, in spite of structuring by a combination of gradient drift and secondary Kelvin-Helmholtz (KH) instabilities, has been attributed to the strong stabilizing influence of dynamics of electrons along the field line and the break-up of the gradient drift instability driven fingers by secondary KH instabilities. Another physical effect that contributes significantly to the robustness of the patch is the variability of the convection of the patch over the polar cap region. Recently we have developed a parallel version of our 3D code, which can run on the IBM SP. We will present results of a set of runs with realistic convective drives obtained from MHD simulations of real event studies of substorms. The goal is to develop a database to provide statistical information on the nature of structuring in high latitude plasma patches. We are also developing diagnostic capabilities to compare with reconstructed images of the 3D transverse as well as parallel structure of the irregularities.

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