

# Ozone abundance on Mars from infrared heterodyne spectra II. Validating photochemical models

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## Abstract

Ozone is an important observable tracer of martian photochemistry, including odd hydrogen ( $\text{HO}_x$ ) species important to the chemistry and stability of the martian atmosphere. Infrared heterodyne spectroscopy with spectral resolution  $\geq 10^6$  provides the only ground-based direct access to ozone absorption features in the martian atmosphere. Ozone abundances were measured with the Goddard Infrared Heterodyne Spectrometer and the Heterodyne Instrument for Planetary Wind and Composition at the NASA Infrared Telescope Facility on Mauna Kea, Hawai'i. Retrieved total ozone column abundances from various latitudes and orbital positions ( $L_S = 40^\circ, 74^\circ, 102^\circ, 115^\circ, 202^\circ, 208^\circ, 291^\circ$ ) are compared to those predicted by the first three-dimensional gas phase photochemical model of the martian atmosphere [Lefèvre, F., Lebonnois, S., Montmessin, F., Forget, F., 2004. *J. Geophys. Res.* 109, doi:10.1029/2004JE002268. E07004]. Observed and modeled ozone abundances show good agreement at all latitudes at perihelion orbital positions ( $L_S = 202^\circ, 208^\circ, 291^\circ$ ). Observed low-latitude ozone abundances are significantly higher than those predicted by the model at aphelion orbital positions ( $L_S = 40^\circ, 74^\circ, 115^\circ$ ). Heterogeneous loss of odd hydrogen onto water ice cloud particles would explain the discrepancy, as clouds are observed at low latitudes around aphelion on Mars.

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## 1. Introduction

The early work of Parkinson and Hunten (1972) and McElroy and Donahue (1972) demonstrated the importance of odd hydrogen species ( $\text{HO}_x$ ) to the chemistry and stability of the 95%  $\text{CO}_2$  atmosphere of Mars. Carbon dioxide is dissociated through photolysis into CO and O, and the odd hydrogen

species OH can react with CO to catalytically form  $\text{CO}_2$  at a rate that is orders of magnitude faster than the direct, spin-forbidden recombination of CO and O. Odd hydrogen species result from water vapor photolysis and play vital roles in photochemical models of the long-term stability of the  $\text{CO}_2$  atmosphere and the short-term chemistry of minor species. Observations of conditions and constituent abundances on Mars are important for testing those models, and the richer and more varied the available data, the greater the burden models must bear to reproduce those conditions. Other than recent detections of hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) (Clancy et al., 2004; Encrenaz et al., 2004), odd hydrogen species have not themselves been directly observed. However, ozone is destroyed by odd hydrogen species and can serve as an important observable for testing and constraining models that simulate the photochemistry of the atmosphere of Mars.

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Ozone is formed through the three-body reaction of O and O<sub>2</sub> that result from CO<sub>2</sub> photolysis and subsequent chemistry. During the daytime, ozone is considered to be in photochemical equilibrium. Photolysis is not a permanent sink for ozone because the atomic oxygen produced can eventually recombine with O<sub>2</sub> to reform ozone. Odd hydrogen species react with ozone to produce O<sub>2</sub> and additional odd hydrogen without releasing atomic oxygen. More importantly, odd hydrogen inhibits ozone production by converting O to O<sub>2</sub>, depleting a building block for ozone. Therefore, reactions involving odd hydrogen species ultimately serve as sinks for ozone, and the abundance of ozone can serve as a sensitive tracer of odd hydrogen abundance.

Observations of ozone on Mars have been made with the Goddard Infrared Heterodyne Spectrometer (IRHS, Kostiuk, 1994) and the Heterodyne Instrument for Planetary Wind and Composition (HIPWAC, Schmillig et al., 1999) at the NASA Infrared Telescope Facility on Mauna Kea, Hawai'i, between 1988 and 2003 (Fast, 2005). The very high spectral resolution ( $\lambda/\Delta\lambda \geq 10^6$ ) of infrared (IR) heterodyne spectroscopy allows martian ozone features to be observed when they are Doppler shifted away from their telluric counterparts, making it the only ground-based technique for directly observing ozone on Mars. The observational and analysis techniques are detailed extensively in Fast et al. (2006) (hereafter Paper I), along with the measured distribution of ozone with latitude for  $L_S = 40^\circ, 74^\circ, 102^\circ, 115^\circ, 202^\circ, 208^\circ,$  and  $291^\circ$  ( $L_S$  is solar longitude, where  $0^\circ$  is the northern spring equinox). Various degrees of anticorrelation of observed ozone abundances with contemporaneous measurements of water vapor (source of ozone-destroying odd hydrogen) are demonstrated. Other techniques for observing ozone are also detailed in Paper I, and a comparison of ozone abundances acquired using IR heterodyne and ultraviolet techniques shows good agreement. Here, we apply the measurements of martian ozone column abundance acquired through IR heterodyne spectroscopy to the specific spatial and orbital predictions of the three-dimensional photochemical model of Lefèvre et al. (2004). Discrepancies are explored as possible indicators of chemical processes or vertical distributions not included in the gas phase model. The role of ozone in testing photochemical models is discussed.

