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RESEARCH ARTICLE

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Key Points:

- The solar occultation technique provides high (ppt) sensitivity to many atmospheric trace gases, due to the long atmospheric paths and the brightness of the Sun
- Dust extinction is a major obstacle in the lower Mars atmosphere to detecting trace gases without strong absorption bands at wavenumbers less than $2,400\text{ cm}^{-1}$ or for spectrometers without coverage at wavenumbers less than $2,400\text{ cm}^{-1}$
- High spectral resolution (0.025 cm^{-1}) offers significant advantages over medium-resolution spectrometers (0.15 cm^{-1}) for detecting trace gases (e.g., CH_4) whose absorptions are overlapped by much stronger interfering absorptions (e.g., from CO_2 or H_2O)

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Solar Occultation FTIR Spectrometry at Mars for Trace Gas Detection: A Sensitivity Study

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Abstract A sensitivity study has been performed to estimate detection limits of various atmospheric trace gases achievable by a Mars-orbiting solar occultation Fourier transform infrared (FTIR) spectrometer. This was accomplished by first computing realistic limb transmittance spectra based on a model (T, P, VMR, and dust profiles) of the Mars atmosphere and adding appropriate noise and systematic errors based on assumed instrument design/configuration/performance. We then performed spectral fits to the resulting synthetic spectra to derive slant column abundances and their uncertainties. A profile retrieval was performed to infer limits of detection. This methodology was applied to a Mars-orbiting FTIR solar occultation spectrometer covering the $850\text{--}4,300\text{ cm}^{-1}$ spectral region at 0.025 cm^{-1} resolution. We conclude that most gases can be retrieved with a single-occultation sensitivity of 20–100 ppt. But this sensitivity varies considerably with the dust loading, especially for gases whose strongest absorption bands are toward higher wavenumbers where scattering is large. We conclude that for CH_4 , the ν_4 band centered at $1,305\text{ cm}^{-1}$, despite being more than 2 times weaker than the ν_3 band centered at $3,015\text{ cm}^{-1}$, offers better sensitivity due to its close spectral proximity to the dust extinction minimum. We also conclude that for the purpose of CH_4 detection, a high-resolution (0.025 cm^{-1}) broadband instrument would have a substantial advantage over a medium-resolution (0.15 cm^{-1}) instrument, despite the latter having a much larger signal-to-noise ratio.

Plain Language Summary We have estimated whether an infrared spectrometer might have enough sensitivity to measure minute amounts of gases (e.g., CH_4 , N_2O , HCN, and OCS) in the Martian atmosphere that might arise due to life or volcanic activity. We conclude that by viewing the Sun at sunset and sunrise, many gases would be detectable at the 20–100 ppt level which would reduce current upper limits of several gases, some by factors of more than a hundred (e.g., N_2O). But airborne dust is a major impediment to detecting gases in the lowest few kilometers of the atmosphere, close to their likely sources.

1. Introduction

Trace gases are a sensitive indicator of planetary activity, whether photochemical in the atmosphere or bio-chemical in the subsurface (Smith et al., 2009; Zurek et al., 2011). Here, we document the capability of a high-resolution, broadband, solar occultation Fourier transform infrared (FTIR) spectrometer, modeled on the canceled Mars Atmosphere Trace Molecule Occultation Spectrometer (MATMOS) to detect and quantify profile abundances of CH_4 and other trace gases in the Martian atmosphere. Unfortunately, the National Aeronautics and Space Administration ended its involvement in the Trace Gas Orbiter (TGO) mission in 2012, which terminated work on the MATMOS instrument and associated science studies. MATMOS was replaced by the Atmospheric Chemistry Suite (ACS), which is described by Korabev et al. (2014, 2018) on TGO, a component of the U.S./European Space Agency ExoMars program. This paper summarizes the performance modeling done in support of MATMOS (Wennberg et al., 2011) in the hope that it might benefit future Mars experiments.

MATMOS had strong heritage from the Atmospheric Chemistry Experiment (ACE), launched into Earth orbit in 2003 (Bernath et al., 2005; Coheur et al., 2007; Olsen et al., 2016), and the Atmospheric Trace

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Molecule Spectroscopy (ATMOS) experiment (Farmer, 1987), which flew on the Space Shuttle in 1985, 1991, 1992, and 1994. Additionally, MATMOS benefitted from advances in 24-bit Analog-to-Digital Converter (ADC) technology, tested in the Jet Propulsion Laboratory MkIV Fourier Transform Spectrometer (FTS), that eliminate the need for gain switching (Bekker et al., 2009).

The existence of methane in the Martian atmosphere has been the subject of much debate in recent years (Formisano et al., 2004; Krasnopolsky et al., 2004; Mumma et al., 2009; Zahnle et al., 2011) but has now been confirmed by the Mars Science Laboratory by Webster et al. (2015, 2018) measuring a local, seasonally varying, background value of 0.41 ± 0.16 ppb (2 sigma) and apparent peak of 7.2 ± 2.1 ppb in Gale crater over a 60-sol period. This background value is 4,500 times smaller than on Earth (1,850 ppb). Combined with the much lower Mars surface pressure, the Mars column CH_4 is 750,000 times less than that on Earth.

The discovery of CH_4 on Mars reorients our understanding of the Martian environment and potential for life. Since CH_4 has a photochemical lifetime of only 300 years, its presence in the atmosphere requires a continually replenishing source, defying the conventional framework of a geologically and biologically inactive Mars. So now the question is as follows: What is producing methane on Mars? Leading hypotheses of Martian methane sources include water-rock chemistry and methanogens (see, e.g., Yung et al., 2018). Distinguishing between hypotheses will require more measurements, and these will in turn require major theoretical, experimental, and technological advancements. In particular, we must integrate source, transport, and (possibly unknown) sink processes in our theoretical and experimental scope to properly identify and interpret observable signatures.

In this work we review high-resolution FTS remote sensing capabilities in the anticipation of a new era of Mars research that will unfold around potential biomarkers like methane, beginning with the ExoMars TGO (Vago et al., 2015). We pay special regard to the ability of FTS to detect and resolve unique spectral fingerprints of trace gases in the infrared. In the context of large observatories, FTS observations of exoplanets transiting the disk of their star may also become a technique of choice to probe the atmospheres of promising exoplanets in the era following the James Webb Space Telescope.

2. Solar Occultation Technique

In the solar occultation technique, illustrated in Figure 1, direct sunlight that has traversed the atmosphere parallel to the surface is measured at local sunrise or sunset. Long limb paths contain large slant column abundances, on Mars ~ 45 times more than a vertical path from the same minimum altitude, and therefore provide very high sensitivity to atmospheric trace gases. This observation geometry also provides a vertical resolution of a quarter of a scale height (~ 3 km for a uniformly mixed gas on Mars) providing a detailed profiling capability. The brightness of the directly viewed Sun provides a high signal-to-noise ratio (SNR).

The long limb paths are also a drawback since they contain large amounts of absorbers *not* of interest (e.g., CO_2 and dust), which black out broad swaths of the spectrum, especially at low altitude. The other drawback is the infrequency of the solar occultations, for example, only two 3-min occultations per 117-min science orbit described by TGO—a 5% duty cycle.

FTIR spectrometers are ideal survey instruments. Their high throughput allows a huge free spectral range and high spectral resolving power simultaneously, allowing measurements of many different gases in the same spectrum, including gases not considered in the prelaunch phase. This, together with their narrow and stable instrumental line shape (ILS), allows weak absorption lines to be cleanly resolved from much stronger adjacent lines of more abundant gases (e.g., CO_2). This technique has been successfully applied to the Earth's atmosphere in the 700- to $4,300\text{-cm}^{-1}$ region where nearly all gases have their strongest absorption bands. For example, the ATMOS (Farmer, 1987), MkIV (Toon, 1991), and ACE (Bernath et al., 2005) solar occultation FTIR instruments have collectively detected more than a dozen gases in the Earth's atmosphere for the first time. This broadband approach also allows for serendipitous science, accomplishing objectives that were not considered important at the time the mission was formulated. For example, the spectra from ATMOS, which last flew in 1994, are still being analyzed.

The MATMOS telescope used a $f/3$, 240-mm focal length, off-axis, paraboloidal primary mirror. The incident beam was limited by an 80-mm diameter aperture stop and a 0.375-mm diameter field stop, the latter setting the external field-of-view (FOV) diameter to 1.56 mrad. Thus, less than 1/15 of the solar disk area was

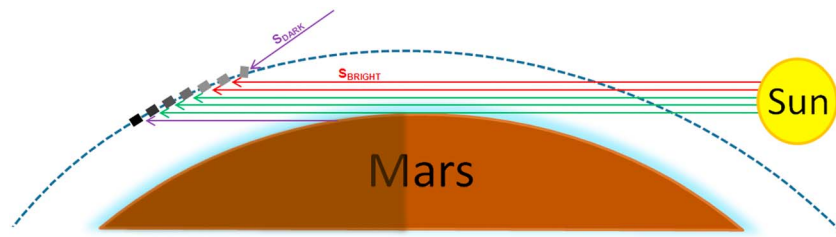


Figure 1. Illustrating the solar occultation observation geometry. As the spacecraft (depicted as black/gray rectangles) enters or emerges from the shadow of Mars (eclipse), the ray path from the Sun traverses the atmosphere at different altitudes, providing information on the vertical structure of the atmosphere. Limb ray paths are depicted by green arrows. Cold calibrations are denoted by purple arrows labeled “SDARK” and include deep space and the nightside of Mars. Bright calibrations are denoted by red arrows labeled “SBRIGHT” and occur viewing the Sun at tangent altitudes above 200 km, where atmospheric absorption becomes negligible.

admitted by the telescope. The beam exiting the telescope and feeding the FTS was collimated by a secondary mirror to 20-mm diameter with 6.25-mrad angular divergence, giving the telescope a magnification of 4.

The MATMOS interferometer subsystem, manufactured by ABB in Quebec City, leveraged heavily from ACE with a double-passed pendulum design pivoting about a flexure. The MATMOS design incorporated several improvements that resulted from ABB’s experience with ACE and GOSAT including switchable scan speed and better mounts for the mirrors.

MATMOS planned to acquire a double-sided interferogram every 2–3 km in tangent altitude during occultations, in order to achieve a quarter scale height vertical resolution (~ 3 km). The external FOV of 1.56-mrad diameter, projected on to the Mars limb, 1,600 km distant from 300-km orbital altitude, also subtends ~ 3 km. MATMOS had a maximum optical path difference of 25 cm. This, together with the 6.25-mrad diameter internal FOV, gave it a spectral resolution of 0.025 cm^{-1} corresponding to a resolving power of 120,000 in the $3,000\text{-cm}^{-1}$ region. The MATMOS instrument planned to process raw interferogram data into spectra in the downtime between occultations, reducing the data volume to be telemetered back to Earth by a factor ~ 100 . A variable scan speed was planned since the rate of change of tangent altitude is strongly beta angle dependent (beta is the angle between the Sun direction and the orbital plane). Taking scans on a fixed time interval, rather than a fixed vertical interval, would have resulted in too many spectra to be on-board processed at high beta angles or too coarse a vertical spacing at low beta angles.

An important consideration is the number of detectors. Although a single HgCdTe detector could easily cover the desired $800\text{--}4,300\text{-cm}^{-1}$ region, the photon noise from this bandpass would be quite large, and so the SNR at the lower wavenumbers, where the solar Planck function is weak, would be poor. By using a dichroic to split the spectral domain over two detectors, the photon noise can be reduced, especially at the low wavenumbers. Increasing the number of detectors from 2 to 3 would produce further improvements in SNR but may not justify the increased complexity, power, and onboard data processing. Furthermore, at lower tangent altitudes where the solar signal is more attenuated and no longer source photon noise limited, there is no advantage of splitting the spectrum domain over multiple detectors. So the choice of the number of detectors depends on the altitudes and wavenumbers that are most important, scientifically. For the remainder of this paper, two detectors are assumed: HgCdTe covering $800\text{--}1,850\text{-cm}^{-1}$ and InSb covering $1,850\text{--}4,320\text{-cm}^{-1}$, as was planned for MATMOS.

3. Simulated Mars Occultation Spectra

The Mars atmosphere used in this work is that described by Nair et al. (1994). The surface pressure was assumed to be 7 mbar with a temperature of 240 K. The main radiation-absorbing gas constituents were CO_2 (95%), H_2O , and CO. Dust opacities in the Mars atmosphere vary considerably, over time and with wavenumber. At $1,075\text{ cm}^{-1}$, nadir opacities, also known as aerosol optical depths (AODs), vary from 0.1 under low-dust conditions to 0.3 more typically and 0.6 under higher dust conditions (Montabone et al., 2015). Even larger opacities are possible during a major dust storm, but these are rare. Based on this, occultations of simulated Mars limb transmittance spectra were computed for four different dust amounts

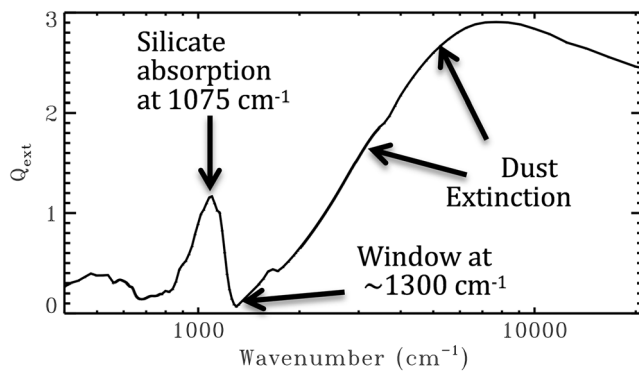


Figure 2. Mars dust extinction (absorption + scattering) efficiency plotted versus wavenumber. Based on a Mie calculation for a particle distribution with an effective radius of $1.06\ \mu\text{m}$ and an effective logarithmic variance of 0.3 (Kleinböhl et al., 2009; Kleinböhl et al., 2011). The strong increase in extinction from $1,300$ to $7,000\ \text{cm}^{-1}$ is caused by scattering by dust particles smaller than the wavelength of the radiation. The secondary peak centered at $1,075\ \text{cm}^{-1}$ is due to silicate absorption.

