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MARS ATMOSPHERE AS SEEN BY ATMOSPHERIC CHEMISTRY SUITE ONBOARD EXOMARS TGO

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Introduction: The Atmospheric Chemistry Suite (ACS) instrument on board the ExoMars TGO dedicated atmospheric spacecraft has been successfully operating since March 2018, delivering unique new data. ACS includes three spectroscopic channels covering from the near IR through thermal IR wavelengths. ACS NIR is a near-IR echelle spectrometer with filtering of diffraction orders using an AOTF. ACS MIR is a crossed dispersion echelle spectrometer, and ACS TIRVIM is a Fourier spectrometer [1]. MIR and NIR are used in solar occultation. These channels remain in perfect health; their operation is being continued. Compared to MIR, whose secondary dispersion grating has to be put in one selected out of 11 positions, MIR delivers a homogeneous and denser dataset. The cryogenic cooler of TIRVIM stopped working in the end of 2019, approaching its expected lifetime and short of one full MY. The channel collected a corpus of atmospheric spectra, mostly in nadir geometry.

The talk will introduce the ACS experiment and outline its main findings, grouped in five sections, methane, trace species, water and escape, CO, O_2, and CO_2, the atmospheric structure.

Methane: The ACS/TGO spectra in the wavelength range where the strongest methane features should be found, established a stringent upper limit on CH_4. The instrument registers faint absorption lines of water vapour but not the neighbouring features of methane. First, ACS observations gave an upper limit of 0.05 ppbv [2], while a more extensive dataset covering MY34-35 resulted in the upper limit of 0.02 ppbv or 20 ppptv [3]. The main difficulty lies in contradiction between the "background" level of methane by Curiosity [4], and the upper limit by TGO. With a lifetime of 300 years [5], methane is expected to add up, sooner or later exceeding the TGO upper limit. Assuming Gale the only source and only the background methane (0.41 ppbv), the accumulation time after which TGO should detect methane is 24y [2]. There are many places on Mars whose geological structure makes them potential sources of methane; the estimate does not take into account spikes and the improved TGO upper limit. Including these factors makes the accumulation time even shorter. Mesoscale simulations of methane dissipating from Gale under the TGO constraints suggest that not only it is the single source on the planet, but a particular location of the putative source within the crater rim can solely explain the observed background and spikes [6, 7]. Moores et al. [8] suggested that the height of the planetary boundary layer in the crater decreases at night, limiting mixing and leading to the accumulation of methane. Indeed, recent SAM-TLS daytime measurements are only upper limits of ≤0.2 ppbv [6]. The night-time scenario could increase the accumulation time of methane or the allowable area on Mars where it can seep. Still, to comply with the TGO upper limits, an as yet unknown mechanism for the rapid methane destruction is needed. ACS continues regular CH_4 measurements.

Trace gases and faint absorptions: "In place of methane", i.e. in the spectral range containing the strongest methane spectral features, two new absorbers are discovered in the ACS MIR spectra. In a range of 2900–3300 cm^{-1}, 30 observed lines were absent from spectroscopic databases. Their frequencies matched the theoretically calculated P-, Q-, and R-branches of the magnetic dipole or electro-quadrupole band of the main CO_2 isotopologue. This band, forbidden for electro-dipole absorption, has been never observed or numerically calculated. The relative depth of branches suggested its magneto-dipole nature [9]. Later, the even weaker electric quadrupole system was also found in the ACS spectra [10].

In the same spectral range, we detected a weak infrared ozone band overlapping one of methane's P-branch features. This band has never been seen in the Mars atmosphere before. Observations in the IR make it possible to reconstruct vertical profiles and explore the lowermost layer of ozone [11, 12].

Hydrogen chloride (HCl) was confidently identified by 12 lines in the ACS MIR spectra [13, 14]. As confirmed by NOMAD, the HCl mixing ratio reaches 4 ppbv, significantly higher than previous upper limits. The gas appeared after the MY34 GDS and in perihelion of MY35, while outside the dusty season it remained ≤0.1 ppbv. A possible mechanism of HCl formation involves atmospheric dust (see talk by K Olsen et al.) The high fidelity of the collected spectra makes it possible to estimate the ratio $H^{37}Cl/H^{35}Cl$ [15]. Unlike for other volatiles on Mars, the isotopic anomaly is indistinguishable. Given its short lifetime, fractionation mechanisms in HCl are too weak to be noticed.