## 2. Photochemical models

Many photochemical models of the martian atmosphere have been published. They are based on CO<sub>2</sub> reformation catalyzed by odd hydrogen, but they differ in how they seek to come into agreement with available atmospheric data. Chemical reactions, reaction rates, eddy diffusion coefficients, photodissociation cross sections, temperature dependencies, hydrogen and oxygen escape rates, ionospheric processes, nitrogen chemistry, and heterogeneous (surface) chemistry are some of the issues that must be considered in modeling. Most photochemical models have been one-dimensional, meaning they examine the height variation of species and simulate transport through a vertical eddy diffusion coefficient.

Early models such as McElroy and Donahue (1972), Parkinson and Hunten (1972), and Kong and McElroy (1977a, 1977b) employed fast eddy mixing or large amounts of water in order to reform CO<sub>2</sub> fast enough. It was later recognized that the room temperature value of the CO<sub>2</sub> absorption cross section needed to be reduced under martian conditions to account for its temperature dependence. This has the effect of increasing the amount of radiation available to photolyze water vapor, creating the opposite problem of an overproduction of odd hydrogen resulting in too much CO<sub>2</sub> reformation and too little CO and ozone compared to observations. Other adjustments to models were needed to compensate.

Development continued on one-dimensional models that examined martian photochemistry under mean global, seasonal, and diurnal conditions (e.g., Shimazaki, 1989; Krasnopolsky, 1993, 1995; Nair et al., 1994; Atreya and Gu, 1994). Some one-dimensional models were applied locally in order to calculate photochemical behavior with latitude or season (e.g., Shimazaki and Shimizu, 1979; Shimazaki, 1981; Clancy and Nair, 1996). A two-dimensional (i.e., zonally averaged) photochemical model of Earth was adapted to Mars by Moreau et al. (1991) to interactively treat photochemical and dynamical effects.

The more recent one-dimensional photochemical models differed in areas such as eddy diffusion, rate constants, water vapor distribution, and the chemistry of minor species. Some required a heterogeneous sink for odd hydrogen (e.g., Krasnopolsky, 1993; Atreya and Gu, 1994) while others found that gas phase chemistry is sufficient for explaining observations (e.g., Nair et al., 1994; Krasnopolsky, 1995). All relied on the pool of available spacecraft and ground-based observations of Mars up to that point with which to construct and test their models. However, Krasnopolsky (2003a) points out that recent ground-based and spacecraft results have brought the models out of agreement with observations and point again to the need for heterogeneous chemistry to bring down odd hydrogen production.

Global mean photochemical models are important for investigating the chemistry of CO, O<sub>2</sub>, and H<sub>2</sub>, whose photochemical lifetimes are much longer than atmospheric transport time scales. The one-dimensional models of the 1990's used ozone abundance retrieved from the IR heterodyne analysis of Espenak et al. (1991) to test their models. However, ozone is not a very meaningful test of global mean photochemical models beyond indicating if modeled ozone abundance is within an acceptable range because of the short photochemical lifetime of ozone and its spatial, seasonal, and orbital variability (e.g., Paper I, Figs. 1 and 2).

The larger pool of ozone abundance information becoming available (e.g., IR heterodyne (Paper I), Mars Express SPICAM (Bertaux et al., 2000, 2004)) is important for testing photochemical models that address specific spatial and seasonal/orbital atmospheric properties. Such models are necessary to explain the variability of ozone and the odd hydrogen chemistry it probes. For example, the seasonal behavior of ozone at  $65^\circ$  N and  $65^\circ$  S was modeled by local one-dimensional models of Shimazaki and Shimizu (1979) and

Shimazaki (1981). The models were developed to reproduce polar winter ozone abundances observed by Mariner 9 (Barth et al., 1973). As the poles come out of winter, the modeled ozone abundances drop due to destruction by odd hydrogen resulting from increased water vapor photolysis. Those models at 65° N predict less than half the ozone seen by IR heterodyne measurements (Paper I) for northern spring.

