LETTER TO THE EDITOR

Double resonance rotational spectroscopy of CH₂D⁺

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ABSTRACT

Context. Deuterated forms of CH₃⁺ are thought to be responsible for deuterium enrichment in lukewarm astronomical environments. There is no unambiguous detection of CH₂D⁺ in space to date.

Aims. Four submillimetre rotational lines of CH₂D⁺ are documented in the literature. Our aim is to present a complete dataset of highly resolved rotational lines, including millimetre (mm) lines needed for a potential detection.

Methods. We used a low-temperature ion trap and applied a novel IR–mm-wave double resonance method to measure the rotational lines of CH₂D⁺.

Results. We measured 21 low-lying ($J \leq 4$) rotational transitions of CH₂D⁺ between 23 GHz and 1.1 THz with accuracies close to 2 ppb.

Key words. astrochemistry – line: identification – molecular data – ISM: molecules – radio lines: ISM

1. Introduction

According to current astrochemical models (Roueff et al. 2007; Parise et al. 2009), CH₃⁺ and its deuterated analogues are thought to be responsible for deuteration processes at lukewarm temperatures ($\sim 20 \text{ K} < T < \sim 80 \text{ K}$) following the reaction chain (Smith et al. 1982; Asvany et al. 2004)

Unfortunately, this hypothesis rests on weak grounds, as none of the involved cationic species is detected in space, and there are only searches and tentative detections of CH₂D⁺ by Wootten & Turner (2008) and Roueff et al. (2013). Those searches and tentative detections used predicted CH₂D⁺ transition frequencies based on laboratory data available at that time. The first predictions of the rotational transition frequencies were provided by the IR data by Rösslein et al. (1991) and Jagod et al. (1992), and those were later refined by the high-resolution IR work by Gärtner et al. (2010, 2013) and, in particular, by the first four pure rotational lines measured by Amano (2010). More recently, two fundamental rotational transitions were measured in the Cologne laboratories (Brünken et al. 2014b) using a helium attachment technique at 4 K (Brünken et al. 2014a). In the work presented here, a double resonance spectroscopy technique is used to measure 21 rotational transitions of CH₂D⁺ between 23 GHz and 1.1 THz with close to 2 ppb accuracy. With this complete dataset, we hope to trigger a renewed search for CH₂D⁺.

2. Laboratory methods

The experiment was performed in a 4 K 22-pole ion trapping machine, which is described in Asvany et al. (2014); the applied IR–millimetre-wave (mm-wave) double resonance technique was

first mentioned in Gärtner et al. (2013) and later documented by Jusko et al. (2014). In brief, CH₂D⁺ ions were produced by ionizing CH₃D gas in a storage ion source. The ions were mass selected and a few 10 000 ions were injected into the 22-pole ion trap (Asvany et al. 2010). On entrance, the ion ensemble was cooled down to the ambient trap temperature by a short helium gas pulse. The trap temperature was adjusted between 9 and 25 K, depending on the probed rotational level. During the trapping time of about 700 ms, the ion ensemble was exposed to cold hydrogen gas. The backwards direction of reaction (1) was induced by vibrationally exciting the stored ions, leading to a detectable CH₃⁺ signal. This process is called laser induced reaction (LIR; Schlemmer et al. 1999, 2002). For this vibrational excitation, a cw optical parametric oscillator (OPO) was held in resonance (within $\pm 2 \times 10^{-4} \text{ cm}^{-1}$) on selected transitions of the ν_1 or ν_4 bands (Jagod et al. 1992; Gärtner et al. 2013). With the IR frequency held on resonance, a cw (sub)mm-wave beam was shone simultaneously onto the trapped ion ensemble. A mirror with a hole was used to superpose the two beams, as shown in Fig. 1 of Jusko et al. (2014). The two coaxial beams then entered the vacuum chamber via a diamond window and reached the 6.6 mm diameter aperture of the 22-pole ion trap. For the generation of long wavelength radiation, synthesizers (Agilent E8257D or Rohde & Schwarz SMF 100A) with suitable horn antennas were used, whereas a modular chain consisting of amplifiers and multipliers (WR9.0M-AMC, Virginia Diodes Inc.) was applied for frequencies beyond 80 GHz. As shown in the inset of Fig. 1, the rotational excitation pumps CH₂D⁺ ions into the state probed by the vibrational transition, increasing the CH₃⁺ signal count. By scanning the rotational excitation frequency over the resonance (symmetrically up and down), a rotational line can be obtained.

