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Trace species in planetary atmospheres: Some results of TGO ExoMars

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The presence of life alters the composition of a planet's atmosphere. This thesis, formulated back in the 1960s, is now gaining importance. The discovery or even suspicion of chemically non-equilibrium compounds in the atmosphere of another planets can influence space policies. The report reviews the discovery of phosphine on Venus and its possible consequences. The main focus is on the issue of methane on Mars and the related results of the *ExoMars* 2016 Trace Gas orbiter.

Keywords: Planets and satellites: atmospheres – planets and satellites: composition – planets and satellites: detection – planets and satellites: Mars – planets and satellites: Venus – radiative transfer

1 Introduction

Forms of life on a planet profoundly alter the planet's atmosphere and regulate its climate. Our Earth offers a striking example: the appearance of oxygen in the atmosphere ∼3.5 billion years ago, in Archea, and a sharp increase in its content, at first ∼2.5 and then, almost to the current level, ∼1 billion years ago was associated with the development of living forms. The O_2 content has remained within 21±5% over the past 200 million years. The Earth's atmosphere contains both oxidising and reducing gases, oxygen and methane. Considering the non-equilibrium atmospheric components allowed Hitchcock and Lovelock (1967) to formulate the thesis: "Knowledge of the composition of the Martian atmosphere may similarly reveal the presence of life there".

The excitement about the discovery of phosphine (PH_3) in the atmosphere of Venus by ALMA observations in the millimetre range (Greaves et al. 2021a), which was announced in October 2020, substantiates the above statement. It was not possible to explain the presence of this gas within the framework of known chemical reactions, and several publications associate it with the presence of anaerobic microorganisms in the Venus clouds (Bains et al. 2019; Seager et al. 2020).

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NASA executives have reacted immediately: "... the most significant argument for life beyond Earth ... It's time to prioritize Venus." Indeed, out of five candidates selected for Discovery-class projects in June 2021, two are dedicated to Venus exploration (launches in 2029–30). Right after this, ESA approved the ENVISION project with an estimated launch date of 2032 (Wilson et al. 2021). Roscosmos plans to develop *Venera-D* mission by 2029–31 (see Section 2).

The ALMA discovery of phosphine at 20 parts per billion (ppbv) has sparked a heated debate. In the IR spectral range, strict upper limits have been established, $\leq$5 ppbv according to data from the airborne observatory SOFIA (Encrenaz et al. 2020) and $\leq$0.2–1 ppbv according to *Venus Express* (Trompet et al. 2021). The finding was criticised pointing to deficiencies in data reduction (Snellen et al. 2020; Thompson, 2021; Akins et al. 2021). It was also noted that the absorption of SO_2 could explain the observed line without the involvement of phosphine (Villanueva et al. 2021; Lincowski 2020). Still, the authors of the discovery insist on the viability of their interpretation (Greaves et al. 2021b) and further hypothesise about the cloud habitability (Seager et al. 2021).

The history of the search, discovery and discussion of methane on Mars is developing just as dramatically, albeit stretched over a longer time frame (see Section 4). After the announced detection of methane in 2003–2004 (Fomisano et al. 2004; Krasnopolsky et al. 2004; Mumma et al. 2009), the idea of a specialised orbital mission aimed at measuring small components in the atmosphere of Mars arose and took shape. In 2012, such a mission was decided as the first part of the joint ESA–Roscosmos *ExoMars* program, the Trace Gas Orbiter (TGO) (Vago et al. 2015). The spacecraft was launched by the Russian *Proton-M* on March 14, 2016 and reached Mars in October of the same year. The circular orbit of observations was formed by the aerobraking by the spring of 2018. There are four scientific instruments on board the satellite, two Russian and two European. The Atmospheric Chemistry Suite (ACS) complex of sensitive IR spectrometers is dedicated to measuring small atmospheric components (Korablev et al. 2018).

This paper follows the lines of the report to the Division of Physical Sciences of Russian Academy of Sciences on April 19, 2021. It briefly discusses the research of Venus planned in Russia and the possibilities of studying small atmospheric components. The primary attention is paid to the results of the ACS experiment onboard *ExoMars* TGO on methane and other trace gases on Mars.

2 Venus studies

A series of successful USSR projects devoted to exploring Venus ended in 1984 with *VeGa* project, the landing of two descent vehicles and the flight of two atmospheric probes. Russian scientific groups have had the opportunity to explore the planet during the ESA *Venus Express* mission (2005–2015). Two science instruments of this project were created with the participation of Russia; most of the experiments had scientific involvement. In particular, Russia has contributed to the spectroscopic complex for studying the above-cloud atmosphere SPICAV-SOIR, created together with scientists from France and Belgium (Bertaux et al. 2007). The dataset accumulated by Venus Express is still in use – for example, the most stringent upper limit

on phosphine (Section 1) is established with SPICAV-SOIR data. Russian scientists have published ∼200 articles in refereed journals. Equally, the data obtained by the Japanese satellite of Venus *Akatsuki* are employed. Participation in foreign projects made it possible to preserve the research teams engaged in Venus studies in Russia.

