

Terahertz spectroscopy of the CHD radical ($\tilde{X}^3 A''$)

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ABSTRACT

Context. Pure rotational spectra in the field-free condition of the CH₂ and CD₂ isotopologues of the methylene radical have already been reported, whereas only six rotational transitions of the mono-deuterated species, CHD, detected by FIR-LMR spectroscopy have been.

Aims. Spectra of the mono-deuterated methylene radical in its ground electronic state ($\tilde{X}^3 A''$) were observed in the field-free condition for the first time in the frequency region below 1 THz.

Methods. CHD was generated in a positive column discharge in a CH₂D₂ – Ar mixture cooled with liquid nitrogen.

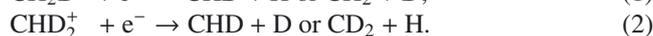
Results. Two rotational transitions, each split into three fine-structure components, were measured. The *B* and *C* rotational constants, the ϵ_{bb} and ϵ_{cc} spin-rotation constants, and the β spin-spin constant were revised.

Conclusions. The reported frequencies are suitable for astronomical searches.

Key words. line: identification – molecular data – ISM: molecules – submillimetre: ISM

1. Introduction

The methylene radical, CH₂, is known as an interstellar molecule that has been detected towards hot cores in dense interstellar clouds (Hollis et al. 1995; Polehampton et al. 2005). In the gas phase chemical models of both dense and diffuse molecular clouds, the methylene radical is thought to be one of the fundamental molecules of the carbon chemistry, and it is produced primarily by dissociative recombination of the methyl ion, CH₃⁺ (Herbst 2001; Vejby-Christensen et al. 1997). Recently tentative detection of the mono-deuterated methyl ion, CH₂D⁺ have been reported toward an infrared source in the vicinity of Orion (Lis et al. 2009), along with its supporting laboratory spectroscopic measurements (Amano 2010; Gärtner et al. 2010). Mono-deuterated methylene CHD can be produced from this ion or its counterpart ion, CHD₂⁺, by dissociative recombination with an electron as shown in the chemical reactions:



Thus, both CHD and CD₂ can be observed in warm interstellar clouds, where the deuterium fractionation process is important (see Turner 2001; Roueff 2007; Parise 2009). Precise laboratory reference data are therefore desirable for such a radio-astronomical observation of these molecules.

More than half a century has passed since the pioneering spectroscopic work on the methylene radicals, CH₂ and its deuterated isotopomers by Herzberg et al. (1959, 1971). However, it is still an ongoing project to characterize or understand the nature of this species by spectroscopy in various wavelength regions. This difficulty arises from the unique chemical and physical properties of the molecule. The methylene radical is the prototype of the “carbene” and is known to be kinetically

a very unstable species (Moss & Jones, Jr. 1975). Therefore this short-lived molecule is very hard to generate in concentrations that are high enough for carrying out spectroscopic studies in laboratory conditions. In the ground electronic state, the CH₂ molecule possesses ³B₁ symmetry with a bent and exceedingly floppy molecular structure. The latter characteristic leads to the breakdown of the Watson model for this species. Such a complicated situation has stimulated many theoretical studies on CH₂, and various models have been proposed in order to represent its bending potential (see Bunker & Landsberg 1977; Bunker & Jensen 1983; Jensen et al. 1982; Bunker et al. 1986; Jensen 1988). The fidelity of these theoretical models can be validated by comparative studies of the energy levels of methylene and its deuterated analogues obtained by high-resolution molecular spectroscopy.

