1994023387

N94- 27890

# PROBING THE MARTIAN ATMOSPHERE IN THE ULTRAVIOLET

Bernhard Lee Lindner

442439

Atmospheric and Environmental Research, Inc.
840 Memorial Drive
Cambridge, Massachusetts 02139
(617)349-2280

Several fundamental differences in atmospheric chemistry exist between Mars and the Earth. The martian atmosphere is primarily $CO_2$ (95%), with strong vertical mixing, cold temperatures (typically 220K), low pressures (6 mb at the surface), high atmospheric dust and cloud particle content, and no man-made atmospheric constituents. Earlier difficulties in explaining why the atmosphere was not more decomposed into CO and $O_2$ have been placated with models using updated reaction rates, 'moderate' eddy mixing of order $10^7$ $cm^2$ $s^{-1}$, and the odd hydrogen catalytic cycle (Shimazaki, 1989; Krasnopolsky, 1992). Odd nitrogen and sulfur catalytic cycles are of marginal importance, and other catalytic cycles shown to be important in the terrestrial atmosphere are unimportant on Mars (Yung et al., 1977; Krasnopolsky, 1992). Currently, much work is being undertaken to examine the importance of heterogeneous chemistry (e.g., Atreya and Blamont, 1990; Krasnopolsky, 1992), but uncertainties in particle properties make efficiencies difficult to evaluate. Also, atmospheric chemistry may significantly alter atmospheric composition on climatic timescales, particularly during periods of low obliquity (Lindner and Jakosky, 1985).

Ozone is a key to understanding atmospheric chemistry on Mars. The $O_3$ abundance has been inferred from UV spectra by several spacecraft, with the most complete coverage provided by Mariner 9 (Lane et al., 1973). The Mariner 9 UV spectrometer scanned from 2100 to 3500 Angstroms in one of its two spectral channels every 3 seconds with a spectral resolution of 15 Angstroms and an effective field-of-view of approximately 300 $km^2$. The only atmospheric absorption in the 2000 to 3000 Angstrom region was assumed to come from the Hartley band system of ozone, which has an opacity of order unity. Therefore the amount of ozone was inferred by fitting this absorption feature with laboratory data of ozone absorption, as shown in Fig. 1. Mars $O_3$ shows strong seasonal and latitudinal variation, with column abundances ranging from 0.2 µm-atm at equatorial latitudes to 60 µm-atm over the northern winter polar latitudes [Lane et al., 1973] (1 µm-atm is a column abundance of $2.689 \times 10^{15}$ molecules $cm^{-2}$). However, the $O_3$ abundance is never great enough to significantly affect atmospheric temperatures (Lindner, 1991) or surface temperatures and frost budgets (Lindner, 1990). Figure 2 shows some of the inferred $O_3$ abundances.

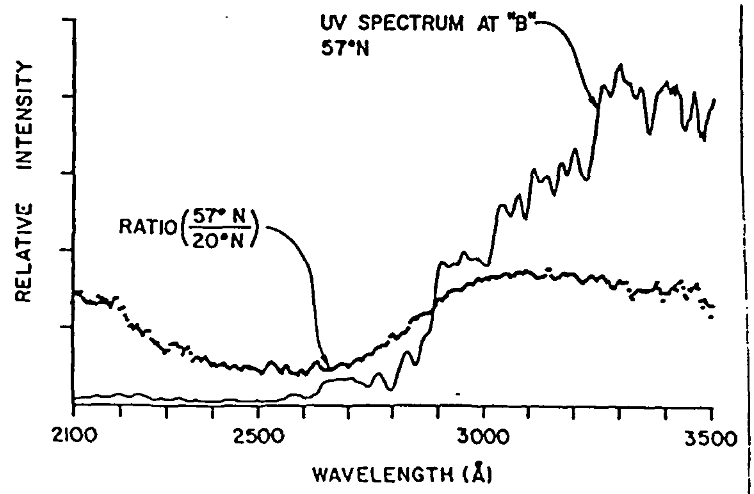

Figure 1. Ultraviolet spectrum measured by Mariner 9 at 57N latitude on orbit 144. To enhance the $O_3$ absorption feature, this spectrum was divided by one obtained at 20N latitude on orbit 144, where $O_3$ abundances are minimal (Lane et al., 1973).

