Revised upper limits for abundances of NH_3, HCN and HC_3N in the Martian atmosphere

A. Trokhimovskiy[1], A. A. Fedorova[1], F. Lefèvre[2], O. Korablev[1], K.S. Olsen[3], J. Alday[4], D. Belyaev[1], F. Montmessin[2], A. Patrakeev[1], N. Kokonkov[1]

[1] Space Research Institute (IKI) RAS, Moscow, Russia
e-mail: trokh@cosmos.ru
[2] LATMOS/CNRS, Guyancourt, France
[3] Department of Physics, University of Oxford, Oxford, UK
[4] The Open University, Milton Keynes, UK

Abstract

The Atmospheric Chemistry Suite (ACS) onboard the ExoMars Trace Gas Orbiter (TGO) spacecraft has been studying Mars' atmosphere since 2018. The sensitivity of the middle infrared channel (MIR) allows it to address many ardent topics and it is capable of improving and establishing upper limits for many trace species. In this work we present analysis of transmittance spectra in the 3332.5-3338.6 cm^{-1} range with 30,000 resolution ($\lambda/\Delta\lambda$), covering absorptions lines of three nitrogen-bearing species: ammonia (NH_3), hydrogen cyanide (HCN) and cyanoacetylene (HC_3N). According to existing models, all of those are not expected to be present in a CO_2-rich Martian atmosphere, but outgassing or unknown chemistry sources cannot be discounted. The upper limits of 14, 1.5 and 11 ppbv are obtained for NH_3, HCN and HC_3N from individual occultation measurements during the warm and dusty perihelion season of martian year 36. For the ammonia and hydrogen cyanide the upper limits are improved compared to previously published results. A search for cyanoacetylene on Mars is reported for the first time.

Keywords: **IR spectroscopy; Mars, atmosphere; Atmospheres, composition**

Main

Molecular nitrogen is the second most abundant species (2.8%) after CO_2 in the Martian atmosphere (Franz et al., 2017). Soil contains oxidised nitrogen-bearing compounds (Stern et al., 2015; Sutter et al., 2017). Also the chemically-derivatized molecules ammonia (NH_3) and hydrogen cyanide (HCN) were detected from sand, among others, with the wet chemistry experiments of the Sample Analysis at Mars (SAM) instrument on NASA's Curiosity rover (Millan et al., 2022). The combination of an elevated abundance of derivatized ammonia and several N-bearing organic species detected in the follow-up analyses suggested that indigenous N-bearing molecules are present in the soil. At the same time, expected atmospheric processes involving nitrogen are limited (Lefèvre and Krasnopolsky, 2017), because the strong N–N bond makes N_2 a relatively inert species. Odd-nitrogen species, N and NO, can be produced as a result of N_2 dissociation at high altitudes only. The nitrogen chemistry in the lower atmosphere thus greatly depends on the downward fluxes. As calculated by the general circulation model of Moudden and McConnell (2007), main nitrogen species below 40 kilometres are NO and NO_2, varying in tiny abundances from 0.1 ppbv to 0.25 ppbv. The current knowledge for NO_2 is <10 ppbv (Maguire, 1977) and less than 1.7 ppb for NO (Krasnopolsky, 2006) The sensitivity of the mid-infrared channel of the Atmospheric Chemistry Suite (ACS MIR) approaches the expected NO_2 0.2 ppbv absorption features in the 2915 cm^{-1} band, which will be a subject of a separate study.

Not considering any release processes, other nitrogen components are modelled to be orders of magnitude less abundant, like the pptv level concentrations of HNO_4 near 20 km in altitude.

In this work we present upper limits of somewhat unexpected molecules for Mars: ammonia, hydrogen cyanide and cyanoacetylene derived from ACS MIR data. The first two have been already searched for on Mars, the third has not yet been considered.

