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Altitude profiles of O_2 on Mars from SPICAM stellar occultations

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ABSTRACT

We determine the first altitude profiles of O_2 in the important photochemical region below 120 km in the atmosphere of Mars by analyzing Mars Express/SPICAM ultraviolet observations of six occultations of stars by the atmosphere. Over the range of 90–130 km the altitude-averaged mixing ratio of O_2 relative to the major constituent CO_2 varies in space and time in the range of 3.1×10^{-3}–5.8×10^{-3}, with a mean value of 4.0×10^{-3}. This mean value exceeds by a factor of 3–4 those reported earlier for the lower atmosphere. However, some of the O_2 abundance and mixing ratio profiles determined here are similar to those measured by Viking in 1976 in the upper atmosphere.

1. Introduction

The stability of the martian atmosphere is linked to the abundance of photochemically-produced constituents. Photolysis destroys CO_2, and a CO_2 atmosphere with little O, CO, and O_2 implies efficient recycling of these products back to CO_2. Early investigations established that CO_2 was probably reformed through catalytic cycles involving odd H compounds (McElroy and Donahue, 1972; Parkinson and Hunten, 1972). The primary chemical processes and densities of the important constituents vary with altitude, location, and season. Until recently however, we lacked sufficient observations to constrain global models of martian dynamics and photochemistry. In particular, the global distribution of O_2, a primary photochemical product, is poorly known. Understanding the distribution of O_2 is important in constraining photochemical, dynamical, and evolutionary models of the martian atmosphere. Global variations in the O_2 mixing ratio are related to variable O_2 production rates from photolysis of O_3, recombination, and other reactions, in balance with loss owing to photolysis of O_2 and odd H and N chemistry. Hence understanding global O_2 variations can enhance our understanding of all these processes. Occultation observations are of particular interest in this regard, because they can supply global information at high vertical and horizontal resolution.

Early determinations of O_2 at Mars were followed by a long interval without new measurements, then a burst of both remote and in situ sensing. Yet today information on the horizontal and vertical distributions of O_2, and their variations with time, is limited. Using Earth-based measurements, Barker (1972), Carleton and Traub (1972) and Trauger and Lunine (1983) detected O_2 by its A band absorption at 763.5 nm. The Viking mass spectrometers determined density profiles of many constituents, including O_2 from 114 km to ∼175 km (Nier and McElroy, 1977). The O_2 mole fraction in the mixed region of the atmosphere from all these measurements is roughly 10^{-3}. Above the homopause, diffusive separation is important and the O_2 mixing ratio increases. Viking found a ratio that varied from 0.001 to 0.002 near 120 km to ∼0.005 at 160 km. Owen et al. (1977) quoted an O_2 mixing ratio of 0.13% at the surface, but noted scatter in the measurements of a factor of two, suggesting uncertainty in the derived ratio.

Hartogh et al. (2010) reported the first detection of O_2 at millimeter wavelengths using Herschel/HIFI. Their inferred mixing ratio of $1.40(\pm0.12) \times 10^{-3}$ is averaged over the disk and over a range of altitudes, although they do not describe the altitude weighting of the measurement. Mahaffy et al. (2013) measured an O_2 mixing ratio of $1.45(\pm0.09) \times 10^{-3}$ at the surface using observations by

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the Surface Analysis at Mars (SAM) investigation on the Curiosity rover. Earth-based measurements average over a vertical column and large portions of the globe, while the Viking measurements and Curiosity refer to single locations, V1 at 22°N and $L_S = 97°$, V2 at 48°N and $L_S = 118°$, and Curiosity at 4.5°S and $L_S = 164–211°$. Thus, these measurements provide little information on the variations of O_2 with location and time.

We use SPICAM observations of stellar occultations to infer the altitude profile of O_2 at several locations. The possibility of measuring O_2 was recognized in the SPICAM instrument design (Korablev et al., 2001); an exciting aspect of our investigation is determining O_2 profiles from 90 to ~140 km. The only previous altitude profiles, those from Viking, referred to altitudes above 128 km except for one point at 114 km, while the earlier remote observations sensed the column-integrated abundance and, in most cases, averaged over much of the visible disk. Chemical production of O_2 through $O + O + M \rightarrow O_2 + M$ and $O + OH \rightarrow O_2 + H$ peaks at an altitude of ~60 km while loss of O_2 through photolysis occurs at a fairly uniform rate below ~80 km (Nair et al., 1994). The models of Krasnopolsky (2002, Figs. 1–3) show that lighter species begin assuming their own scale heights at ~130 km, and this signature marks the beginning of diffusive separation. These SPICAM occultations therefore explore O_2 in a previously unstudied region where the atmosphere is well mixed but still subject to photochemical processes.