The nearest opportunity to study phosphine by approaching the planet will be offered onboard the planned ISRO *Schukrayaan-1* orbiter (Haider et al. 2018). Its launch is scheduled for early 2025. Based on the *ExoMars* TGO developments, the Russian–French VIRAL instrument is designed to measure atmospheric gases and wind speed from orbit in the IR range with a high spectral resolution.

The *Venera-D* project (Zasova et al. 2020), being prepared as part of the Roscosmos Venus research program, presents unique opportunities for studying the biomarker gases. Using IR spectroscopy, it will be possible to conduct sensitive measurements of gases above the clouds and in the upper cloud layer from a satellite in polar orbit. During the lander's descent, the analysis of gases and aerosols will be carried out using an analytical complex, including gas chromatography, a mass spectrometer, a laser spectrometer, and an X-ray fluorescence analysis. It is also planned to analyze gas and aerosols on the balloon probe using mass and laser spectrometry.

3 Solar occultation studies of the Mars' atmosphere

The method of sounding the atmosphere, observing eclipses of the Sun by a planet from the spacecraft has several advantages. The solar disk is 10^6 times brighter than the illuminated surface of Mars, which is observed from the Earth or a nadir-looking spacecraft. The optical path at the limb depends on the aiming height and can reach 50 heights of a homogeneous atmosphere. On Mars, depending on the aerosol content, the gain in the optical path (compared to ∼3 for observations in nadir) is ∼10 times. Combining these two factors makes it possible to reduce the detection threshold or increase the measurement accuracy by a factor of 100–300. Also, the solar occultation allows us to obtain vertical profiles of measured values with good altitude resolution (Fig. 1). The disadvantages of the method are restrictions on the location (the spacecraft orbit binds the coordinates of eclipses) and the difficulty to measure at low altitudes. Generally, aerosol strongly weakens the signal below ∼10 km.

This method was first implemented on Mars in the Auguste experiment onboard the *Phobos-2* spacecraft (Krasnopolsky et al. 1989). Later, our group conducted several solar occultation experiments studying atmospheres of Mars, Venus and the Earth in the infrared range: SPICAM / *Mars Express* (2003–) (Bertaux 2006; Korablev et al. 2006), SPICAV and SOIR / *Venus Express* (2006–2014) (Bertaux et al. 2007; Korablev et al. 2012; Nevejans et al. 2006), Rusalka onboard the ISS (2009–2012) (Korablev et al. 2011), ACS/*ExoMars* TGO (2016–) (Korablev et al. 2014, 2018). Instrumentation on the same principles was created for the *Mars-96* and *Phobos-Grunt* unsuccessful projects.

Onboard TGO, ACS includes three channels. ACS NIR is a near-IR echelle spectrometer with filtering of diffraction orders using an acousto-optical filter. ACS MIR is a cross-dispersion echelle spectrometer, and ACS TIRVIM is a Fourier spectrometer. Most of the results presented here were obtained with the ACS MIR channel

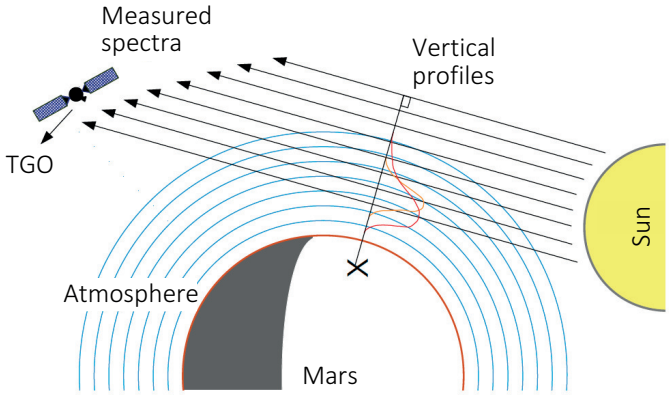


Figure 1 A sketch of atmospheric profiles measurements when observing a solar occultation from a spacecraft. The refraction of light in the atmosphere of Mars is negligible.

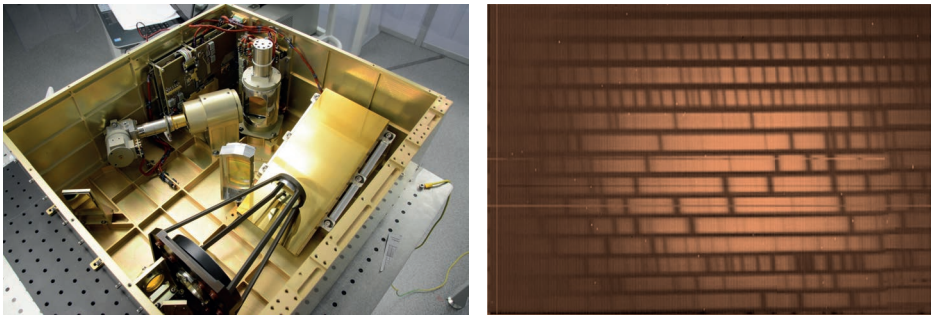


Figure 2 ACS MIR, one of the channels of the ACS instrument onboard TGO *ExoMars 2016* with the cover removed. The echelle diffraction grating is visible. On the right is the arrangement of diffraction orders at the detector.

data, which provides a high spectral resolution ($\lambda/\Delta\lambda \geq$30,000) in the wavelength range of 2.3–4.2 μm (Trokhimovskiy et al. 2017; Korablev et al. 2018), see Fig. 2.

