

UNIDENTIFIED CHEMISTRY ON MARS? STRONG TESTS OF CURRENT PHOTOCHEMICAL MODELS VIA GLOBAL MAPPING OF WATER AND OZONE (SAMPLED VIA O₂ DAYGLOW)

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Abstract: We report maps of ozone (probed via O₂[a¹Δ_g] dayglow) and water across the Martian globe obtained using high-resolution infrared spectroscopy. The maps reveal a strong dependence of the O₂ emission and water burden on local orography, while the spatial distribution and vertical profile of the observed emission are in strong disagreement with current climatological models. Could this be the signature of heterogeneous chemistry?

Introduction: Ozone and water are powerful tracers of photochemical processes on Mars. Considering that water is a condensable with a multifaceted hydrological cycle and ozone is continuously being produced / destroyed on short-time scales, their maps can test the validity of current 3D photochemical and dynamical models. Ozone and water are closely linked through photochemistry and they are anticorrelated with each other, because atomic hydrogen (a photolysis product of water vapor) is a powerful catalyst destroying ozone.

Ozone can be studied in the Martian atmosphere by probing its immediate photolysis product (excited O₂), which readily emits at 1.27 μm (O₂[a¹Δ_g] dayglow emission) when returning to its ground-state with a lifetime of 1.25 hours. Consequently, Mars O₂[a¹Δ_g] dayglow enables critical studies of Mars oxygen and hydrogen photochemistry, as well as atmospheric water vapor content/saturation conditions.

Comparisons of modern GCM models (1) with certain datasets (e.g., 2,3) point to significant disagreement, which in some cases have been related to heterogeneous (gas-dust) chemistry beyond the classical gas-gas homogeneous reactions.

We address these concerns by acquiring full 2D maps of water and ozone (via O₂ dayglow) on Mars, employing high spectral infrared spectrometers at ground-based telescopes (CRIRES/VLT/ and CSHELL/NASA-IRTF/). By performing a rotational analysis on the O₂ lines, we derive molecular temperature maps that we use to derive the vertical level of the emission (e.g., (4)). We target several lines of a broad range of rotational energies, that sensitively sense the 120-200 K range (0-80 km), establishing a third dimension (3D, altitude).

Spectral lines of these bands on Mars are observable through our atmosphere when measured from high-altitude observatories at moderately high Doppler shifts (>11 km s⁻¹), i.e., when Mars' lines are displaced sufficiently far from the cores of their counterpart telluric absorbing lines. CO₂ is co-measured with water in each

setting, thereby providing an unambiguous metric of column abundance on Mars for each footprint along the slit.

Mapping: Two-dimensional maps of the targeted species were obtained by orienting the slit N-S or E-W and by stepping the slit across the planet, achieving full disk coverage. For each footprint on Mars, we estimated the local atmospheric conditions by querying the Mars Climate Database v4.2 (5), that is based on a realistic general-circulation-model (GCM) as constrained by authentic Mars parameters obtained from spacecraft results. These parameters were fed to a multi-layer planetary radiative transfer model adapted for Mars (GENLN3, see methodology also in 6-8), and the apparent martian column densities were derived from the measured spectral line intensities (O₂, O₃, H₂O, CO₂) using a Levenberg-Marquardt (LM) algorithm (see Figure 1). The influence of aerosol scattering was removed from the processed data prior to final abundance retrievals for the gaseous species.

Datasets: The data were collected over several years and seasons on Mars from March/2008 until January/2014. We will present results from the best datasets targeting O₂ dayglow and water, obtained at times of low telluric water, high-Doppler shift and maximum spatial coverage (CSHELL: March/25/2008, NIRSPEC: January/24/2014, CRIRES: January/29-30/2014), spanning seasons from late northern winter to late northern spring on Mars (Ls = 50°, 80°, 83°). The dates span the critical interval when the northern polar cap sublimates and replenishes the atmosphere with water.

Results: We observe strong O₂[a¹Δ_g] dayglow emission (after correcting for observational airmasses) at equatorial regions. The distribution of the emission follows certain orographic features on Mars, and could be related to heterogeneous processes induced by clouds.

Yet, our observations show low emission dayglow emission at polar latitudes, where the LMD climatological models predicts maximum emission. The latest version of the GCM that we consider (LMD v5.2) includes an ad-hoc parameterization for heterogeneous chemistry. In fact, heterogeneous chemistry may explain the O₂ dayglow that we observe at equatorial latitudes induced by water ice clouds, but it may overestimate its effectiveness at polar latitudes.

At polar latitudes, and in particular at low altitudes (10-20 km), the climatology model predicts too much ozone. Is heterogeneous chemistry less effective at polar latitudes, leading to a stronger ozone sink via HOx? Is

the model predicting too many water ice clouds at polar latitudes? MARCI images do not show polar clouds.

Conclusions: We obtained global maps of $O_2[a^1\Delta_g]$ and water vapor, and have compared these to the currently most advanced climatological models. Our results for late Northern Spring show strong enhancement at equatorial latitudes, that could be inconsistent with heterogeneous chemistry, yet at polar latitudes, the data reveal substantially lower emission than the GCM model predicts. These new measurements set new constraints on the effectiveness of heterogeneous process across Mars, which may have implications for the stability of other trace species (e.g., methane) on Mars.

