

THz rotational spectroscopy of weakly polar CH₃D and non-polar CH₄ molecules using a widely tunable photomixing synthesizer based on a frequency comb

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The Terahertz (THz) group of the Laboratory of Physical Chemistry of the Atmosphere has developed a THz synthesizer exploiting a photomixing source widely tunable between 0.3 and 3.3 THz with a frequency metrology precise to the ten kHz through the locking of optical laser sources on an ultra-stable frequency comb.¹ The performances of this unique instrument contribute to improve and complete international databases such as HITRAN or JPL by means of rotational spectroscopy studies (positions and line profiles) on stable and unstable species that play a key role in Earth or planetary atmospheres.^{2,3}

Recently, the sensitivity thresholds have been overcome through measurements on deuteromethane CH₃D, a primary target for measurements of the origin of atmospheric gases and methane CH₄, one of the most abundant gases in planetary atmospheres. Direct THz absorption measurements between 1 and 2.5 THz have been performed with an optical path of 20 m allowing line positions and line profiles studies of rotational transitions with intensities lower than 10⁻²⁵ cm⁻¹/(molecules.cm⁻²). In the case of CH₃D, the line positions of K multiplets with 6 < J < 10 have been measured for the first time with relative uncertainties better than 10⁻⁷ allowing to improve the accuracy of ground state molecular parameters⁴ and consequently, the prediction of pure rotational frequency and intensity transitions in the THz domain. In addition, a first determination of self-broadening coefficient from pure rotational transitions of CH₃D have been performed with measurements in a small pressure range from 1 to 4 mbar. Finally, we demonstrated the capability of the THz synthesizer to measure THz pure rotational transitions of non-polar CH₄ molecules where a very weak transition dipole moment is induced by centrifugal distortion effects. Our new measurements in the 2.5 THz region were compared with the distortion dipole rotational spectrum of CH₄ measured by Boudon *et al.* using synchrotron based FT-Far-IR spectroscopy.⁵ With a resolution of the order of tens of kHz, we improved by at least 2 orders of magnitude the accuracy of measured line frequencies providing a better agreement with simulations based on the tensorial formalism developed in the Dijon group for spherical-top molecules.

References

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