($\tau_{\text{nadir}} = 0.0, 0.1, 0.3, 0.6$). The zero value is unrealistic but was included for reference purposes and to compare with earlier studies that assumed no dust.

Figure 2 shows the dust extinction efficiency (Q_{ext}) used in this study. It is based on the Mie scattering calculation of Kleinböhl et al. (2009, 2011) and assumes an effective particle radius of $1.06\ \mu\text{m}$ and an effective variance of 0.3 in $\log_e$ space. Q_{ext} is the dimensionless ratio of the effective extinction cross section ($\text{cm}^2/\text{particle}$) of the particles to their actual cross-sectional areas. Both scattering and absorption terms are included. The general increase in extinction between $1,300$ and $7,000\ \text{cm}^{-1}$ is due to the increase of scattering with wavenumber. The secondary peak at $1,075\ \text{cm}^{-1}$ is due to silicate absorption. Around $1,300\ \text{cm}^{-1}$, there is a minimum in the dust opacity, which is fortunate for low-altitude measurements of the ν_4 CH_4 band centered at $1,305\ \text{cm}^{-1}$. The extinction at $21,500\ \text{cm}^{-1}$ ($0.89\ \mu\text{m}$) is roughly 2.6 times that at $1,075\ \text{cm}^{-1}$ ($9.3\ \mu\text{m}$), which is 2.7 times that at $450\ \text{cm}^{-1}$ ($21.6\ \mu\text{m}$). The shape of this extinction spectrum is assumed to be independent of altitude.

Mars also has ice clouds, with absorption peaking at 800 and $3,000\ \text{cm}^{-1}$.

These were not included in the calculation, since we believe that these mainly occur in the polar winter, which is never sampled by MATMOS. The effects of small amounts of ice clouds at seasons and latitudes that are sampled by MATMOS is not within the scope of this study.

Simulated Mars limb transmittance spectra under low ($\tau = 0.1$) and high ($\tau = 0.6$) dust conditions are shown in Figure 3. The dust is assumed to be uniformly mixed, meaning that the extinction decreases exponentially with altitude with a scale height of $\sim 10\ \text{km}$. The broad absorption features are due to dust absorption and scattering, mirroring the Q_{ext} shown in Figure 2. The narrow absorption features are due to gases. The spectral dependence of the dust opacity is dominated by scattering at large wavenumbers and by the silicate absorption band around $1,075\ \text{cm}^{-1}$. Since the limb opacity is ~ 45 times larger than the vertical opacity, the limb path just above the surface is virtually opaque under most conditions except for the window around $1,300\ \text{cm}^{-1}$. At higher tangent altitudes, however, the dust extinction diminishes rapidly. At 160-km tangent altitude the only discernable gas absorptions are from CO_2 and CO .

4. Instrument Performance Model

To investigate design trade-offs, we built a computer model of the MATMOS performance using Matlab. This was coupled to the simulated Mars limb transmittance spectra described above and a solar irradiance spectrum, allowing the various error terms to be quantified as a function of tangent altitude. The noise terms considered in the model include source photons, background photons, detector noise, preamplifier noise, ADC noise, and calibration error. Some of these terms depend on the scene (e.g., source photon noise), whereas others do not. Some depend on the spectral bandwidth; some depend on the detector temperature. The ADC noise depends on the number of bits to which the signal is digitized.

The performance model also considers the throughput and modulation efficiencies of the interferometer, which depend on the quality of the optics and their alignment. It also includes metrology system errors, dark current, pointing jitter, Doppler shift due to pointing, self-emission, stray light, and channel fringes (etaloning).

The throughput efficiency is the probability of a photon, within the instrumental FOV, reaching the photo-sensitive part of the detector. Throughput efficiency is wavenumber dependent but independent of optical path difference. The modulation efficiency (ME) is the depth of modulation of the varying signal. It depends on how completely the radiation from the two arms of the interferometer interferes with each other and therefore depends on the relative intensities of radiation from the two arms and the conformity of the wavefronts. Poor alignment or surface flatness in one arm of the interferometer, not matched in the other arm, degrades the ME. Typically this degradation varies with wavenumber as $\exp[-(\nu\Delta x)^2]$,

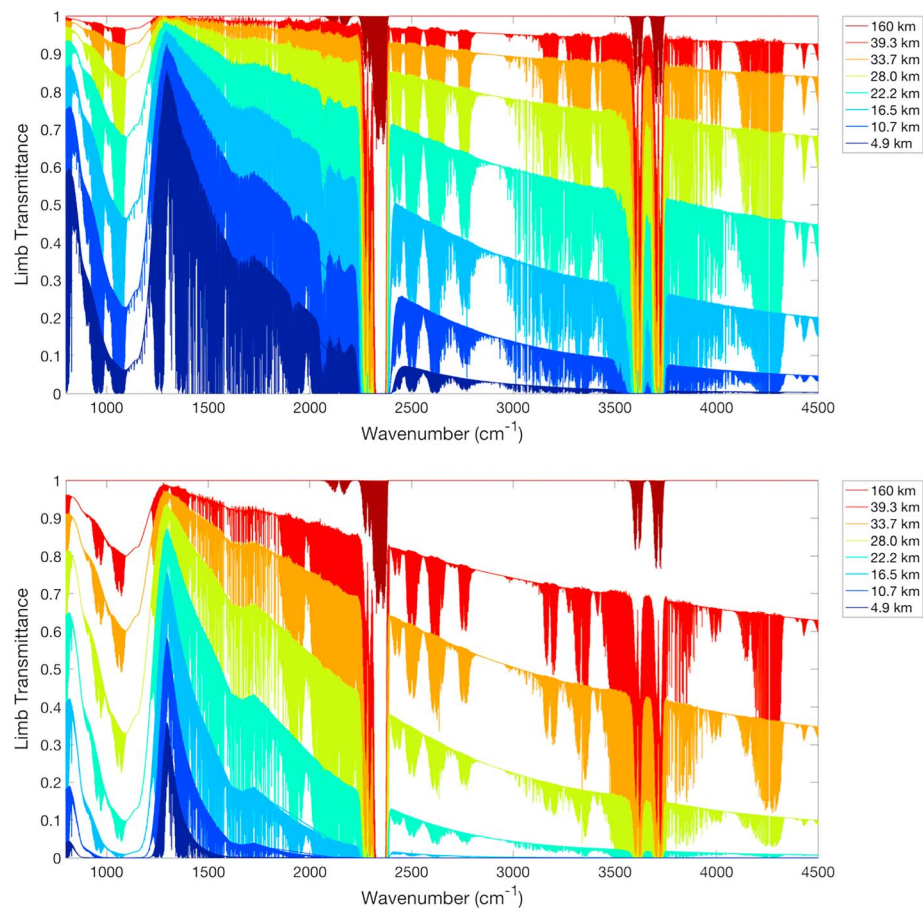


Figure 3. Simulated Mars limb transmittance spectra. Colors denote different tangent altitudes from purple (4.9 km), to red (160 km). (top) Low-dust conditions ($\tau_{\text{nadir}} = 0.1$). (bottom) High-dust conditions ($\tau_{\text{nadir}} = 0.6$). Broad features are due to dust, narrow features due to gases.

where ν is the wavenumber, so a given wavefront error (Δx) causes a much more severe drop in ME at high wavenumbers than at low wavenumbers.

The performance model does not consider noise terms that our off-line sensitivity studies had previously showed to be negligible in MATMOS. These include sampling jitter, ghosts from detection nonlinearity and periodic sampling errors, scan velocity variations, detector temperature variations, and digitization noise (assuming 24-bit ADCs).

Figure 4 shows a validation of the spectral dependence of the SNR predicted by the performance model under high-Sun conditions (i.e., no atmosphere). The top panel shows the SNR achieved by ACE (Soucy et al., 2007). Over most of the 1,000- to 2600- cm^{-1} region ACE achieves a SNR of 300–350. At lower wavenumbers, the SNR is poorer due to the dimmer solar Planck function. At larger wavenumbers the SNR declines due to degradation of the interferometer ME. The middle panel shows the prediction of our performance model for the ACE instrument. Although the details of the dips and peaks are not reproduced, the general behavior is well rendered. The bottom panel shows the predicted SNR of the MATMOS instrument using our performance model. The SNR values are approximately double those of ACE (note the doubling of the y scale). There are several reasons for the much improved performance of MATMOS:

1. Improved ME at high wavenumbers. In ACE, ME was degraded by distortion of the interferometer end mirror and the cube corner retroreflectors by their mounts.
2. MATMOS detectors were smaller (0.5 vs. 0.8 mm). Hence, they had less detector noise.
3. MATMOS HgCdTe detector has an 850 cm^{-1} cut-on versus 750 cm^{-1} for ACE.
4. MATMOS used 24-bit ADCs, as compared with 14-bit for ACE, avoiding the need for gain switching.

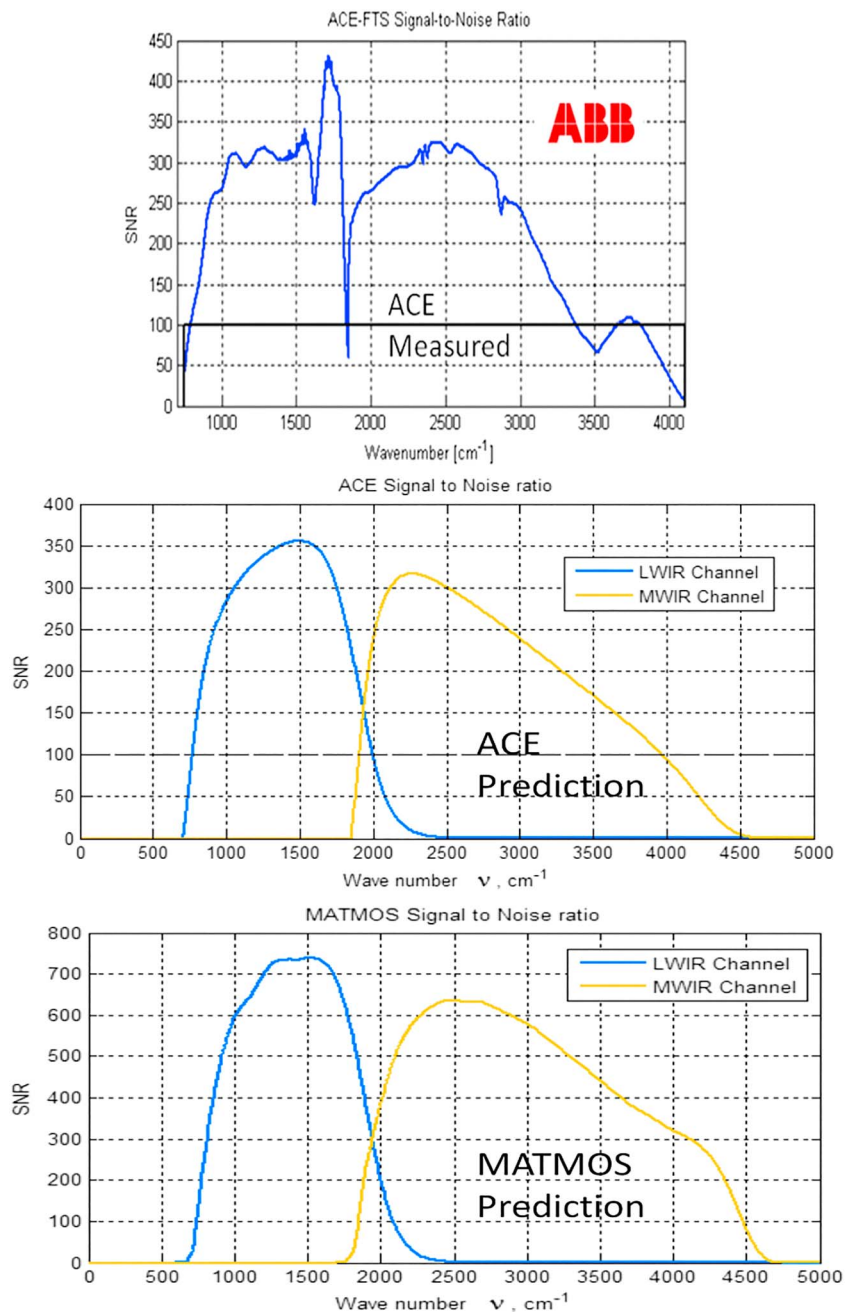


Figure 4. Validation of performance model. (top) Achieved ACE performance. (middle) Our prediction for ACE. (bottom) Our prediction for a MATMOS exo-atmospheric spectrum. ACE = Atmospheric Chemistry Experiment; MATMOS = Mars Atmosphere Trace Molecule Occultation Spectrometer.

5. MATMOS acquired data more slowly due to the smaller orbital velocity at Mars (4.5 km/s) compared with 7.8 km/s in low Earth orbit and therefore had longer integration times.