In solar occultation, the instrument's optical axis should be pointed to the solar disk, and the spacecraft should remain in an inertial attitude. In each occultation, the solar spectrum is measured above any significant atmospheric absorption. The spectra at all levels are then normalized to this reference spectrum. For one sunset or sunrise, the resulting series of atmospheric transmission spectra allows for the retrieval of atmospheric parameters (Figs 1, 3).

First, the direct problem of atmospheric sounding is solved – the transmission spectrum of the atmosphere is sought for known parameters (temperature, pressure, content of atmospheric gases). In the IR range, the absorption cross-sections depend on temperature and pressure. The width of spectral lines depends on the velocity of molecules and the frequency of their collisions. The absorption in each line is computed, considering the spectral broadening profile. The line parameters are taken from spectroscopic databases (e.g., HITRAN 2016, Gordon et al. 2017). A layer-

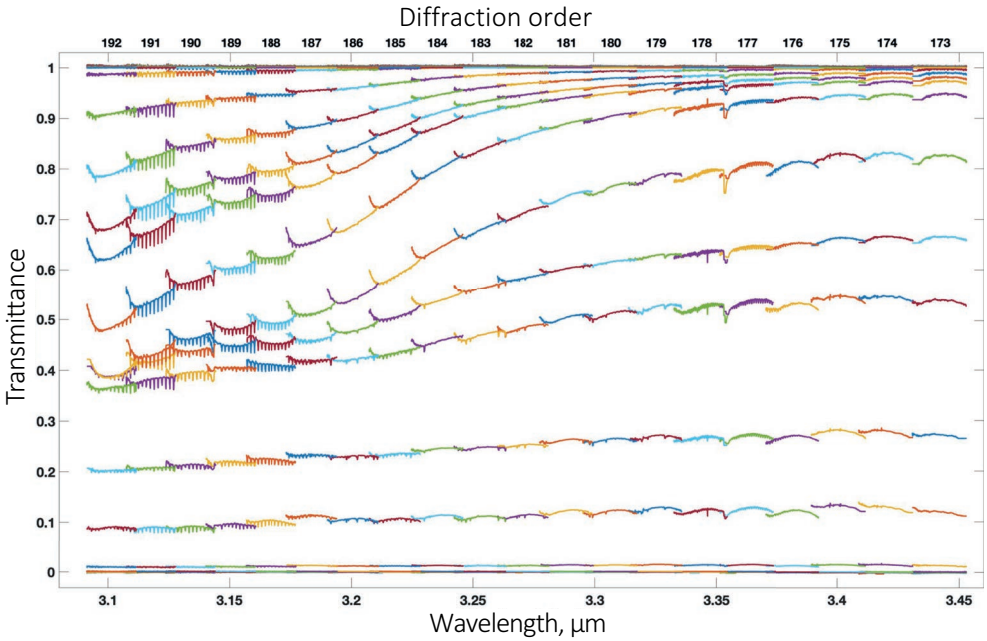


Figure 3 An example sequence of transmission spectra measured by the ACS MIR spectrometer as the atmosphere of Mars eclipses the Sun. The main features of methane are sought in the spectral range 3.1–3.45 μm. Visible gaseous absorption features belong to CO_2. Strong continual absorption at $\lambda \leq 3.25$ μm corresponds to a band of water ice and is explained by clouds (Korablev et al. 2019).

by-layer spherically symmetric model of the atmosphere is used (Fig. 1), and the spectrum of "infinite" resolution is calculated as the sum of absorptions from each line. Finally, the spectrum is convolved with the spectral profile of the instrument. The direct problem entails lengthy computations, calling for multidimensional look-up tables to solve the inverse problem.

The inverse problem reconstructs vertical profiles of density, temperature, and atmospheric components mixing ratios from the measured spectrum. The contribution of absorption from all layers along the optical path is taken into account simultaneously. For Mars, the density is usually first retrieved from the carbon dioxide absorption, followed by the temperature, using the uneven dependence of the CO_2 and other gases lines on temperature. The atmospheric profile in the hydrostatic approximation is then sought iteratively, using regularization. The content of the trace components is restored at the concluding steps (Fedorova et al. 2020; Belyaev et al. 2021).

