The 5.8 µm absorption bands for nitric acid ($H^{14}N^{16}O_3$): line positions and intensities for the ν_2 band at 1709.567 cm.1 and for its first associated hot bands ($\nu_2+\nu_9-\nu_9$, $\nu_2+\nu_7-\nu_7$, and $\nu_2+\nu_6-\nu_6$)

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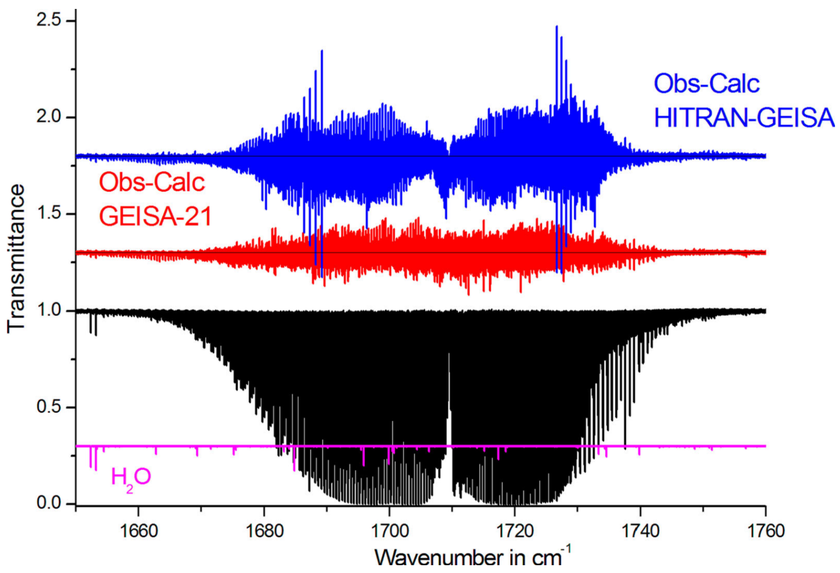
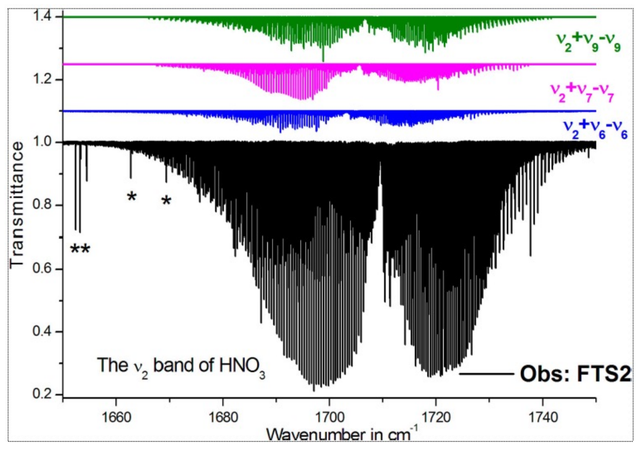
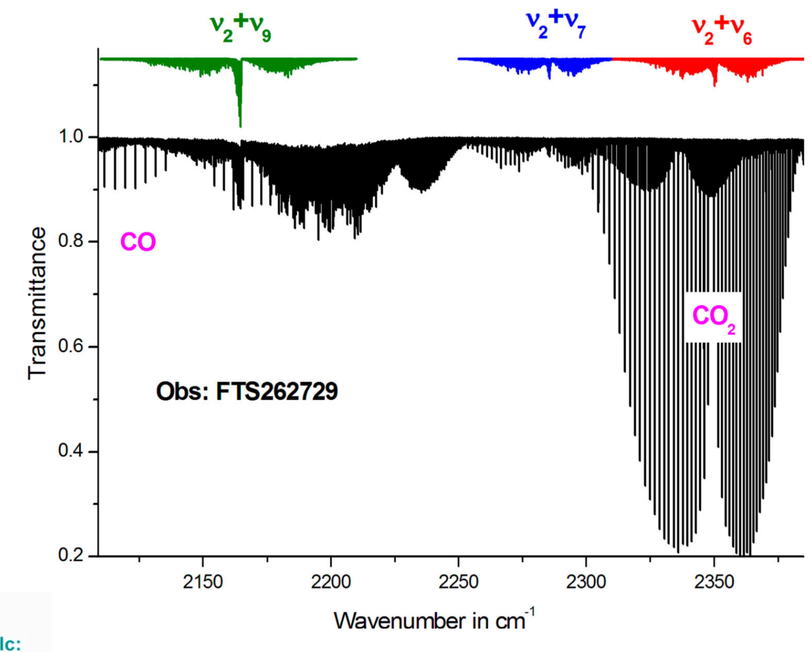
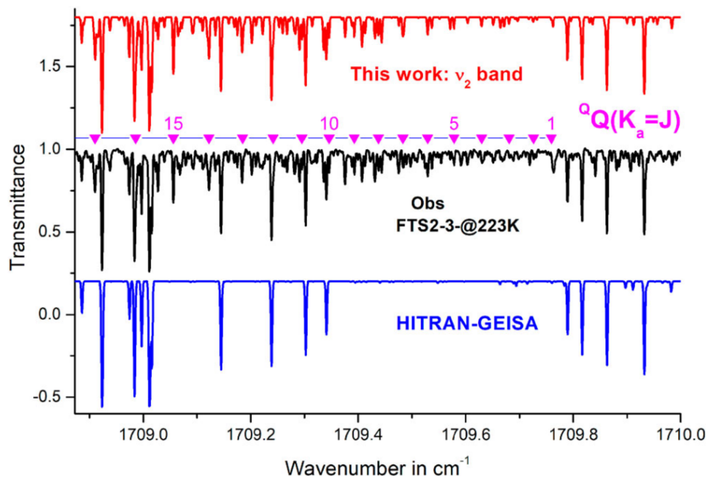
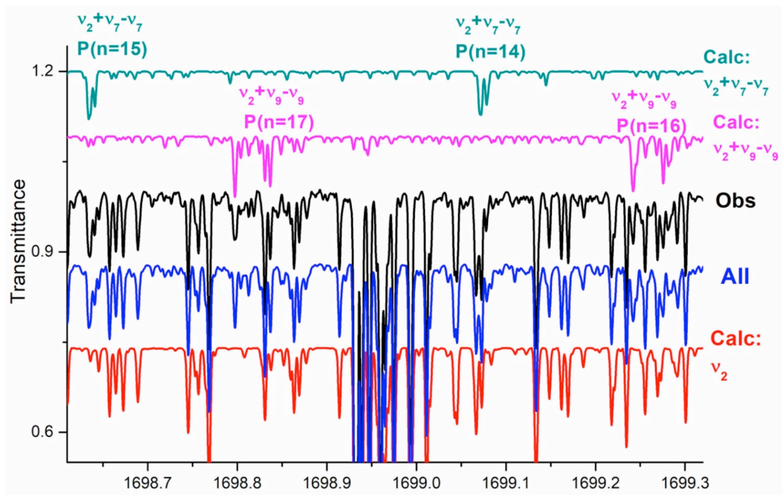
These two papers present the generation of a more accurate linelist for the 5.8µm absorption band of HNO_3 (the ν_2 band together with the $\nu_2+\nu_9-\nu_9$, $\nu_2+\nu_7-\nu_7$, and $\nu_2+\nu_6-\nu_6$ first hot bands). For this, we recorded four high-resolution Fourier transform spectra for the ν_2 band, centered at 1709.567 cm^{-1}, and one spectrum in the 4.5 µm region. Using these spectra, a new extended line position analysis was performed for the ν_2 band, leading to more accurate line positions and the first identification of the $\nu_2+\nu_9$, $\nu_2+\nu_7$, and $\nu_2+\nu_6$ bands. In parallel, individual line intensities were measured at 5.8 µm. It appears that, although the ν_2 band is mainly of B-type, it also possesses a (very) weak A-type component that cannot be ignored. Our final linelist for HNO3 at 5.8 µm includes lines from the ν_2 band together with those of the $\nu_2+\nu_9-\nu_9$, $\nu_2+\nu_7-\nu_7$, and $\nu_2+\nu_6-\nu_6$ associated hot bands that were generated during the first part of this study. Surprisingly, both $\nu_2+\nu_9-\nu_9$ and $\nu_2+\nu_9$ bands exhibit large amplitude torsional splittings of ~0.043 cm^{-1}. This is presumed to be due to the existence of an anharmonic resonance that couples together the 2^19^1 energy levels with those of a dark state involving high excitation in the ¦Í9 large amplitude OH torsional mode

