GROUND-BASED DIRECT ACCESS TO MARTIAN OZONE THROUGH INFRARED HETERODYNE SPECTROSCOPY

K. E. Fast, T. Kostiuk, *NASA's Goddard Space Flight Center, Greenbelt, MD, USA (Kelly.E.Fast@nasa.gov),* **T. Hewagama**, *University of Maryland, College Park, MD, USA*, **T. A. Livengood**, *Sagan Center, Washington, DC, USA.*

Introduction:

Ozone is an observable tracer of odd hydrogen (HO_X) species important to the chemistry and stability of the atmosphere of Mars, and ozone measurements are used to test models of Martian atmospheric chemistry. Infrared heterodyne spectroscopy ($\lambda/\Delta\lambda \geq 10^6$) is currently the only technique that provides direct access to Martian ozone absorption line shapes from the surface of the Earth. The high spectral resolution allows Martian ozone lines to be measured when they are Doppler shifted away from their terrestrial counterparts into regions of higher telluric transmittance.

Total ozone column abundances were obtained from various latitudes and orbital positions (Table 1) on Mars between 1988 and 2003. Those ozone measurements are compared with contemporaneous water vapor measurements and with predictions of photochemistry in order to test the understanding of Martian atmospheric chemistry.

IR Heterodyne Ozone Measurements:

Instrumentation. Spectroscopic measurements of ozone features on Mars were acquired with the NASA/Goddard Space Flight Center Infrared Heterodyne Spectrometer [IRHS, Kostiuk and Mumma, 1983; Kostiuk, 1994] between 1988-1999 and with the Heterodyne Instrument for Planetary Wind and Composition [HIPWAC, Schmülling *et al.* 1999] in 2003 at the NASA Infrared Telescope Facility (IRTF) on Mauna Kea, Hawai'i.

The heterodyne technique involves mixing 9.7 μm infrared signal from Mars with infrared signal from a frequency-stabilized $^{16}O^{12}C^{16}O$ gas laser local oscillator (LO). The two signals are focused together onto a liquid nitrogen-cooled HgCdTe photomixer, providing a radio-frequency (RF) signal at the absolute difference frequency between the source and the laser frequency. The frequency and the intensity information of the infrared spectrum are preserved in this beat frequency spectrum. The source signal is chopped with an in-system ("on-the-table") chopper or the telescope wobbling secondary mirror for synchronous detection of the difference between the source and background sky. A local blackbody source provides the system intensity calibration, verified with direct measurements of continuum emission from the Moon. RF filter banks or an acousto-optic spectrometer (AOS) are used to analyze the RF beat-frequency signal, providing high spectral resolution in excess of 10^6.

Observations. Target ozone features in the 9.7 μm are chosen so that the relative velocity of Mars and Earth Doppler shifts the Martian ozone features away from their terrestrial counterparts into regions of higher telluric transmittance. Observations were made during periods detailed in Table 1 at various latitudes on Mars with a beam that covered ~10° of latitude in most cases (~15° at high latitudes). The pointing was maintained at a constant Mars local time, and each spectrum covers ~20°-40° of longitude on Mars.

Table 1. IR Heterodyne Ozone Observations of Mars

L_S	UT Date	Northern Martian Season
40°	14-16 Feb 1993	Mid-Spring
74°	17-23 Mar 1995	Late Spring
102°	4-7 Jul 1993	Early Summer
115°	24-29 Mar 1999	Early Summer
202°	10-16 Jun 2003	Early Autumn
208°	3-7 Jun 1988	Early Autumn
291°	1-3 Nov 2003	Early Winter

Data Reduction and Analysis. Spectra are assembled by co-adding scans according to their date of observation and position on Mars. The resulting spectra contain features of both Earth and Mars, so observations of the telluric absorption spectrum taken against the Moon [Fast *et al.* 2004] are used to characterize the telluric contribution for removal from the Martian spectra. The Martian components of the spectra are modeled using the radiative transfer package BEAMINT [Hewagama *et al.* 1998] and the terrestrial components are generated and fine-tuned through calls to GENLN2 [Edwards 1992].

