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THz spectrum of monodeuterated methane

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Abstract

We report new measurements of the rotational spectrum of monodeuterated methane (CH_3D) in the range of 690–1200 GHz which allow for an accurate prediction of all lines in the range of the high-resolution spectrometer of the Herschel Space Observatory. Comparison is also made with the previous analysis based on infrared combination differences. Three lines of $^{13}CH_3D$ were measured in natural abundance.

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1. Introduction

We report extended measurements of the rotational spectrum of monodeuterated methane (CH_3D). This species is important for the study of planetary atmospheres and of the interstellar medium (ISM).

Since the first detection of CH_3D in the atmosphere of Jupiter [1], the deuterium-to-hydrogen (D/H) ratio has played a major role in the study of the origin and evolution of planetary atmospheres (e.g. [2]). The large mass difference between hydrogen and its isotope deuterium induces significant differences in both the thermodynamics and the kinetics of various processes, such as thermal escape, chemical reactivity and condensation, resulting in an isotopic fractionation. Therefore observed D/H ratios act as tracers of the physical and chemical history of planetary atmospheres as they evolve from the initial interstellar ices and gases. CH_3D has been observed on Jupiter [3,4], Saturn [5,6], Titan [7–10], Uranus [11,12] and Neptune [13] by, for example, ISO and the IRIS instrument on Voyager. The weaker rotational spectrum of CH_4 has been observed with the CIRS instrument on Cassini and has been used to determine the methane abundance in Saturn and Titan: see Ref. [14] (Saturn) and Ref. [15] (Titan). Recently the Cassini-CIRS instrument has also reported measurements of the isotopic methane species CH_3D [16] and $^{13}CH_3D$ [17] on Titan.

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The deuterium present in the atmospheres of the giant planets is thought to be representative of the protosolar composition, a quantity of high interest in astrophysics [18]. The D/H ratio of methane has also been used to estimate the formation temperature of cometary molecules [19]. The authors used this determination as an evidence that our Sun was born in a warm cloud of 30 K rather than a cold one at 10 K. It should be noted that this conclusion was based on the non-detection of CH_3D in the near-infrared.

The launch of the Herschel Space Observatory in 2008 will enable measurements of astrophysical spectra in the far-infrared that are not possible from earth-based observatories because of the atmospheric absorption. In particular the HIFI instrument will allow for very high-resolution spectral studies to be taken over a wide spectral range from around 500–1900 GHz, increasing the region in which new spectral lines can be searched for and allowing wide and long scans unaffected by local weather conditions. Laboratory spectral data for CH_3D in this region are lacking and only three precisely measured rotational transitions, all below 500 GHz, have been reported.

Chemical models predict methane to be one of the most abundant polyatomic species in dense interstellar clouds and it is thought to have enhanced abundance in hot, dense gas such as the Orion hot core region because of evaporation from grain mantles. Although its rovibrational spectrum has been detected toward IRC +10216 [20], vibrational excitation is limited in interstellar molecules, especially in regions of extended gas that dominate molecular clouds, since even toward star-forming objects temperatures are typically only around 10–100 K. Hence, infrared spectra must be measured in absorption. Furthermore, vibrational spectra cannot be used to study far inside clouds containing dust since the latter absorbs and scatters infrared radiation. However, far-infrared radiation can penetrate throughout the cloud. Since it is completely symmetric CH_4 has no permanent dipole moment and is not easily identified in the ISM from its rotational spectrum.

The dipole moment of CH_3D that arises from the isotopic substitution is small but non-zero ($\sim 6 \times 10^{-3} D$) [21,22]. This being measured via direct absorption methods in the THz spectrum at low resolution and using the electric resonance spectrum in the first two rotational states. The dipole was later shown to have a significant rotational dependence [23]. CH_4 also has a centrifugally induced dipole moment that is around a 1000 times weaker than the isotopically induced electric dipole of CH_3D [24]. The cosmic elemental D/H ratio is expected to be around $1.5-2.3 \times 10^{-5}$ (see, for example, Ref. [25]). However, for molecular species the fractionation ratio, defined as the ratio of the column density of a deuterated molecule to its hydrogen counterpart, is found to be up to five orders of magnitude higher than this elemental abundance ratio [26]. The deuterium enhancement results from chemical processes, which can involve both gas-phase and surface reactions. Hence it is not clear whether CH_3D or CH_4 is most likely to be first detected. An attempt to identify CH_3D in Orion proved inconclusive [27], giving an upper limit to the column density of the order of 10^{18} cm^{-1}. The ALMA interferometer which will come progressively into service at the end of this decade will give not only high spatial resolution allowing searches to concentrate on specific areas of supposed high concentration but also highly increased sensitivity due to the cumulative surface area of the array of telescopes used (up to 64).

Previous laboratory measurements of the rotational spectrum of deuterated methane have been limited by available technology. Until recently only three lines had been measured, the $J(0 \rightarrow 1)$, by Pickett et al. [28], and the two K-components of $J(1 \rightarrow 2)$ by Womack et al. [27], who also measured the first transition as well. The predictive analysis available from ground-state combination differences (GSCDs) [29] and the available pure rotational data have been the basis of the JPL catalog compilation. The present work extends the basis of high precision pure rotational data.

We now report 12 new measured rotational frequencies in the range of 697–1162 GHz, completing measurements of the rotational spectrum up to $J'_{K'} = 5_4$.

2. Experimental

The measurements were carried out at JPL. The spectrometer system has been described earlier [30,31]. Briefly, a millimeter-wave module, with 10–100 mW of output power, and a series of commercial (Virginia Diodes) and JPL built multiplier chains were used to produce THz radiation. The radiation source was a sweep synthesizer phase-locked to a frequency standard with a precision of one part in 10^{12}; so the frequency