Another important aspect of the performance model is predicting the variation of SNR with tangent altitude. Many of the trace gases of interest will be most abundant close to the surface since this is close to their sources and also where the atmospheric pressure is highest. But at these low tangent altitudes, much of the solar signal will have been extinguished by Mars dust. If the instrument can maintain source photon noise limited performance, even at these lowest altitudes, then the noise will get smaller as the square root of the average signal. So even if the signal were diminished by a factor 25, if the noise also reduces by a

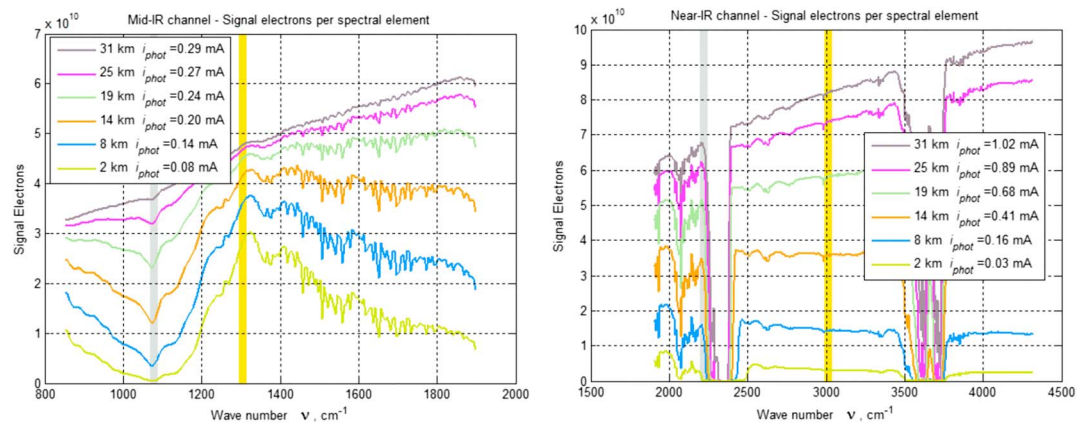


Figure 5. Signal electrons as a function of wavenumber for various tangent altitudes in the HgCdTe (left) and InSb (right) channels.

factor 5, then the SNR would still be reasonable. In many ways, the SNR at low altitudes is more important for short-lived trace gas detection than the SNR predictions for high altitudes shown in Figure 4. In the design of the MATMOS instrument, we optimized performance under conditions of dim illumination. For example, reducing the detector size reduces its noise at the risk of increased nonlinearity under high flux conditions, as does increasing the cut-on wavenumber to 850 cm^{-1} .

An unexpected prediction of the performance model is that in some of the “window” spectral regions, the SNR actually increases as the Sun gets dimmer due to dust extinction. This is because the photon noise (which depends on the *average* flux seen by the detector) drops faster than the local signal. Figure 5 shows the vertical behavior of the SNR as a function of wavenumber. The $1,305\text{-}$ and $3,015\text{-cm}^{-1}$ regions containing the two strongest CH_4 bands are highlighted in yellow.

5. In-Flight Calibration

One of the advantages of the solar occultation approach is that calibration spectra can be easily obtained. By viewing direct sunlight at large tangent altitudes at the beginning and/or end of each occultation, a “bright” solar spectrum free of atmospheric absorptions can be obtained. And by viewing deep space (or the nightside of the planet), a “dark” calibration spectrum can be obtained, which essentially describes the instrument self-emission. Under the assumption that the bright and dark calibration spectra are sufficiently close in time to the limb spectra that the instrument did not change significantly, the limb transmittance can be calculated by the equation

$$T_i(\nu) = [S_i(\nu) - S_{\text{DARK}}(\nu)] / [S_{\text{BRIGHT}}(\nu) - S_{\text{DARK}}(\nu)] \quad (1)$$

where $S_i(\nu)$ are the raw, uncalibrated, limb spectra. This ratioing removes the instrumental and solar features from the resulting limb transmittance spectra (provided the solar features are fully resolved). The main problem with this calibration approach is that the instrument will most rapidly change temperature at sunrise and sunset, which will introduce artifacts if the calibration spectra are acquired too long before or after the limb spectra. For example, if the MATMOS spectral response contains channel fringes, these will shift as a function of instrument temperature and therefore may not completely cancel between limb spectra and the calibration spectra. Also, since MATMOS sees only one ninth of the solar disk, and since the solar spectrum is not uniform across the disk, changes in the pointing between the acquisition of the limb spectra and S_{BRIGHT} will leave residual solar features in the calibrated limb transmittance spectra.

For detection of Mars trace gases, the altitudes of main interest are near the surface, and so having the calibration spectra several minutes earlier/later could be problematic. If the instrument temperature were drifting, it might be better to use spectra of the nightside of Mars, acquired immediately presunrise, for a cold calibration (S_{DARK}) rather than a deep space spectrum measured ~ 5 min before/after the sunrise. The nightside of Mars (180 K) is 13–45 times dimmer than the instrument self-emission, depending on the

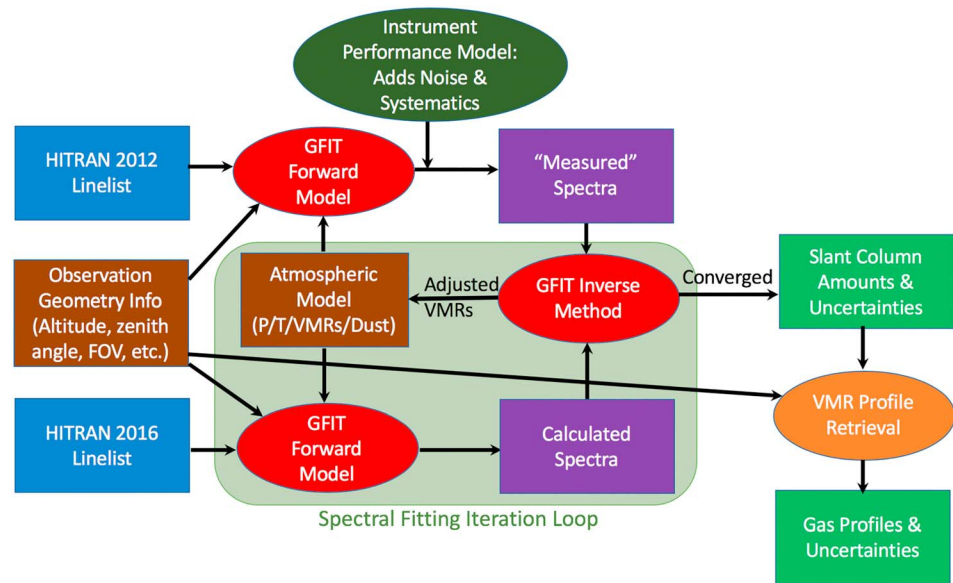


Figure 6. Flow diagram of the sensitivity analysis. Rectangular boxes represent data files. Ovals represent software. Colors are arbitrary.

wavenumber. It would therefore allow the self-emission to be quantified to 0.2–0.7%, which is $<0.03\%$ of the solar Planck function. So using the nightside as a cold calibration is likely better than a deep-space calibration spectrum, by virtue of being closer in time to the limb spectra. Of course, this all depends on the instrument temperature stability. If the instrument changes slowly, the timing of the calibration spectra becomes less critical. The ACE FTS instrument was shaded by the solar panels, which kept short-term temperature changes small. But on TGO, this was not an option for MATMOS.

The requirement that a high quality $S_{\text{BRIGHT}}(\nu)$ spectrum can be recorded every occultation imposes severe constraints on the mission and instrument design. Even though the primary science comes from the lower altitudes close to the Mars surface where the Sun will be dim, the instrument still has to accommodate the high-altitude spectra, where the total solar signal may be 10 times larger.

6. Retrieval Method

Gas profile retrieval simulations were performed using the “GGG” software, developed at Jet Propulsion Laboratory for quantitative analysis of solar absorption spectra of the Earth’s atmosphere. This software has been used extensively for analysis of solar occultation spectra of the Earth’s atmosphere, including MkIV balloon profiles (Sen et al., 1998), the Version 3 ATMOS shuttle spectra (Irion et al., 2002), and also ground-based solar absorption spectra such as the Total Column Carbon Observing Network (Wunch et al., 2011). For the MATMOS experiment, the GGG software package was adapted for Mars, which involved changing the planet radius, the gravity, the mean molecular weight, the $T/P/Z$ profiles, and the gas VMR profiles. This was then validated by fitting (nadir) spectra acquired by the Mars Express Planetary Fourier Spectrometer instrument (Formisano et al., 2005), obtaining sensible results for easily measured gases (e.g., H_2O and CO_2) and plausible upper limits for CH_4 .

The retrieval consists of two parts: (1) In the “spectral inversion” a nonlinear, least-squares, spectral fitting program (GFIT) computes the slant column abundances of each gas and their uncertainties from the spectral fits to simulated Mars spectra. (2) The “vertical inversion” solves the matrix equation relating the “measured” slant column abundances to the unknown concentration profiles and the computed slant path distances (Figure 6).

GFIT consists of two parts: a “Forward Model” that computes a spectrum over a user-defined window based on atmospheric models, the observation geometry, and a user-prescribed linelist, and an “Inverse Method” that compares the measured and calculated spectra and decides how to adjust the assumed gas VMRs to

improve the match. A Gauss-Newton iteration scheme is employed that solves the normal equations by QR factorization of the Jacobian matrix.

In the vertical inversion the concentration profiles were retrieved onto a 2-km vertical grid, which is less than the separation of the tangent altitudes, which were calculated to vary from 2.9 km near the surface to 2.1 km at 200-km tangent altitude. The slant column uncertainties are directly proportional to the root-mean-square spectral fits and also depend on the number and strength of the absorption lines of interest.

The matrix equation solved by the vertical inversion can be represented as

$$\left(S^{-1/2} K\right) x \cong S^{-1/2} Y \quad (2)$$

where S is the measurement covariance matrix, K is the matrix of calculated slant path distances, Y is the vector of measured slant columns, and x is the unknown concentration profile. The least-squares solution is

$$x = \left(K^T S^{-1} K\right)^{-1} K^T S^{-1} Y \quad (3)$$

The uncertainty in the retrieved concentration profiles is computed from the diagonal elements of the covariance matrix $\left(K^T S^{-1} K\right)^{-1}$.

For a trace gas, perhaps assumed to be present at an abundance of only a few parts per thousand, the errors bars on the retrieved VMR profile will generally encompass zero at most altitudes, implying that the gas is not detectable. But in this case the error bars still provide upper limits: estimates of the minimum detectable VMR at each retrieval altitude. As the absorptions become deeper than the spectral noise, the errors bars start to increase due to the effects of systematic errors. So whereas a gas like CH_4 may have a minimum detectable abundance of 80 ppt for a single occultation, if 7,000 ppt (7 ppb) of CH_4 were to exist on Mars, in line with the Mars Science laboratory detection (Webster et al., 2015), the errors bars would grow to ~ 250 ppt since the CH_4 lines would become optically thick in the occultation spectra which would increase the residuals due to the effects of systematic errors (ILS, temperature, zero-level offsets, etc.) on the CH_4 lines.

7. Error Sensitivity Analysis

Various types of spectral errors were added to the simulated Mars occultation spectra described in section 3. Their impact on the retrieval uncertainty was calculated by fitting the perturbed spectra using GFIT and then performing the retrieval as described in section 6. Figure 7 shows examples of spectral fits in the $3,016$ - to $3,088\text{-cm}^{-1}$ region containing the R branch of the ν_3 CH_4 band. Seven different types of error were considered: six systematic and one random.

Random noise. The performance model computed a 0.16% contribution from photon source noise plus 0.08% from detector noise. The former varies as the square root of the mean limb transmittance seen by that detector, whereas the latter is constant. Combined in quadrature, these two random terms result in a spectral SNR of 560 for a limb transmittance of 100%, $\text{SNR} = 156$ for a limb transmittance of 16%, and $\text{SNR} = 12$ for a limb transmittance of 1%. In the latter case, detector noise is dominant, so the SNR can be approximated by $1\%/0.08\% = 12$.

Residual channel fringes. Two sets of fringes were added, each with an amplitude of 0.04% with periods of ~ 0.4 and 1.0 cm^{-1} . In Figure 7b you can see these two frequencies beating against each other. These would arise from incomplete cancellation of much larger channel fringes (perhaps 0.4% in amplitude) between the limb spectra and the bright calibration spectrum, due to changes in the instrument temperature.

Spectroscopic errors. Spectroscopic errors were estimated by computing simulated limb transmittance spectra with the HITRAN 2016 linelist (Gordon et al., 2017), then performing retrievals using HITRAN 2012 (Rothman et al., 2013). This approach has the advantage of simplicity but underestimates the true spectroscopic errors in bands that did *not* change between HITRAN 2012 and 2016 but are imperfect in both. A more comprehensive spectroscopic error analysis would be much more complicated. In general, the impact of spectroscopic errors on the residuals will diminish with increasing altitude as the absorption lines weaken. Since the trace gas absorptions will also weaken, the impact on the retrieval precision will be roughly constant with altitude.