As in the case of methane (CH_4), the ammonia could be considered as a biomarker. But in contrast to methane, whose lifetime is considered to be on the order of a hundred years (Lefèvre and Krasnopolsky, 2017), ammonia is not a stable molecule in the atmosphere of Mars and would be quickly photolyzed within hours. Hydrogen cyanide is also not expected to be produced in the Martian atmosphere (Mancinelli and Banin, 2003): its permanent presence would require a continuous source, like active volcanoes or biota, both actively sought, but never detected on Mars.

The first NH_3 3 σ upper limit of 8 ppbv was set by the Mariner 9 Infrared Interferometer Spectrometer (IRIS; Maguire, 1977). The results were obtained from an average of spectra from all over the planet, covering a full Martian year (MY), starting from L_s = 293° in MY 9. In 2004, the detection of ammonia in the atmosphere of Mars by the Planetary Fourier Spectrometer (PFS) was announced; the report was not followed by a publication. The NH_3 was then sought using NIRSPEC at Keck-2 observatory (Villanueva et al., 2013). The observations at L_s = 352° in MY 27 provided a 57 ppbv 3 σ upper limit, and at L_s = 83° in MY 30, a 45 ppbv upper limit. In parallel, they have established HCN upper limits of 4.5 and 2.1 ppbv, respectively.

HC_3N was not considered as a goal for Martian atmospheric surveys, while it has a notable astrochemical importance (e.g. Thelen et al., 2019; Jiang et al., 2017). The most recent version of the spectroscopy database HITRAN2020 (Gordon et al., 2022) includes, for the first time, ro-vibrational transitions relative to all seven vibrational modes of HC_3N up to 3400 $cm^{-1,}$ and rotational data in the ground state and many vibrational states of all normal modes. In this work, we used the recently documented band around 3327 cm^{-1} to set the first upper limit on HC_3N in Mars atmosphere.

The ACS package for the Trace Gas Orbiter (TGO) is a part of the ExoMars mission (Korablev et al., 2018; Vago et al., 2015). ACS includes the mid-infrared channel (MIR), a versatile instrument for the spectral range 2.3-4.2 μm. It is a cross-dispersion echelle instrument dedicated to solar occultation measurements. The resolving power of 30,000 and a signal-to-noise ratio (SNR) of 5,000 per pixel per 2 s acquisition make it perfect for detecting weak absorptions (Trokhimovskiy et al., 2020; Olsen et al., 2020). We use the ACS MIR measurements obtained using secondary grating position 13, which includes 27 diffraction orders (190-216) encompassing a spectral range of 3178-3643 cm^{-1}. Order 199 covers a range 3330.5-3355.1 cm^{-1}, where all three gases, NH_3, HCN, and HC_3N, have absorption lines . This range also contains CO_2 and H_2O lines, which are used for additional pixel-to-wavenumber calibration. To retrieve upper limits in this work, we used a narrower 3332.5-3338.6 cm^{-1} fitting window (see Figure 1 Panel A for model spectra of sought gases and data example).

Regular and optimised position 13 measurements have started mid MY 36. The dataset analysed includes 135 ACS MIR occultations performed in MY 36 during southern summer at the perihelion season (L_s = 212°-360°; TGO orbits 19,656-22,705). The observation period is characterised by greater dust load, higher temperatures, elevation of water vapour up to 120 km (Belyaev et al., 2021; Fedorova et al., 2023). Recently discovered by ACS, hydrogen chloride is being observed exceptionally in the perihelion season (Korablev et al., 2021; Olsen et al., 2021), emphasising more active atmospheric chemistry. The observed latitudes range from –77°S to 90°N, with the majority of occultations occuring at high latitudes (Korablev et al., 2018).