High-resolution spectroscopy of the methylene radical has been conducted mainly by infrared/far-infrared laser magnetic resonance spectroscopy (IR/FIR-LMR) or infrared diode laser spectroscopy (Bunker 1985). Thanks to these extensive works in mid 70's to early 80's, pure rotational transitions frequencies for CH₂ and CD₂ can be predicted with the accuracy of less than several tens of MHz, and laboratory microwave spectra of CH₂ and CD₂ were successfully observed (Lovas 1983; Ozeki & Saito 1995, 1996). In the best-studied case of CH₂, six rotational transitions having *K_a* = 0, 1 have been observed up to almost 2 THz with microwave spectroscopic precision (Michael et al. 2003; Brünken et al. 2004, 2005). Since *b*-type transitions are allowed, those measured near 1 and 2 THz involve *N* = 1, 2 and include the 1₁₀ ← 1₀₁ ground-state transition of *para*-CH₂ (see the definition of *ortho*- and *para*-CH₂ in the results and discussion section), while the ones measured in the lower frequency region correspond to higher rotational quantum numbers with

energy levels of several hundred Kelvin. The inadequacy of a Watson-type Hamiltonian for fitting spectra of methylene radical also led Brünken et al. (2005) to employ a Hamiltonian based on Euler functions to successfully carry out the global analysis of the experimental spectrum of CH₂. The number of observed lines is, however, still limited due to its lightness and the fact that *b*-type asymmetric rotor selection rules apply. As for CD₂, only four rotational transitions below 600 GHz have been reported so far by laboratory microwave spectroscopy (Ozeki & Saito 1996). To our knowledge, no field-free high-resolution spectrum has been reported for the CHD radical. Nolte et al. (1994) published FIR-LMR spectroscopy of the CHD radical in the ground electronic state. An insufficient number of observed spectral lines (six rotational transitions) meant that their proposed set of molecular constants was a composite of the ones derived both experimentally and theoretically (Bunker et al. 1983). As a consequence the energy levels of CHD are not as reliable as those of CH₂ and CD₂, which presumably makes it hard to achieve spectral measurement of this species. We report in the present paper field-free, pure rotational spectra of the CHD radical up to the terahertz frequency region with an accuracy the same order as conventional microwave spectroscopy.

2. Experiment

The spectrometer used in this experiment has been described extensively elsewhere (Bailleux et al. 2002). Submillimetre-wave and terahertz radiations in the frequency range 0.55–0.97 THz were provided by two phase-locked backward-wave oscillators (Istok company, Russia). Emitted power at observed transition frequencies was in the mW range. A liquid-helium-cooled InSb bolometer (QMC Instruments) was used as detector. Source modulation at 5 kHz and lock-in detection at twice the modulation frequency was employed for improved sensitivity, resulting in a second-derivative line shape. A positive column discharge in various isotopologues of methane used as precursors, CH₂D₂ and CD₄ (Cambridge Isotope Laboratories Inc., USA), was setup. The absorption cell was a 2 m long, 5 cm inner diameter, double-jacketed Pyrex tube, allowing liquid-nitrogen flow through the outer jacket to cool the plasma. The cell was equipped with a solenoid coil for creating an axial magnetic field to ensure that the lines are paramagnetic by on/off measurements. The precursor was pre-mixed with argon used as buffer gas before it entered the absorption cell's inlet for in situ production of reactive species. In addition to the above-mentioned precursors, CH₄ was also available in order to check for the chemistry of the reactions that occur in the absorption cell.

3. Spectroscopic measurements

We first optimized the experimental conditions to produce CH₂ as trial species using CH₄ as precursor. For this purpose, reported rotational lines below 600 GHz were observed. The conditions were further confirmed by the observation of the di-deuterated analogue, CD₂, using CD₄ as precursor. We found that the optimum discharge current was in the range 20–30 mA and that the partial pressures (measured downstream at room temperature) giving the best signal-to-noise ratio were 13 and 2.5 mTorr for Ar and CH₄ or CD₄, respectively. The outer jacket of the cell partially filled with liquid nitrogen (~30% of the maximum liquid nitrogen load) resulted in an increase in the intensity of the signals. Using these conditions, we have successfully observed the as yet unreported three fine-structure components of the

$N_{K_a K_c} = 7_{07} \leftarrow 6_{16}$ rotational transition of CD₂ near 799 GHz, which will be published elsewhere with additional lines measured, if possible. Optimization of the conditions also allowed us to gauge both the production efficiency and the line intensity we could expect for the mono-deuterated methylene radical. Indeed, our method of production differs markedly from the one reported in previous studies, continuous glow discharge in ketene. As a result, our production efficiency, although lower than the one obtained with the discharge in ketene, was satisfactory to expect the detection of rotational transitions of CHD.