3. Experimental results

Owing to the existing predictions, no tedious searches were necessary and the targeted lines were usually found within minutes.

Fig. 1. Measurement of the $2_{02} \leftarrow 1_{01}$ rotational ground state transition with the IR-mm-wave double resonance technique at 11 K. The energy level diagram (inset) explains the double resonance method: with the IR light held in resonance (OPO; long green arrow) at $3029.6352 \text{ cm}^{-1}$, more than 5100 CH_3^+ signal counts are obtained. When the submm-wave source (THz; small red arrow) is tuned into resonance, additional CH_2D^+ ions are pumped into the 2_{02} rotational level, leading to an increase of the signal by about 500 counts. In this example, the submm-wave source has been tuned up and down six times, stepping 10 kHz after each 1 s trapping cycle. A Gaussian fit of the seen signal gives a centre frequency of 534 280.0217(24) MHz and a kinetic temperature of about 30 K. Eight such measurements lead to the final value given in Table 1.

A sample measurement of the transition $2_{02} \leftarrow 1_{01}$ is shown in Fig. 1 together with a Gaussian fit and more explanations. To improve the statistics, such measurements were typically repeated five to ten times. In total we detected 21 rotational lines. These are summarized in Table 1 and are compared to the 4 rotational lines measured by Amano (2010), whose conservative error limits are confirmed and improved by at least one order of magnitude in this work. Surprisingly, our measured values also agree extremely well with the very first prediction of rotational transitions of CH_2D^+ given by Rösslein et al. (1991).

The cold temperatures and good signal-to-noise ratio in this work usually permit us to determine the transitions with uncertainties close to 2 ppb. Transitions with higher uncertainties in the table stem either from weakly populated levels (e.g. $4_{13} \leftarrow 4_{14}$), or are transitions with weak intrinsic transition strength ($\Delta K_a = 2$, e.g. $3_{22} \leftarrow 3_{02}$ or $2_{21} \leftarrow 2_{02}$) and/or with limited submm-wave source power (in upper frequency range, e.g. $4_{23} \leftarrow 3_{22}$). We also want to point out the low frequency transitions, for which the unresolved hyperfine splittings, caused mainly by the electrical quadrupole moment of the deuterium nucleus, start broadening and skewing the Doppler line shapes; see Figs. 2 and 3 for the 23 GHz and 67 GHz lines, respectively. For these lines, some residual power broadening effects cannot be excluded. As simple simulations of the hyperfine structure did not fully recover the seen structures, we kept using Gaussian functions, leading to less reliable definitions of the line centres given in Table 1. But because of the large dataset given in Table 1, the line centres and their error limits can be checked by forming combination differences. For instance, the difference between the rotational levels 2_{11} and 3_{13} can be formed in two different ways (see level scheme in Fig. 4 and Table A.1), and shows that our data is reasonable. A full list of 32 such combination differences is given in Table A.1. In this

Fig. 2. Transition $2_{20} \leftarrow 2_{21}$ at 23 GHz measured at a nominal trap temperature of 15 K. The broadness of this feature can be recognized by comparison with the narrow Gaussian curve, which is the shape expected for a single line at 40 K. Since pressure or Doppler broadening to this extent can be excluded, unresolved hyperfine structure is the most reasonable explanation for this broadening, whereas some residual power broadening effect cannot be excluded. These hyperfine splittings are dominated by the small electrical quadrupole moment of the deuterium nucleus. To better identify the structure in this feature, the data of 13 single measurements (shown as pale grey dots) have been normalized (to the off-resonant CH_3^+ counts), averaged, and binned into 6 kHz steps. The result is shown as a red curve, where two smaller peaks become discernible on both sides of the feature.