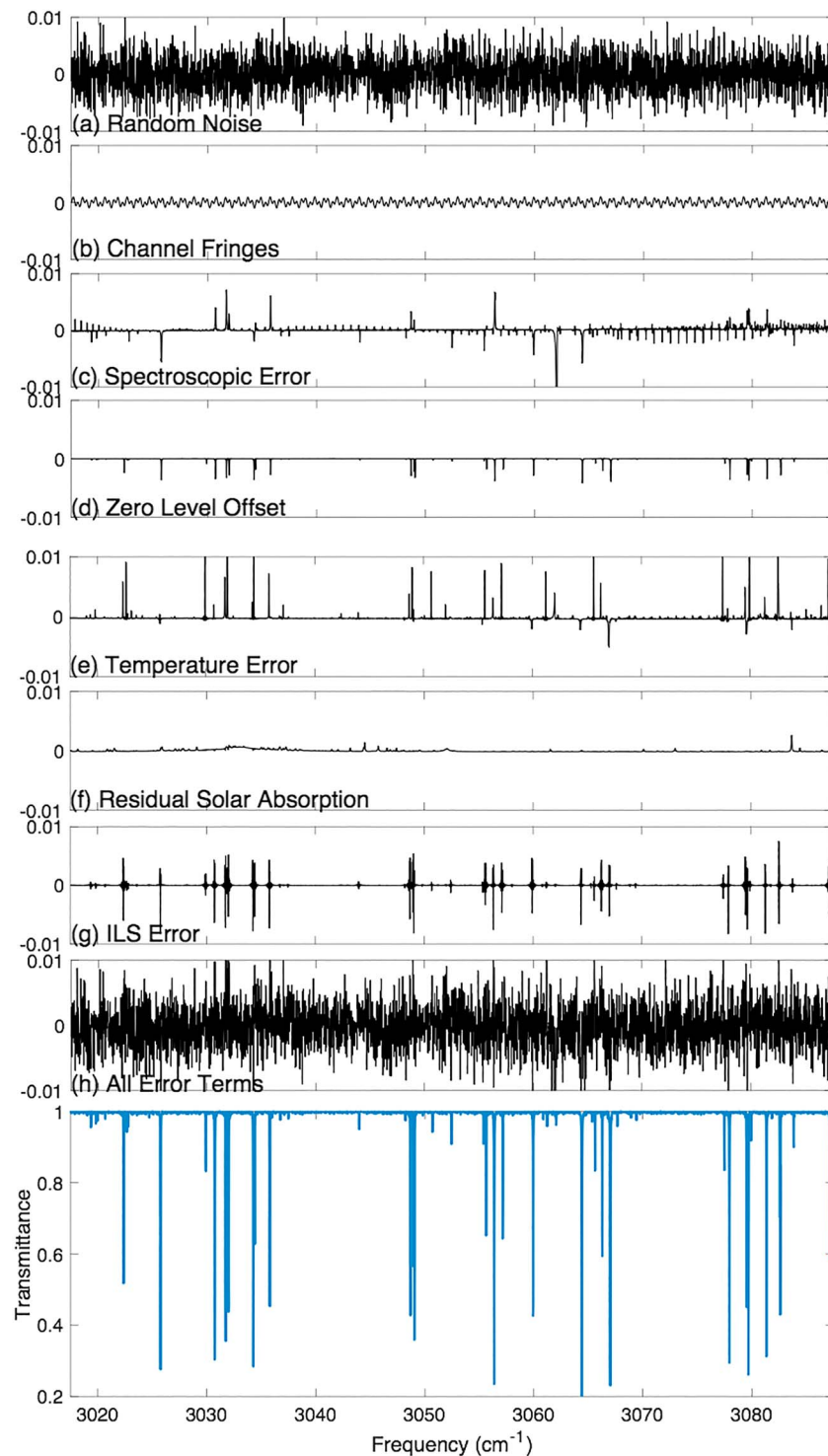


Figure 7. Fits to simulated Mars limb transmittance spectra at 10.7-km tangent altitude in the R branch region of the ν_3 CH_4 band for conditions of no dust. In each panel, a different spectral error type is introduced. Lowest residual panel shows the effect of all errors. (a) Random noise. (b) Channel fringes. (c) Spectroscopic error. (d) Zero level offset. (e) Temperature error. (f) Residual solar absorption. (g) Instrumental line shape error. (h) All error terms.

Zero level offset. This can arise due to drifts in the instrument temperature between the acquisition of the limb spectra $S_L(\nu)$ and the dark calibration $S_{\text{DARK}}(\nu)$. This problem is largest below $1,000 \text{ cm}^{-1}$. In FTIR spectrometers detection nonlinearity can lead to a zero offset in the spectrum. This latter problem can be severe

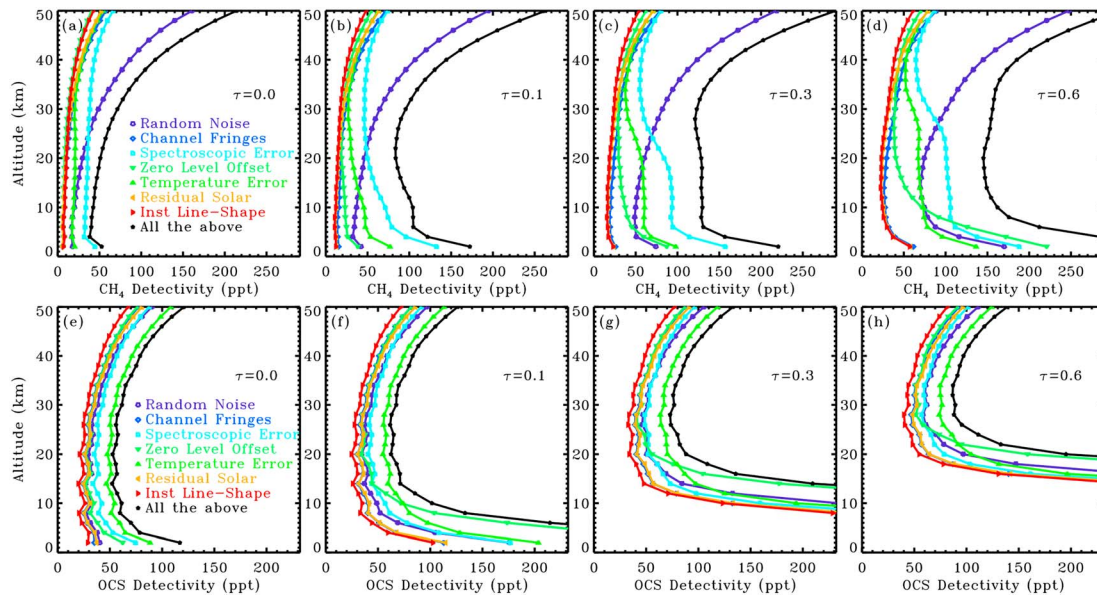


Figure 8. Illustrating the detectivity for CH₄ (a–d) and OCS (e–h) as a function of altitude for four different dust loadings: $\tau = 0.0, 0.1, 0.3$, and 0.6 . The contributions of the various noise terms are included, including the total. In the case of CH₄, random noise dominates at all altitudes and dust loadings. For OCS the effects of atmospheric temperature errors dominate.

for solar occultation spectrometers because of the high photon fluxes. Unfortunately, this offset is signal dependent and so will not be canceled by subtraction of the S_{DARK} spectrum. This effect is represented by a 0.5% zero level offset in the spectra.

Atmospheric temperature error. Although MATMOS will retrieve temperature from its own spectra, these retrievals will not be perfect and the temperature errors will cause spectral fitting residuals for temperature-sensitive, high ground-state energy (E'') lines of the strongly absorbing gases (e.g., CO₂, CO, and H₂O). Any weak trace gas absorption feature in the vicinity of one of these temperature error-induced residuals will be strongly perturbed. To represent this effect, the temperature was biased by 4 K at all altitudes. The effect of T errors will decrease with increasing altitude as the absorption lines weaken. Since the trace gas absorptions also weaken, the net effect of T errors is roughly constant with altitude.

Residual solar absorption. The solar disk is nonuniform (e.g., limb darkening and sunspots). To obtain good vertical resolution, the MATMOS external FOV is only one third of the solar diameter. This means that any drift of the location of the FOV on the solar disk between acquisition of limb spectra and S_{BRIGHT} can lead to imperfect cancellation of the solar features when performing the calibration. For this analysis, we assumed that only 98% of each solar absorption feature was removed by ratioing, such that residual solar features remained in the limb transmittance spectrum at 2% of their original depth. Since solar features can reach 50% in depth in the Mid-Infrared, this can lead to a transmittance error of up to 1%. In the spectral window shown in Figure 7f, this error reaches 0.3% at $3,084 \text{ cm}^{-1}$.

ILS errors. ILS errors cause distortion of the line shapes from the theoretical expression. Although the ILS can be parameterized in the laboratory (prelaunch) and/or from the high-tangent-altitude spectra, the parameterization is never perfect at all wavenumbers. This results in spectral fitting residuals in the vicinity of strong absorption lines (e.g., CO₂, CO, and H₂O), which can corrupt overlapped trace gas absorptions in their vicinity. Figure 7g shows the effect of a 3% error in the assumed ILS width, resulting from a 7% error in the assumed divergence of the radiation inside the interferometer. ILS errors decrease with increasing altitude as the absorption lines weaken. Thus, the impact of ILS errors is constant with altitude.

Dust has not been considered an explicit systematic error because its extinction signature is very smooth and can therefore be clearly distinguished from the narrow, discrete gas absorption lines of interest by fitting a polynomial to the slowly varying (with wavenumber) continuum signal in each fitted window. But dust

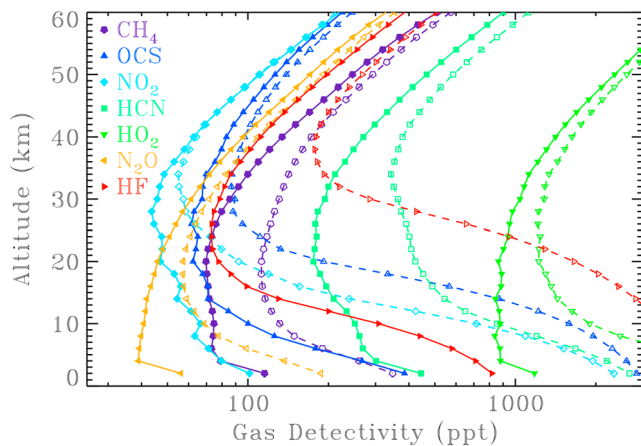


Figure 9. Mars Atmosphere Trace Molecule Occultation Spectrometer single-occultation detectivity profiles for seven gases plotted as a function of altitude. Solid symbols and connecting lines denote low-dust conditions ($\tau_{\text{nadir}} = 0.1$). Empty symbols with dashed connecting lines denote high-dust conditions ($\tau_{\text{nadir}} = 0.6$).

reduces the signal and hence the SNR. Furthermore, layering of the dust causes rapid variations of the incident solar flux during the course of acquiring a single interferogram, which distorts the ILS. So indirectly, the effects of dust are partly considered via the ILS.

Figures 8a–8d show the retrieved CH_4 uncertainty as a function of altitude for dust loadings of $\tau_{\text{nadir}} = 0.0, 0.1, 0.3$, and 0.6 . The spectral windows fitted for CH_4 cover the entire ν_4 band centered at $1,305 \text{ cm}^{-1}$ and the entire ν_3 band centered at $3,015 \text{ cm}^{-1}$. These are the two strongest CH_4 bands in the infrared. The assumed CH_4 amount was only 14 ppt, so these uncertainties represent single-occultation single-altitude detection limits (detectivities). It can be seen that in the no-dust case, the detectivity gets larger with altitude. When dust is added, the detectivity near the surface progressively degrades.

Figures 8e–8h show the detectivity of OCS as a function of altitude for dust loadings of $\tau = 0.0, 0.1, 0.3$, and 0.6 . Due to the strong ν_3 OCS absorption bands occurring at $2,200 \text{ cm}^{-1}$, a region of high dust extinction, the detectivity of OCS degrades rapidly with increasing dust loading. In the OCS case, temperature uncertainties dominate for low dust loading below 35-km altitude. At high dust loadings, random noise and residual solar CO

absorptions dominate below 20 km. The latter is due to the proximity of the ν_3 OCS absorption band (by far the strongest) centered at $2,062 \text{ cm}^{-1}$ to the CO fundamental. Over the $1,800$ - to $2,300\text{-cm}^{-1}$ region there are solar CO absorptions exceeding 40% in depth, giving rise to residuals exceeding 0.8% in our spectral fits.

The more dust the worse the sensitivity to trace gases, and the altitude of best sensitivity moves upward. For a uniformly mixed gas and dust, this best altitude occurs where the absolute depths of the gas absorption lines reach a maximum, which happens where the optical depth (OD; on Mars, primarily due to dust) is unity (see Appendix A). At higher altitudes the gas density falls off exponentially. At lower altitudes the dust extinction increases, reducing the source brightness exponentially and eventually completely blacking out. The altitude of peak sensitivity will therefore vary with the dust loading. For a gas with its main absorption around $3,000 \text{ cm}^{-1}$, the peak sensitivity will occur at $\sim 15\text{-km}$ altitude under low-dust conditions ($\tau_{\text{nadir}} = 0.1$), and $\sim 30 \text{ km}$ under higher dust conditions ($\tau_{\text{nadir}} = 0.6$). For a gas with its strongest absorption around $1,000 \text{ cm}^{-1}$ (e.g., O_3), where dust absorbs more weakly, these altitudes of peak detectivity are lower.

For CH_4 , random noise is dominant, which is actually a good thing because when aggregating results over multiple occultations, the random errors will decrease as $1/\sqrt{N}$ but the systematic errors (channel fringes, spectroscopy, ILS, etc.) will decrease more slowly. So although random errors dominate in a single occultation, systematic errors will limit the overall measurement performance over the entire mission.

There are other gases in different spectral regions where systematic errors are dominant even in a single occultation. For example, the OCS detectivity is dominated by the effects of temperature errors below 50 km. This is because the main OCS absorption band is centered at $2,062 \text{ cm}^{-1}$ where there are strong overlapping CO_2 and CO lines, some with high E'' and hence temperature sensitivity.

Figure 9 shows six examples of single-occultation detectivity profiles for CH_4 , OCS, NO_2 , HCN, HO_2 , and N_2O under low- and high-dust conditions. In every case, at every altitude, the detectivity is larger (poorer) under high-dust conditions. Gases with strong absorption bands near the dust window at $\sim 1,300 \text{ cm}^{-1}$, for example, N_2O , CH_4 , and HO_2 , show less than a factor of 2 deterioration/increase in detectivity above 10 km with increasing dust opacity from 0.1 to 0.6. On the other hand, gases whose only strong absorption band is at high wavenumber, for example, HF, show more than a factor 10 deterioration/increase in detectivity with increasing dust opacity.

Table 1 shows the spectral windows that were fitted for the weakly absorbing gases shown in Figure 9 and in Table 2. In cases such as CH_4 where multiple windows were fitted, the results were combined before the vertical inversion was performed.