References: 1. Lefèvre, F. et al. (2004). *J. Geophys. Res. Pl*, 109, 1–20; 2. Clancy, R.T. et al. (2012). *J. Geophys. Res. Pl*, 117, E00J10; 3. Bertaux, J.-L. et al. (2012). *J. Geophys. Res. Pl*, 117, 1–9; 4. Novak, R.E. et al. (2002). *Icarus*, 158, 14–23; 5. Millour, E. et al. (2008). *Mars Atmosphere: Modeling and Observations Conf*, #9029; 6. Villanueva, G.L. et al. (2008). *Icarus*, 195, 34–44; 7. Villanueva, G.L. et al. (2011). *J. Geophys. Res. Pl*, 116, 1–23; 8. Villanueva, G.L. et al. (2012). *J. Quant. Spectrosc. Radiat. Transfer*, 113, 202–220

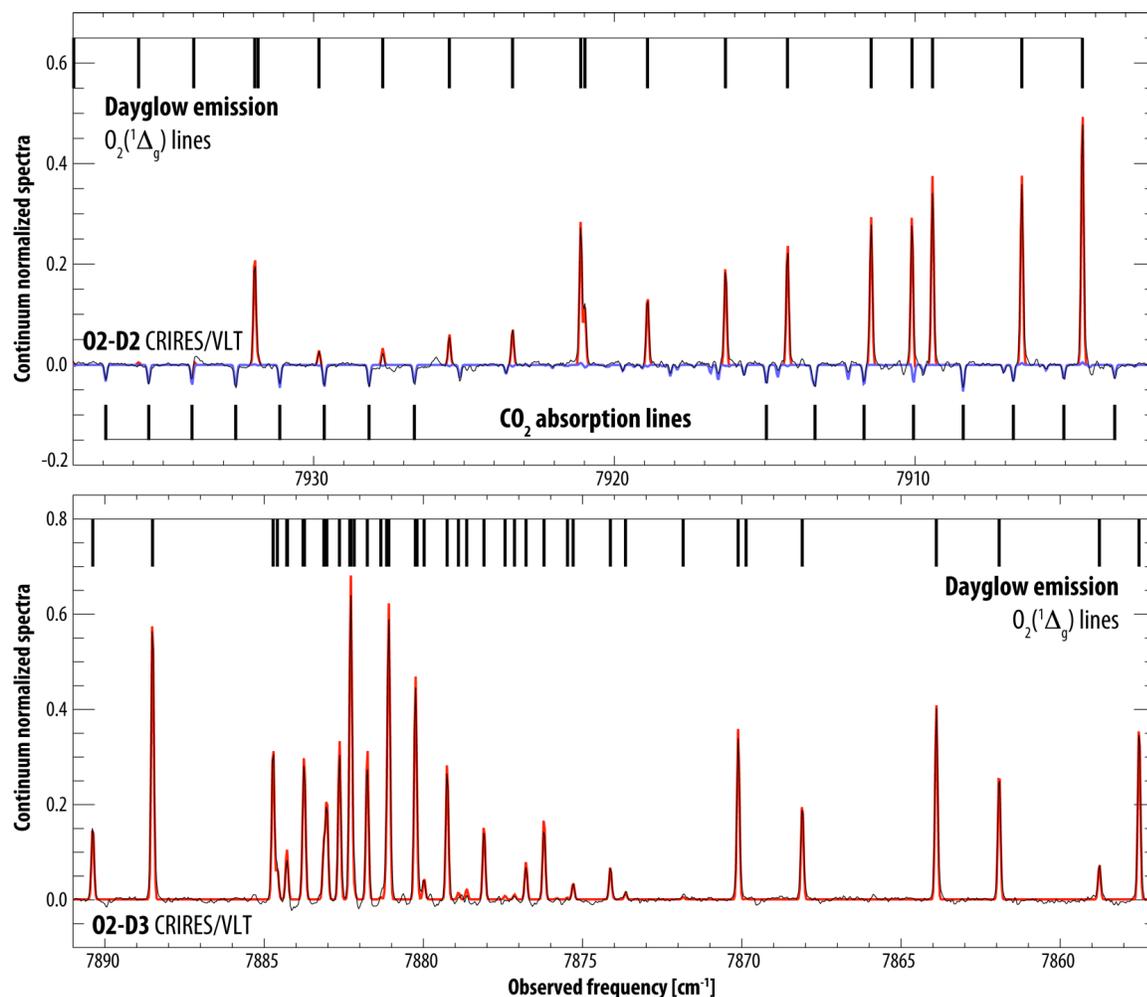


Figure 1: Observations of excited oxygen on Mars (L_s 83° - Jan/29/2014), acquired with the high-resolution spectrometer (CRIRES) at the VLT observatory (Paranal, Chile). The data are overlaid with a model of $O_2[a^1\Delta_g]$ at 165 K presented with a red trace, and a Martian absorption model of CO_2 shown in blue.