Since then, chemical parameters have been updated, and the groundwork was laid to move further beyond global mean modeling. For instance, Clancy and Nair (1996) and Clancy et al. (1996) modeled water vapor distribution and saturation altitude with season, which strongly impacts water vapor transport and ozone distribution. Recently, a three-dimensional photochemical model has been developed by Lefèvre et al. (2004) that examines local martian photochemistry on a global and seasonal basis. Spatial, temporal, and seasonal ozone abundances retrieved using IR heterodyne spectroscopy (Paper I) are an excellent tool for testing specific predictions of this model.

### 3. Testing the first three-dimensional model

The three-dimensional model of martian atmospheric photochemistry of Lefèvre et al. (2004) combines photochemistry with the general circulation model (GCM) of Forget et al. (1999). Chemistry resulting from local conditions (including topography) is combined with three-dimensional atmospheric circulation and an annual water cycle in order to develop a comprehensive global, diurnal, and seasonal photochemical model. The GCM-calculated water vapor profiles have column abundances consistent with those measured by Mars Global Surveyor (Smith, 2002). Although the GCM uses a time-varying dust distribution consistent with Mars Global Surveyor data, this has not yet been coupled to the photochemical code, which uses a constant dust optical depth corresponding to seasons of minimal dust. The model includes simplified nitrogen chemistry and water cloud transport, and it does not include heterogeneous processes.

Slices of the model corresponding to the orbital positions ( $L_S$ ), longitudes, and local times of the heterodyne observations are shown in Fig. 1, along with the IR heterodyne ozone column density retrievals and conservative  $1\sigma$  uncertainties that were presented in Paper I. Each model curve is for a different longitude and local time (indicated by colored text), and color indicates the correspondence between observed and modeled column density. The following behavior is noted:

- During the near-perihelion periods of  $L_S = 202^\circ$ ,  $208^\circ$ , and  $291^\circ$ , modeled ozone abundances agree fairly well with observations and upper limits (except at high northern latitudes at  $L_S = 202^\circ$ ).
- During the near-aphelion periods of  $L_S = 40^\circ$ ,  $74^\circ$ , and  $115^\circ$ , although there is general agreement at higher latitudes, the model consistently underestimates low latitude ozone abundance as compared to observations.

The overall qualitative agreement in the behavior of ozone between aphelion and perihelion periods is good, with both

observed and modeled ozone abundances decreasing over that period (aphelion is at  $L_S = 71^\circ$  and perihelion is at  $L_S = 251^\circ$ ). During cooler aphelion orbital positions, water vapor transport is inhibited due to a combination of circulation and the lower hygropause altitude (e.g., Clancy et al., 1996) and water vapor freezes out of the atmosphere, removing the source of odd hydrogen and allowing the abundance of ozone to increase. Toward perihelion, warmer conditions result in the increased global presence of water vapor, the photolysis of which provides odd hydrogen to destroy ozone. The quantitative agreement around perihelion is good, with the some departure seen at higher latitudes. That could be attributed to a larger sampling of latitudes by the instrument beam toward a polar limb or to dynamical effects near the poles that result in ozone abundance variations (as seen by Mariner 9 (Barth et al., 1973) and as predicted by the model). During the aphelion periods of  $L_S = 40^\circ$ ,  $74^\circ$ , and  $115^\circ$ , the agreement is good at higher latitudes, but the low latitude abundance is consistently underestimated by the model as compared to observations.

Similar behavior was noted by Lefèvre et al. (2004) when comparing their model to a limited set of observations (one  $O_2(^1\Delta)$  dayglow and two ultraviolet data sets, and the published IR heterodyne analysis of Espenak et al., 1991). The ozone retrievals in this work provide a more extensive sampling of orbital periods with which to test the model. The updated analysis of Paper I also revised the Espenak et al. (1991) retrievals at  $L_S = 208^\circ$  downward by  $\sim 30\%$ , bringing them into better agreement with the perihelion model.