The retrieval is performed by the iterative Levenberg–Marquardt iterative algorithm with Tikhonov regularisation developed to analyse data from SPICAM IR spectrometer on Mars Express (Fedorova et al., 2018) and TGO's ACS near-infrared channel (NIR) data (Fedorova et al., 2020) and adapted for ACS MIR data (Trokhimovskiy et al., 2021; Fedorova et al., 2022). The CO_2 density and temperature profiles were not retrieved, but taken from ACS NIR simultaneous measurements (Korablev et al., 2018; Fedorova et al., 2023). The free parameters are aerosol extinction and volume mixing ratios of gases. In the absence of detection, the uncertainty on the retrieved quantities is given by the covariance matrix of the solution, which defines the upper limit. The retrieved values are generally within a 1σ away from zero; we present the three-sigma upper limits as a confident non-detection case. The vertical dependence of the upper limits is typical for occultation experiments and for Mars reaches the best values at altitudes of about 10-25 km. At higher altitudes, the line-of-sight captures only a miserable number of searched molecules, at lower altitudes the signal is diminished by aerosol load. On Figure 1 Panel B we present a collection of three-sigma upper limits for NH_3 from different orbits. The vertical pattern for HCN and HC_3N is similar.

The best upper limits are achieved at L_s = 233°, latitude 64°N and altitude 10 km, and accordingly for NH_3, HCN and HC_3N are 14, 1.5 and 11 ppbv. Tens of observations provide upper limits below 33, 3.5 and 30 ppbv at high latitudes in both hemispheres during the whole season observed. The upper limit for HC_3N is not restrictive since HCN is typically the most abundant nitrile. At lower latitudes, with more aerosols and less occultations available, the best upper limits by ACS MIR for NH_3, HCN and HC_3N were 114, 12 and 95 ppbv. These numbers were achieved at L_s = 287°, latitude -12°S and altitude 39 km.

The upper limits for ammonia and hydrogen cyanide are several times below those obtained by Villanueva et al. (2013) for the end of MY 27. Moreover, the ACS data cover the entire perihelion season and different latitudes. The upper limits for cyanoacetylene in the Martian atmosphere are obtained for the first time. Tracing these species, unexpected on Mars, with stringent upper limits is important to monitor potential outgassing events and constrain chemical models. As the ExoMars mission continues, ACS will extend the trace species search further.

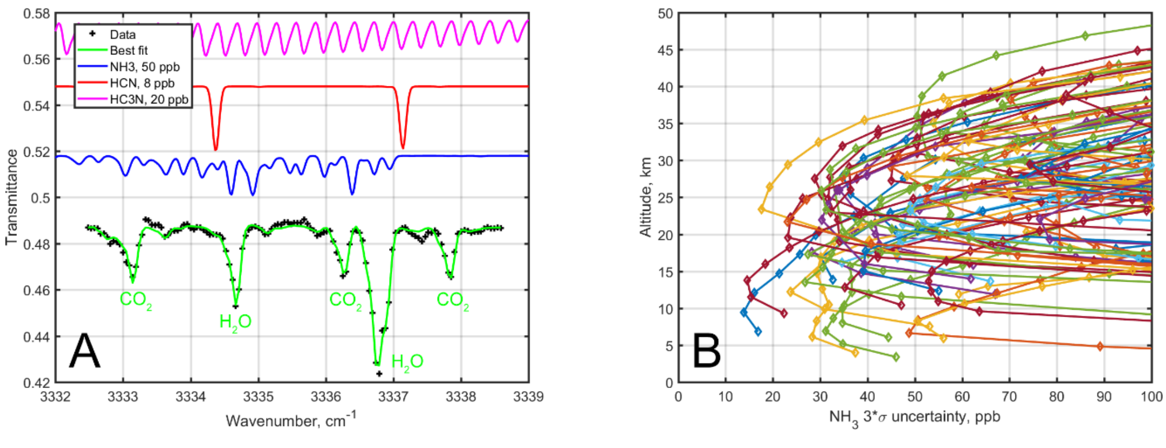

Figure 1. Panel A. Example of ACS MIR data from order 199 and the best fit at tangent altitude 18 km, orbit 21352 N1, L_s = 299°, latitude -55°S. The model spectra for NH_3, HCN and HC_3N are shown shifted and with abundances of 50, 8 and 20 ppbv, respectively. The noticeable lines fitted in the data are due to CO_2 and are located at 3333.1, 3336.2 and 3337.8 cm^{-1}, the H_2O line is at 3334.6 cm^{-1} and a doublet around 3336.8 cm^{-1}. Panel B. The vertical dependency