I use a radiative transfer model based on the discrete ordinate method to calculate synthetic radiance spectra. Assuming a constant mixing ratio for ozone and no chemical or radiative interaction between $O_3$ and clouds/dust, Fig. 3

shows that when typical amounts of dust and cloud are present that significant underestimation of $O_3$ occurs. A factor of 3 times as much $O_3$ is needed to generate the same spectrum as for a clear atmosphere. If the scattering properties of martian clouds and dust were well known, then their appearance would not be a problem, as a model would be capable of retrieving the $O_3$ abundance. However, these properties are not well known, which raises doubts about the effectiveness of the current UV reflectance spectroscopy technique used to measure $O_3$.

Spatial and temporal variability in temperature and water vapor account have been claimed to account for the scatter of the data points in Fig. 2 (Barth and Dick, 1974). A decrease in temperature would result in a decrease in water vapor, if saturated as expected at prevalent temperatures. A decreased water vapor abundance decreases the availability of odd hydrogen, which converts CO and O into $CO_2$ catalytically, decreasing the abundance of O needed to form $O_3$. However, water vapor is a small source of odd hydrogen in the winter polar atmosphere compared to $H_2$, and may not account for most of the variability in Fig. 2 (Lindner, 1988). Masking by clouds and dust may also account for some of the observed $O_3$ variability, because the nature and opacity of the clouds and dust in the polar hood change dramatically in latitude and even on a day-to-day basis. As the maximum $O_3$ abundance resides near the surface (Lindner, 1988), spacecraft must be able to observe through the entire cloud and dust abundance in order to actually see the total $O_3$ column abundance. If reflectance spectroscopy is used, as on Mariner 9, then the cloud and the airborne dust must be traversed twice; first by the incoming solar flux down to the surface, and then once again upon reflection from the surface out to the spacecraft. In addition, the large solar zenith angles at winter polar latitudes mean several times the vertical opacity of cloud and dust must be traversed. Indeed, part of the observed latitudinal variation in $O_3$ in Fig. 2 may be due to the inability of the spacecraft to observe through the increasing effective optical depths as one goes poleward.

By using a photochemical model which included multiple scattering of solar radiation, Lindner (1988) showed that the absorption and scattering of solar radiation by clouds and dust actually increased $O_3$ abundances at winter polar latitudes. Hence, regions with high dust and cloud abundance could contain high $O_3$ abundances (heterogeneous chemistry effects have yet to be worked out). It is quite possible that the maximum $O_3$ column abundance observed by Mariner 9 of 60μm-atm is common. In fact, larger quantities may exist in some of the colder areas with optically thick clouds and dust. As the Viking period often had more atmospheric dust loading than did that of Mariner 9, the reflectance spectroscopy technique may even have been incapable of detecting the entire $O_3$ column abundance during much of the Mars year that Viking observed, particularly at high latitudes.