A Martian CO_2 line is present in the instrument bandpass along with the ozone features. The fully-resolved Martian CO_2 absorption line shape is sensitive to the combination of surface temperature, surface pressure, and atmospheric temperature profile. The surface pressure is externally constrained [Tillman *et al.* 1993] using surface altitudes from MGS-MOLA [D. E. Smith *et al.* 2001]. Initial thermal profiles and surface temperatures are from MGS-TES [M. D. Smith *et al.* 2001] and are iteratively modified in the fitting process until a best fit to the CO_2 line shape is achieved. The final fit parameters ultimately deviate somewhat from the MGS results because of local time and pointing variations, and this thermal information is important for accurate ozone abundance retrieval.

IR heterodyne measurements probe ozone column abundance down to the surface, and retrieved column abundances are not strongly affected by reasonable variations to a constant-with-height ozone distribution [Fast 2005]. A constant-with-height ozone mole fraction is therefore assumed in the model, modified by a fitted multiplicative factor. A data calibration factor is also allowed to vary in the fitting process to account for calibration and tracking uncertainty, seeing and telluric transmittance variation. This allows the fully-resolved line shapes themselves to drive the modeling of the Martian atmospheric parameters.

The shape and depth of the measured CO_2 line can indicate the presence of large amounts of dust. These measurements at 9.7 μm are not strongly sensitive to normal amounts of dust. Possible extinction greater than 10-20% was not evident in the CO_2 lines shapes and retrieved surface temperatures for any of the observing campaigns. Uncertainties in dust extinction are smaller than derived errors (≥20%) in the ozone abundance from the IR heterodyne measurements.

The 1σ uncertainties on retrieved ozone column abundances reflect correlations with the other parameters (atmospheric and surface temperature, calibration factor, telluric ozone and CO_2) as well as the variance between the observed and model spectra. Displayed uncertainties are therefore more conservative representations of the accuracies of the retrievals than uncertainties in ozone abundance when the other parameters are held fixed. The column abundances themselves are integrated above the local topography on Mars.

IR Heterodyne Ozone Measurements Applied: *Ozone/Water Vapor Anticorrelation and Vertical Distribution.* Example IR heterodyne ozone column densities from L_S=115° (March 1999) are displayed in Fig. 1, along with contemporaneous water vapor column densities from MGS-TES [M. D. Smith *et al.* 2001, Smith 2004]. Spatial anticorrelation of the two species is clearly evident. This is expected by photochemistry, as water vapor photolysis provides odd hydrogen that destroys ozone.

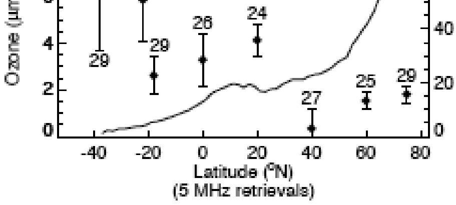

Fig. 1. IR heterodyne ozone retrievals and uncertainties at L_S=115° (March 1999) with contemporaneous water vapor measurements from MGS-TES [M. D. Smith *et al*. 2001, Smith 2004]. Demonstrated is here is spatial anticorrelation of ozone with water vapor.

Spatial and orbital anticorrelation is consistently seen between all heterodyne data sets and contemporaneous water vapor measurements, but the degree of anticorrelation varies. This lack of consistent strict anticorrelation may have to do with the vertical distribution of the species. The orbital variability of the water vapor saturation altitude [e.g. Clancy and Nair 1996, Clancy *et al.* 1996a, Lefévre *et al.* 2004] points to the need to measure the vertical distribution of ozone in order to study its response to the water vapor profile and to understand the degree of anticorrelation of total column abundance.

Since different altitudes (pressures) contribute to different parts of the ozone line shape, fully-resolved IR heterodyne ozone spectra can probe the vertical profile of ozone through targeted measurements. Measurements of $O_2(^1\Delta)$ dayglow emission indirectly probe ozone above ~20 km [e.g. Krasnopolsky 2003, Novak *et al.* 2002]. These in combination with IR heterodyne measurements that are sensitive to the total column can be used to investigate the vertical profile of ozone [Fast 2005].