A 1-D chemical model in the meteorological context from LMD MGCM [16] reproduces the seasonal and vertical behaviour of HCl. It also suggests that chlorine chemistry might shorten the lifetime of methane down to weeks or days, potentially resolving the methane conundrum. This hypothesis needs further validation.

The sensitive search for more trace species resulted in improving of several upper limits. ACS has established upper limits of ≤50 pptv on C_2H_6, ≤1 ppbv on CH_3Cl, ≤0.4 ppbv on OCS [17], ≤0.1 ppbv on phosphine PH_3 [18]. The model-predicted NO_2 abundance of ~0.2 ppmv is tentatively confirmed (see talk by A. Trokhimovskiy et al.)

Water and escape: ACS measures water vapour profiles in occultation with NIR (1.38-µm band) and with MIR in broader range, covering isotopologues and the strongest 2.56-µm band. The vertical distribution of water vapour was measured up to 120 km [19-21]. During the MY34 GDS, smaller scale events like the MY34 C-storm, and the perihelion season of MY35 the H_2O mixing ratio of ~100 ppmv is observed at 100 km and higher. The Lyman-alpha measurements by MAVEN showed simultaneous increase of escaping H atoms during the MY34 C-storm, implying such dust events can boost the planetary H loss by a factor of 5–10 [22]. Still, ACS measurements and modelling suggest that the seasonal signal is water elevation and H escape is comparable to that during GDS [21, 23]. Given the duration of the perihelion dusty season and the fact that GDS occurs every third MY at most, we infer the seasonal contribution to escape is prevailing [23].

ACS MIR measures altitude profiles of H and O isotope ratios in H_2O. HDO and H_2O profiles combined with expected photolysis rates, also reveal the prevalence of the perihelion season for the formation of atomic H and D at altitudes relevant for escape [20]. This study shows that while condensation-induced fractionation is the main driver of variations of D/H in water vapour, the differential photolysis of HDO and H_2O mainly controls the isotopic composition of the dissociation products. Observed variations of the D/H ratio, lower HDO/H_2O ratios in the colder regions of Mars, the impact of the MY34 GDS were simulated with GCM [24-26] (See talk by Vals et al.) MIR measurements allowed, for the first time, the measurement of vertical profiles of the $^{18}O/^{16}O$ and $^{17}O/^{16}O$ ratios in atmospheric water vapour. They are enriched with respect to Earth ($\delta^{18}O = 200 \pm 80‰$ and $\delta^{17}O = 230 \pm 110‰$ and do not show any evidence of altitudinal variations [27].

Both NIR and MIR ACS water profiles are accompanied with simultaneous density-temperature profiles retrieved from CO_2 absorptions, allowing to assess the saturation state. Fedorova et al. [19, 28] concluded about nearly ubiquitous supersaturation of water, particularly during the dust season, thereby promoting water escape on an annual average. The robustness of the supersaturation detected in the specific terminator geometry was supported by hourly-resolved OU MGCM modelling with assimilation [29]. Within the same framework, ACS water profiles serve to define the varying hygropause altitude (See talk by J. Holmes et al.)

Water ice clouds detected by ACS MIR and TIRVIM were studied in the context of atmospheric and water profiles [19]. The seasonal distribution of condensation clouds and also dust, and the aerosol properties were investigated [30, 31] (See talk by Stcherbinine et al.)

The effort to constrain the abundances of odd-hydrogen species OH and HO_2 from MIR spectra is ongoing (See talk by J. Alday et al.)