Another view of the behavior of the observations and the model is given in Fig. 2, where measured ozone abundances from each target latitude are compared to model abundances as a function of season or orbital period ( $L_S$ ). The model curves show maximum and minimum calculated local noon abundances at each latitude, indicating extremes due to topography. The following behavior is noted:

- At 60° N, the behaviors of the model and observations are generally consistent over the aphelion periods sampled.
- At 40° N, generally good agreement between the model and observations is seen around aphelion in spite of the scatter at  $L_S = 74^\circ$ .
- At 20° N, 0° N, and 20° S, there is excellent agreement between the model and observations approaching perihelion, but the model underestimates the amount of ozone during the aphelion periods.
- At 40° S, there is large scatter and uncertainty in the observations around aphelion, but generally within the model range. There is excellent agreement between the model and the data approaching perihelion,

There is generally good agreement between observed and modeled ozone abundances except at low latitudes during aphelion orbital periods, and this is the most significant and repeatable departure of the model from the observations. Although the qualitative seasonal/orbital behavior of ozone at low latitudes is reproduced by the model, the quantitative results around apher-

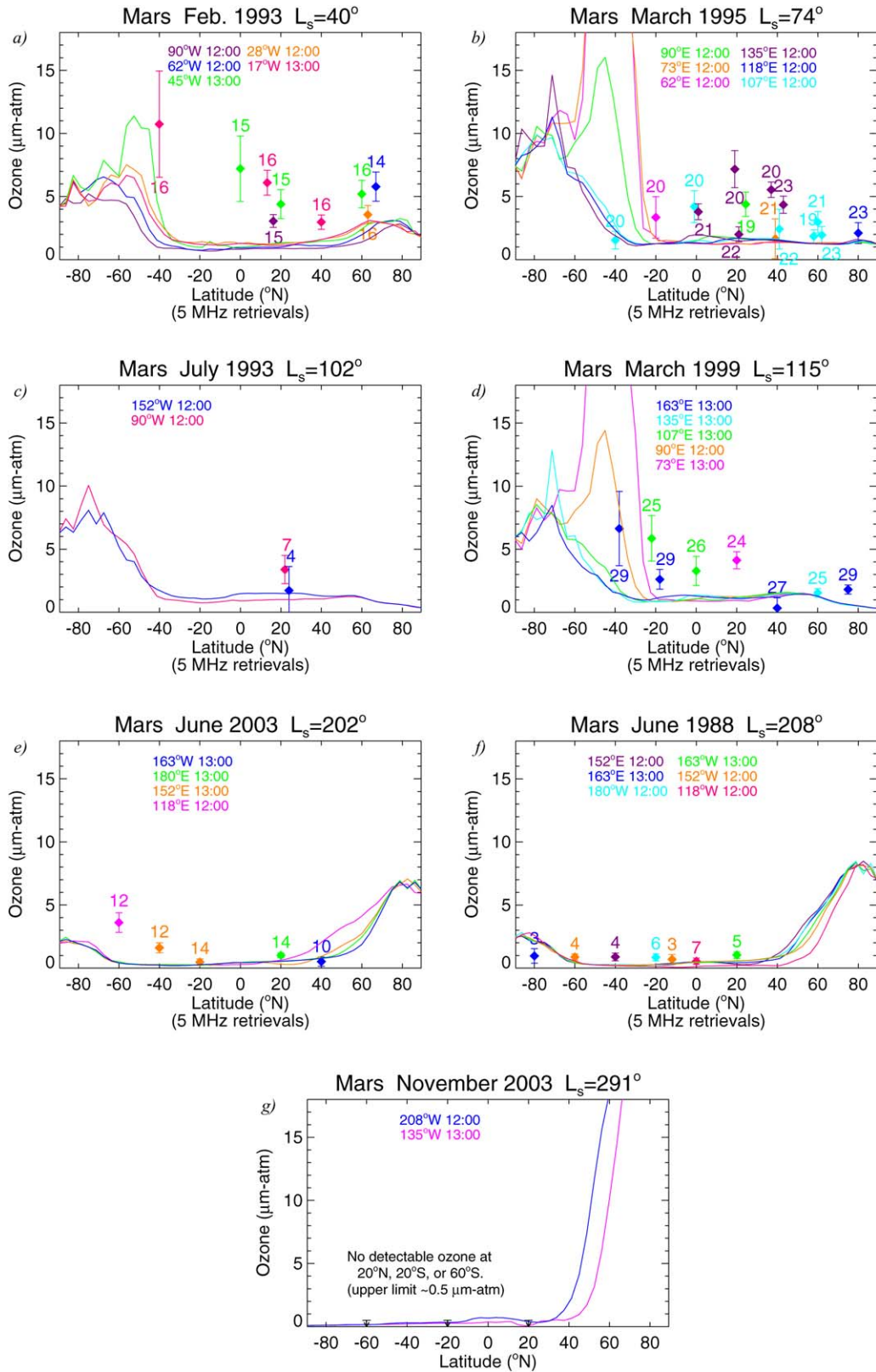


Fig. 1. Ozone column abundances and  $1\sigma$  accuracies from infrared heterodyne spectra (Fast et al., 2006) are displayed with corresponding slices from the three-dimensional photochemical model of Lefèvre et al. (2004). The longitudes and local times of the model curves are indicated on the plots by color-coded text, and are close to those of the observations. Color also indicates the correspondence between observed and modeled ozone column densities. Numbers displayed with data points indicate day of month of observation. The general behavior of ozone column abundance with  $L_s$  seen in the data is reproduced by the model, but there is significant quantitative departure of the model from the observed values at lower latitudes during aphelion periods. Good agreement overall is seen during perihelion periods. (Aphelion is at  $L_s = 71^\circ$  and perihelion is at  $L_s = 251^\circ$ .) The large ozone abundances modeled in the polar regions occur during their respective winters when those latitudes are not visible from Earth.