4 Search for methane on Mars

A targeted search for organics on Mars began in the middle of the 20th century. Astronomical observations in the then-new infrared range and instruments on the first flyby and orbiting USSR and NASA spacecraft were looking for C–H absorption

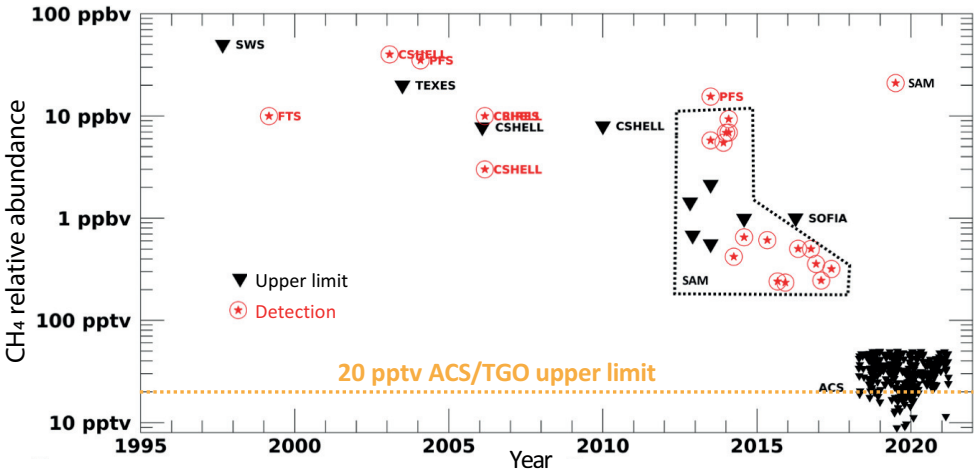


Figure 4 History of attempts to detect methane since 1997. The upper limits and detections are shown from Earth-based IR spectroscopy (Krasnopolsky et al. 2004, 2007, 2012; Encrenaz et al. 2005; Mumma et al. 2009; Villanueva et al. 2013), *Infrared Space Observatory* (Lellouch et al. 2000), *Mars Express* (Formisano et al. 2004; Giuranna et al. (2019), the *Curiosity* rover (Webster et al. 2013, 2015, 2018, 2021) and TGO *ExoMars* (Korablev et al. 2019; Montmessin et al. 2021).

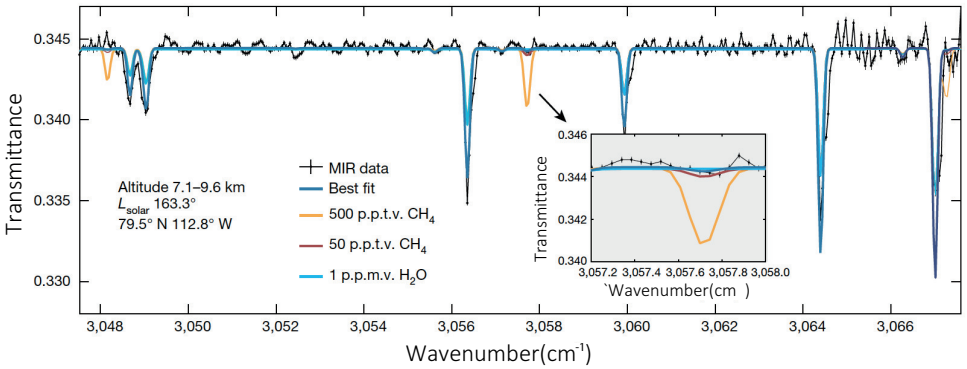


Figure 5 One ACS/TGO spectrum in the interval where the spectral features of methane should be present (Korablev et al. 2019).

bands (in the spectral range of 3–3.5 μm or, significantly weaker, at 1.6 μm). A few false-positive detections, e.g., the New York Times announcement after the *Mariner 7* flyby, had attracted broad public attention. At that time, narrow absorptions caused by solid carbon dioxide on the polar cap were mistaken for the methane spectral features.

Data from the next Mars satellite, *Mariner 9*, were disappointing (Maguire 1977). For a long time, the search for methane invariably yielded negative results. Several upper limits below 10–20 parts per billion by volume (ppbv) have been established. It was only in 2003, when three independent research groups announced methane

detection in the amount of 10–45 ppbv using the data of PFS on *Mars Express* and Earth-based high-resolution spectra (Formisano et al. 2004; Krasnopolsky et al. 2004; Mumma et al. 2009). Having gained confidence, several researchers have subsequently found methane in ground-based spectra, PFS and even TES/*Mars Global Surveyor* data. Upper limits intermitted positive detections, some of which were later withdrawn or criticized. The history of efforts to search for methane on Mars since 1997 is presented graphically in Fig. 4.

In the ensuing discussion about the origin of methane (summarised by Yung et al. 2018), external sources (comets, micrometeorites) were excluded. Methane could flow from the ground, indicating residual volcanic or geothermal activity, or anaerobic microorganisms could produce it. Fossil methane could be stored as gas hydrates, slowly seeping into the atmosphere, a hypothesis not addressing its origin though. Because the gas in the Earth's atmosphere is predominantly biological, methane on Mars reached far beyond the attention of atmospheric scientists.

In 2011, the *Curiosity* rover with the Sample Analysis on Mars (SAM) analytical complex, which includes a Tunable Laser Spectrometer (TLS), specifically designed to measure methane in a sample of the Martian atmosphere, began operation in Gale Crater. The first SAM-TLS measurements gave only a strict upper limit: $\leq$1.3 ppbv (Webster et al. 2013), then several spikes of 5–8 ppbv of methane were detected (Webster et al. 2015, 2018). Measurements in a more sensitive mode, with sample enrichment, showed the "background" methane changing with the season, 0.2–0.5 ppbv (Webster et al. 2018). The most vigorous methane spike (20.5$\pm$4 ppbv) according to SAM-TLS data is reported by Webster et al. (2021).