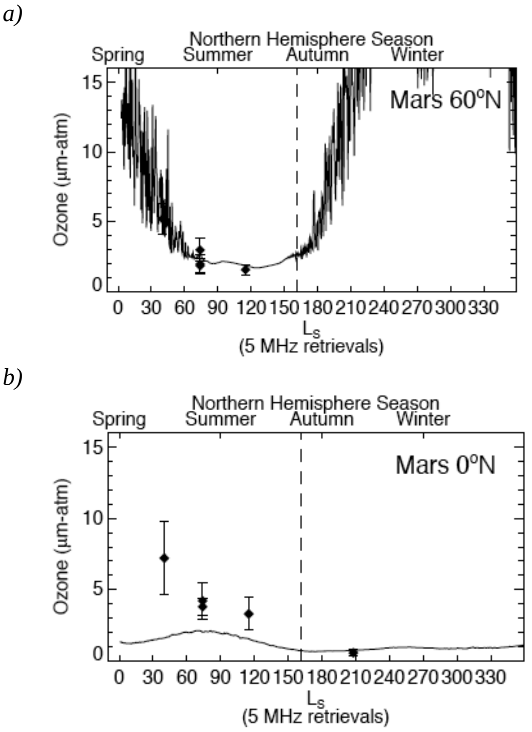

Fig. 2. IR heterodyne ozone column abundances and uncertainties at 60°N (a) and 0°N (b) shown with model abundances from the three-dimensional photochemical model of Lefèvre *et al.* [2004] (0° longitude, 12:00 local time). The dotted line divides the aphelion (left) and perihelion (right) periods, with aphelion at L_S=71° and perihelion at L_S=251°.

Testing Photochemical Models. Ozone abundance is sensitive to the abundance of chemically active odd hydrogen species, therefore ozone measurements provide an important constraint for photochemical models. IR heterodyne ozone measurements were compared to predictions of the first three-dimensional Martian photochemical model of Lefèvre *et al.* [2004]. Orbital behavior at example latitudes is shown in Fig. 2. The model and measurements show excellent agreement at latitudes from 60°N to 40°S during orbital periods around perihelion. Excellent agreement is also seen at high latitudes during orbital periods around aphelion, but at low latitudes the model underestimates ozone abundance compared to the measurements. Lefèvre *et al.* [2004] note a similar disagreement when comparing with a smaller set of observations.

The disagreement between the model and measurements at low latitudes around aphelion is an important clue to possible processes not included in the model. The gas-phase model does not include heterogeneous chemistry. Water ice clouds have been observed at low latitudes around aphelion [e.g. Smith 2004] and may provide a heterogeneous sink for odd hydrogen, allowing ozone abundance to rise above that predicted by the gas-phase model. The addition of heterogeneous chemistry to the model may bring the low latitude aphelion abundances into closer agreement with measurements.

Comparison to UV Measurements. Other than the IR heterodyne measurements detailed here, direct observations of ozone have been made exclusively through UV techniques above Earth's atmosphere. A comparison of ozone abundance retrieved through two very different means is a useful test of both techniques.

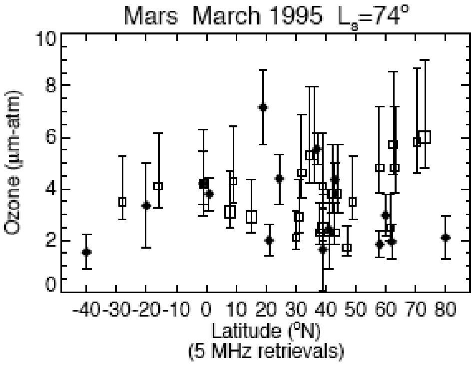

Fig. 3. Example comparison of IR heterodyne ozone measurements (filled diamonds) and HST UV measurements (open squares) [Clancy *et al.* 1996, 1999] with quoted accuracies. The two techniques show overall consistency here at L_S=74° and during other seasons.

IR heterodyne observations were compared with UV measurements from HST [Clancy *et al.* 1996, 1999]. An example comparison is shown in Fig. 3, and the two techniques show overall consistency during all orbital periods compared.