Fig. 3. Transition $1_{10} \leftarrow 1_{11}$ at 67 GHz measured at a nominal temperature of 9 K. Similar to Fig. 2, the narrow Gaussian is the shape expected for a single line at 40 K. Averaging over several measurements and binning into 4 kHz steps yields the red curve, revealing deviations from a Gaussian shape.

list, the combination differences involving the 67 GHz line show deviations beyond the expected level, the most probable reason being the unresolved hyperfine structure mentioned above. Thus, excluding this line, our data were used as input to an asymmetric rotor model (Western 2016). Transitions from previous publications (Jagod et al. 1992; Amano 2010; Gärtner et al. 2013) were not included here as they did not significantly improve the ground state constants. The obtained rotational constants for the ground state of CH_2D^+ are summarized in Table 2.

Table 1. Measurements of low-lying ($J \leq 4$) rotational transitions (in MHz) of CH₂D⁺ up to 1.1 THz (for comparison, the hitherto available discharge cell measurements of [Amano 2010](#) are also listed).

$J'_{K'_a K'_c} \leftarrow J_{K_a K_c}$	This work	Amano (2010)
2 ₂₀ 2 ₂₁	23 015.9690(12)	
1 ₁₀ 1 ₁₁	67 273.6872(11)	
3 ₂₁ 3 ₂₂	101 483.1327(5)	
2 ₁₁ 2 ₁₂	201 754.0373(5)	
4 ₂₂ 4 ₂₃	251 007.7368(42)	
1 ₀₁ 0 ₀₀	278 691.7708(9)	
3 ₁₂ 3 ₁₃	398 038.7155(11)	
2 ₁₂ 1 ₁₁	490 012.2588(7)	490012.247(30)
2 ₀₂ 1 ₀₁	534 280.0198(11)	
2 ₂₁ 2 ₀₂	588 663.4054(14)	
2 ₁₁ 1 ₁₀	624 492.6351(9)	624492.648(20)
4 ₁₃ 4 ₁₄	637 667.8351(57)	
3 ₂₂ 3 ₀₃	666 869.7354(38)	
3 ₁₃ 2 ₁₂	722 354.6106(9)	722354.622(25)
3 ₀₃ 2 ₀₂	757 258.1056(11)	
3 ₂₂ 2 ₂₁	835 464.4209(47)	835464.376(50)
3 ₂₁ 2 ₂₀	913 931.5916(19)	
3 ₁₂ 2 ₁₁	918 639.2934(20)	
4 ₁₄ 3 ₁₃	945 398.0638(15)	
4 ₀₄ 3 ₀₃	963 380.5889(18)	
4 ₂₃ 3 ₂₂	1 095 332.1756(153)	

Notes. Uncertainties are given in parentheses.

Table 2. Best-fit spectroscopic parameters for the ground state of CH₂D⁺ (in MHz) obtained using 20 rotational lines of this work.

Symbol	Value	Symbol	Value
A	280 862.61(4)	Φ_J	0.000219(4)
B	173 019.812(3)	Φ_{JK}	
C	105 686.555(3)	Φ_{KJ}	0.0058(1)
Δ_J	3.64968(8)	Φ_K	
Δ_{JK}	10.8915(5)	ϕ_J	0.000041(3)
Δ_K	8.089(9)	ϕ_{JK}	0.00358(3)
δ_J	1.39841(5)	ϕ_K	-0.0069(3)
δ_K	12.103(2)		

Notes. Only parameters of statistical significance are listed.