Table 1
Windows Fitted for the Weakly Absorbing Gases in the Mars Atmosphere as Defined by the Window Center Wavenumber and the Full Width

Gas	Center (cm ⁻¹)	Width (cm ⁻¹)	$S_{\max}$ (cm ⁻¹ /molecules cm ⁻²)	S_{tot} (cm ⁻¹ /molecules cm ⁻²)
N ₂ O	1,285.0	105.0	1.69E-19	9.59E-18
	2,220.0	125.0	1.00E-18	5.66E-17
CH ₄	1,305.0	105.0	9.62E-20	4.50E-18
	3,015.0	180.0	2.09E-19	9.46E-18
NO	1,813.0	80.0	1.99E-20	1.41E-18
	1,895.0	80.0	2.32E-20	2.98E-18
SO ₂	1,360.0	80.0	4.85E-20	2.88E-17
	2,500.0	90.0	1.02E-21	5.97E-19
NH ₃	975.0	248.0	5.49E-19	1.84E-17
	1,650.0	295.0	6.94E-20	4.30E-18
NO ₂	1,615.0	75.0	1.30E-19	5.66E-17
	2,900.0	75.0	6.64E-21	2.88E-18
OH	3,555.0	400.0	6.13E-20	9.10E-19
OCS	860.0	42.0	1.54E-20	1.40E-18
	1,050.0	60.0	5.20E-21	5.45E-19
H ₂ S	2,055.0	55.0	1.25E-18	1.12E-16
	1,280.0	200.0	1.81E-21	6.44E-20
	2,685.0	90.0	3.61E-22	1.46E-20
HCl	3,805.0	250.0	1.83E-21	1.83E-19
	2,890.0	205.0	5.03E-19	4.52E-18
HF	3,970.7	300.0	2.37E-18	1.26E-17
HCN	1,410.0	175.0	5.06E-20	1.49E-18
	3,310.0	85.0	3.48E-19	7.60E-18
H ₂ O ₂	1,270.0	125.0	3.89E-20	1.83E-17
HCOOH	1,106.0	8.0	2.35E-20	4.34E-18
H ₂ CO	2,840.0	221.0	6.13E-20	2.29E-17
HO ₂	1,096.0	120.0	4.05E-21	1.24E-18
	1,395.0	120.0	6.69E-21	2.07E-18
CH ₃ Cl	1,420.0	200.0	3.36E-21	2.60E-18
	2,965.0	51.0	6.70E-21	2.80E-18
C ₂ H ₂	1,320.0	105.0	1.38E-19	2.43E-18
	3,280.0	125.0	2.46E-19	9.45E-18
C ₂ H ₄	950.0	125.0	8.41E-20	9.79E-18
	3,000.0	125.0	8.96E-21	2.41E-18
C ₂ H ₆	835.0	50.0	1.11E-21	5.80E-19
	1,475.0	100.0	3.55E-21	3.05E-18
	2,980.0	22.0	1.03E-19	5.51E-18
PH ₃	1,100.0	250.0	3.68E-20	5.52E-18
	2,335.0	188.0	2.52E-19	1.86E-17
CH ₃ OH	1,030.0	100.2	4.58E-20	1.74E-17
	2,925.0	250.0	7.50E-21	1.97E-17

Note. The maximum line intensity ($S_{\max}$) for each gas in each window is included, as is the sum of all the 296-K target line intensities (S_{tot}).

The MATMOS instrument would have obtained a spectrum every 2–3 km in the vertical. Its overall ability to detect a gas is therefore better than the sensitivity at any particular altitude. We have therefore defined a single-occultation-aggregated detection limit (SOADL) as

$$\text{SOADL}_{\text{GAS}} = \left\{ \sum_i (D_{\text{GAS}}(z_i))^{-2} \right\}^{-0.5} \quad (4)$$

where $D_{\text{GAS}}(z_i)$ is the detectivity (uncertainty in the retrieved VMR) of GAS at the altitude z_i . This equation assumes that the detectivities, $D_{\text{GAS}}(z_i)$, at the different tangent altitudes have a Gaussian distribution with no correlation between adjacent levels. SOADL is smaller/better than any of the best single-altitude detectivities, typically by a factor of 3–4. The SOADL provides a single number that conveniently summarizes the overall, vertically integrated sensitivity to a particular gas. Table 2 shows values of $\text{SOADL}_{\text{GAS}}$ computed for 21 different gases under four different dust loadings. In all cases SOADL worsens (becomes larger) the higher the dust loading. But for gases whose main absorption is at larger wavenumbers (e.g., HCl: 2,900 cm⁻¹; C₂H₆: 3,000 cm⁻¹; and HF: 4,000 cm⁻¹) this degradation happens faster than for gases whose main absorption is at lower wavenumbers (e.g., SO₂, 1,350 cm⁻¹).

Despite the solar occultation geometry being highly sensitive to dust, the single-occultation SOADL values shown in Table 2 are typically 2 orders of magnitude better than current upper limits (CUL). For N₂O the MATMOS is 3^{1/2} orders of magnitude better than the CUL value. To make the CUL values directly comparable with the 1 sigma MATMOS values and with each other, we have divided them by the number of sigma that they represented. For example, Villanueva et al. (2013) reported 3 sigma values. Maguire (1977) reported 2 sigma uncertainties. And Krasnopolsky (2012) appears to have quoted a 2.5 sigma upper limit of 0.2 ppb for C₂H₆. In cases where the original reported upper limit was not 1 sigma, the VMRs in Table 2 will not reflect the reported value.

Appendix B provides a “back-of-the-envelope” calculation of the detectivity of CH₄ and NO₂, in the absence of dust and systematic errors, based on the spectral line intensities, the spectral resolution and SNR, and the total atmospheric slant column.

8. Isotopologue Ratios

Isotopic abundances provide important constraints on the evolution of planetary atmospheres. The high spectral resolution of MATMOS allows separation of weak isotopic lines from nearby much stronger lines of the parent isotopologue. Figure 9 shows the expected single-occultation

precisions of the isotopic ratios of the named isotopologues and their parents. For abundant gases (CO₂ and CO) and abundant isotopologues, the precision is generally about 1% and independent of altitude since the isotopologue spectral signatures remain strong even at 100-km altitude. For the less abundant gases, the fractionation precision degrades rapidly once the isotopologue spectral absorption depths fall below the noise level. At lower altitudes the precision of the isotopic fractionation degrades toward the surface as spectral bands with the strongest isotopologue lines become blacked out by the parent band. And of course, under high-dust conditions ($\tau_{\text{nadir}} = 0.6$) the precision is far worse/larger at low altitudes than under low-dust conditions ($\tau_{\text{nadir}} = 0.1$). The HDO/H₂O ratio can be determined to 1% over the 20- to 35-km altitude range. The H₂¹⁸O/H₂O ratio has a similar shape but with a slightly superior precision. Under high-dust conditions, the H₂O fractionation sensitivity is completely lost below 15-km altitude.

Table 2
Single-Occultation-Aggregated Detection Limits (ppt) for 19 Trace Gases for Four Different Dust Loadings

Gas	$\tau = 0.0$	$\tau = 0.1$	$\tau = 0.3$	$\tau = 0.6$	CUL
CH ₄	7	17	24	33	2,200 ^a , 600^b
C ₂ H ₂	9	17	22	30	1,400 ^a
C ₂ H ₄	27	47	87	138	1,370 ^a
C ₂ H ₆	11	32	67	109	66 ^a , 80 ^c
OCS	6	9	12	17	5,000 ^d
SO ₂	16	18	21	26	550 ^e , 500 ^c , 150 ^f
N ₂ O	8	9	11	16	22,000 ^a
NH ₃	7	11	20	31	2,700 ^d
HF	4	19	40	65	N/A
HCl	6	22	47	80	100
H ₂ CO	12	37	76	122	1,300 ^a
HCOOH	7	38	85	133	N/A
HCN	13	34	58	84	700 ^a
NO	77	113	184	274	850 ^c
NO ₂	4	6	8	11	5,000 ^d
HO ₂	101	128	167	214	66,000 ^a
CH ₃ Cl	53	118	179	243	4,800 ^a
CH ₃ OH	26	54	98	151	2,300 ^a
PH ₃	35	66	127	202	50,000 ^d

Note. The sixth column shows 1 sigma current upper limits (CUL) from remote sensing measurements. Bold values in the CUL column represent detections.

^aBased on the work of Villanueva et al. (2013). ^bBased on the work of Webster et al. (2018). ^cBased on the work of Krasnopolsky (2005, 2006). ^dBased on the work of Maguire (1977). ^eBased on the work of Khayat et al. (2015). ^fBased on the work of Encrenaz et al. (2011).

It is perhaps surprising that ¹⁷OCO and ¹⁸OCO can be determined more precisely than the ¹³CO₂ given that they are less abundant by factors of 15.1 and 2.8, respectively. This is because the ν_1 band (symmetric stretch), centered at 1,376 and 1,366 cm⁻¹ for ¹⁷OCO and ¹⁸OCO respectively, is infra-red inactive for symmetrical isotopologues, so ¹⁷OCO and ¹⁸OCO can be measured without interference from much more abundant but symmetrical ¹²CO₂ and ¹³CO₂. So most of the low-altitude information on these asymmetric isotopologs comes from the ν_1 band, the stronger ν_3 region (asymmetric stretch centered at 2,350 cm⁻¹) being completely blacked out by ¹²CO₂ and ¹³CO₂. Also, in terms of dust absorption, the CO₂ ν_1 band is near the minimum.

The precision of the ¹³CH₄/¹²CH₄ ratio varies inversely with the assumed CH₄ amount—the more CH₄ the smaller/better the precision. For a 14-ppt CH₄ amount, the precision was found to be best at around 15 km with a value of 320 (32,000%) and 600 for dust opacities of 0.1 and 0.6, respectively. For a CH₄ amount of 45 ppb (assumed in Korablev et al., 2018), the MATMOS precision of the ¹³CH₄/¹²CH₄ ratio was 10% and 19% for nadir dust extinctions of 0.1 and 0.6, respectively. Using only the ν_3 band degraded these precisions to 15% and 45%. Since the atmosphere will be opaque below 10 km in the 3,000-cm⁻¹ region, we conclude that MATMOS would be unable to make a scientifically useful (10%) measurement of the CH₄ fractionation in a single occultation, unless more than 45 ppb of CH₄ were to be present above 10-km altitude. In contrast, Korablev et al. (2018) claimed that ACS would achieve a 2% precision for the ¹²CH₄/¹³CH₄ ratio from a 1-s integration, using just the ν_3 band.

Table 3 shows the occultation aggregated isotopic ratio precisions, defined as in by equation (1) but with the precisions of the isotopic ratios replacing the detectivities. For the abundant isotopologues, where a high level of measurement precision is maintained to high altitudes, the reduction in the occultation aggregated precision is about a factor 6 smaller than the best point on the profile (Figure 10). And the variation with dust amount is small because the bulk of the information is coming from above the dust. For less abundant gases like H₂O whose isotopologues are difficult to measure above 40 km, the occultation aggregated precision is only a factor 2–3 times better than the best point on the profile. It is interesting that increasing the CH₄ abundance by a factor 3,200 (from 14 ppt to 45 ppb) improves the precision by only a factor ~1,000. This is because as the ¹²CH₄ lines grow in depth, they cause extra fitting residuals (via the ILS, zero level offset, temperature errors, or CH₄ spectroscopic errors) that affect the much weaker ¹³CH₄ lines nearby.

Table 3
Occultation Aggregated Precisions (%) of Various Isotopic Ratios

Isotopic ratio	Assumed total VMR	$\tau = 0.0$	$\tau = 0.1$	$\tau = 0.3$	$\tau = 0.6$
¹³ CH ₄ / ¹² CH ₄	14 ppt	3,600	10,700	15,300	21,000
¹³ CH ₄ / ¹² CH ₄	45 ppb	5	10	15	19
¹³ CO ₂ / ¹² CO ₂	0.95	0.17	0.18	0.19	0.20
¹⁸ OCO/ ¹² CO ₂	0.95	0.13	0.13	0.13	0.14
¹⁷ OCO/ ¹² CO ₂	0.95	0.16	0.16	0.17	0.19
¹⁷ OCO/ ¹⁸ OCO	0.95	0.19	0.19	0.19	0.20
¹³ CO/ ¹² CO	800 ppm	0.38	0.39	0.40	0.41
¹² C ¹⁸ O/ ¹² CO	800 ppm	0.47	0.49	0.52	0.54
H ₂ ¹⁸ O/H ₂ O	< 200 ppm	0.6	0.6	0.6	0.8
HDO/H ₂ O	< 200 ppm	0.7	0.7	0.8	0.9

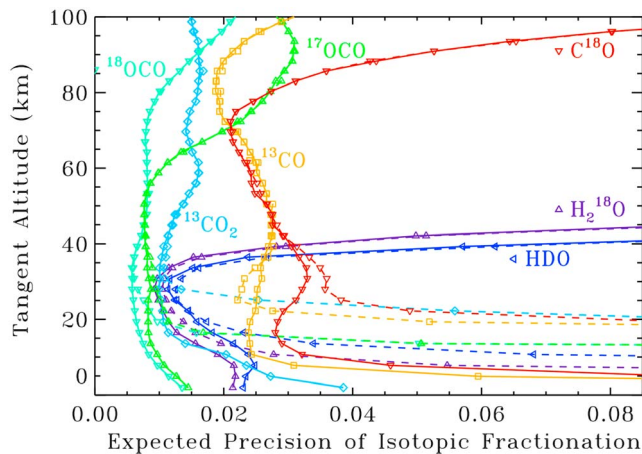


Figure 10. Expected single-occultation precisions of the isotopic ratios of the named isotopologues, plotted versus tangent altitude. Solid lines show results for low-dust conditions ($\tau = 0.1$), whereas dashed lines show results for high-dust conditions ($\tau = 0.6$). The $^{13}\text{CH}_4/^{12}\text{CH}_4$ ratio was also computed but does not fit on this plot.