of the three-sigma upper limits for ammonia from the ACS MIR solar occultation observations. The vertical pattern for HCN and HC_3N is similar. Different colours stand for distinct occultations.

Belyaev, D., Fedorova, A.A., Trokhimovskiy, A., Alday, J., Montmessin, F., Korablev, O.I., Lefèvre, F., Patrakeev, A.S., Olsen, K.S., Shakun, A.V., 2021. Revealing a high water abundance in the upper mesosphere of Mars with ACS onboard TGO. J. Geophys. Res. Letters, Volume48, Issue10. https://doi.org/10.1029/2021GL093411

Franz, H.B. et al. 2017. Initial SAM calibration gas experiments on Mars: Quadrupole mass spectrometer results and implications. Planetary and Space Science 138, 44–54. doi:10.1016/j.pss.2017.01.014

Fedorova, A., Bertaux, J.-L., Betsis, D., Montmessin, F., Korablev, O., Maltagliati, L., Clarke, J., 2018. Water vapor in the middle atmosphere of Mars during the 2007 global dust storm. Icarus. 300, pp. 440-457. https://doi.org/10.1016/j.icarus.2017.09.025.

Fedorova, A.A., Montmessin, F., Korablev, O., Luginin, M., Trokhimovskiy, A., Belyaev, D.A., Ignatiev, N.I., Lefèvre, F., Alday, J., Irwin, P.G.J., Olsen, K.S., Bertaux, J.-L., Millour, E., Määttänen, A., Shakun, A., Grigoriev, A.V., Patrakeev, A., Korsa, S., Kokonkov, N., Baggio, L., Forget, F., Wilson, C.F., 2020. Stormy water on Mars: The distribution and saturation of atmospheric water during the dusty season. Science. 367, pp. 297-300. https://doi.org/10.1126/science.aay9522.

Fedorova, A., Trokhimovskiy, A., Lefèvre, F., Olsen, K.S., Korablev, O., Montmessin, F., Ignatiev, N., Lomakin, A., Forget, F., Belyaev, D., Alday, J., Luginin, M., Smith, M., Patrakeev, A., Shakun, A., Grigoriev, A., 2022. Climatology of the CO vertical distribution on Mars based on ACS TGO measurements. J. Geophys. Res.: Planets. 127, e2022JE007195. https://doi.org/10.1029/2022JE007195.

Fedorova, A.A., Montmessin, F., Trokhimovskiy, A., Luginin, M., Korablev, O., Alday, J., Belyaev, D., Holmes, J., Lefevre, F., Olsen, K., Patrakeev, A., Shakun, F. 2023. A two-martian years survey of the water vapor saturation state on Mars based on ACS NIR/TGO occultations. J. Geophys. Res.: Planets. e2022JE007348. https://doi.org/10.1029/2022JE007348

