

LETTER TO THE EDITOR

Rotational transitions of CH₂D⁺ determined by high-resolution IR spectroscopy

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ABSTRACT

Context. Deuterated forms of CH₃⁺ are responsible for deuterium fractionation in warmer environments. Current searches for CH₂D⁺ are hampered by a lack of accurate laboratory data.

Aims. We demonstrate that IR spectroscopy at very high resolution can make accurate rotational predictions.

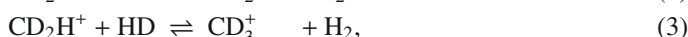
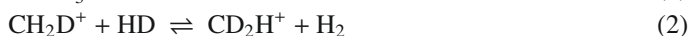
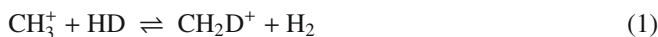
Methods. By combining a low-temperature ion trap with a narrow-bandwidth IR light source, we are able to measure vibrational transitions with high accuracy. A subsequent fit using an asymmetric rotor model allows predictions of MHz accuracy or even better.

Results. We predict rotational transitions up to 1.5 THz.

Key words. methods: laboratory – ISM: molecules – submillimeter: ISM

1. Introduction

In cold interstellar clouds, the deuterium content of some molecules is enhanced by several orders of magnitude relative to the cosmic D/H ratio of 1.5×10^{-5} . While gas-phase ion-molecule reactions involving H₃⁺-isotopologues are responsible for this fractionation in the coldest regions, as proven by several detections of H₂D⁺ (Stark et al. 1999) and a single observation of D₂H⁺ by Vastel et al. (2004), CH₃⁺ is assumed to mediate the fractionation in warmer (50 K) clouds (Roueff et al. 2007). This can be traced back to the exchange reactions



which are quite effective (Asvany et al. 2004) and whose relatively high exothermicity of about 370 K (Smith et al. 1982) prevents the formed deuterated species being destroyed in the warmer H₂ gas. To support this CH₃⁺ hypothesis, there are currently astronomical searches for the rotational signatures of CH₂D⁺. Unfortunately, these searches have been hampered by the lack of accurate laboratory data of the rotational transitions, only measurements of the IR vibrational transitions being available to date (Rösslein et al. 1991; Jagod et al. 1992). Jagod et al. (1992) recorded some hundred lines of the ν_1 and ν_4 IR bands of CH₂D⁺ and the ν_1 band of CD₂H⁺, and a subsequent fit yielded molecular constants of the molecular ground state, in particular predictions of the rotational transitions. The IR spectroscopic techniques 20 years ago permitted predictions with uncertainties up to ~10 MHz for the range 200–600 GHz, as documented currently in the Cologne Database for Molecular Spectroscopy (CDMS, Müller et al. 2005).

Submm-spectroscopy of carbon-containing species remains a challenge. To support future laboratory and astronomical searches for rotational transitions of CH₂D⁺, as a first step, we revisit the IR spectroscopy of CH₂D⁺ at very high resolution.

We achieve this by applying a low temperature ion trap combined with a narrow-bandwidth IR source, permitting us to push the predictions into the sub-MHz domain. A full experimental account will be given elsewhere, but the predictions for the astronomically important rotational transitions can be found at the end of this letter.

2. Laboratory methods

We recorded the ν_1 and ν_4 IR-active bands of CH₂D⁺ by applying the method of laser-induced reactions (LIR, Schlemmer et al. 1999, 2005; Asvany et al. 2005, 2007, 2008). In brief, typically 3000 CH₂D⁺ ions were stored and cooled in a low-temperature 22-pole ion trap (Gerlich 1995) held at 14 K and subject to cold hydrogen gas. The IR light traversing the trap was then able to induce the reaction in Eq. (1) in the backward direction. Thus, by counting the laser-induced reaction products CH₃⁺ as a function of the laser frequency, we were able to record a spectrum. As the IR light source we used a home-made optical parametric oscillator (OPO), characterized by high power up to 1 W, a narrow bandwidth (~100 kHz), and a tunability between 2500 and 4000 cm⁻¹. The relative frequency measurement has been achieved with a commercial wavemeter, and placed on an absolute basis with a calibration gas contained in a multipass reflection cell. Because of the high accuracy requirements, only lines of OCS (Saupe et al. 1996; Guelachvili & Rao 1993, NIST¹) and H₂O (Toth 1993) known with better accuracy than 1 MHz have been used as reference. In summary, because of the cold ions, the vanishing linewidth of the laser, and use of accurate calibration gases, the center frequencies of the measured transitions were able to be determined with high accuracy of typically 3 MHz. We checked this by comparing combination differences in the ground and excited states.