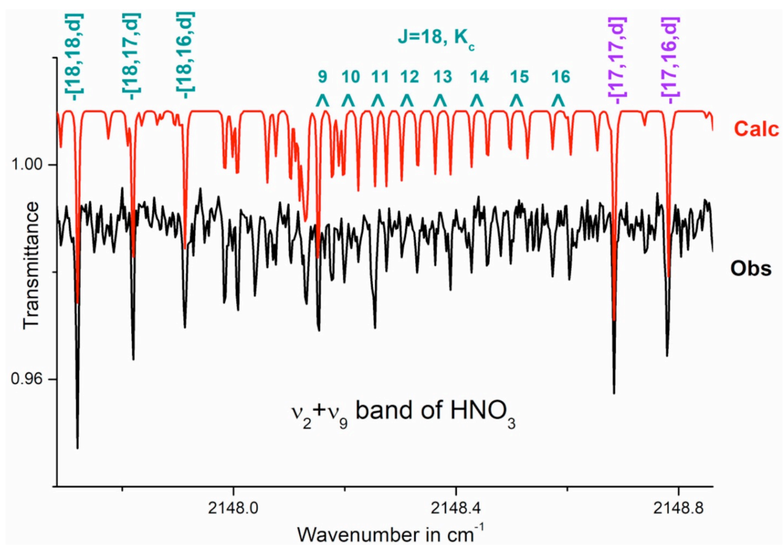


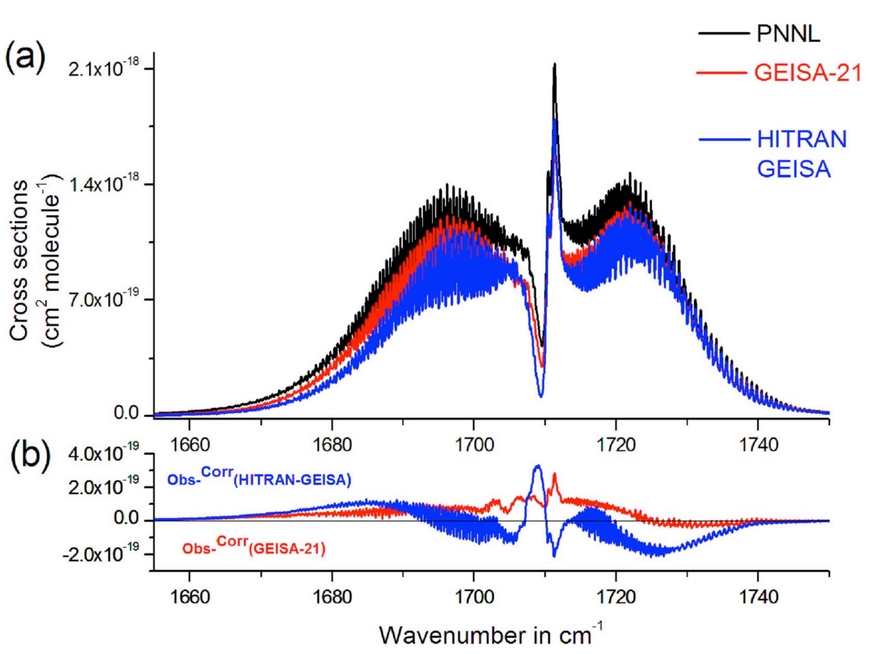


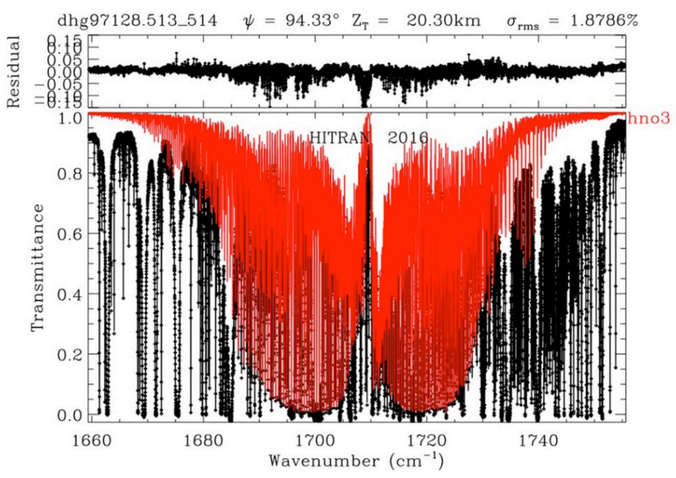


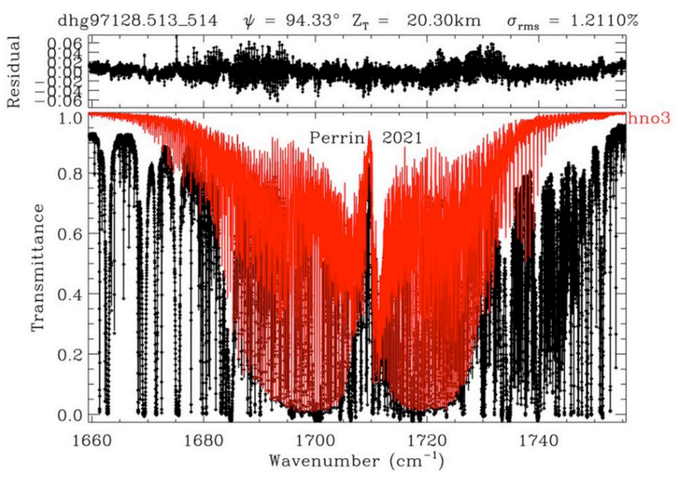












Overview of the experimental spectrum in the ν_2 region (5.8 µm) and comparison with the calculated spectra for the $\nu_2+\nu_9-\nu_9$, $\nu_2+\nu_7-\nu_7$, and the $\nu_2+\nu_6-\nu_6$.

Overview of the spectrum in the 4.5 µm region comparison with the calculated spectra generated in this work for the $\nu_2+\nu_9$, $\nu_2+\nu_7$, and $\nu_2+\nu_6$ bands of HNO_3.

Portion of the P branch part of the $\nu_2+\nu_9$ band in the 2148.2 cm^{-1} spectral region. Strongest lines involve [J, K_a, K_c] values in the 2^19^1 upper state for very high Ka values (Kc is degenerated) for J = 18 and J = 17. The identified weaker lines involve low K_a values and J = 18, and the torsional (K_a = J-Kc ⇔K_a = J-K_c+1) splitting doublets are indicated by the K_c values in 2^19^1.

Portion of the HNO_3 spectrum in the 1699 cm^{-1} spectral region. The calculated plots are the ν_2 cold band , the $\nu_2+\nu_9-\nu_9$ and $\nu_2+\nu_7-\nu_7$ hot bands, and all bands (ν_2 and hot bands). Within those of the P branch of the ν_2 cold band, transitions belonging to several hot bands are observable. The P(n) clusters have a different shape for the $\nu_2+\nu_9-\nu_9$ and $\nu_2+\nu_7-\nu_7$ hot bands because of the existence of large amplitude torsional splittings in the 2^19^1 excited state.

Central part of the **A-type Q branch** of the (**mainly B type**) ν_2 band of HNO3. The assignments for the $^QQ_{(Ka = J)}$ transitions are also shown (triangles).

Comparison of the PNNL cross sections (in cm^2/molecule at 296K) with their corresponding values using the HITRAN-GEISA linelist and the GEISA-21 linelist.

Overview of the HNO3 spectrum recorded at 223K in the 5.8 µm region. The (Observed – Calculated) signals are compared for the old (HITRAN-GEISA) and new (GEISA-21) line lists.

Example of a spectral fit to a MkIV balloon spectrum using the HITRAN 2016 HNO3 linelist (left panel) and the present work (right panel). Black diamonds represent the measured spectrum, the black line the fitted calculation, and the red lines the contribution of HNO_3. This particular spectrum was measured at 20.3 km tangent altitude above Alaska in 1997, where the tangent temperature and pressure were 230K and 50 mbar. The upper panels display the residuals (Obs-Calc.); note the scale change between left and right residuals. The main absorbers in this region are HNO3, H2O, and O3, but the spectroscopy of these other gases was unchanged, so the differences between the left- and right-hand panels are entirely attributable to HNO3 spectroscopy changes.

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