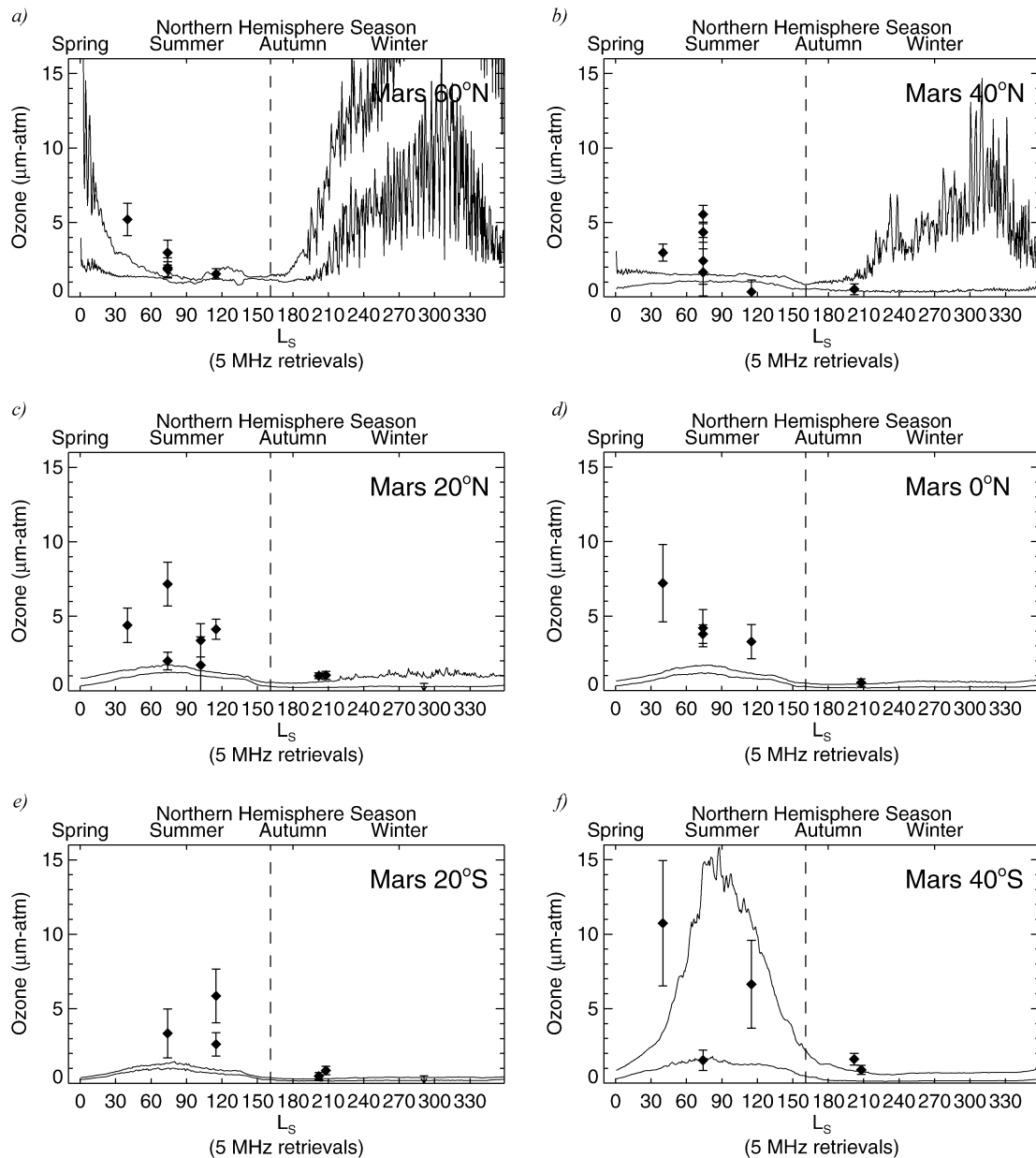


Fig. 2. Ozone column abundances and  $1\sigma$  accuracies from infrared heterodyne spectra (Fast et al., 2006) are displayed for various latitudes as a function of season or orbital period ( $L_S$ ) with model abundances from the three-dimensional photochemical model of Lefèvre et al. (2004). The model curves show maximum and minimum calculated local noon abundances at each latitude, indicating extremes due to topography. The dotted line divides the aphelion (left) and perihelion (right) periods, with aphelion at  $L_S = 71^\circ$  and perihelion at  $L_S = 251^\circ$ . Good agreement is seen for the most part in the seasonal behavior at  $60^\circ$  N, and during perihelion seasons at lower latitudes, but the model consistently underestimates ozone at low latitudes during aphelion seasons.

lion require an examination of the chemistry and assumptions incorporated in the model.

Lefèvre et al. (2004) noted the low latitude problem in their comparison of limited ultraviolet and infrared observations to their model and explored possible reasons for the underestimation of ozone at low latitudes around aphelion. An overabundance of water vapor would lead to increased odd hydrogen production and ozone destruction, but they note that the water vapor column abundances in the GCM compare well with those from Mars Global Surveyor. They point to uncertainties in photochemical and kinetics parameters, and the fact that a constant, low dust abundance is assumed. They see better ab-

sorption cross section data at low temperatures as important and also point to updated reaction rates from terrestrial research, but it still does not solve the aphelion problem.

Lefèvre et al. (2004) see heterogeneous chemistry as promising for resolving the discrepancy, and that is further indicated in the comparison of the model to IR heterodyne measurements (Figs. 1 and 2). A heterogeneous sink for ozone-destroying odd hydrogen would lead to an increase in ozone abundance. The fact that IR heterodyne observations at low latitudes agree with modeled ozone abundances at perihelion but not at aphelion is an important clue. A heterogeneous sink of odd hydrogen onto dust particles would not solve the problem at apher-