We afterwards guided our search for the $N_{K_a K_c} = 7_{07} \leftarrow 6_{16}$ rotational transition of CHD, CH₂D₂ serving as precursor. The three fine-structure components were expected to occur near 944.5 GHz, based on the predictions made using the molecular constants provided by the FIR-LMR work (Nolte et al. 1994). A careful search of 2 GHz around the predicted frequencies using the same experimental conditions as for CH₂ and CD₂ showed very clean spectra. A limited number of unidentified lines were detected, but all were found to belong to diamagnetic species. We thus decided to extend the search region further, proceeding toward the high frequencies. We detected one set of three paramagnetic lines within 512 MHz. We checked the chemistry to produce these lines and found that they were not observable when CD₄ or CH₄ were used as precursors instead of CH₂D₂. However, they could be detected when CD₄ and CH₄ were introduced simultaneously, with a signal-to-noise ratio about five times weaker than with CH₂D₂. These chemical tests showed that the newly observed species contains both H and D atoms. Convinced that this species was the monodeuterated methylene radical, we decided to detect the $N_{K_a K_c} = 6_{06} \leftarrow 5_{15}$ rotational transition predicted around 580.3 GHz and started to scan upwards. We subsequently discovered another set of three paramagnetic transitions above 581 GHz that showed identical behaviour with the chemical tests. The detection of two additional rotational transitions, the $N_{K_a K_c} = 5_{05} \leftarrow 4_{14}$ and the $N_{K_a K_c} = 1_{11} \leftarrow 2_{02}$, predicted near 221 and 821 GHz, respectively, was attempted. It is likely that the lack of accurate predictions (within 100 MHz) and their weaker intensity, especially for the $N_{K_a K_c} = 1_{11} \leftarrow 2_{02}$, $J = 2 \leftarrow 3$ fine-structure component that is expected to be split into several hyperfine-structure components, prevented us from detecting them.

4. Results and discussion

Although the number of observed lines is limited, we are confident that identification of the CHD radical in its ground electronic state (\bar{X}^3A'') is secure. Three fine-structure components for each rotational transition were detected, as expected for a species in a triplet ground electronic state. Wide regions were scanned (several GHz) around the predictions, and only the transition frequencies reported in Table 1 showed paramagnetic behaviour. The chemistry for all six lines was carefully checked, proving that they belong to a species that contains both H and D atoms. As for CH₂ and CD₂, all fine-structure components were found to be very sensitive to the magnetic field applied: a magnetic field in the range 2–50 Gauss was sufficient to observe the disappearance of the lines, the F_3 and F_2 components being the most and least sensitive, respectively. Similar to the spectrum of CD₂ at 799 GHz, the F_2 component was detected with stronger signal-to-noise ratio than the F_1 and F_3 components. These observations are in accordance with the prediction that includes the hyperfine-structure due to H and D nuclei since all hyperfine-structure components are overlapped on a single line only for the F_2 component. An example of the

Table 1. Observed rotational transitions frequencies of CHD (\tilde{X}^3A''), in MHz.

Transition	Component ^a	ν_{obs}^b	$\nu_{\text{obs}} - \nu_{\text{calc}}$
$6_{06} \leftarrow 5_{15}$	F_1	581 021.489(60) ^c	0.046
	F_2	581 506.679(20)	-0.012
	F_3	581 580.606(50)	0.040
$7_{07} \leftarrow 6_{16}$	F_1	946 609.805(40)	-0.022
	F_2	946 800.636(25)	0.019
	F_3	947 121.971(60)	-0.060

Notes. The standard deviation of the fit is 38 kHz. Calculated frequencies were obtained from molecular constants given in Table 2. ^(a) $\Delta J = \Delta N = 1$ fine-structure components. For the upper and lower energy levels, $F_1: J = N + 1$, $F_2: J = N$, $F_3: J = N - 1$. ^(b) Values in parentheses are 1σ experimental error on the last digits. ^(c) Hyperfine-structure for this line was partly resolved as a doublet, and the average of the two observed transition frequencies was used in the least-squares analysis.