Conclusions:

Ozone is an important tracer of odd hydrogen chemistry, and IR heterodyne spectroscopy provides a ground-based means for directly measuring Martian ozone abundance. We have detailed the technique and have compared IR heterodyne ozone column abundances to contemporaneous water vapor measurements and to ozone abundances predicted through photochemical modeling. Contemporaneous and seasonal/orbital comparisons of ozone measurements from IR heterodyne spectra and from HST UV observations show good agreement.

Spatial and seasonal anticorrelation is seen in the IR heterodyne ozone and contemporaneous water vapor column abundances. However, the quantitative behavior of total ozone abundance did not show the same degree of variation as the water vapor. This and the variability of the hygropause altitude with orbital position suggest that the vertical distribution of the constituents is important to photochemical processes and the accurate interpretation of measured data by all methods and the optimization of atmospheric models of Mars. Fully-resolved IR heterodyne line shapes have the potential to probe the vertical distribution of ozone down to the surface on their own and in combination with $O_2(^1\Delta)$ measurements.

The IR heterodyne ozone measurements were compared to the spatial and seasonal/orbital variability of ozone predicted by the first three-dimensional gas-phase photochemical model of the Martian atmosphere [Lefèvre *et al.* 2004]. Observed and model ozone abundances show good agreement at all measured latitudes at perihelion orbital positions. Observed low-latitude ozone abundances are significantly higher than those predicted by the model at aphelion orbital positions. This clue points to the need to add heterogeneous processes to the gas-phase model. Low latitude water ice clouds observed around aphelion may provide a heterogeneous sink for odd hydrogen. Inclusion of heterogeneous chemistry would decrease odd hydrogen available for destroying ozone and increase low-latitude ozone abundance in the model, bringing it into closer agreement with observations.

Ozone has been shown to be an important tool for tracing odd hydrogen chemistry and for validating photochemical models of the Martian atmosphere that make specific spatial, orbital/seasonal, and diurnal predictions. Such models require a very extensive pool of observations in light of the observed variability of ozone abundance. IR heterodyne spectroscopy is an important technique for studying ozone on Mars, and it can enable long-term ground-based studies of Martian atmospheric chemistry and stability and can serve as a useful consistency check for spacecraft data.

The Mars Express instrument SPICAM [Bertaux *et al.* 2000] is conducting the first long-term study of ozone from orbit since Mariner 9. IR heterodyne spectroscopy can provide an important test of those results, complement such spacecraft campaigns, and provide long-term ground-based monitoring when spacecraft data are unavailable

References:

Bertaux, J. -L., D. Fonteyn, O. Korablev, E. Chassefière, E. Dimarellis, J. P. Dubois, A. Hauchecorne, M. Cabane, P. Rannou, A. C. Levasseur-Regourd, G. Cernogora, E. Quemerais, C. Hermans, G. Kockarts, C. Lippens, M. De. Maziere, D. Moreau, C. Muller, B. Neefs, P. C. Simon, F. Forget, F. Hourdin, O. Talagrand, V. I. Moroz, A. Rodin, B. Sandel, and A. Stern 2000. The study of the Martian atmosphere from top to bottom with SPICAM light on Mars Express. *Planet. Space Sci*. **48**, 1303-1320.

Clancy, R. T., A. W. Grossman, M. J. Wolff, P. B. James, D. J. Rudy, Y. N. Billawala, B. J. Sandor, S. W. Lee and D. O. Muhleman 1996*a*. Water vapor saturation at low altitudes around Mars aphelion: A key to Mars climate? *Icarus* **122**, 36-62.

Clancy, R. T. and H. Nair 1996. Annual (perihelioin-aphelion) cycles in the photochemical behavior of the global Mars atmosphere. *Journal Geophys. Res.* **101**, 12,785-12,790.

Clancy, R. T., M. J. Wolff, and P. B. James 1999. Minimal aerosol loading and global increases in atmospheric ozone during the 1996-1997 Martian northern spring season. *Icarus* **138**, 49-63.

Clancy, R. T., M. J. Wolff, P. B. James, E. Smith, Y. N. Billawala, S. W. Lee, and M. Callan 1996*b*. Mars ozone measurements near the 1995 aphelion: Hubble Space Telescope ultraviolet spectroscopy with the Faint Object Spectrograph. *Journal Geophys. Res.* **101**, 12,777-12,783.

