Sub-Doppler Spectroscopy of Methane in the THz range

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Methane plays a crucial role in atmospheric and planetary sciences, as one of the primary anthropogenic greenhouse gases. [1] Its accurate spectroscopic characterization is essential for climate modeling and improvement of databases. Over the past decades, extensive spectroscopic studies have been carried out in the mid-infrared and visible regions, providing large datasets of transition frequencies, intensities and pressure broadening coefficients. [2-4] However, in the THz domain, experimental data remain deficient and no sub-Doppler measurements have been reported in the THz range so far. This lack of high-precision data limits the refinement of spectroscopic model and datasets.

Methane as a spherical top molecule, has no permanent dipole moment. As a result, pure rotational transitions are electric-dipole forbidden, making conventional microwave and terahertz spectroscopy very challenging. However, weak transitions can arise through different mechanism that induce a dipole moment. [5] Such mechanisms are centrifugal distortion and vibration-rotation interaction. These effects relax the strict selection rules and enable otherwise forbidden transition to be observed. In the 100-1000 GHz range, the most intense transitions observed at the room temperature are pure rotational transitions in the v_4 vibrational mode. In this work, we present sub-Doppler double-resonance (DR) measurements of methane in the v_4 vibrational band allowing for first Sub-Doppler measurements of these lines. Our DR scheme, exploit a MIR pump radiation that selectively pump molecules into v_4 state while THz radiation probe pure rotational transitions in this state. Resolving pure rotational transitions in 300-1100 GHz in the sub-Doppler regime enables improvement of frequency accuracy for refining effective Hamiltonian models and spectroscopic databases.

[1] *Intergovernmental Panel On Climate Change (Ipcc), Climate Change 2021 – The Physical Science Basis: Working Group I Contribution to the Sixth Assessment Report of the Intergovernmental Panel on Climate Change, 1st ed. (Cambridge University Press, 2023).*

[2] A. V. Nikitin, V. Boudon, Ch. Wenger, S. Albert, L. R. Brown, S. Bauerecker, and M. Quack, High resolution spectroscopy and the first global analysis of the Tetradecad region of methane 12CH4, Physical Chemistry Chemical Physics 15, 10071 (2013).

[3] S. Kassi, B. Gao, D. Romanini, and A. Campargue, The near-infrared (1.30–1.70 μm) absorption spectrum of methane down to 77 K, Physical Chemistry Chemical Physics 10, 4410 (2008).

[4] A. Campargue, E. V. Karlovets, S. S. Vasilchenko, and M. Turbet, The high resolution absorption spectrum of methane in the 10 800–14 000 cm–1 region: Literature review, new results and perspectives, Physical Chemistry Chemical Physics 25, 32778 (2023).

[5] I. Ozier and A. Rosenberg, The vibrationally induced rotational spectrum of CH4 in the (v4=1) state, The Journal of Chemical Physics 69, 5203 (1978).

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