¹ Wavenumbers for Calibration of IR Spectrometers, data taken from <http://www.nist.gov/physlab/data/wavenum/>

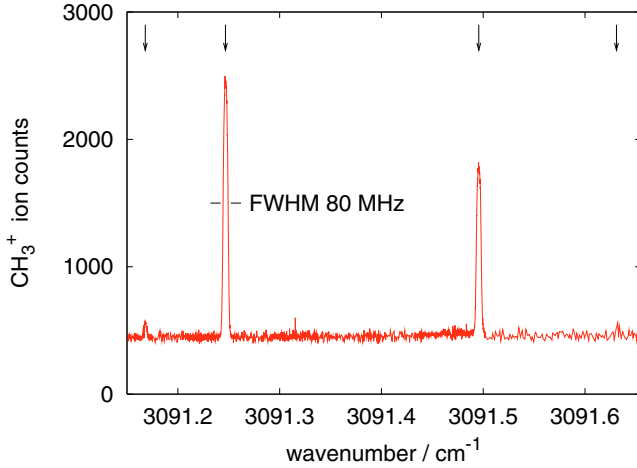


Fig. 1. Four lines of the the ν_4 vibrational band of CH_2D^+ . The strongest one is the transition $3_{03} \leftarrow 3_{12}$ at $(3091.24687 \pm 0.0001) \text{ cm}^{-1}$.

Table 1. Best-fit parameters in the ground state of CH_2D^+ given in MHz. For the sextic distortion constants on the right, only those of statistical significance are given.

Symbol	Value	Symbol	Value
A	280 861.17(72)	Φ_J	
B	173 020.15(62)	Φ_{JK}	
C	105 684.83(64)	Φ_{KJ}	-0.0088(35)
Δ_J	3.6124(94)	Φ_K	
Δ_{JK}	10.824(51)	ϕ_J	0.00075(63)
Δ_K	7.822(71)	ϕ_{JK}	0.0181(39)
δ_J	1.4314(269)	ϕ_K	
δ_K	12.556(111)		

3. Results and predicted rotational spectra

We measured in total 112 lines in the two bands, some coinciding with those of Jagod et al. (1992). As an example, Fig. 1 shows four lines of the ν_4 vibrational band. An asymmetric rotor model was fitted to the lines using SPFIT (Pickett 1991) and PGOPHER² with our data only, our data and those of Jagod et al. (1992), and our 61 ground state combination differences. All fits show consistent results, as long as sextic distortion constants are included. As expected, the average deviation of our IR data from the fit is about 4 MHz. The ground state molecular constants based on our lines alone are summarized in Table 1 and the resulting predictions for the rotational transitions are collected in Table 2. They are given up to 1.5 THz for potential high-frequency searches (APEX, Herschel). A comparison to the values of Rösslein et al. (1991) and CDMS (essentially a re-fit of the lines of Jagod et al. 1992), shows that the predictions are in very good agreement, and are substantially refined by this work. Further improvements of the presented high resolution IR technique will thus aid laboratory and astronomical searches of species whose pure rotational spectra are difficult to measure.

During the review process we learned that Amano had submitted a paper on the pure rotational lines of CH_2D^+ , also published in this volume. The predicted frequencies based on both works will be available at CDMS.

Table 2. Prediction of low-lying ($J < 6$) rotational transitions (in MHz) of CH_2D^+ up to 1.5 THz.