The ACS/TGO spectra in the wavelength range where the strongest methane features should be found (Fig. 5) immediately lowered the upper limit, to an order of magnitude under the SAM-TLS background values. The instrument registers faint absorption lines of water vapour but not the neighbouring features of methane. The first ACS publication has established an upper limit of $\leq$0.05 ppbv (Korablev et al. 2019), followed by $\leq$0.06 ppbv (2σ) according to the NOMAD/TGO data (Knutsen et al. 2020). Recently, a more extensive ACS data set covering two Martian years MY34–35 resulted in the upper limit of $\leq$0.02 ppbv or 20 parts per trillion (3σ) (Montmessin et al. 2021).

The TGO eclipses occurring in the vicinity of Gale Crater are assigned the highest priority. In these cases, ACS always operates, tuned to measure methane. Unfortunately, aerosols present in the low-latitude atmosphere of Mars in all seasons impede measurements at altitudes where the maximum sensitivity could be achieved. The aerosol loading explains the seasonal dependence of the upper limits of the ACS (Figure 6). The most stringent upper limits are obtained at aphelion season when dust activity on Mars is minimal and at high latitudes. Even then, condensation clouds are present in the equatorial latitudes of Mars, where *Curiosity* conducts its measurements. Nevertheless, it was possible to constrain methane at 65–150 ppbv near Gale (Fig. 7).

Any known physical or chemical processes could not explain the variability of methane in the atmosphere of Mars (Lefèvre, Forget, 2009; Holmes et al. 2015; Etiope, Oehler, 2019). The solar radiation slowly destroys methane resulting in its photochemical lifetime of 300–330 years. On the other hand, the atmosphere is wholly mixed by circulation within 1–3 months. A mechanism of rapid destruction is required

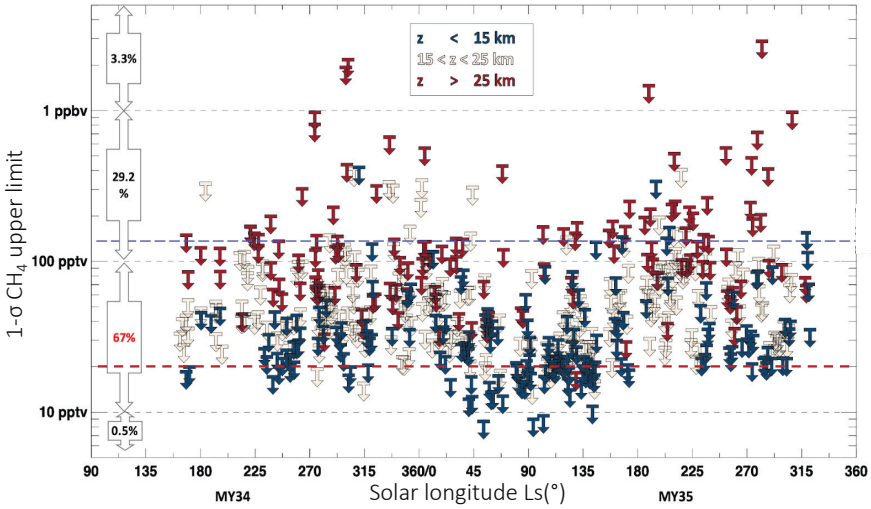


Figure 6 Upper limits for methane by ACS/TGO versus time (Ls, the heliocentric solar longitude, indicates season on Mars) (Montmessin et al. 2021).

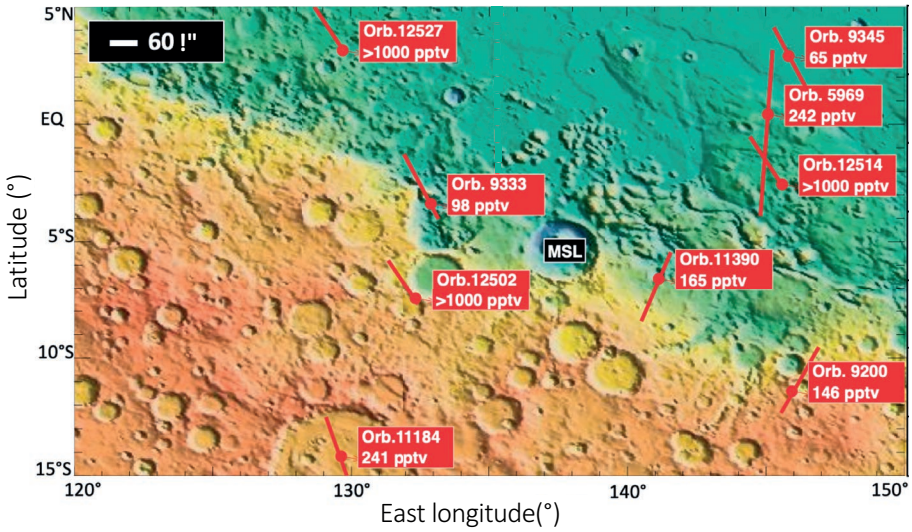


Figure 7 Upper limits on methane by ACS/TGO in the vicinity of Gale crater where *Curiosity* detects methane (Montmessin et al. 2021).

to explain the variability of methane, its emissions and spikes. Numerous laboratory experiments to search for such mechanisms, for example, under the action of UV or higher-energy radiation, have not solved the problem. It is relatively easy to break down methane, but this would also affect other chemically active compounds, such as CO, which the existing atmospheric models describe well, without any new mechanism.