CO, O_2 and CO_2: The first vertical profiles of carbon monoxide CO before and during the MY34 GDS were retrieved from MIR spectra at 2.35 µm [32]. They showed a prominent depletion of CO up to 100 km, pointing to the importance of CO oxidation during wetter GDS conditions. A complete climatology of CO vertical profiles from the beginning of the mission to the end of MY35 was obtained from NIR data using a weaker CO band at 1.6 µm, overlapped with stronger CO_2 band. CO profiles show strong enrichment of 3000-4000 ppmv at 10–20 km in southern winter and early spring in mid-high southern latitudes. An enrichment is also found above 50 km at equinoxes [33]. The mean CO VMR is ~950 ppmv, higher than Curiosity *in situ* measurements [34] and closer to CRISM, PFS and NOMAD nadir results [35–37].

Another incondensable species, O_2, is also measured by ACS NIR in its 0.76 µm band. The as yet unpublished two-MY dataset includes O_2 profiles measured up to 40-50 km and exhibit enrichments similar to those observed in CO. The average O_2 mixing ratio is 1800 ppmv; the O_2/CO ratio of ~2. (see talk by A. Fedorova et al.)

Isotopic ratios in atmospheric CO_2 were monitored using MIR data to obtain the O and C isotopic composition at 70–130 km. Their vertical trends are consistent with the expectations from diffusive separation above the homopause, with average values below showing Earth-like fractionation. Results suggest that at least 20-40% of primordial carbon has been lost from Mars throughout history [38].

Atmospheric structure: ACS TIRVIM measures spectra of the outgoing thermal radiation in nadir. The spectral range (600–1300 cm^{-1}) includes the 15-µm CO_2 band. Inversion of spectra in this band yields vertical temperature profiles from the surface up to 60 km of altitude. The continuum spectrum at shorter wavelength permit to measure surface temperatures and estimate column optical depths of dust and H_2O clouds. TIRVIM operated from Ls=143° MY34 to Ls=115° MY35. The nadir coverage during this period varied within 500–9000 spectra per orbit, allowing, despite several gaps due to hardware issues, a uniquely dense coverage of the diurnal cycle. Two methods of inversion are developed and validated against MCS/MRO profiles [39, 40]. Most differences between TIRVIM and MCS atmospheric temperatures can be attributed to differences in vertical sensitivity.

The atmospheric thermal structure and the column dust content during the MY34 GDS was analysed, capturing its evolution and the atmospheric response to the changing dust load. The global storm caused asymmetric atmosphere heating, predominantly in the southern hemisphere, and changed diurnal contrast of atmospheric thermal structure. Also, at the peak of the GDS we see a reduced diurnal contrast of surface temperatures [40]. To understand the meteorology of GDS, in particular the atmospheric properties that cannot be measured directly, such as wind, data assimilation was applied using LMD MGCM and the Local Ensemble Transform Kalman Filter [41]. The model predicts the atmospheric state every three hours. At the peak of the storm, a strong asymmetry developed in the midlatitude jets, modifying the diurnal and semidiurnal tides. The reconstructed surface pressure was verified against Curiosity measurements (See talk by R. Young et al.)

Thermal tides in the Martian atmosphere were analysed using temperature the TIRVIM nadir profiles near the northern summer solstice of MY35. The observations have a full local time coverage, which enables analyses of daily temperature anomalies. Wave mode decomposition showed dominant diurnal tide, important semi-diurnal tide and diurnal Kelvin wave, with maximal amplitudes of 5, 3, and 2.5 K, respectively, at 10–100 Pa. The results agree with the LMD MGCM, yet with noticeable earlier phases of diurnal and semi-diurnal tides [41].

The thermal structure at the limb was reconstructed from ACS MIR occultation spectra in CO_2 bands. Belyaev et al. [42] using the strongest 4.3-µm band of CO_2 retrieved the atmospheric structure up to 180 km and traced the homopause and mesopause over seasons. The homopause was detected from 80 km at aphelion to 110 km at perihelion thorough MY34-35, depending on dust activity. The mesopause altitude rises from 70-90 km in the high-winter latitudes to 130-150 km in summer (See talk by D. Belyaev et al.)

Starichenko et al. have used MIR profiles to study the gravity waves at 20-160 km. For the first time such a wide altitude range was analysed. The waves' amplitude increases up to ~100 km, and they break up above, in the mesopause region 100–130 km (See talk by E. Starichenko et al.)

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