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Introduction

The ExoMars Trace Gas Orbiter (TGO) has been making high resolution spectroscopic measurements of the atmosphere of Mars since April 2018. By MAMO 2022, it will have acquired 4 Earth-years of data, which will be just over two full years on Mars. Observations began just before the autumnal equinox in Mars year (MY) 34, we observed the global dust storm in 2018, then two full perihelion and aphelion periods. MAMO will take place over solar longitude (L_s) 245° in MY 36, which is into the third dusty season observed by TGO.

While observing the dusty season of Mars, observations made using the Atmospheric Chemistry Suite mid-infrared channel (ACS MIR) revealed the first novel trace gas found during the TGO mission: hydrogen chloride (HCl) [1]. Over the perihelion periods, while it is spring and summer in the southern hemisphere, the atmosphere of Mars is characterized by lifted dust, warmer temperatures, increased water vapour content, and an elevated hygropause. Towards the vernal equinox, the dust subsides, water content falls, and the absorption signal of HCl vanishes in the ACS MIR data.

Over the aphelion period, the atmosphere is much colder and dryer, except for near the surface in the northern hemisphere. Without water vapour, odd-hydrogen chemistry is greatly reduced. The odd-hydrogen family of gases contains the hydroxyl and hydroperoxyl radicals (OH and HO_2), which are formed after the photolysis of water vapour. Reactions with these radicals is the main pathway to removing odd-oxygen (O, O_3) from the atmosphere of Mars by forming a more-stable O_2 bond. Therefore, over the aphelion period we are able to observe elevated levels of ozone (O_3) in the atmosphere of Mars.

HCl and Ozone are both closely linked to the seasonal cycles of water. Ozone is reduced when water vapour, and its odd-hydrogen photolysis products, is present [2], while those same products are needed to form HCl from free chlorine, resulting in a positive correlation between HCl and H_2O [3].

Both of these species may be closely linked to aerosols as well. Chloride minerals in dust may be a source of atmospheric chlorides, while water vapour condensation and cloud formation may contribute to its removal from the atmosphere. Ozone is rapidly reduced as water vapour abundances increase, and changes in atmospheric temperature that lead to cloud formation limit the production of odd-hydrogen (OH, HO_2) from H_2O photolysis.

Here we present a comparison of the vertical profiles of H_2O, O_3, and HCl volume mixing ratios (VMRs) with each other and other data sources: temperatures measured with the near-infrared channel of ACS [4], and dust and ice aerosols measured by the Mars Climate Sounder [5].

ACS MIR

ACS MIR is a cross-dispersion spectrometer on TGO that operates in solar-occultation mode. It consists of an optical telescope that makes direct observations of the sun, an echelle grating whose diffraction orders are in the infrared, and a secondary, steerable grating that separates overlapping diffraction orders. The secondary grating is steerable, and its position determines the instantaneous spectral range for a series of solar occultation observations. The absorption features of the HCl $1 \leftarrow 0$ band are measurable between 2710–3020 cm^{-1}, which is observed using grating positions 11 (2680–2950 cm^{-1}) and 12 (2920–3210 cm^{-1}). The absorption features of the $003 \leftarrow 000$ vibration-rotation band of O_3 are measurable between 3010–3060 cm^{-1} in position 12. Position 12 also features several strong water vapour absorption lines.

As TGO goes into, or comes out of, the shadow of Mars, ACS MIR makes a series of observations of the sun while the limb of the atmosphere lies between the spacecraft and the sun. Spectra are obtained at unique tangent heights every 2–4 km. By comparing the observations through the atmosphere with those made above the atmosphere, we can determine how much sunlight was absorbed by the atmosphere along the line-of-sight (LOS). ACS MIR uses a 2D detector and the vertical field of view of the fore-optics allow ~ 12 spectra to be acquired at each tangent height. By analyzing each of the detector rows and then taking the average of the retrieved VMR vertical profiles, we can greatly improve the accuracy of our results and the sensitivity of the re-