The main difficulty of the current state of the problem lies in the apparent contradiction between the "background" level of methane, recorded by *Curiosity*, and the upper limits by TGO, by an order of magnitude lower. With a lifetime of 300 years, methane must accumulate in the atmosphere, sooner or later exceeding the TGO upper limit. Assuming that Gale Crater is the only source of methane on the planet – an implausible scenario – and only the background methane (0.41 ppbv), Korablev et al. (2019) estimated the accumulation time after which TGO should detect methane at 24 years. There are many places on Mars the geological structure of which makes them potential sources of methane; this estimate does not take into account the spikes recorded by Curiosity and the recently improved TGO upper limit. Including these factors makes the accumulation time even shorter. Ongoing mesoscale simulations of methane dissipating from Gale under the TGO constraints suggest that not only is it 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 (Webster et al. 2021; Luo et al. 2021).

Until recently, all SAM-TLS measurements were carried out at night. Moores et al. (2019) hypothesized that the height of the planetary boundary layer in the crater decreases at night, limiting mixing and leading to the accumulation of methane. New SAM-TLS measurements carried out in MY35 tend to confirm this inference (Webster et al. 2021). While their nighttime values fall on the previously established seasonal curve (Webster et al. 2018), two daytime measurements can only be interpreted as upper limits of $\leq$0.2 ppbv. The nighttime scenario could increase the accumulation time of methane or the allowable area on Mars where it can seep. Still, in all cases, to comply with the TGO upper limits, an as yet unknown mechanism for the rapid methane destruction is needed.

This unresolved controversy and criticism of spectroscopic detections from the ground, PFS/*Mars Express* and *Curiosity* (Zahnle et al. 2011; Zahnle 2015) caused a split in the scientific community. Some researchers believe that the methane detections are real, while others deny its presence. The question of methane on Mars remains open.

5 Measurements of trace atmospheric components

Setting a strict upper limit on methane – orders of magnitude below the sensitivity of the Curiosity instrument – requires exceptional instrumentation performance. At the same time, in certain media, the negative result from TGO appeared in a negative connotation. We are therefore pleased to discuss the discovery of new atmospheric absorbers.

"In place of methane", i.e. in the spectral range containing the strongest methane spectral features (Fig. 5), two new absorbers are discovered. Weak features of the absorption spectrum (Fig. 5), attributed previously to systematic errors, the fixed-pattern noise (Korablev et al. 2019), belong to the magnetic dipole band of CO_2 and the IR band of ozone.

In a wide spectral range of 2900–3300 cm^{-1}, it was possible to identify 30 weak lines absent from the spectroscopic bases. A periodic structure near the Q-branch of methane absorbing up to 1.6% was systematically present in the spectra measured

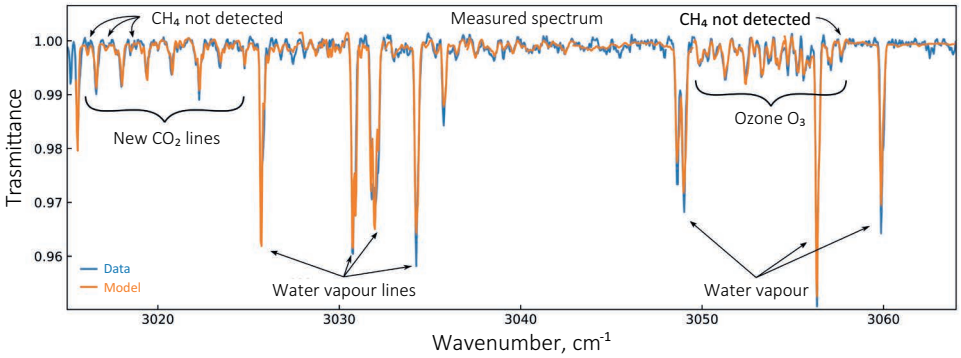


Figure 8 An ACS/TGO spectrum composed of several diffraction orders showing newly detected lines of CO_2 and ozone. After Olsen et al. (2020), Trokhimovskiy et al. (2020).

below 20 km (Fig. 8). The new lines' position suggested comparing them with the theoretically calculated frequencies of the P-, Q-, and R-branches of the magnetic dipole or electro-quadrupole band of the main CO_2 isotopologue. This band is forbidden for ordinary electro-dipole absorption. Neither band has been previously observed or numerically calculated. The relative depth of the branches made it possible to conclude about the magneto-dipole nature of the new band (Trokhimovskiy et al. 2020). During an eclipse, the solar light travels up to 400 km in the atmosphere, an optical path unattainable in laboratory conditions. For the second time (see Villanueva et al. 2008), the carbon dioxide atmosphere of Mars has allowed the discovery of new absorption bands.