Gordon, I.E., Rothman, L.S., Hargreaves, R.J., Hashemi, R., Karlovets, E.V., Skinner, F.M., Conway, E.K., Hill, C., Kochanov, R.V., Tan, Y., Wcisło, P., Finenko, A.A., Nelson, K., Bernath, P.F., Birk, M.,Boudon, V., Campargue, A., Chance, K.V., Coustenis, A., Drouin, B.J., Flaud, J.–M., Gamache, R.R., Hodges, J.T., Jacquemart, D., Mlawer, E.J., Nikitin, A.V., Perevalov, V.I., Rotger, M., Tennyson, J., Toon, G.C., Tran, H., Tyuterev, V.G., Adkins, E.M., Baker, A., Barbe, A., Canè, E., Császár, A.G., Dudaryonok, A., Egorov, O., Fleisher, A.J., Fleurbaey, H., Foltynowicz, A., Furtenbacher, T., Harrison, J.J., Hartmann, J.–M., Horneman, V.–M., Huang, X., Karman, T., Karns, J., Kassi, S., Kleiner, I., Kofman, V., Kwabia–Tchana, F., Lavrentieva, N.N., Lee, T.J., Long, D.A., Lukashevskaya, A.A., Lyulin, O.M., Makhnev, V.Yu., Matt, W., Massie, S.T., Melosso, M., Mikhailenko, S.N., Mondelain, D., Müller, H.S.P., Naumenko, O.V., Perrin, A., Polyansky, O.L., Raddaoui, E., Raston, P.L., Reed, Z.D., Rey, M., Richard, C., Tóbiás, R., Sadiek, I., Schwenke, D.W., Starikova, E., Sung, K., Tamassia, F., Tashkun, S.A., Vander Auwera, J., Vasilenko, I.A., Vigasin, A.A., Villanueva, G.L., Vispoe, B., Wagner, G., Yachmenev, A., Yurchenko, S.N., 2022. The HITRAN2020 molecular spectroscopic database. J.Q.S.R.T. 277, 107949. https://doi.org/10.1016/j.jqsrt.2021.107949.

Jiang, X.-J., Wang, J.-Z., Gao Y., Gu, Q.-S., 2017. HC3N observations of nearby galaxies. A&A. 600, A15. https://doi.org/10.1051/0004-6361/201629066.

Korablev, O., Montmessin, F., Trokhimovskiy, A., Fedorova, A.A., Shakun, A.V., Grigoriev, A.V., Moshkin, B.E., Ignatiev, N.I., Forget, F., Lefèvre, F., Anufreychik, K., Dzuban, I., Ivanov, Y.S., Kalinnikov, Y.K., Kozlova, T.O., Kungurov, A., Makarov, V., Martynovich, F., Maslov, I., Merzlyakov, D., Moiseev, P.P., Nikolskiy, Y., Patrakeev, A., Patsaev, D., Santos-Skripko, A., Sazonov, O., Semena, N., Semenov, A., Shashkin, V., Sidorov, A., Stepanov, A. V., Stupin, I., Timonin, D., Titov, A.Y., Viktorov, A., Zharkov, A., Altieri, F., Arnold, G., Belyaev, D.A., Bertaux, J. L., Betsis, D.S., Duxbury, N., Encrenaz, T., Fouchet, T., Gérard, J.-C., Grassi, D., Guerlet, S., Hartogh, P., Kasaba, Y., Khatuntsev, I., Krasnopolsky, V.A., Kuzmin, R.O., Lellouch, E., Lopez-Valverde, M.A., Luginin, M., Määttänen, A., Marcq, E., Martin Torres, J., Medvedev, A.S., Millour, E., Olsen, K.S., Patel, M.R., Quantin-Nataf, C., Rodin, A.V., Shematovich, V.I., Berkenboschs, I., Thomas, N., Vazquez, L., Vincendon, M., Wilquet, V., Wilson, C.F., Zasova, L.V., Zelenyi, L.M., Zorzano, M.P., 2018. The Atmospheric Chemistry Suite (ACS) of Three Spectrometers for the ExoMars 2016 Trace Gas Orbiter. Space Sci. Rev. 214, 7. https://doi.org/10.1007/s11214-017-0437-6.

