

High Accuracy Line Lists of CH₄ and H₂CO in the 8 μ m Range from Optical Frequency Comb Fourier Transform Spectroscopy

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Spectral data in the 8 μ m region – a water window where many molecules show strong rovibrational features – are currently derived mostly from conventional FTIR measurements, with line position uncertainties of the order of a few to few tens of MHz [1]. Recently, we developed a Fourier transform spectrometer (FTS) based on a compact 8 μ m frequency comb that allows line position retrieval with sub-MHz accuracy [2]. We record and interleave spectra at different repetition rates to obtain sampling point spacing of ~ 10 MHz using the sub-nominal resolution sampling-interleaving method to analyze the FTS data [3]. Here, we use this spectrometer to measure high-resolution absorption spectra of two species important in atmospheric sensing and astrophysics: methane, Fig. 1(a), a greenhouse gas and a constituent of exoplanetary atmospheres, and formaldehyde, Fig. 1(c), a toxic pollutant and a species found in the interstellar medium. By fitting Voigt functions to the individual absorption lines in spectra measured over a wide range of partial pressures, we determine center frequencies of transitions with intensities spanning more than 3 orders of magnitude, with typical uncertainties of a few hundred kHz.

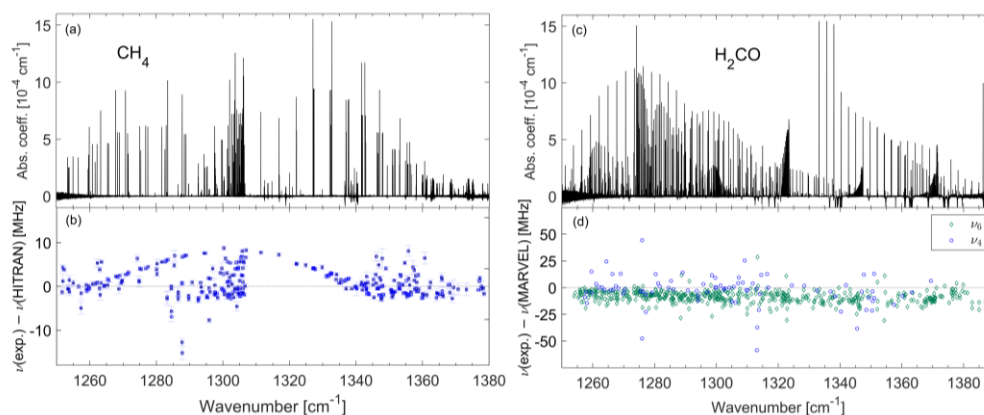


Fig. 1 (a) Absorption spectrum of 5% methane (CH₄) in N₂ at a total pressure of 0.04 mbar. (b) Observed line positions of the v_4 band of CH₄ relative to the HITRAN2020 database [1]. (c) Absorption spectrum of 0.02 mbar of pure formaldehyde (H₂CO). (d) Observed line positions of the v_4 and v_6 bands of H₂CO relative to MARVEL predictions.

For methane, we compiled a list of >800 lines belonging to the v_4 fundamental band of $^{12}\text{CH}_4$ [Fig. 1(b)] and $^{13}\text{CH}_4$ and two hot bands of $^{12}\text{CH}_4$, with a frequency accuracy more than an order of magnitude better than previous FTIR data [4]. We used this line list to improve the global fit of an effective CH₄ Hamiltonian. For formaldehyde, we retrieved the positions and intensities of >700 fundamental-band and >40 hot-band transitions. Reference data for this range is missing in HITRAN [1], but a large fraction of the measured lines can be assigned using predictions from the MARVEL (measured active rotation vibration energy levels) procedure [Fig. 1(d)] [5]. We assigned other lines using an effective Hamiltonian based on the MARVEL-predicted lines and used them to revise the MARVEL analysis, which yielded new energy levels. The line lists obtained using comb-based FTS will significantly improve the accuracy of line positions available in molecular databases.

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