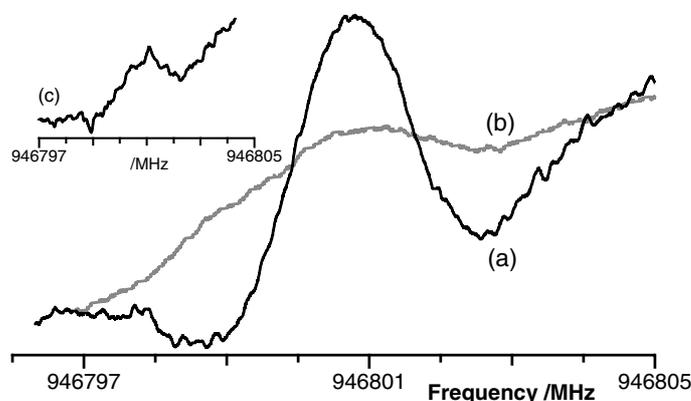


Fig. 1. Observed spectra of the $N_{K_a K_c} = 7_{07} \leftarrow 6_{16}$, $J = 7 \leftarrow 6$ (F_2 component) rotational transition of the CHD radical produced in dc glow discharge (~ 20 mA) using CH_2D_2 as precursor recorded **a**) without magnetic field applied and **b**) with a magnetic field of only 15 Gauss applied. Inset **c**): same transition detected using CH_4 and CD_4 as precursors, about five times less intense. These spectra were recorded by integrating 36 scans with 0.5 Hz repetition rate and 10 ms time constant of the lock-in amplifier.

$N_{K_a K_c} = 7_{07} \leftarrow 6_{16}$, $J = 7 \leftarrow 6$ (F_2 component) recorded near 946 801 MHz is depicted in Fig. 1.

In the present study, no hyperfine-structure due to H and D nuclei could be observed for these high N rotational transitions, except for the F_1 component of the $6_{06} \leftarrow 5_{15}$ rotational transition, which appeared as a weak, partly resolved doublet with a frequency gap of 1.34(12) MHz. This value was obtained from a nonlinear line profile analysis for individual components using IGOR Pro (wavemetrics). The line frequencies and the peak intensities for this doublet were adjusted by assuming a second derivative Voigt line shape with the same linewidth for both hyperfine-structure components. This result is consistent with our preliminary prediction of the hyperfine-structures by assuming that the hyperfine interaction constants for H and D nuclei are the same as those of CH_2 and CD_2 , respectively. The calculated hyperfine pattern for these high N rotational quantum numbers shows that the F_2 components should be observed as a singlet, while the F_1 and F_3 components should each appear as a doublet with a frequency gap of less than 3.0 and 2.5 MHz,

Table 2. Molecular constants for CHD (\tilde{X}^3A''), in MHz.

Constant	Present study	FIR LMR work ^a
B	170 344.0470(28)	170 233.7(21)
C	148 139.235(32)	149 100.6(21)
ϵ_{bb}	-112.66(18)	-105.527
ϵ_{cc}	-110.93(50)	-83.342
β	1339.584(75)	1382.0(75)

Notes. Only constants determined in this preliminary study are reported. All other molecular constants have been fixed to their values reported in Table IV from Reference 1. ^(a) Reference 1. Values originally reported in cm^{-1} were converted to MHz.

References. (1) Nolte et al. (1994).

respectively. It should also be noted that, at these high frequencies, the Doppler broadening of the lines prevents the observation of the hyperfine-structure. The observed transition frequencies (Table 1) were subjected to least-squares analysis (which does not include hyperfine constants) using Pickett's program SPFIT (Pickett 1991). The rotational constants B and C , the electron spin-rotation constants ϵ_{bb} and ϵ_{cc} , and the electron spin-electron spin constant β were the adjustable parameters. A least-squares analysis using the combinations of constants $A - \frac{1}{2}(B + C)$, $\frac{1}{2}(B + C)$, $\epsilon_{aa} - \frac{1}{2}(\epsilon_{bb} + \epsilon_{cc})$, and $\frac{1}{2}(\epsilon_{bb} + \epsilon_{cc})$, in addition to β , resulted in a fit with a standard deviation of ~ 0.7 MHz. The determined constants are provided in Table 2, together with their values obtained from the previous FIR-LMR study for comparison. We checked that no significant correlation occurred between the floated parameters.