lion because dust is less abundant than at perihelion, when the sink would only lead to an overestimate of ozone abundance by the model. Heterogeneous chemistry involving water ice cloud particles may be a solution because that sort of chemistry would dominate during the cooler aphelion period when low latitude clouds have been observed by Mars Global Surveyor to be more abundant (Smith, 2004). Increased ozone production in the presence of water ice clouds was suggested by Krasnopolsky and Parshev (1979) as a way of explaining the abundance of ozone in a morning layer observed by Mars 5, and Krasnopolsky (2005) explored loss efficiencies of odd hydrogen species onto water ice particles. Heterogeneous loss may also explain why modeled  $\text{H}_2\text{O}_2$  abundances are similar between  $L_S = 112^\circ$  and  $206^\circ$ , yet observations show far less  $\text{H}_2\text{O}_2$  at  $L_S = 112^\circ$  than at  $L_S = 206^\circ$  (Encrenaz et al., 2004; Clancy et al., 2004).

A sink of odd hydrogen onto ice particles could be implemented in the model in such a way as to resolve the discrepancy between the model and observations. However, the accuracy of such a model would be questionable without laboratory studies to back up the choice of efficiency for the odd hydrogen sink. Laboratory studies of heterogeneous processes involving water and other ices and dust under martian conditions are required in order to produce a model that is consistent with observed ozone behavior and has a basis in tested chemistry. Preliminary results using available laboratory data indicate that heterogeneous loss of odd hydrogen onto water ice particles holds promise for resolving the discrepancies between modeled and observed ozone abundances (F. Lefèvre, private communication).