Korablev, O., Olsen, K.S., Trokhimovskiy, A., Lefèvre, F., Montmessin, F., Fedorova, A.A., Toplis, M.J., Alday, J., Belyaev, D.A., Patrakeev, A., Ignatiev, N.I., Shakun, A.V., Grigoriev, A.V., Baggio, L., Abdenour, I., Lacombe, G., Ivanov, Y.S., Aoki, S., Thomas, I.R., Daerden, F., Ristic, B., Erwin, J.T., Patel, M., Bellucci, G., Lopez-Moreno, J.-J., Vandaele, A.C., 2021. Transient HCl in the atmosphere of Mars. Sci. Adv. 7, eabe4386. https://doi.org/10.1126/sciadv.abe4386.

Krasnopolsky, V.A. 2006. A sensitive search for nitric oxide in the lower atmospheres of Venus and Mars: Detection on Venus and upper limit for Mars. Icarus 182, 80–91. doi:10.1016/j.icarus.2005.12.003

Lefèvre, F., Krasnopolsky, V., 2017. Atmospheric Photochemistry. In: Haberle, R.M., Clancy, R.T., Forget, F., Smith, M.D., Zurek, R.W. (Eds.), The Atmosphere and Climate of Mars, pp. 405 - 432. http://dx.doi.org/10.1017/9781139060172.013.

Maguire, W.C., 1977. Martian isotopic ratios and upper limits for possible minor constituents as derived from Mariner 9 infrared spectrometer data. Icarus. 32, pp. 85–97. https://doi.org/10.1016/0019-1035(77)90051-3.

Mancinelli, R.L., Banin, A., 2003. Where is the nitrogen on Mars? Int. J. Astrobiol. 2, pp. 217–225. https://doi.org/10.1017/S1473550403001599.

Millan, M., Teinturier, S., Malespin, C.A., Bonnet, J.Y., Buch, A., Dworkin, J.P., Eigenbrode, J.L., Freissinet, C., Glavin, D.P., Navarro-González, R., Srivastava, A., Stern, J.C., Sutter, B., Szopa, C., Williams, A.J., Williams, R.H., Wong, G.M., Johnson, S.S., Mahaffy, P. R., 2022. Organic molecules revealed in Mars's Bagnold Dunes by Curiosity's derivatization experiment. Nat. Astron. 6, pp. 129–140. https://doi.org/10.1038/s41550-021-01507-9.

Montmessin, F., Korablev, O.I., Trokhimovskiy, A., Lefèvre, F., Fedorova, A.A., Baggio, L., Irbah, A., Lacombe, G., Olsen, K.S., Braude, A.S., Belyaev, D.A., Alday, J., Forget, F., Daerden, F., Pla-Garcia, J., Rafkin, S., Wilson, C.F., Patrakeev, A., Shakun, A., Bertaux, J.L., 2021. A stringent upper limit of 20 pptv for methane on Mars and constraints on its dispersion outside Gale crater. A.&A. 650, A140. https://doi.org/10.1051/0004-6361/202140389.

Moudden Y., McConnell, J.C., 2007. Three-dimensional on-line chemical modelling in a Mars general circulation model. Icarus. 188, pp. 18-34. http://dx.doi.org/10.1016/j.icarus.2006.11.005.

Olsen, K.S., Lefèvre, F., Montmessin, F., Trokhimovskiy, A., Baggio, L., Fedorova, A.A., Alday, J., Lomakin, A., Belyaev, D.A., Patrakeev, A., Shakun, A., Korablev, O.I., 2020. First detection of ozone in the mid-infrared at Mars: implications for methane detection. A.&A. 639, A141. https://doi.org/10.1051/0004-6361/202038125.

Olsen, K.S., Trokhimovskiy, A., Montabone, L., Fedorova, A.A., Luginin, M., Lefèvre, F., Korablev, O.I., Montmessin, F., Forget, F., Millour, E., Bierjon, A., Baggio, L., Alday, J., Wilson, C.F., Irwin, P.G.J., Belyaev, D.A., Patrakeev, A., Shakun, A., 2021. Seasonal reappearance of HCl in the atmosphere of Mars year 35 dusty season. A.&A. 647, A161. https://dx.doi.org/10.1051/0004-6361/202140329.