In the same spectral range, overlapping one of methane's P-branch spectral features, a weak infrared ozone band was detected (Fig. 8; Olsen et al. 2020). This band has never been observed on Mars before. The amount of ozone in the Mars' atmosphere is small, and a much stronger UV band has always been used to measure it (e.g., Montmessin et al. 2017). Observations in the IR make it possible to reconstruct vertical profiles and explore the lowermost layer of ozone, unattainable for occultations in the UV range.

6 The first detection of HCl in the atmosphere of Mars

For the first time since 2004 (when the methane detection was reported), a new chemical compound has been discovered in the atmosphere of Mars. Hydrogen chloride (HCl) was confidently identified by 12 lines in the ACS MIR spectrum (Fig. 9; Korablev et al. 2021; Olsen et al. 2021a). Its relative content reaches four ppbv, significantly higher than upper limits previously established by the Earth-based and orbital measurements ($\leq$0.3 ppbv 3σ; Hartogh et al. 2010; Villanueva et al. 2013). In the ACS spectra, hydrogen chloride appeared after the global dust storm of MY34, while outside the dusty season, its content remained below 0.1 ppbv, resolving the apparent contradiction.

As suggested by the coincidence of the detection with the dust season, the preferable mechanism of gas formation involves atmospheric dust (Korablev et al. 2021).

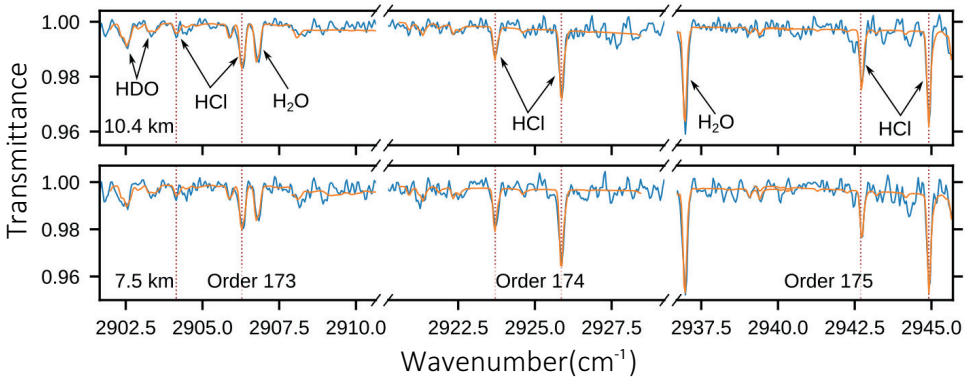


Figure 9 ACS/TGO spectra at two tangent altitudes demonstrating the detection of HCl lines (Korablev et al. 2021).

Chlorine is abundant at the surface of Mars in the form of NaCl or perchlorates and is identified within the surface dust. Both forms can be lifted into the lower atmosphere during a dust storm, where they might serve as a source of Cl. The transition to the gas phase could be a consequence of the hydration of chlorine salts with the release of radicals. This mechanism, although speculative under Martian conditions, may eventually lead to the formation of HCl. Another argument supporting this hypothesis is the high degree of correlation between HCl and H_2O in the atmosphere (Aoki et al. 2021; Olsen et al. 2021a).

The high fidelity of the collected spectra makes it possible to estimate the $H^{37}Cl/H^{35}Cl$ isotope ratio (Trokhimovskiy et al. 2021). Unlike for other volatiles on Mars, this relationship is indistinguishable from that on Earth. On average, the atmosphere of Mars may be slightly depleted in ^{37}Cl ($-7\pm20‰$) compared to Earth's value. This result is consistent with the known meteorites and measurements at the the Martian surface, confirming the idea of the formation of HCl from chlorine-containing dust particles. Within accuracy, we were unable to detect variations in ^{37}Cl over time or across the planet. The known fractionation mechanisms are apparently too weak to be noticed, given the short lifetime of HCl in the atmosphere. It is also unlikely that the chlorine isotopes participate in any long-term exchange between the atmosphere and the surface.

Alternatively, the source of HCl can be degassing, i.e., one could not exclude its volcanic origin. On Earth, HCl is a significantly less abundant volcanic gas than SO_2, not yet found on Mars (Khayat et al. 2015). However, HCl reappeared in similar quantities during the next Martian year MY35, although dust activity was much lower (Olsen et al. 2021a; Fig. 10). Also, several trustable detections in aphelion ($Ls = 120°$, at low dust amount) challenge the correlation with dust.

From the gas chemistry viewpoint, HCl should be a stable chlorine reservoir in the lower atmosphere of Mars (Lefèvre, Krasnopolsky, 2017). The observed variability suggests an unexplained chemical or physical chlorine loss. Perhaps this is due to the absorption of HCl on the surface of water ice clouds, present throughout the dusty period, when we see HCl (Luginin et al. 2020).