Although total column abundances were compared here, the vertical distributions of ozone and water should be considered. The degree of anticorrelation of the total column abundances of IR heterodyne ozone and contemporaneous water vapor measurements was less than strict (Paper I), indicating the need to consider the vertical distribution of the constituents within the column. Clancy and Nair (1996) used the Nair et al. (1994) model to investigate photochemistry at  $30^\circ$  latitude over the course of the martian year by utilizing observed variations in temperature and water saturation altitude, or hygropause, in their model. They showed that variation in ozone number density at 20 and 40 km between perihelion and aphelion is much greater than that of the total ozone column because of the behavior of the ozone distribution in response to the water vapor vertical distribution and the hygropause altitude. Clancy et al. (1996) modeled the effect of circulation and the hygropause altitude on water vapor transport, which ultimately affects the spatial and vertical distribution of ozone.

Similarly, the three-dimensional model of Lefèvre et al. (2004) predicts the vertical distribution of ozone based on the chemistry resulting from the changing water vapor distribution as calculated by the GCM over the course of the year on Mars. A high altitude layer of ozone forms during the cooler seasons around aphelion when the hygropause is at lower altitude ( $\sim 10$ – $15$  km). During the perihelion seasons, that layer disappears due to the warmer conditions and higher hygropause ( $\sim 30$ – $40$  km). The modeled behavior of ozone and water vapor indicates why strict anticorrelation of total ozone column den-

sity with total water vapor abundance is not observed (Paper I). Total column abundance provides a good test of photochemical models and GCMs, and measurement of the vertical distribution of constituents provides an even stricter test of model predictions. Vertical distribution of ozone has been investigated by combining IR heterodyne total ozone column abundances with observations of  $\text{O}_2(^1\Delta)$  dayglow emission that probe ozone above  $\sim 20$  km (e.g., Krasnopolsky, 2003b; Novak et al., 2002). The combination can indicate deviations from a constant-with-height mole fraction distribution (Fast, 2005). Vertical distribution of water vapor and ozone on Mars (above  $\sim 10$ – $20$  km) is being explored through occultation measurements made with Mars Express SPICAM (Bertaux et al., 2000, 2004).

Dust storms affect the warmer perihelion season and, although IR heterodyne ozone abundances are consistent with the three-dimensional photochemical model around perihelion, the work by Atreya et al. (2004) on oxidant production in dust devils and storms should be considered. They find that triboelectricity (electricity produced through friction) in dust devils and storms results in increased production of OH and  $\text{O}^-$  and ultimately  $\text{H}_2\text{O}_2$  at levels much higher than from photochemical production alone. The life issue is of course the thrust of that study, but the effect on ozone would be worth exploring to be able to support interpretation of perihelion observations and model predictions. Increased OH production during dust activity would lead to ozone destruction, and the model predicts a significant decrease in ozone abundance, not accounting for dust opacity (A.S. Wong, private communication). Observations of ozone during global dust storms would not be able to probe the abundance near the surface. Localized dust phenomena could lead to localized depletion of ozone relative to model predictions or previous observations.

#### 4. Conclusions

We have applied total ozone column abundances on Mars acquired through IR heterodyne spectroscopy (Fast et al., 2006) to the testing of 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). Both measured and modeled ozone column abundances show an overall decrease between aphelion and perihelion orbital positions. This general consistency gives confirmation to the role of odd hydrogen chemistry in the  $\text{CO}_2$  atmosphere of Mars and validates the model. Modeled total ozone abundances agree fairly well with IR heterodyne measurements at all latitudes and orbital periods except at low latitudes during aphelion periods, where the model underestimates ozone abundance relative to observations. This provides an important clue to the nature of additional processes that must be taken into account in order to better reproduce the atmospheric conditions. In particular, heterogeneous loss of odd hydrogen onto water ice cloud particles that are observed to be present around aphelion is not included in the gas-phase model. 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 martian 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. Infrared heterodyne spectroscopy is an important technique for studying ozone on Mars, and can enable long-term ground-based studies of the atmospheric chemistry and stability.

Underlying assumptions about chemistry adopted by photochemical models must also be validated. Laboratory measurements of chemical properties under martian conditions are important for validating photochemical models, as well as expanding them to include processes such as heterogeneous chemistry.

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