9. Methane Discussion

CH_4 is an interesting case, having strong bands at lower ($1,305\text{ cm}^{-1}$) and higher ($3,015\text{ cm}^{-1}$) wavenumbers, conferring an intermediate dust dependence to its detectivity. The $3,015\text{ cm}^{-1}$ band is more than double the strength of the $1,305\text{ cm}^{-1}$ band, and the solar Planck function ($\text{ph/s/m}^2/\text{sr/cm}^{-1}$) is nearly double (see Appendix C). So at altitudes above the dust, the combined CH_4 sensitivity is dominated by the $3,015\text{ cm}^{-1}$ band. But most of the CH_4 resides close to the surface, where the signal loss due to dust extinction is many times larger at $3,015$ than at $1,305\text{ cm}^{-1}$. So our ability to detect low-altitude CH_4 is much better at $1,305$ than at $3,015\text{ cm}^{-1}$. Figure 11 illustrates the location of these two CH_4 bands superimposed onto simulated Mars limb transmittance spectra at various tangent altitudes. The dip around $1,000\text{--}1,100\text{ cm}^{-1}$ is due to the silicate absorption band of the dust. The gradual decrease in transmittance with increasing wavenumber is due to extinction by dust particles. Since these dust particles have to be very small to stay aloft in the thin Mars atmosphere, they scatter high wavenumbers much more. The sharp absorptions are due to gases, especially CO_2 .

Figure 12 shows the altitude dependence of the CH_4 detectivity broken down by band and by dust extinction. It is clear from Figures 12a and 12b that the $1,305\text{ cm}^{-1}$ window is much less sensitive to dust than the $3,015\text{ cm}^{-1}$ window. Above 40 km the $3,015\text{ cm}^{-1}$ window provides more sensitivity to CH_4 than the $1,305\text{ cm}^{-1}$ window due to its lines being more than 2 times stronger and the Sun brighter. Under high-dust conditions (red) and at low altitudes, the $1,305\text{ cm}^{-1}$ band provides far more information and hence sensitivity. By measuring both bands simultaneously (Figure 12c), MATMOS achieves good sensitivity at all altitudes, even under high-dust conditions. Under low-dust conditions ($\tau = 0.1$; blue curves), the MATMOS CH_4 detectivities are never better than 80 ppt (Figure 12c) and that without access to the $1,305\text{ cm}^{-1}$ band the detectivity would worsen to 160 ppt . Under high-dust conditions ($\tau = 0.6$; red) the corresponding detectivities are double.

Our simulations, indicating that MATMOS would have had a best CH_4 profile sensitivity of 160 to 360 ppt using just the ν_3 band, depending on the amount of dust, are in contrast to claims of much better CH_4 sensitivities for the NOMAD-SO (Nadir and Occultation for Mars Discovery Solar Occultation) grating spectrometer, recently inserted into Mars orbit, covering the same spectral region. For example, Drummond et al.

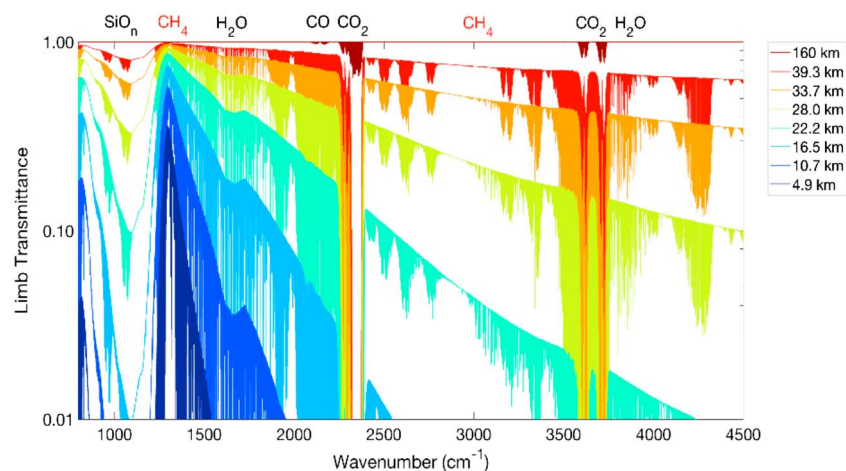


Figure 11. Simulated limb transmittance spectra for high-dust conditions ($\tau = 0.6$ at $1,075\text{ cm}^{-1}$). The locations of the main absorption bands of CO_2 , H_2O , CO , and CH_4 are indicated at the top of the panel. Limb transmittance at 28 km (lime green) is 90% at $1,300\text{ cm}^{-1}$ and 25% at $3,000\text{ cm}^{-1}$. Limb transmittance at 16.5 km (light blue) is 80% at $1,300\text{ cm}^{-1}$ and $<1\%$ above $2,600\text{ cm}^{-1}$.

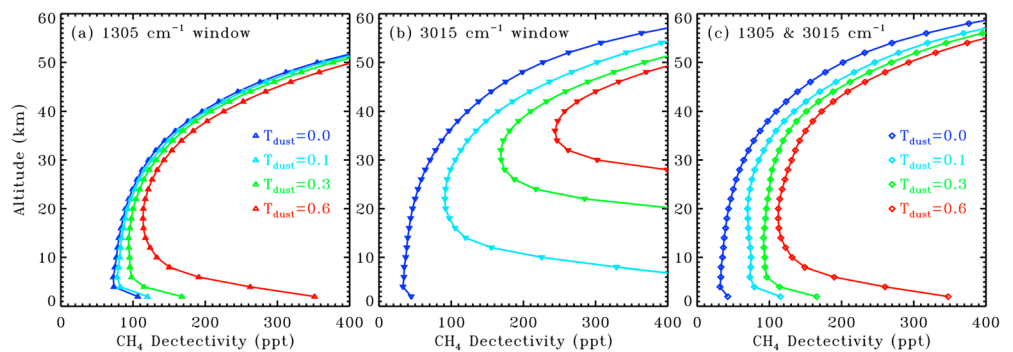


Figure 12. Single-occultation CH_4 detectivities, broken down by band and dust loading, plotted versus altitude. Colors represent dust loading. (a) The detectivity obtained from Mars Atmosphere Trace Molecule Occultation Spectrometer using the $1,305\text{-cm}^{-1}$ window alone. (b) The detectivity obtained from the $3,015\text{-cm}^{-1}$ window alone. (c) The detectivity obtained by combining these two windows.

(2011) claimed a 10-ppt detectivity for CH_4 , Vandaele et al. (2015) claimed 20–25 ppt, and Robert et al. (2016) claimed detectivities as low as 18 ppt for 20-km altitude with a possible factor $\sqrt{6}$ further improvement by dedicating all six multiplexed channels to CH_4 . See Appendix C for a more detailed discussion of published NOMAD performance and CH_4 detection limits.

We decided to investigate whether the seemingly superior NOMAD CH_4 sensitivity was an inherent advantage of its much higher SNR, or simply due to different assumptions in the performance modeling. So we applied our MATMOS performance modeling methodology to a hypothetical 0.15-cm^{-1} resolution spectrometer covering most of the $\text{CH}_4 \nu_3$ band with a SNR of 3,000 and with no coverage of the ν_4 band. We call this instrument the Moderate Resolution Fourier Transform Spectrometer (MRFTS).

We do not directly equate the MRFTS with NOMAD-SO spectrometer. The former is a Fourier transform spectrometer whereas the latter is a grating spectrometer and therefore has different noise characteristics. Moreover, we have no information on the magnitude of potential systematic errors in NOMAD spectra. We nevertheless ascribe to the MRFTS the same spectral coverage, resolution and SNR as NOMAD from Neefs et al. (2015). In terms of systematic errors, we use the same terms and magnitudes as used in our MATMOS analysis. This seems reasonable because there is no reason why the systematics (e.g., spectroscopic inadequacies) would be any less important in MRFTS than in MATMOS. In fact, one could argue that due to MATMOS's broader free spectral range, it will do a better job at retrieving atmospheric temperature and pressure than MRFTS because the T -sensitive CO_2 lines (at 950 and $2,400\text{ cm}^{-1}$) and T -insensitive CO_2 lines (at $3,300\text{ cm}^{-1}$) are available in every spectrum.

Because the SNR of MRFTS is so high, systematic errors are much larger relative to the random noise and therefore more important in limiting the retrieval detectivity. So whereas in a high-resolution instrument, random noise is the most important error term at most altitudes, this is less true for the MRFTS. Even if we were to assign an infinite SNR to the MRFTS, the detectivities would improve by less than a factor 2 because the systematic errors would quickly become dominant.

A fundamental difference between a grating spectrometer (e.g., NOMAD) and an FTS (MATMOS) is that in the latter the detector sees all wavelengths simultaneously and so the noise is spectrally white; having the same value at all wavenumbers. In a multidetector grating spectrometer, on the other hand, each detector pixel sees only a narrow spectral bandpass. So when the signal is small at a particular wavenumber/pixel, the source photon noise will be reduced, conferring a potentially large advantage to the grating spectrometer at strongly absorbed wavenumbers. But in solar occultation spectrometry the best opportunities for trace gas detections occur in spectral regions where the solar flux is large. In this situation there is no noise advantage to the grating spectrometer, relative to an FTS, so we believe that our MRFTS analysis is not inapplicable to a grating spectrometer in solar occultation mode.

Figure 13 shows CH_4 detectivity profiles for the MATMOS and MRFTS instruments. The former uses both the ν_4 and ν_3 bands in their entirety, the latter uses just the Q and R branches of the ν_3 band. In the

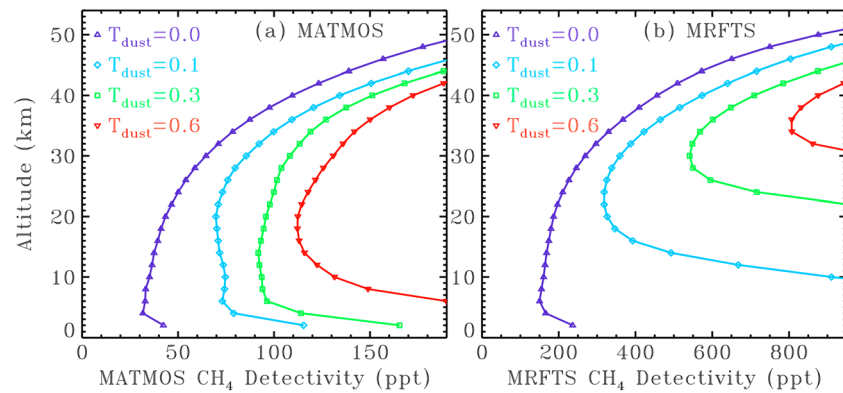


Figure 13. CH₄ detectivity profiles calculated for MATMOS (a) and MRFTS (b) under different dust conditions. Note the factor 5 x -scale change between the two panels. The dark blue curves represent no dust, the red curves represent a nadir dust optical depth at $1,075\text{ cm}^{-1}$ of 0.6. The inflections in the curves, particularly noticeable in (a) below 15 km for $T_{\text{dust}} = 0.1$, are due to the ν_3 and ν_4 contributions peaking at different altitudes under nonzero dust conditions. MATMOS = Mars Atmosphere Trace Molecule Occultation Spectrometer; MRFTS = Moderate Resolution Fourier Transform Spectrometer.

presence of dust the MATMOS detectivities are orders of magnitude superior at lower altitudes due to the high transparency of the atmosphere in the region occupied by the ν_4 CH₄ band, not used by MRFTS. For example, at 10-km altitude and with $\tau = 0.1$, the MATMOS detectivity is 72 ppt as compared with 915 ppt for MRFTS. At higher altitude where the ν_3 band dominates, the MATMOS advantage is only a factor ~ 4 . Below 10 km, even a small amount of dust ($\tau = 0.1$) degrades the MRFTS CH₄ sensitivity by more than an order or magnitude, as compared with no dust. For MATMOS the degradation is less than a factor 3 due to the availability of the ν_4 band.

The first two data rows of Table 4 reveal that, even confining the MATMOS coverage to the $3,016\text{--}3,088\text{ cm}^{-1}$ region to match MRFTS, it still outperforms MRFTS by a factor 4 to 6 in terms of CH₄ SOADL. Considering that the MATMOS SNR is only 560 at $3,050\text{ cm}^{-1}$ as compared with 3,000 for MRFTS, this result seems surprising at first. The superior MATMOS sensitivity arises because the MATMOS spectral resolution is 6 times better than MRFTS and so isolated CH₄ features appear 6 times deeper in MATMOS spectra. And there are more of them since many CH₄ lines that are blended at the MRFTS spectral resolution are well separated in the MATMOS spectra. The high spectral resolution of MATMOS also means that many more of the CH₄ lines are away from large residuals associated with the inability to correctly fit much stronger interfering H₂O and CO₂ lines (due to spectroscopic errors, ILS uncertainties, atmospheric T/P errors,

Table 4

CH₄ Single-Occultation-Aggregated Detection Limits (SOADLs) in ppt for MRFTS and MATMOS, the Latter With Various Window Combinations

Instrument	Spectral window fitted	Nadir optical depth at $1,075\text{ cm}^{-1}$			
		$\tau = 0.0$	$\tau = 0.1$	$\tau = 0.3$	$\tau = 0.6$
MRFTS	ν_3 band Q & R ($3,016\text{--}3,088\text{ cm}^{-1}$)	53	134	268	442
MATMOS	ν_3 band Q & R ($3,016\text{--}3,088\text{ cm}^{-1}$)	8	31	70	119
MATMOS	entire ν_3 band ($2,925\text{--}3,105\text{ cm}^{-1}$)	8	28	63	103
MATMOS	entire ν_4 band ($1,252\text{--}1,357\text{ cm}^{-1}$)	20	22	26	35
MATMOS	both ν_3 and ν_4 bands	7	17	24	33

Note. The MRFTS covering the Q and R branches of the ν_3 band simultaneously ($3,016\text{--}3,088\text{ cm}^{-1}$) achieves a single-occultation SOADL of 134 and 442 ppt for the low and high-dust cases, $\tau = 0.1$ and $\tau = 0.6$, respectively. Covering the exact same spectral window, the MATMOS instrument provides a factor 4–6 improvement in detectivity, depending on the dust amount. Adding the rest of the ν_3 band (P branch and high-J, R branch manifolds) and the entire ν_4 band (centered at $1,305\text{ cm}^{-1}$) to the MATMOS measurements provides improvements of factors of 8 to 13, depending on the dust conditions. MATMOS = Mars Atmosphere Trace Molecule Occultation Spectrometer; MRFTS = Moderate Resolution Fourier Transform Spectrometer.

etc.). So fundamentally, the higher spectral resolution of MATMOS provides many more opportunities to measure the depths of the CH₄ lines.