Edwards, D. P. 1992. GENLN2: A general line-by-line atmospheric transmittance and radiance model: Version 3.0 description and users guide, Rep. NCAR/TN-367+STR, Natl. Cent. for Atmos. Res., Boulder, Colorado.

Fast, K. E. Mars ozone abundances from infrared heterodyne spectra and their application to study of the stability of the Martian atmosphere. Ph.D. dissertation, University of Maryland, 2005.

Fast, K. E., T. Kostiuk, F. Espenak, T. A. Livengood, T. Hewagama, and M. F. A'Hearn 2004. Stratospheric ozone profiles from Mauna Kea, Hawai'i (19.8°N, 155.5°W) using infrared heterodyne spectroscopy, 1988-2003, *Geophys. Res. Lett*. **31**, L08109, doi:10.1029/2004GL019443.

Fast, K. E., T. Kostiuk, F. Espenak, J. Annen, D. Buhl, T. Hewagama, M. F. A'Hearn, T. A. Livengood, G. Sonnabend and F. Schmülling 2005. Ozone abundance on Mars from infrared heterodyne spectra I: Acquisition, retrieval, and anticorrelation with water vapor. *Icarus,* submitted.

Hewagama, T., J. Goldstein, D. Buhl, F. Espenak, K. Fast, T. Kostiuk, T. A. Livengood 1998. Spectral line analysis for planetary atmospheric dynamics retrieval, *BAAS* **#30**, #41.P11.

Kostiuk, T. 1994. Physics and chemistry of upper atmospheres of planets from infrared observations. *Infrared Phys. Technol.* **35**, 243–266.

Kostiuk, T., and M. J. Mumma 1983. Remote sensing by IR heterodyne spectroscopy. *Appl. Opt. 17*, 2644-2654.

Krasnopolsky, V. A. 2003. Mapping of Mars O_2 1.27 μm dayglow at four seasonal points. *Icarus* **165**, 315-325.

Lefèvre, F., S. Lebonnois, F. Montmessin, F. Forget 2004. Three-dimensional modeling of ozone on Mars. *J. Geophys. Res*., **109**, E07004, doi:10.1029/2004JE002268.

Novak, R. E., M. J. Mumma, M. A. DiSanti and N. Dello Russo 2002. Mapping of ozone and water in the atmosphere of Mars near the 1997 aphelion. *Icarus* **158**, 14-23.

Schmülling, F., T. Kostiuk, D. Buhl, P. Rozmarynowski, K. Segal, T. Livengood and T. Hewagama 1999. A new infrared heterodyne instrument for measurements of planetary wind and composition. *BAAS*, DPS meeting **#31**, #08.03

Smith, D. E., M. T. Zuber, H. V. Frey, J. B. Garvin, J. W. Head, D. O. Muhleman, G. H. Pettengill, R. J. Phillips, S. C. Solomon, H. J. Zwally, W. B. Banerdt, T. C. Duxbury, M. P. Golombek, F. G. Lemoine, G. A. Neumann, D. D. Rowlands, O. Aharonson, P. G. Ford, A. B. Ivanov, P. J. McGovern, J. B. Abshire, R. S. Afzal and X. Sun 2001. Mars Orbiter Laser Altimeter (MOLA): Experiment summary after the first year of global mapping of Mars, *J. Geophys. Res.,* **106**, 23,689-23,722.

Smith, M. D. 2004. Interannual variability in TES atmospheric observations of Mars during 1999-2003. *Icarus* **167**, 148-165.

Smith, M. D., J. C. Pearl, B. J. Conrath, and P. R. Christensen 2001. Thermal Emission Spectrometer results: Mars atmospheric thermal structure and aerosol distribution. *J. Geophys. Res* **106**, 23,929-23,945

Tillman, J. E., N. C. Johnson, P. Guttorp, D. B. Percival 1993. The Martian annual atmospheric pressure cycle – Years without great dust storms. *J. Geophys. Res* **98**, 10,963-10,971.