The question about the sources and sinks of HCl remains open. Additional re-

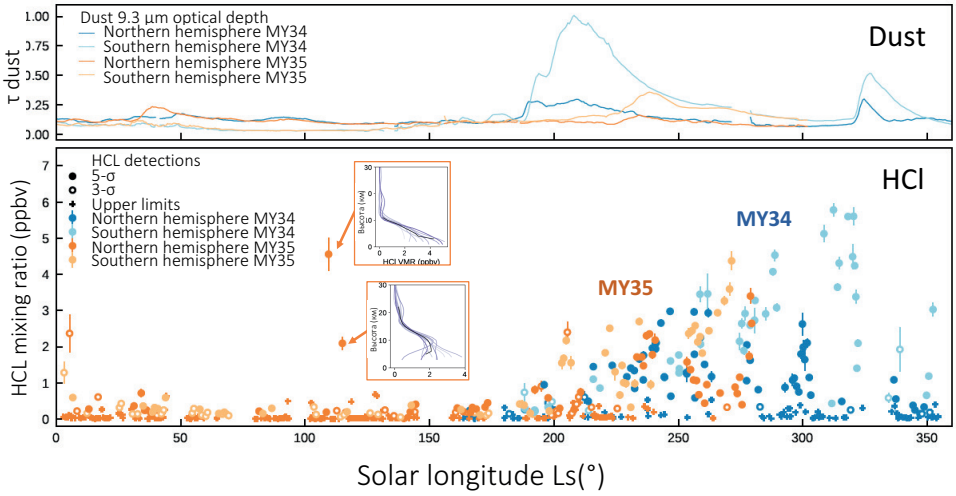


Figure 10 Evolution of HCl mixing ratio over Martian years MY24 and MY35 (Olsen et al. 2021a).

search is needed to limit the rate of formation and destruction of HCl or to identify possible degassing sources. Similarly to methane, it is unlikely that the processes responsible for the production and destruction of HCl would not affect the rest of the Martian atmosphere chemistry. Peak HCl concentrations on Mars are comparable to those in the Earth's upper stratosphere and mesosphere. The ozone depletion cycle, well known in the Earth's stratosphere, would be effective on Mars as well. The discovery of hydrogen chloride suggests the photochemistry of Mars be revisited to account for heterogeneous reactions or surface degassing.

7 Conclusions

Astronomy observations and remote measurements of planet's atmospheres, once the high point of planetary science, were progressively replaced by geology and surface studies. Anew, we see a growing interest in this field of research. First, there are reasons to believe that the composition of a planet's atmosphere gauges active processes in its interior and even its habitability – for example, in the case of phosphine on Venus. Second, one can judge the nature of extrasolar planets by observing their atmospheres and exospheres.

The ACS instrument onboard the *ExoMars* TGO dedicated atmospheric spacecraft has been successfully operating since March 2018, delivering unique new data. Here we reported three results: a low limit for methane, new atmospheric absorbers in the spectral range of methane and the discovery of a new species – hydrogen chloride in the atmosphere of Mars. The established upper limit for methane is of an order of magnitude lower than the "background" methane level recorded by Curiosity, necessitating a yet unexplained mechanism of methane breakdown. The discovery of gaseous hydrogen chloride in the atmosphere of Mars makes it another marker of

chemical or physical processes in the interaction of the surface and atmosphere. In both cases, new measurements show that we do not understand the atmosphere of Mars well enough and make us look for new processes in the atmosphere or between the atmosphere and the surface. Further efforts in atmospheric chemistry modelling and laboratory research are needed.

A range of results obtained with the ACS instrument remained outside the scope of the article. The seasonal distribution of aerosols, including dust, H_2O and CO_2 clouds (Luginin et al. 2020; Stcherbinine et al. 2020) was investigated. The first vertical profiles of carbon monoxide CO were obtained (Olsen et al. 2021b). The processes of water dissipation and the boundary where the lower atmosphere interacts with the exosphere were studied. The distribution of water vapour was measured up to an altitude of 120 km (Fedorova et al. 2020; Belyaev et al. 2021; Chaffin et al. 2021). The altitude profiles of hydrogen and oxygen isotope ratios in CO_2 and H_2O were first obtained (Alday et al. 2019, 2021; Vandaele et al. 2019; Rossi et al. 2021). For the first time, an upper limit for phosphine in the atmosphere of Mars was established $[PH_3] \leq 0.1$–0.6 ppbv (Olsen et al. 2021c). The work is ongoing to establish and improve upper limits on sulfur and nitrogen compounds.

The future offers opportunities for studying biomarker gases on Venus in greater detail. The Russian–French VIRAL instrument will investigate atmospheric gases from the planned Indian orbiter *Schukrayaan-1*. In the *Venera-D* project of Roscosmos, it will be possible to carry out sensitive measurements of gases above clouds or in the upper cloud layer from the orbiter. Gas and aerosol analysis will also be carried out during the lander descent. Studies of trace atmospheric components on the nearest planets will be continued.

Acknowledgements

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