When MATMOS uses the entire ν_3 band, rather than just the Q and R branches, its CH₄ SOADL further improves due to the lines in the P branch. The improvement is only modest because the P branch CH₄ lines are weaker than those in the Q and R branches.

Using the ν_4 band alone, centered at 1,305 cm⁻¹, the MATMOS SOADLs are nearly 3 times worse in the no-dust case ($\tau = 0.0$), due to the ν_4 band being more than 2 times weaker than the ν_3 band and the solar Planck function being only half as strong. But the ν_4 SOADLs grow/worsen much more slowly with increasing dust than the ν_3 values, due to the much greater transparency of the atmosphere at around 1,305 cm⁻¹ as compared with 3,015 cm⁻¹. So, for the low-dust case ($\tau = 0.1$) the ν_4 band is already better than the ν_3 band in terms of CH₄ SOADL and this advantage grows even larger with increasing dust. For the high-dust case ($\tau = 0.6$) the ν_4 band is 3 times better than the ν_3 band, as compared with nearly 3 times worse in the no-dust case.

In our simulations, the MRFTS CH₄ detectivities did not reach the values claimed for NOMAD-SO: (10–25 ppt) by Drummond et al. (2011), Robert et al. (2016), and Vandaele et al. (2018). Even by setting all systematic errors to 0 and assuming no dust whatsoever in the Martian atmosphere, the best (lowest) MRFTS CH₄ detectivity was 40 ppt at 4-km altitude for a single occultation. More realistically, with dust OD optical depths of 0.1/0.3/0.6 and with the systematic error terms reintroduced, the best MRFTS single-occultation detectivities were 310/540/800 ppt occurring at altitudes of 23/30/35 km, respectively. The MRFTS results were, however, in reasonable agreement with the very recent NOMAD-SO calculations of Liuzzi et al. (2018).

In terms of SOADL the MRFTS values were 134/268/442 ppt for the dust optical depths of $\tau = 0.1/0.3/0.6$, which is 2–3 times better than the single-altitude detectivities quoted in the previous paragraph.

So according to our simulated retrievals, MATMOS outperforms the MRFTS for two main reasons: (1) MATMOS has access to the ν_4 CH₄ band centered at 1,305 cm⁻¹, where dust extinction is much weaker than in the ν_3 band at 3,015 cm⁻¹. (2) MATMOS's 6 times higher spectral resolving power provides many more useful CH₄ lines; useful in the sense that you can ascertain their depths accurately. Even if we were to confine the MATMOS retrievals to the Q and R branches of the ν_3 band, exactly matching the MRFTS coverage, MATMOS would still outperform MRFTS by a factor 4–6, despite having a nearly 6 times worse SNR.

In fact, we have been generous to MRFTS in ascribing similar systematic errors to MATMOS. In reality, the high-resolution instrument will have so much redundant information in each spectrum that systematic errors can often be identified and (partly) remedied. A MATMOS spectrum will contain $(4300 - 800)/0.025 = 140,000$ independent pieces of spectral information. Although there is much redundancy among these, they nevertheless can help identify systematic errors in the spectra and facilitate their correction or remediation. For example, spectroscopic errors are easily identified in a high-resolution spectrum, as are channel fringes. And as mentioned earlier, you could argue that due to MATMOS's broader free spectral range, it will do a better job at retrieving atmospheric temperature and pressure than MRFTS because the T -sensitive CO₂ lines (at 950 and 2,400 cm⁻¹) and T -insensitive CO₂ lines (at 3,300 cm⁻¹) are available in every spectrum. Although some of the systematic errors considered here may not be applicable to a grating spectrometer, there are likely other compensating systematic errors, for example, overlap of grating orders, that were not considered here.

10. Low Resolution Versus High Resolution

There is a long-standing debate in the remote sensing community on the comparative virtues of high- versus low-resolution spectrometers. Increasing the spectral resolving power (R) strongly reduces the SNR of a spectrometer. Not only are there fewer photons per spectral element, but the instrument FOV and hence etendue has to be limited, further reducing the photons. And the number of spectra acquired per unit time decreases. So the net effect of these factors is that the SNR varies as $R^{-\beta}$ where the exponent β is -1.5 when the dominant noise is source photons, and -2.0 otherwise. So in a source photon noise limited FTS, increasing the resolving power by a factor 6 (from 0.15 to 0.025 cm⁻¹) may be expected to lower the SNR per unit

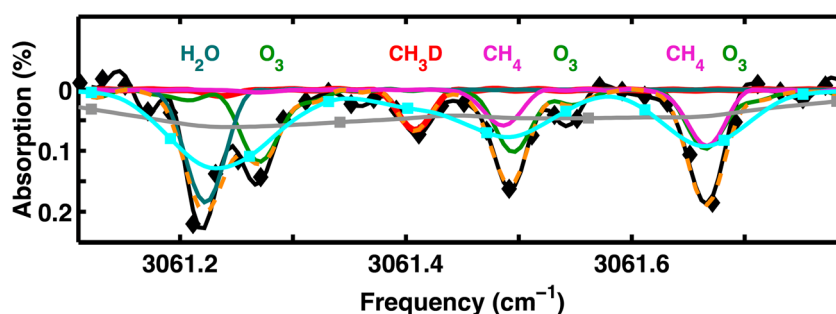


Figure 14. Fit to an average of 189 spectra acquired by the Atmospheric Chemistry Experiment Fourier transform infrared spectrometer at ~ 50 -km tangent altitude in the Earth's stratosphere by Atmospheric Chemistry Experiment-Fourier Transform Spectrometer. The black diamond-shaped points are the data; the black line shows the fitted calculation. The colored lines show the contributions of the various absorbing gases including CH_3D (red), CH_4 (purple), and O_3 (green). The light blue line represents the spectrum degraded to 0.05-cm^{-1} resolution and the gray line to 0.12 cm^{-1} . The root-mean-square fitting residual is ~ 10 times smaller than for a single spectrum, indicating that the dominant error seems to vary as $1/\sqrt{N}$, where N is the number of coadded occultations.

time by a factor $6^{1.5} = 15$. Whether this improved R is beneficial or not depends on the spectrum, in particular the depths and locations of the spectral features of interest in relation to the systematic spectral errors. If the systematic errors are small compared with the random spectral noise, then the low-resolution approach generally wins. And obviously, if the features of interest are fully resolved in the low-resolution spectrum, there is no growth in absorption depth by increasing R and the SNR worsens. But if the features of interest are narrow, and the systematic errors large, then the high-resolution approach offers the best chance to avoid them, or to identify and correct them.

It should also be pointed out that the high R approach has much lower photon fluxes and is therefore less prone to detection nonlinearity, which can cause zero-level offsets in FTIR spectra. This is particularly true when using the Sun as a source. So we cannot keep reducing R to increase the photon flux, and hence SNR, without limit.

The high-resolution approach is also more definitive, in the sense that more spectral features of the trace gas of interest will be clearly observable in the spectrum and so their consistency can be checked. In a low-resolution spectrum, where fewer features may be clearly observable, it may be difficult to assess whether the errors bars assigned to the detection is realistic. Finally, the broad-band, high-resolution approach is able to measure all gases simultaneously in every spectrum and therefore provide a much more thorough characterization of any nonequilibrium processes such as life.

11. Co-Addition of Occultations

All discussion up to this point has concerned single occultations. From 350-km altitude Mars-orbit there will be two occultations every 117 min, the orbital period. Over a 2-year mission there will be $\sim 15,000$ occultations, after accounting for the high beta angle periods when the spacecraft never enters the shadow of Mars. Aggregating the detectivities over the entire mission (e.g., by averaging spectra or retrieved VMR profiles) has the potential to reduce/improve the detectivity values quoted earlier by more than a factor 100, provided the dominant errors are random on an occultation-to-occultation basis. Our error analysis is not sufficiently sophisticated to determine how quickly the total error will reduce as a function of the number of occultations.

Fortunately, we have solar occultation spectra of the Earth's atmosphere measured by the ACE instrument (Bernath et al., 2005), a precursor of MATMOS. We coadded 189 high altitude ACE spectra and then tested whether we could detect CH_3D in the Earth's atmosphere at 50-km altitude, where the pressure (0.5 mbar) is similar to that on Mars at 15 km. The CH_3D absorptions are less than 0.1% deep and so cannot be seen in a single ACE spectrum ($\text{SNR} = 250:1$) in this spectral region. In the average spectrum, however, the CH_3D absorptions could be seen clearly, as illustrated in Figure 14. The fitting residuals were a factor ~ 12 smaller

than for a single spectrum, implying that this type of FTIR instrument has the potential to substantially reduce/improve the detection limits cited earlier by aggregating occultations.

We do not know how much further this averaging of spectra will continue improving spectral fits and hence the gas detectivities. At some point systematic errors will become dominant, preventing further improvements in detectivity. But if the MATMOS spectra were to behave similar to those of ACE, at least one order of magnitude improvement would be achieved, and quite possibly more.

12. Summary and Conclusions

We have computed the sensitivity of a solar occultation spectrometer to trace gases and to isotopologues of major gases in the Martian atmosphere. This involved simulating Mars limb transmittance spectra for various tangent altitudes under four different dust conditions. Appropriate amounts of random noise and systematic errors were added, and then spectral fitting retrievals were performed using an algorithm (GGG) with established credentials for Earth remote sensing. Detectivities were inferred from the retrieval uncertainties. We have validated this approach by application to trace gases in the Earth's atmosphere (Figure 14) to show that detectivities obtained from a weakly absorbing band are consistent with the actual gas amounts, retrieved from an average spectrum. This method has been applied to the MATMOS instrument to compute detectivities for various gases under various dust loadings. Results imply that for several gases MATMOS would have had the potential to reduce trace gas detectivities by 2–3 orders of magnitude with respect to pre-TGO ExoMars values. In doing so, it would likely detect several gases for the first time. Moreover, these new detections would utilize several lines from multiple absorption bands (for CH₄), making the detections highly definitive in the sense that the probability of a false positive would be small.

The same methodology was also applied to a moderate resolution spectrometer (MRFTS) based on our limited knowledge of the NOMAD-SO spectrometer. Our analysis reveals that despite its much higher SNR, the MRFTS would produce CH₄ detectivities of 300/800 ppt, for low/high-dust conditions, respectively. This is nearly an order of magnitude worse than those of MATMOS (55/90 ppt), due to the poorer resolving power of the MRFTS and its lack of access to the ν_4 CH₄ band centered at 1,305 cm⁻¹, located in a dust extinction window (see Figure 11). Consistency with pre-2018 published NOMAD detectivities could not be reached in the best case scenario: dedicating all MRFTS observations to the CH₄ ν_3 region, assuming zero dust, and no systematic errors.

Access to the 850- to 2,300-cm⁻¹ region gives MATMOS a big advantage, not just because of the lower dust extinction there, but also because there are several gases whose strongest absorption bands lie below 2,300 cm⁻¹. For example, the NO₂ band centered at 1,600 cm⁻¹ is 15 times stronger than the one at 2,900 cm⁻¹. The OCS band at 2,260 cm⁻¹ is 80 times stronger than any of its higher wavenumber bands. The O₃ ν_3 band centered at 1,042 cm⁻¹ is nearly 100 times stronger than its second overtone at 3,050 cm⁻¹. The N₂O ν_1 band centered at 2,224 cm⁻¹ is 25 times stronger than any of its higher wavenumber bands.

MATMOS can also gather information on isotopic ratios. In CO₂ the ¹³C/¹²C ratio can be determined to 1.5% in a single occultation over 20- to 100-km altitude, the ¹⁸O/¹⁶O ratio to <1% over 10- to 80-km altitude, and the HDO/H₂O ratio to 1.5% between 20 and 32 km. This latter figure is more than 15 times poorer than that claimed for the ACS instrument (Table 1, Korabev et al., 2018), a medium-resolution grating spectrometer.

Since the 2-year MATMOS mission would have gathered ~15,000 occultations, and since fits to averaged ACE spectra of the Earth's atmosphere seem to improve as $\sqrt{N}$, there is a good likelihood that the mission-aggregated detection limits will be 1–2 orders of magnitude better than the single-occultation detectivities presented earlier.

Finally, we hope that this paper dispels the notion that a high-SNR, medium-resolution spectrometer, operating in the Short-Wave-Infrared region only, could achieve a superior CH₄ detection limits to a high-resolution, broad-band instrument such as MATMOS, a conclusion that might well be reached by surveying currently available literature.

Appendix A: Altitude of Best Sensitivity

The fractional depth of a narrow, unresolved, absorption line of a gas of interest (e.g., CH₄) varies as

$$1 - \exp(-SX/\Delta\nu) \quad (\text{A1})$$

where S is the line strength in $\text{cm}^{-1}/(\text{molecules cm}^{-2})$, $\Delta\nu$ is the spectral resolution (cm^{-1}), and X is the absorber slant column (molecules cm^{-2}), which varies with altitude as

$$X = X_0 \exp[-z/H] \quad (\text{A2})$$

where H is the scale height and X_0 is the slant column at the surface.

The transmission of the continuum is reduced by dust by the factor $\exp[-D]$, where D is the dust optical depth, which varies with altitude as $D = D_0 \exp(-z/H)$ (assuming the same H as the gas). The absolute depth of the absorption line of interest is the product of these two terms

$$(1 - \exp(-SX_0 \exp[-z/H]/\Delta\nu)) \exp(-D_0 \exp(-z/H)) \quad (\text{A3})$$

As we get lower into the atmosphere, the first term gets larger but the second term gets smaller. There is a maximum of the absolute absorption depth at some altitude, before the dust blacks everything out.