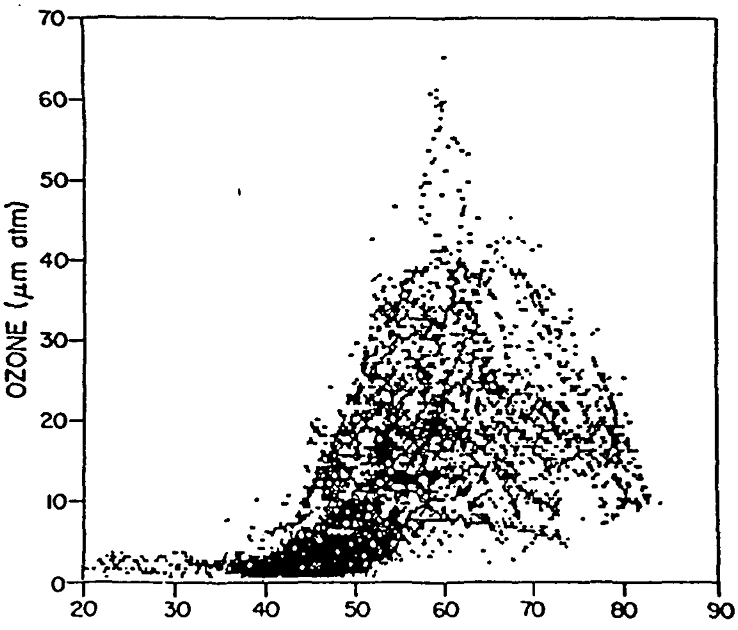

Figure 2. Measurements of the $O_3$ column abundance inferred from the Mariner 9 UV spectrometer data during the northern winter, $L_s$ = 330-360, in the northern hemisphere (Barth, 1985).

However, observing the UV spectrum from the surface would greatly reduce the effects of clouds and dust, and hence significantly increase the accuracy of ozone abundance retrievals. A lander with a simple photometer having only 2 channels, one in the $O_3$ absorption band at 2500 Angstroms and one out of the band at 3500 Angstroms, would achieve this. Other possibilities for measuring ozone include solar occultation (Blamont et al., 1989), IR observations in the 9.6 μm $O_3$ band (e.g., Espenak et al., 1990), and observations of the $O_2$ dayglow at 1.27 μm, produced by photolysis of $O_3$ (Traub et al., 1979). However, further studies of these other techniques are required, especially as regards the effects of clouds and dust.

Atreya, S.K. and J.E. Blamont, 1990: Stability of the martian atmosphere: Possible role of heterogenous chemistry, *Geophys. Res. Lett.*, 17, 287-290.

Barth, C.A., 1985: Photochemistry of the atmosphere of Mars, in *The Photochemistry of Atmo-spheres. Earth, other Planets, and Comets* (Ed. J. Levine). Academic Press, Orlando, Fla.

Barth, C.A. and M.L. Dick, 1974: Ozone and the polar hood of Mars, *Icarus*, 22, 205-211.

Blamont, J.E., E. Chassefiere, J.P. Goutail, B. Mege, M. Nunes-Pinharanda, G. Souchon, V.A. Krasnopolsky, A.A. Krysko and V.I. Moroz, 1989: Vertical profiles of dust and ozone in the martian atmosphere deduced from solar occultation measurements, *Nature*, 341, 600-603.

Espanek, F., M.J. Mumma, T. Kostiuk, and D. Zipoy, 1990: Ground based IR measurements of the global distribution of O3 in the atmosphere of Mars, *Bull. Amer. Astron. Soc.*, 22, 1077.

Krasnopolsky, V.A., 1992: Photochemistry of the martian atmosphere (mean conditions), *J. Geophys. Res.*, in Press.