$J'_{K'_a K'_c} \leftarrow J''_{K''_a K''_c}$	This work	(1)	(2)
2 ₂₀ 2 ₂₁	23 015.03 ± 0.42	23 016.83 ± 1.18	23 015.95 ± 0.46
4 ₃₁ 4 ₃₂	34 063.57 ± 0.77	34 070.76 ± 2.13	34 065.77 ± 0.68
1 ₁₀ 1 ₁₁	67 273.80 ± 0.86	67 272.91 ± 1.78	67 273.71 ± 1.35
3 ₂₁ 3 ₂₂	101 479.95 ± 0.96	101 487.42 ± 4.28	101 482.82 ± 2.03
5 ₃₂ 5 ₃₃	116 348.72 ± 2.51	116 361.74 ± 5.69	116 343.38 ± 2.32
2 ₁₁ 2 ₁₂	201 753.84 ± 1.60	201 752.39 ± 5.12	201 753.99 ± 4.04
4 ₂₂ 4 ₂₃	251 004.10 ± 1.85	251 019.73 ± 8.30	251 006.92 ± 5.02
1 ₀₁ 0 ₀₀	278 690.53 ± 0.44	278 693.05 ± 2.51	278 691.62 ± 5.57
3 ₁₂ 3 ₁₃	398 038.11 ± 1.39	398 036.25 ± 9.26	398 037.70 ± 7.96
5 ₂₃ 5 ₂₄	466 146.23 ± 3.85	466 163.41 ± 11.9	466 137.32 ± 9.32
2 ₁₂ 1 ₁₁	490 011.00 ± 0.79	490 015.33 ± 4.16	490 012.30 ± 9.80
2 ₀₂ 1 ₀₁	534 279.32 ± 0.71	534 282.33 ± 4.45	534 279.91 ± 10.7
2 ₁₁ 1 ₁₀	624 491.04 ± 0.86	624 494.81 ± 5.70	624 492.58 ± 12.5
4 ₁₃ 4 ₁₄	637 668.62 ± 1.84	637 663.21 ± 12.8	
3 ₂₂ 3 ₀₃	666 868.24 ± 0.93	666 865.74 ± 8.50	
3 ₁₃ 2 ₁₂	722 356.35 ± 0.86	722 357.77 ± 5.92	
3 ₀₃ 2 ₀₂	757 259.87 ± 0.79	757 260.81 ± 6.15	
4 ₂₃ 4 ₀₄	798 820.76 ± 1.66	798 814.54 ± 9.80	
3 ₂₂ 2 ₂₁	835 464.15 ± 0.98	835 467.35 ± 6.20	
5 ₁₄ 5 ₁₅	890 257.97 ± 3.59	890 243.87 ± 15.0	
3 ₂₁ 2 ₂₀	913 929.07 ± 1.23	913 937.95 ± 8.27	
3 ₁₂ 2 ₁₁	918 640.62 ± 0.86	918 641.64 ± 7.22	
4 ₃₂ 4 ₁₃	921 337.21 ± 1.72	921 351.70 ± 14.2	
5 ₃₃ 5 ₁₄	937 383.22 ± 2.61	937 400.94 ± 10.8	
4 ₁₄ 3 ₁₃	945 401.66 ± 1.43	945 400.35 ± 7.41	
4 ₀₄ 3 ₀₃	963 383.72 ± 1.30	963 382.76 ± 7.60	
5 ₂₄ 5 ₀₅	970 995.05 ± 3.23	970 979.36 ± 12.7	
4 ₂₃ 3 ₂₂	1 095 336.24 ± 1.13	1 095 331.57 ± 7.16	
4 ₃₂ 3 ₃₁	1 147 303.78 ± 1.36	1 147 313.43 ± 8.22	
5 ₁₅ 4 ₁₄	1 161 984.97 ± 2.96	1 161 989.15 ± 8.60	
5 ₀₅ 4 ₀₄	1 169 118.83 ± 2.90	1 169 123.51 ± 8.69	
4 ₃₁ 3 ₃₀	1 176 099.37 ± 1.56	1 176 114.69 ± 9.40	
4 ₁₃ 3 ₁₂	1 185 032.17 ± 1.15	1 185 027.31 ± 7.61	
4 ₂₂ 3 ₂₁	1 244 860.39 ± 1.45	1 244 863.87 ± 9.48	
5 ₂₄ 4 ₂₃	1 341 293.12 ± 1.74	1 341 288.32 ± 7.64	
5 ₁₄ 4 ₁₃	1 414 574.32 ± 2.20	1 414 569.81 ± 7.75	
5 ₃₃ 4 ₃₂	1 430 620.33 ± 1.78	1 430 619.04 ± 8.53	
5 ₄₂ 4 ₄₁	1 439 955.31 ± 3.73	1 439 977.95 ± 10.7	
5 ₄₁ 4 ₄₀	1 447 413.00 ± 3.73	1 447 437.27 ± 11.0	

References. (1) CDMS; (2) Rösslein et al. (1991).

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² PGOPHER, a Program for Simulating Rotational Structure, C. M. Western, University of Bristol, <http://pgopher.chm.bris.ac.uk>