

# High Accuracy Line Lists of CH<sub>4</sub> and H<sub>2</sub>CO in the 8 $\mu\text{m}$ Range from Optical Frequency Comb Fourier Transform Spectroscopy

Matthias Germann<sup>1</sup>, Adrian Hjältén<sup>1</sup>, Vincent Boudon<sup>2</sup>, Cyril Richard<sup>2</sup>, Jonathan Tennyson<sup>3</sup>, Sergey Yurchenko<sup>3</sup>, Iouli E. Gordon<sup>4</sup>, Christian Pett<sup>5</sup>, Isak Silander<sup>1</sup>, Karol Krzempek<sup>6</sup>, Arkadiusz Hudzikowski<sup>6</sup>, Aleksander Gluszek<sup>6</sup>, Grzegorz Soboń<sup>6</sup>, and Aleksandra Foltynowicz<sup>1</sup>

1. Department of Physics, Umeå University, 901 87 Umeå, Sweden

2. Laboratoire ICB, UMR 6303 CNRS/Université Bourgogne Franche-Comté, F-21078 Dijon Cedex, France

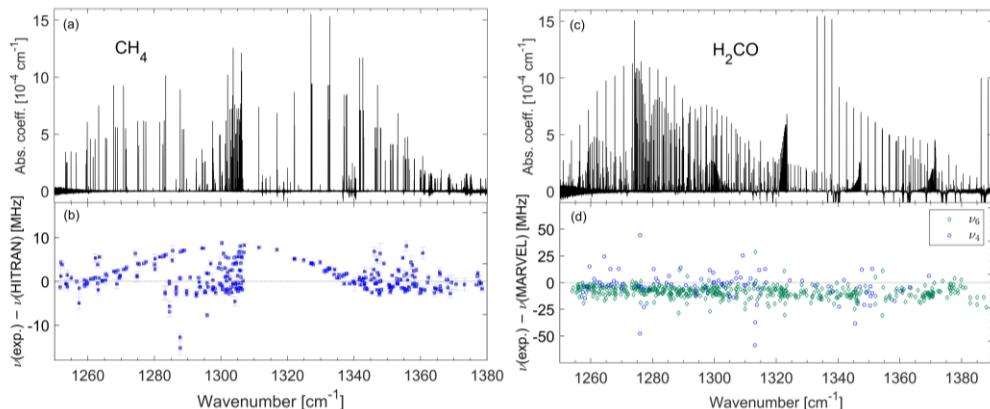
3. Department of Physics and Astronomy, University College London, London WC1E 6BT, United Kingdom

4. Center for Astrophysics, Harvard & Smithsonian, Atomic and Molecular Physics Division, Cambridge, MA 02138, US

5. Department of Chemistry, Umeå University, 901 87 Umeå, Sweden

6. Faculty of Electronics Photonics and Microsystems, Wroclaw University of Science and Technology, 50-370 Wroclaw, Poland

Spectral data in the 8  $\mu\text{m}$  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  $\mu\text{m}$  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  $\sim$ 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 (CH<sub>4</sub>) in N<sub>2</sub> at a total pressure of 0.04 mbar. (b) Observed line positions of the v<sub>4</sub> band of CH<sub>4</sub> relative to the HITRAN2020 database [1]. (c) Absorption spectrum of 0.02 mbar of pure formaldehyde (H<sub>2</sub>CO). (d) Observed line positions of the v<sub>4</sub> and v<sub>6</sub> bands of H<sub>2</sub>CO relative to MARVEL predictions.

For methane, we compiled a list of  $>800$  lines belonging to the v<sub>4</sub> fundamental band of <sup>12</sup>CH<sub>4</sub> [Fig. 1(b)] and <sup>13</sup>CH<sub>4</sub> and two hot bands of <sup>12</sup>CH<sub>4</sub>, 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 CH<sub>4</sub> 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.

**Acknowledgments:** Knut and Alice Wallenberg Foundation (KAW 2015.0159, 2020.0303), Swedish Research Council (2016-03593), and the Foundation for Polish Science (POIR.04.04.00-00-434D/17-00); European Research Council (Advanced Grant 883830).

## References

1. I. E. Gordon, et al., "The HITRAN2020 molecular spectroscopic database," *J. Quant. Spectros. Radiat. Transfer* **277**, 107949 (2022).
2. A. Hjältén, M. Germann, K. Krzempek, A. Hudzikowski, A. Gluszek, D. Tomaszewska, G. Soboń, and A. Foltynowicz, "Optical frequency comb Fourier transform spectroscopy of <sup>14</sup>N<sub>2</sub><sup>16</sup>O at 7.8  $\mu\text{m}$ ," *J. Quant. Spectros. Radiat. Transfer* **271**, 107734 (2021).
3. P. Maslowski, et al., "Surpassing the path-limited resolution of Fourier-transform spectrometry with frequency combs," *Phys. Rev. A* **93**, 021802(R) (2016).
4. M. Germann, et al., "A methane line list with sub-MHz accuracy in the 1250 to 1380 cm<sup>-1</sup> range from optical frequency comb Fourier transform spectroscopy," *J. Quant. Spectros. Radiat. Transfer* **288**, 108252 (2022).
5. A. R. Al-Derzi, J. Tennyson, S. N. Yurchenko, M. Melosso, N. Jiang, C. Puzzarini, L. Dore, T. Furtenbacher, R. Tóbiás, and A. G. Császár, "An improved rovibrational linelist of formaldehyde, H<sub>2</sub><sup>12</sup>C<sup>16</sup>O," *J. Quant. Spectros. Radiat. Transfer* **266**, 107563 (2021).