Obviously, the rotational constants determined in the present study do not fit the quoted error range of the ones obtained by the previous FIR-LMR work. This is true in particular for the C constant. In contrast, the fine-structure parameters of the two studies compare much better. Indeed, the frequency differences between two successive fine-structure components of the $N = 6 \leftarrow 5$ and $7 \leftarrow 6$ rotational transitions predicted from the LMR work can be compared with those obtained from our measurements. The frequency differences from the LMR work, given in MHz as $(F_2 - F_1, F_3 - F_2)$ are (460, 112) and (168, 363) for the $N = 6 \leftarrow 5$ and $7 \leftarrow 6$ transitions, respectively. The corresponding differences calculated from Table 1 are (485, 74) and (191, 321).

The set of molecular constants reported by Nolte et al. (1994) consisted of eight adjusted and nine fixed parameters for both the rotational and spin-rotational parts. The fitted parameters were determined by a limited number of measured lines and theoretically calculated energy levels, while eight out of the nine fixed parameters were constrained to the average of their values for CH_2 and CD_2 . The estimated errors (10 to 15 MHz) for their measured lines are almost certainly underestimated, as they stated. Considering these facts, it is not surprising that the transition frequencies observed in the present study are found shifted by as much as 1 to 2 GHz from the FIR-LMR predicted values. This shows a striking contrast to the cases of spectroscopy of CH_2 and CD_2 , as FIR-LMR data for those species were quite reliable. Our constants will undoubtedly evolve as further rotational transitions of this species will be measured in the future. Since the errors on our constants are model-dependent, they are underestimated as well. Our reported frequencies can be useful as the precise laboratory reference data for astronomical observation, though the upper levels of the observed transitions are

relatively high (220–300 cm⁻¹, corresponding to temperatures of 300–400 K).

Finally, the ground-state rotational transition deserves a few comments. There are no two equivalent nuclei in CHD. Thus no spin statistics have to be obeyed, and only one ground-state transition for this species exists, the $1_{11} \leftarrow 0_{00}$. The rest frequencies of this transition, not taking the fine and hyperfine interactions into account, is predicted to occur near 1773 GHz and 1774 GHz, based on our results and on the LMR work, respectively. In contrast, CH₂ and CD₂ have ³B₁ as a ground state and should follow the Fermi-Dirac and Bose-Einstein spin statistics, respectively. Therefore *ortho*- and *para*-states, which are represented by even and odd values of $K_a + K_c$, respectively, co-exist. The ground-state transitions of the two *ortho*-species lie near 2.35 and 1.23 THz, and in addition, two fundamental transitions of the *para*-species occur, namely the $1_{10} \leftarrow 1_{01}$ and the $2_{12} \leftarrow 1_{01}$. Their lower energy level is 15.1 cm⁻¹ and 7.4 cm⁻¹ above the ground in the case of CH₂ and CD₂, respectively. None of these ground-state transitions has yet been measured with microwave accuracy.

It is also worthwhile mentioning that the $7_{07} \leftarrow 6_{16}$ transition at 0.94 THz lies in the centre of one of the “atmospheric windows” around 1 THz (Matsushita et al. 2000), through which astronomical observations are feasible from ground-based observatories.

5. Conclusions

The two strongest field-free pure rotational transitions of the CHD radical in the electronic ground state (\widetilde{X}^3A'') have been successfully observed below 1 THz for the first time. It is necessary to increase the CHD production efficiency and/or the detection sensitivity of the spectrometer for further detection of the unobserved lines below or above 1 THz. We intend in the near future to carry out such measurements using the “conventional” method, that is, in situ flash pyrolysis of partially deuterated diketene (to generate partially deuterated ketene) combined with continuous glow discharge.

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