Differentiating with respect to z and setting to zero yields

$$\log_e(-\log_e(1 + SX_0/(\Delta\nu D_0)))\Delta\nu/SX_0 = -z'/H \quad (\text{A4})$$

where z' is the altitude at which the absolute line absorption is a maximum.

Assume that the trace gas absorption line is much weaker than the dust absorption

$$SX_0/\Delta\nu \ll D_0$$

in which case $\log_e(1 + SX_0/(\Delta\nu D_0)) \approx SX_0/(\Delta\nu D_0)$

$$\begin{aligned} 1/D_0 &= \exp(-z'/H) \\ D &= D_0 \exp(-z'/H) = 1 \end{aligned} \quad (\text{A5})$$

So the (dust) slant column optical depth is 1 at the altitude (z') where the gas absorption line has its largest absolute depth.

Appendix B: Approximate Lower-Limit Detectivities

A back-of-the-envelope estimate of gas detection limits can be performed for the simple case of no systematic errors, no atmospheric dust, and no interfering absorption. Random noise is the only error term.

The Mars atmospheric pressure is $P_s = 5$ mbar, or 500 N/m^2 , or 0.05 N/cm^2 at the minimum usable tangent altitude of 2 km. This pressure represents the weight of all molecules (mostly CO₂). With a surface gravity of $g = 3.7 \text{ m/s}^2$, and a mean molecular mass of 44 g/mole or $m = 44 \times 1.66 \times 10^{-27} \text{ kg/molecule}$, a vertical column abundance of VC molecules m^{-2} would exert a pressure of

$$\text{m.g.VC} = P_s \quad (\text{B1})$$

VC is the vertical column of all molecules. For a gas with a mole fraction of VMR, the VC is

$$\text{VC} = \text{VMR} \cdot P_s / \text{mg} \quad (\text{B2})$$

The limb column will exceed the vertical column by a factor $\sqrt{(2\pi R/H)} = \sim 45$ for Mars, where R is the distance of the tangent point to center of Mars and H is the scale height. So a limb path grazing the Mars surface will contain a Slant column (SC) of $45 \cdot \text{VC} = 45 \cdot \text{VMR} \cdot P_s / \text{mg}$ molecules cm^{-2} .

The strongest CH₄ absorption lines in the ν_3 band have strengths of $S_{\text{max}} = 1 \times 10^{-19} \text{ cm}^{-1}/(\text{molecules cm}^{-2})$ per resolution element. Multiplying this by the SC gives an equivalent width of $S_{\text{max}} \cdot 45 \cdot \text{VMR} \cdot P_s / \text{mg}$. At a

spectral resolution of $\Delta\nu = 0.025 \text{ cm}^{-1}$ the absorption depth of is $S_{\text{max}} \cdot 45 \cdot \text{VMR} \cdot P_s / \text{mg} \Delta\nu$. In a spectrum with a signal-to-noise ratio of SNR, a single CH_4 feature is just detectable when its absorption depth matches the noise level

$$\begin{aligned} \text{VMR}^\# &= \text{mg } \Delta\nu / (\text{SNR} \cdot S_{\text{max}} \cdot 45 \cdot P_s) \\ &= 44 \times 1.66 \times 10^{-27} \times 3.7 \times 0.025 / (560 \times 1 \times 10^{-19} \times 45 \times 0.05) \approx 50 \text{ ppt} \end{aligned} \quad (\text{B3})$$

Assuming no dust, the MATMOS SNR will be ~ 560 in the ν_3 band of CH_4 . There are about 25 such CH_4 features across the entire band, providing an extra factor $\sqrt{25} = 5$ in sensitivity, which means that 10 ppt will be at the detection limit from a single low-altitude spectrum. This analysis ignores all systematic error terms, dust attenuation, and the effect of interfering absorptions. It therefore represents a best case scenario. The similarity of this best case 10 ppt value with the 20 ppt no-dust MATMOS at 4-km altitude in Figure 12a suggests that only a quarter of the 25 CH_4 features are actually contributing to the sensitivity, the others being wiped out by interference.

For NO_2 the lines are stronger and there are more of them. Peak intensities are 2×10^{-19} per resolution element and there are probably 50 such features across the window. This should give NO_2 a best case detectivity of 3 ppt that is 3 times better/smaller than that of CH_4 . This is not inconsistent with the $\tau = 0$ case in Table 2 (4 ppt) and suggests that most of the NO_2 lines are contributing to the detectivity, at the MATMOS spectral resolution, the others being blocked by H_2O absorptions.

The strongest N_2O lines of the ν_3 band at $2,050 \text{ cm}^{-1}$ has an intensity of 1×10^{-18} . There are ~ 25 such lines. So the N_2O detection limit should be 1 ppt in the absence of dust, systematic error, and interfering absorption. The value of 6 ppt in Table 2 indicate that systematic error and interference from strong absorption lines of other gases plays a major role in limiting the N_2O detectivity. This shows that neglecting these factors can lead to the sensitivity being exaggerated.

We stress that the no-dust assumption in this appendix is totally implausible, so the sensitivities discussed here are not at all realistic. They are calculated only to provide some validation of the full calculation of the detectivity of section 6 for the no-dust case.

It is noteworthy that the ratio $\Delta\nu/\text{SNR}$ appears in equation (B3). This gives the impression that a factor 2 decrease in $\Delta\nu$ (spectral resolution) is equivalent to a factor 2 improvement in SNR, which would be true in the absence of systematic errors and interfering absorptions. But when looking for weak absorptions in a cluttered spectrum, a small $\Delta\nu$ is more valuable than a large SNR, as is clear from the MATMOS sensitivities being several times better than those of MRFTS.

Appendix C: Spectral Coverage

Nearly all gases have their strongest (fundamental) vibrational bands in the $650\text{- to }4,200\text{-cm}^{-1}$ region. Toward lower wavenumbers, the absorption lines get weaker. Overtone bands at double the frequency of the fundamental are 20–40 times weaker. Combination band intensities are smaller by a similar factor. Figure C1a shows the integrated line intensities in 1-cm^{-1} bins for a dozen different gases of interest. Figure C1b shows the solar Planck function, which peaks at $\sim 6,000 \text{ cm}^{-1}$ expressed in units appropriate for an FTIR spectrometer with photo-detectors ($\text{ph/s/m}^2/\text{sr/cm}^{-1}$). Figure C1c shows the product of the curves in C1a and C1b, illustrating that the $650\text{- to }4,200\text{-cm}^{-1}$ region offers the best sensitivity in terms of absorbed solar photons per molecule.

Another consideration in selecting the wavenumber coverage is detector noise. This is less of an issue for instruments viewing direct sunlight because the source photon noise tends to drown everything else, except under conditions when the sunlight is highly attenuated. And although detector noise can be mitigated by cooling, this may be expensive and inconvenient. Detector performance improves toward larger wavenumbers as the necessary bandgap widens, relieving the requirement on detector cooling. So after consideration of spectral line intensities, the solar Planck function, and detector/cooler technology, the $650\text{ to }4,200 \text{ cm}^{-1}$ is generally acknowledged to be the best place to detect trace gases having very weak absorptions by solar absorption spectrometry.

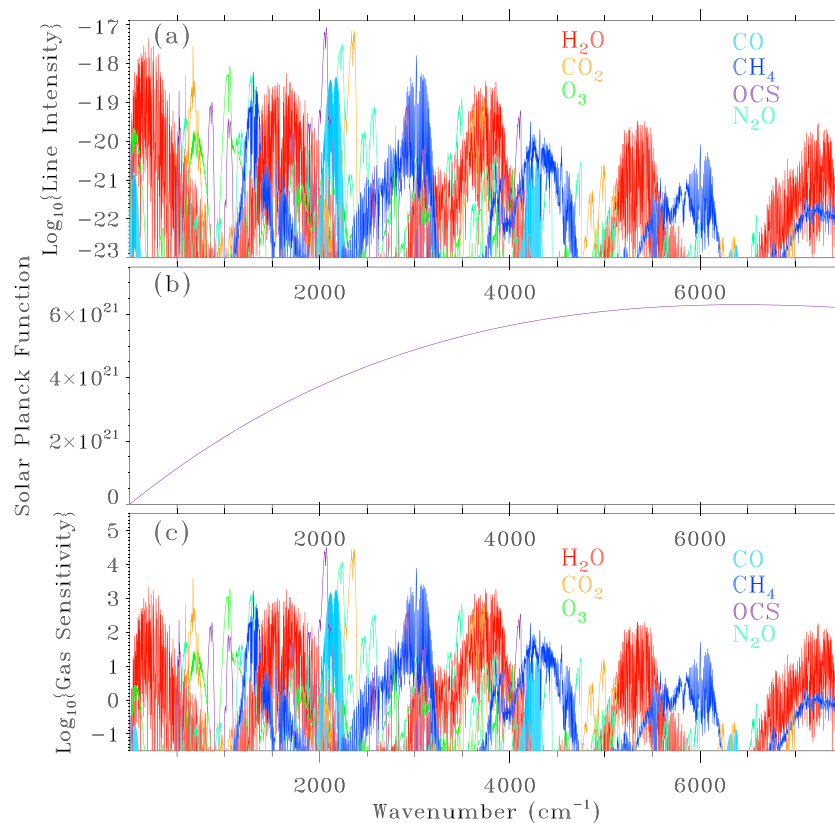


Figure C1. (a) The 296-K line intensities of various gases in units of $\text{cm}^{-1}/(\text{molecule}/\text{cm}^2)$ on a $\log_{10}$ scale, from the HITRAN 20 linelist. (b) The 5800-K Planck function in units of $\text{photons}/\text{s}/\text{cm}^2/\text{sr}/\text{cm}^{-1}$. (c) Their product: photons absorbed per gas molecule encountered ($\text{photons}/\text{s}/\text{sr}/\text{molecule}$).

The broader the spectral coverage the more atmospheric information is obtained, but the noisier the spectra. At low wavenumbers, extending the coverage requires a detector of smaller bandgap, which dramatically increases its thermal detector noise (unless steps are taken to cool the detectors to a lower temperature). At the high wavenumber end, broader coverage increases the photon flux incident upon the detector, increasing the source photon noise and the risk of detection nonlinearity. So the low wavenumber limit is a trade-off between detector noise and low altitude science. The high wavenumber limit is a trade-off between photon noise and high-altitude science.

Appendix D: CH₄ Detection Limits Published by NOMAD Team

Drummond et al. (2011) reported a solar occultation (SO) detection limit of 10 ppt assuming a SNR of 4,000 in their Table 1. The integration time period that the 10 ppt corresponds to is not stated, nor is the spectral interval that was fitted, although Figure 5 suggests that it was the 3,016–3,088 interval. The authors assert “it would be possible to go below a 10 ppt detection limit with averaging”.

Neefs et al. (2015) report that the NOMAD-SO spectrometer has a $\text{SNR} \geq 900$ and an instrument line profile of 0.22 cm^{-1} full width at half maximum, reducing to 0.15 cm^{-1} at $3,000 \text{ cm}^{-1}$ for CH₄. A spectral coverage of 2.3 to $4.3 \text{ }\mu\text{m}$ is claimed with a free spectral range of 23 cm^{-1} .

Robert et al. (2016) assert that the NOMAD-SO spectrometer will have a “relative SNR of 2000–2800” and can multiplex six different 23-cm^{-1} -wide spectral domains in 1 s. In their Table 3 CH₄ detection limits are provided for eight different grating orders, each $\sim 24 \text{ cm}^{-1}$ wide. The two best have detection limits of 24 and 25 ppt for a SNR of 2,000 and 18 ppt each for a SNR of 3,000. Robert et al. claim that the SNR could be further improved by a factor ~ 2.5 by dedicating all six of the multiplexed orders to CH₄, which would lead to a sub-10 ppt detection limit. Finally, in their Table 4, Robert et al. state a 25-ppt detection limit for CH₄, which seems to correspond to dedicating only one of the grating orders and assuming a SNR of 2,000. Robert

et al. assert that their assumed SNR of 2000 is very conservative and therefore compensates for the neglect of aerosol in their sensitivity analysis. (We disagree. A reduced SNR degrades the higher altitudes most, whereas aerosol degrades mostly the lower altitudes, where the vast majority of the CH₄ resides). Robert et al. further claim a 20-ppt CH₄ detection limit in the Limb-Nadir Observation mode, despite this having a factor 2 poorer resolving power and only a slightly larger SNR (due to a narrower bandpass).

Vandaele et al. (2018) appear to have taken dust into account in their analysis; their Figure 20A shows the substantial effect of dust on the detection limits at low altitudes with best CH₄ detectivities of 4 ppt for the no-dust case, 45 ppt in the $\tau = 0.1$ case, and 145 ppt in the $\tau = 1.0$ case. They do not specify what wavelength their dust AODs correspond to. If it is 10,000 cm⁻¹ (1 μ m), used for example by Korabiev et al. (2018) in the same special issue, the dust extinction is 2.3 times larger than at 1,075 cm⁻¹. So the AOD values would need to be divided by 2.3 to be compared with those in the current work (Toon et al.). Despite illustrating the large detrimental impact of dust at lower altitudes, Vandaele et al. nevertheless claim (their Table 2) CH₄ detection limits of 25 ppt in SO mode for a SNR of 2,000 and 20 ppt for a SNR of 3,000. Figure 6 shows an expected SNR of over 5,500 in SO mode.

Finally, we thank an anonymous reviewer for pointing out the recent Liuzzi et al. (2018) paper, which was accepted after submission of our work. Liuzzi et al. claim that under low-dust conditions ($\tau = 0.375$ at 3.3 μ m) in solar occultation mode, NOMAD's best CH₄ detectivity is 330 ppt at 18-km altitude, degrading to 1,000 ppt at 15 and 30 km. These values are more than an order of magnitude poorer than those reported in earlier NOMAD papers and are therefore much closer to our MRFTS calculations (e.g., Figure 13b).

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