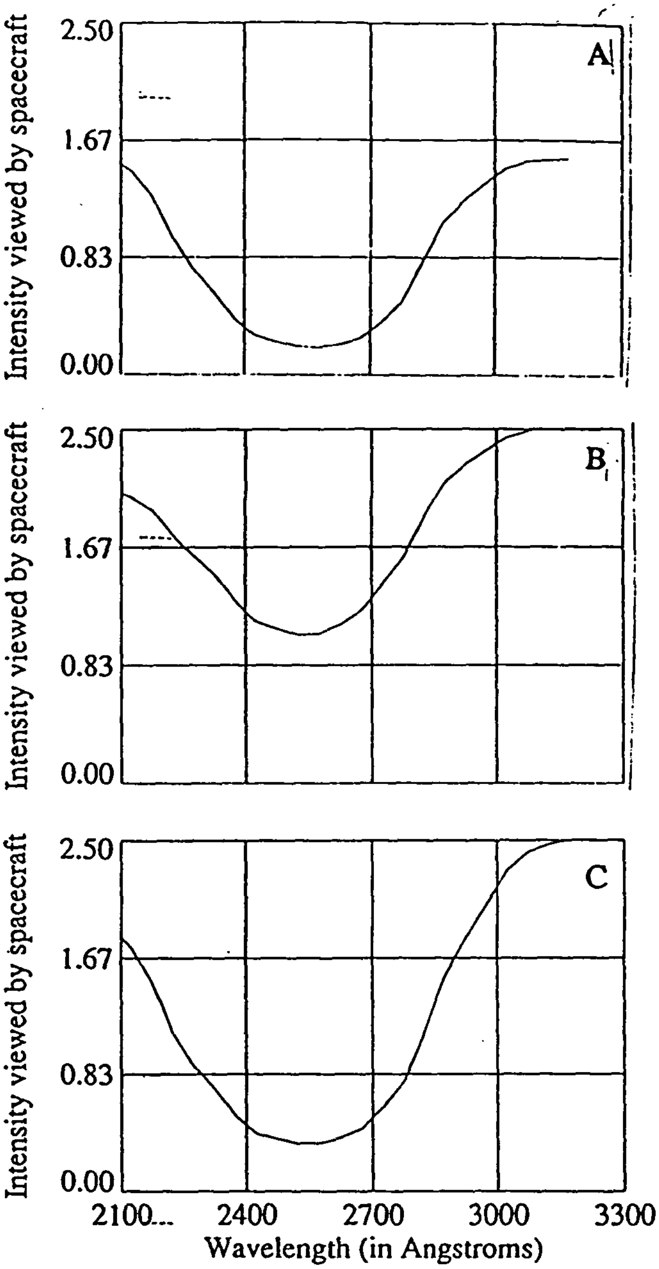

Figure 3. Synthetic spectra as would be observed by spacecraft for atmospheres with (A) no cloud or dust and 30 μm-atm $O_3$, (B) vertical opacities of dust and cloud of 0.3 and 1.0, respectively, and 30 μm-atm of $O_3$, and (C) vertical opacities of dust and cloud of 0.3 and 1.0, respectively, and 100 μm-atm of $O_3$. All cases assume a solar a zenith angle of 75 (typical for winter polar observations), and viewing angle of 60, with azimuth angle of 0 (typical for Mariner 9). Polar-cap albedo of 0.8 (new ice).

Lane, A.L., C. Barth, C. Hord, and A.I. Stewart, 1973: Mariner 9 UV spectro-meter experiment: Obser-va-tions of ozone on Mars, *Icarus*, 18, 102-108.

Lindner, B.L., 1988: Ozone on Mars: The effects of clouds and airborne dust, *Planet. Space Sci.*, 36, 125-144.

Lindner, B.L., 1990: The martian polar cap: Radiative effects of ozone, clouds, and airborne dust, *J. Geophys. Res.*, 95, 1367-1379.

Lindner, B.L., 1991: Ozone heating in the martian atmosphere, *Icarus*, 93, 354-361.

Lindner, B.L. and B.M. Jakosky, 1985: Martian atmospheric photochemistry and composition during periods of low obliquity, *J. Geophys. Res.*, 90, 3435-3440.

Shimazaki, T., 1989: Photochemical stability of CO2 in the martian atmosphere: Reevaluation of the eddy diffusion coefficient and role of water vapor, *J. Geomag. Geoelectr.*, **41**, 273-301.

Traub, W.A., N.P. Carleton, P. Connes and J.F. Noxon, 1979: The latitudinal variation of O2 dayglow and O3 abundance on Mars, *Astrophys. J.*, 229, 846-850.

Yung, Y.L., T.Y. Strobel, T.Y. Kong, and M.B. McElroy, 1977: Photochemistry of nitrogen in the martian atmosphere, *Icarus*, 30, 26-41.