2. The observations

SPICAM's UV spectrograph covers the spectral range 110–310 nm at ~1.5 nm spectral resolution (Bertaux et al., 2006). The occultations consist of observing a star as the orbital motion carries the line of sight to the star through the atmosphere. The measurements determine the transmission of the atmosphere, which we analyze to infer the density of absorbing species (Quémerais et al., 2006). Interpreting occultation observations does not require information about the absolute calibration of the spectrograph used for the measurements. This is because the measured quantity is the atmospheric transmission, which is inferred by computing the ratio of a spectrum for which absorption is present to a reference (unabsorbed) spectrum of the source. The reference spectrum is acquired by observing the star along lines of sight well above the level at which absorption is measurable.

Identifying the absorption signature of O_2 in the presence of the stronger CO_2 absorption requires observations with high signal-to-noise ratios. Thus the brighter of the available occultation stars are preferred. On the other hand, the possibility of using dimmer stars increases the number of useful observations and hence expands coverage in space and time. For this initial investigation we report results from two occultations of each of three stars having a range of brightnesses. Table 1 summarizes the occultation observations that we use here. In this investigation we are interested primarily in establishing that O_2 can be reliably measured in the SPICAM occultation experiment. We therefore concentrate on these bright stars and reserve for later the study of the geographic variations of O_2 enabled by the full data set.

Deriving transmission spectra requires several steps. We begin with Level 1A data, which has been corrected for dark current and electronic offsets. We remove the effects of scattered light using the technique described by Quémerais et al. (2006). We compute the stellar reference spectrum required to calculate the transmission by averaging all spectra at tangent heights above 180 km, where our analysis verifies the absence of absorption. The ratio of the spectra with tangent heights within the absorbing region of the atmosphere to this reference spectrum is a measure of the atmospheric transmission. For these occultations, the number of spectra summed to create the reference spectrum ranged from 84 to 344, with a mean value of 229. As a rough indication of the corresponding signal to noise ratio, we consider the occultation of ζ Pup, the star intermediate in brightness, in orbit 977. For this orbit, 207 spectra were available for averaging into the reference spectrum, a number similar to the mean value over all these occultations. Over most of the spectral range used in our analysis, the signal to noise ratio in the individual spectra was ~26, and the averaging increased this to ~370 for the reference spectrum.

The integration time for each star was 0.64 s, except for β Cen, the brightest, for which it was 0.32 s. For all occultations, the spectrum was sampled at intervals of 1 s. From occultation to occultation, the rate of change of the altitude of the tangent ray from the star to SPICAM varied from 1.05 to 1.90 km s^{-1}, with a mean value of 1.42 km s^{-1}. During each occultation the rate was effectively constant. The accuracy of the altitude assigned to a measurement is independent of the pointing of the spectrograph and depends only on the accuracy with which Mars Express's position in its orbit is known (Quémerais et al., 2006; Bertaux et al., 2006), which is a few meters, negligible in this context. For stellar occultations SPICAM's slit is retracted to enlarge the field of view. Thus the wavelength calibration, but not the dispersion, depends on the position of the star in the field. Following Quémerais et al. (2006) we establish the wavelength offset for each occultation by fitting the prominent CO_2 absorption signature. Our analysis shows that wavelength registration is determined to a precision that ensures that uncertainties in wavelength have a negligible effect on the analysis.

Our analysis determines uncertainties and confidence intervals as well as the most probable value for the column density of each species. Reliably assessing the uncertainty in a measurement of a faint signal demands a good understanding of the statistical behavior of the detector. SPICAM's detector, an intensified CCD operated in a pulse integrating mode, has characteristics of both photon-counting and integrating devices. In this circumstance, departures from purely photon-counting statistical performance are expected (Sandel and Broadfoot, 1986). Accordingly we have measured the statistical characteristics of the signal recorded by SPICAM, as we describe in the next paragraph.

The characteristic of chief interest is the variance of the distribution of signals recorded when a signal of constant level is

Table 1
Occultation observations.

	Time	Orbit	Star	Flux[a]	Lat (°)	LST (h)[b]	L_S (°)	O_2 MF[c]
1	2004-05-13/10:34	0395	ζ Pup	18,000	16.7	21.05	32.7	5.3 ± 1.1
2	2004-08-03/02:49	0687	β Cen	56,200	−38.0	18.67	68.9	5.8 ± 1.5
3	2004-08-11/20:14	0718	γ Ori	16,000	−75.4	7.29	72.7	3.2 ± 1.1
4	2004-09-28/04:56	0887	γ Ori	16,000	−75.1	3.77	93.5	3.6 ± 1.3
5	2004-10-23/06:22	0977	ζ Pup	18,000	−16.4	3.74	104.7	3.1 ± 0.6
6	2005-04-18/13:54	1610	β Cen	56,200	37.7	21.99	195.4	3.3 ± 1.8

[a] Stellar flux in photons cm^{-2} s^{-1} nm^{-1} averaged over 130–155 nm.
[b] Local Solar Time.
[c] O_2 mole fraction in units of 10^{-3}.