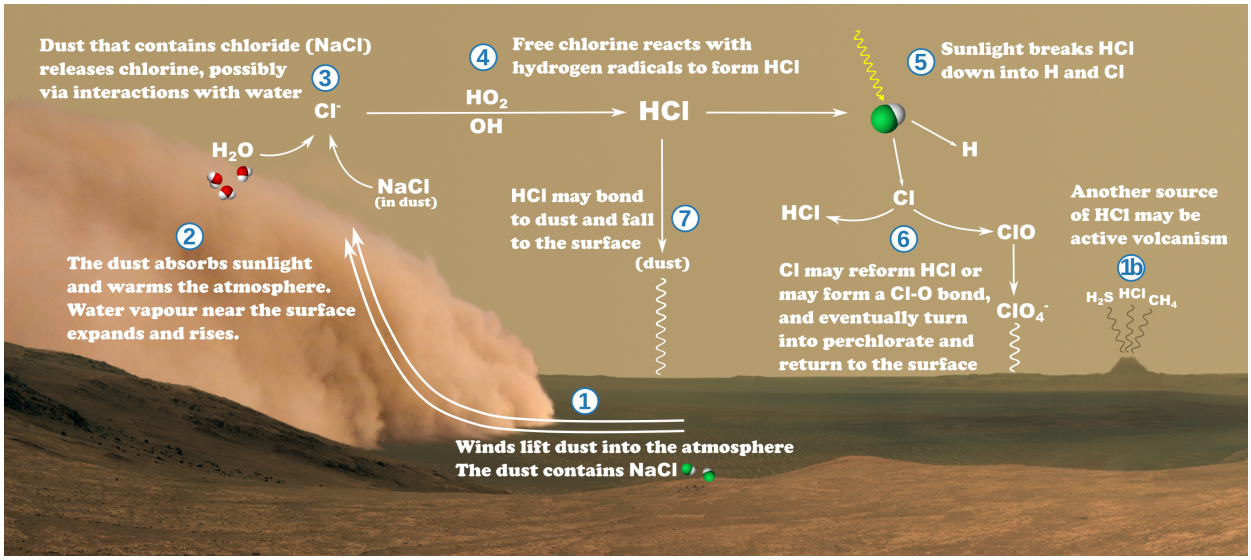

Figure 1: Schematic of possible surface-atmosphere interactions involving chlorine. 1 Dust-bearing minerals are lofted into the Mars atmosphere; 2 atmospheric warming caused by the dust raises the hygropause and increases the water vapour content; 3 hydrated dust aerosols may make chlorine ions available for reaction; 4 reactions between Cl^- and HO_2 or OH will form HCl; 5 HCl will break down in sunlight; 6 free Cl will either re-form HCl, or form a bond with oxygen, eventually leading to perchlorate formation; 7 HCl may adhere to dust or ice aerosols and return to the surface. Volcanic emissions cannot be ruled out (1b).

trievals to trace gases, or low VMRs towards the limits of our sensitivity. Instrument details can be found in [6, 7].

Spectral fitting is done using the JPL Gas Fitting Software (GGG) [8, 9] which uses a non-linear Levenberg-Marquardt least squares method to compare the measurements to a computed spectrum. Absorption coefficients are calculated line-by-line using the HITRAN2020 line list [10], with line broadening parameters in a CO_2-rich atmosphere for HCl from [11] and for H_2O from [12]. Temperature and pressure are measured from simultaneous measurements of CO_2 made with ACS NIR along the same LOS. VMR vertical profiles are retrieved from the spectral fits by inverting the matrix of slant path abundances with the matrix of ray paths through atmospheric layers. For details about these retrievals, see [13, 3].

HCl

HCl was first observed in the atmosphere of Mars using ACS MIR shortly after the onset of the 2018 global dust storm [1]. It appeared simultaneously in both hemispheres, but with larger VMRs in the south. The southern VMRs fell quickly after solar longitude (L_s) $\sim 300°$ as the atmosphere above 30 km began to cool, shortly before the late-season 'C' dust storm. This behaviour was repeated in MY 36 [3].

While HCl was a target gas of the ExoMars mission because of its link to active volcanism, the nature of atmospheric HCl does not seem to support such an origin. Other trace gases associated with active volcanism, such those bearing sulphur, have not been detected by ACS [14, 15]. Some sort of surface emission, maybe related to magma pockets, or to clathrates experiencing seasonal thawing, remains a possibility. In the northern summer, around L_s 110°, two ACS MIR observations featured distinct HCl absorptions below 10 km [3].

On the other hand, we have posited that HCl may be derived from aerosol minerals lofted from the surface, which would be a novel surface-atmosphere interaction with implications for our interpretation of chloride and perchlorate reservoirs [16, 17]. Figure 1 shows a schematic of possible HCl pathways. First, dust loaded with chloride-bearing minerals, possibly NaCl, is lofted into the atmosphere. The atmosphere warms, the hygropause elevates, and conditions become suitable for the dust aerosols to become hydrated. This allows for reactions between chlorine ions and HO_2 (or OH) to form HCl. HCl will rapidly photolyze, but the free chlorine should also rapidly find odd-hydrogen molecules to reform HCl. A ClO bond may be formed, eventually leading to perchlorate formation and surface deposition [18], but this may not be rapid enough for the observed seasonal behaviour. Another possibility is that HCl leaves the gas phase after adhering to dust or ice aerosols.

1 Ozone

Odd-oxygen chemistry plays a crucial role in the atmosphere of Mars. CO_2 photolysis leads to the the formation of atomic oxygen and carbon monoxide (CO). Atomic oxygen will lead to O_3 production via a three-body reaction with O_2, and will become the dominant form of reactive odd-oxygen in the lower atmosphere. Unlike O, O_3 is also directly measurable via remote sensing.

It was first detected by the Mariner ultraviolet spectrometers [19, 20] and its seasonal behaviour along the vertical was more recently examined with the ultraviolet component of the NOMAD instrument on TGO [21]. Observations of O_3 on Mars have been dominantly performed in the ultraviolet range, but with the sensitivity of ACS MIR, we have been able to identify its spectral signature in the mid-infrared as well [22].

Ozone is not visible at mid-to-low altitudes or in the southern hemisphere while it is spring or summer in the south (over the perihelion). This is due to the abundance of water vapour in the atmosphere that results from the perihelion dust activity. At high northern latitudes the TGO observations are made around the region of polar night (though not within). Rarely, observations of ~ 200 ppbv O_3 are made below 10 km. These may be indicative of dynamic excursions of polar air from within the polar vortex.

Around the aphelion, when it is fall and winter in the southern hemisphere, the atmosphere is much cooler and dryer. This allows for frequent observations of O_3 across Mars. In the time periods surrounding the equinoxes, the atmosphere is fairly symmetric and 200–500 ppbv O_3 is seen from around 30 km to near the surface. In the southern hemisphere, this behaviour persists throughout the year. In the north, where it is summer, there is more water vapour present in the lower atmosphere and its abundance increases from ~ 20 km to the surface, leading to an O_3 VMR that is reduced below 20 km. Around the equator, the aphelion cloud belt is formed. As the atmosphere cools and water vapour condenses, odd-oxygen is no longer suppressed by HO_2, and we observe an equatorial ozone layer centred just below 40 km.

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