4. Conclusions and outlook

While the IR-mm-wave double resonance technique has been applied before on single fundamental transitions of H₂D⁺ ([Gärtner et al. 2013](#)) and OH⁺ ([Jusko et al. 2014](#)), its full power is unfolded by measuring the complete set of all low-lying rotational transitions of CH₂D⁺ up to 1.1 THz, thereby leading to highly accurate spectroscopic parameters. A level diagram summarizing the rotational transitions studied in this work is shown in Fig. 4. We hope to trigger renewed searches of CH₂D⁺ in space given the complete set of rotational transitions. As the hyperfine structure might become important for the lower frequency transitions, we also want to encourage high-level

Fig. 4. Ground state rotational levels of CH₂D⁺ illustrating the 21 rotational transitions measured in this work.

ab initio calculations of the hyperfine structure, as carried out previously for H₂D⁺ and D₂H⁺ by [Jensen et al. \(1991, 1997\)](#). A full account of similar rotational experiments for CD₂H⁺ will be given in a later publication.

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Appendix A: combination differences

From the 21 rotational lines measured for CH_2D^+ , the 32 combination differences listed in Table A.1 could be obtained by forming sums and differences (see also Fig. 4). The eight combination differences which could be formed in two different ways show that our rotational line centres and their errors are reasonable, except for the 67 GHz line, which exhibits a deviation on the order of 20 kHz. This line is most probably affected by unresolved hyperfine structure (and power broadening effects).

Table A.1. The combination differences (CD) obtained by forming sums or differences of the two rotational transitions T1 and T2 are listed here in ascending order.

Up	Low	CD	T1	T2
3 ₀₃	2 ₂₁	168594.6855(60)	666870	835464
3 ₀₃	2 ₂₁	168594.7002(18)	588663	757258
4 ₀₄	3 ₂₂	296510.8535(42)	666870	963381
2 ₁₂	1 ₁₀	422738.5716(13)	67274	490012
2 ₁₂	1 ₁₀	422738.5978(10)	201754	624493
3 ₁₃	2 ₁₁	520600.5733(10)	201754	722355
3 ₁₃	2 ₁₁	520600.5779(23)	398039	918639
4 ₁₄	3 ₁₂	547359.3483(19)	398039	945398
2 ₂₀	2 ₀₂	611679.3744(18)	23016	588663
2 ₁₁	1 ₁₁	691766.2961(9)	201754	490012
2 ₁₁	1 ₁₁	691766.3223(14)	67274	624493
3 ₂₁	3 ₀₃	768352.8681(38)	101483	666870
3 ₂₂	2 ₂₀	812448.4519(49)	23016	835464
3 ₂₂	2 ₂₀	812448.4589(20)	101483	913932
2 ₀₂	0 ₀₀	812971.7906(14)	278692	534280
3 ₂₁	2 ₂₁	936947.5536(47)	101483	835464
3 ₂₁	2 ₂₁	936947.5606(22)	23016	913932
4 ₂₃	3 ₂₁	993849.0429(153)	101483	1095332
3 ₁₂	2 ₁₂	1120393.3261(14)	398039	722355
3 ₁₂	2 ₁₂	1120393.3307(21)	201754	918639
2 ₂₁	1 ₀₁	1122943.4252(18)	534280	588663
3 ₁₃	1 ₁₁	1212366.8694(11)	490012	722355
3 ₀₃	1 ₀₁	1291538.1254(16)	534280	757258
4 ₂₂	3 ₂₂	1346339.9124(159)	251008	1095332
3 ₂₂	2 ₀₂	1424127.8263(49)	588663	835464
3 ₂₂	2 ₀₂	1424127.8410(40)	666870	757258
3 ₁₂	1 ₁₀	1543131.9285(22)	624493	918639
4 ₁₃	3 ₁₃	1583065.8989(59)	637668	945398
4 ₁₄	2 ₁₂	1667752.6744(17)	722355	945398
4 ₀₄	2 ₀₂	1720638.6945(21)	757258	963381
4 ₂₃	3 ₀₃	1762201.9110(158)	666870	1095332
4 ₂₃	2 ₂₁	1930796.5965(160)	835464	1095332

Notes. All values in MHz; uncertainties are given in parentheses.