Stern, J.C., Sutter, B., Freissinet, C., Navarro-González, R., McKay, C.P., Archer Jr., P.D., Buch, A., Brunner, A.E., Coll, P., Eigenbrode, J.L., Fairen, A.G., Franz, H.B., Glavin, D.P., Kashyap, S., McAdam, A.C., Ming, D.W., Steele, A., Szopa, C., Wray, J.J., Martín-Torres, F.J., Zorzano, M.-P., Conrad, P.G., Mahaffy, P.R. and the MSL Science Team, 2015. Evidence for indigenous nitrogen in sedimentary and aeolian deposits from the Curiosity rover investigations at Gale crater, Mars. PNAS. 112, pp. 4245-4250. https://doi.org/10.1073/pnas.1420932112.

Sutter, B., McAdam, A.C., Mahaffy, P.R., Ming, D.W., Edgett, K.S., Rampe, E.B., Eigenbrode, J.L., Franz, H.B., Freissinet, C., Grotzinger, J.P., Steele, A., House, C.H., Archer, P.D., Malespin, C.A., Navarro-González, R., Stern, J.C., Bell, J.F., Calef, F.J., Gellert, R., Glavin, D.P., Thompson, L.M., Yen, A.S., 2017. Evolved gas analyses of sedimentary rocks and eolian sediment in Gale Crater, Mars: Results of the Curiosity rover's sample analysis at Mars instrument from Yellowknife Bay to the Namib Dune. J. Geophys. Res. Planets. 122, pp. 2574-2609. https://doi.org/10.1002/2016JE005225.

Thelen, A.E., Nixon, C.A., Chanover, N.J., Cordiner, M.A., Molter, E.M., Teanby, N.A., Irwin, P.G.J., Serigano, J., Charnley, S.B., 2019. Abundance measurements of Titan's stratospheric HCN, HC3N, C3H4, and CH3CN from ALMA observations. Icarus. 319, pp. 417-432. https://doi.org/10.1016/j.icarus.2018.09.023.

Trokhimovskiy, A., Perevalov, V., Korablev, O., Fedorova, A.A., Olsen, K.S., Bertaux, J.-L., Patrakeev, A., Shakun, A., Montmessin, F., Lefèvre, F., Lukashevskaya, A., 2020. First observation of the magnetic dipole CO2 main isotopologue absorption band at 3.3 µm in the atmosphere of Mars by ExoMars Trace Gas Orbiter ACS instrument. A.&A. 639, A142. https://dx.doi.org/10.1051/0004-6361/202038134.

Trokhimovskiy, A., Fedorova, A.A., Olsen, K.S., Alday, J., Korablev, O., Montmessin, F., Lefèvre, F., Patrakeev, A., Belyaev, D., Shakun, A.V., 2021. Isotopes of chlorine from HCl in the Martian atmosphere. A.& A. 651, A32. https://doi.org/10.1051/0004-6361/202140916.

Vago, J., Witasse, O., Svedhem, H., Baglioni, P., Haldemann, A., Gianfiglio, G., Blancquaert, T., McCoy, D., de Groot, R., 2015. ESA ExoMars program: The next step in exploring Mars. Sol. Sys. Res. 49, pp. 518-528. https://doi.org/10.1134/S0038094615070199.

Villanueva, G.L., Mumma, M.J., Novak, R.E., Radeva, Y.L., Käufl, H.U., Smette, A., Tokunaga, A., Khayat, A., Encrenaz, T., Hartogh, P., 2013. A sensitive search for organics (CH4, CH3OH, H2CO, C2H6, C2H2, C2H4), hydroperoxyl (HO2), nitrogen compounds (N2O, NH3, HCN) and chlorine species (HCl, CH3Cl) on Mars using ground-based high-resolution infrared spectroscopy. Icarus. 223, pp. 11-27. https://doi.org/10.1016/j.icarus.2012.11.013.