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LETTER TO THE EDITOR

Submillimeter-wave spectrum of CH_2D^+

T. Amano

Department of Chemistry and Department of Physics and Astronomy, University of Waterloo, 200 University Avenue West, Waterloo, ON, N2L 3G1, Canada
e-mail: `tamano@uwaterloo.ca`

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ABSTRACT

Aims. Recently a tentative identification of CH_2D^+ in interstellar space has been reported. To facilitate astronomical identifications, laboratory measurements of precise rest frequencies for the rotational lines of CH_2D^+ should be carried out.

Methods. A submillimeter-wave spectrometer is used for detection of CH_2D^+. The CH_2D^+ ion is generated in an extended negative glow discharge operated at liquid nitrogen temperature. The optimum gas mixture is found to be CH_4 (~3 mTorr), CD_4 (~1 mTorr), and H_2 (~2 mTorr) in helium buffer.

Results. Four rotational lines have been detected in the frequency range of 280−890 GHz. The measured frequencies agree very well within a MHz with the predictions given by Rösslein et al. from the infrared spectra.

Conclusions. Two rotational lines of this ion have been tentatively identified toward Ori IRc2. The rest frequencies obtained here should facilitate identifications and analysis of astronomical spectra.

Key words. molecular data – methods: laboratory – ISM: molecules – submillimeter: ISM – radio lines: ISM

1. Introduction

In interstellar carbon chemistry, CH_3^+ is likely to be one of the more abundant molecular ions, and its deuterated species, CH_2D^+, is thought to play an important role in deuterium fractionation in warmer interstellar clouds (Turner 2001; Roueff et al. 2007; Parise et al. 2009). However, because CH_3^+ is a symmetric planarmolecule and as a result has no permanent dipole moment, it is almost impossible to detect this species by radio astronomical observations. Its deuterated species, CH_2D^+ and CHD_2^+, possess the dipole moment, so the rotational lines should be observable. Rösslein et al. (1991) and Jagod et al. (1992) observed the infrared spectra of these deuterated species by using a high-resolution infrared spectroscopic technique with difference frequency radiation as a radiation source. Demuynck and coworkers (see for example Demuynck 1994) tried to observe CH_2D^+ rotational lines in submillimeter-wave region in an extended negative glow discharge with no success. Wootten & Turner (2008) searched for CH_2D^+ in several molecular sources without definite identifications. More recently Lis et al. (2009) reported a tentative identification of CH_2D^+ toward Ori IRc2. Thus laboratory measurements of the rest frequencies for this ion is urgently needed. This letter reports the first laboratory identification and the precise measurements of the submillimeter-wave lines of CH_2D^+.

2. Experimental procedure and results

A backward-wave oscillator (BWO) based submillimeter-wave spectrometer (Amano & Maeda 2000; Amano & Hirao 2005) was used in conjunction with an extended negative glow electrical discharge cell (De Lucia et al. 1983). With three BWO oscillators, the frequency range of 280−890 GHz is covered with two frequency gaps, 530−560 GHz and 750−770 GHz. The frequency of submillimeter-wave radiation was phase-locked to harmonics of millimeter-wave radiation (80−110 GHz) from a Gunn oscillator that could be controlled by phase-locking to harmonics of centimeter-wave radiation from a stabilized microwave synthesizer. The phase-locked submillimeter-wave radiation has the frequency stability of a couple of kHz and the output power on the order of milliwatts. An InSb hot electron bolometer cooled with liquid helium was used for the detection of the submillimeter-wave radiation. A double modulation scheme was used as described in Amano & Maeda (2000); Amano & Hirao (2005).

The molecular constants and the predicted rotational transition frequencies given by Rösslein et al. (1991) and Jagod et al. (1992) were a good starting point in searching for the rotational lines. The electric dipole moment is calculated to be 0.329 D, which lies along the *a* principal inertia axis, resulting in the *a*-type rotational transitions. Due to equivalent protons, the 3:1 nuclear spin statistics appears to the K_a odd (*ortho*) and K_a even (*para*) states.

At first, a very weak feature was found almost exactly at the calculated frequency for the 2_{12}−1_{11} transition. Eventually the line appeared strong enough for precise frequency measurements after adjusting the reaction conditions. The observations were made with the discharge current of about 16 mA with liquid nitrogen cooling. The optimum gas mixture was found to be CH_4 (~3 mTorr), CD_4 (~1 mTorr), H_2 (~2 mTorr), and He (~35 mTorr). Here helium played an important role more than a buffer gas, but was found to be essential to produce CH_2D^+. No signals were detectable with the Ar buffer. In the helium-dominated plasma, the electron temperature is higher than that in argon dominated plasma, and helium ion and metastable exited helium are abundant. The ionization of CH_4 and CD_4 should be the initial step of the formation processes. Energetically all CH_4^+, CH_3^+, CH_2^+, and CH^+ can be generated (Crofton et al. 1985). The

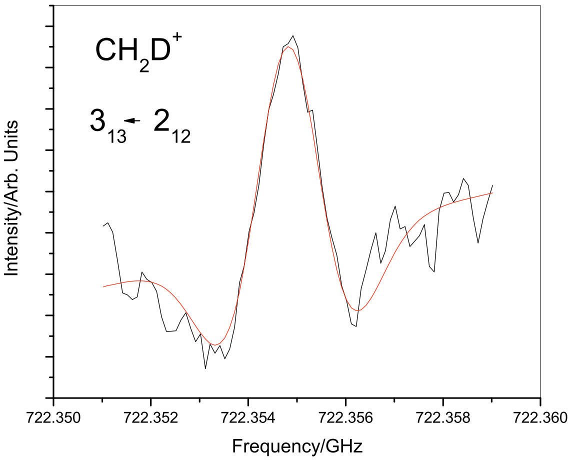

Fig. 1. The 3_{13}–2_{12} line of CH_2D^+. The line profile was fitted to the second derivative of the Gaussian profile, and the fitted curve is also shown. This is a result of accumulation of 80 scans with a scanning rate of 1 MHz/s.

Table 1. Observed transition frequencies for CH_2D^+ (in MHz).

Transition		This work[a]	Rösslein et al. (1991)[b]
2_{12}–1_{11}	*o*	490 012.247(30)	490 012.30
2_{11}–1_{10}	*o*	624 492.648(20)	624 492.58
3_{13}–2_{12}	*o*	722 354.622(25)	722 354.74[c]
3_{22}–2_{21}	*p*	835 464.376(50)	835 465.29[c]

Notes. [a] The numbers in parentheses indicate estimated uncertainties to the last significant digits.
[b] The uncertainties of these predicted values is given to be 2×10^{-5}. It translates to 12 MHz uncertainty for the 624.5 GHz line.
[c] Calculated value obtained by using the molecular constants given by Rösslein et al. (1991).

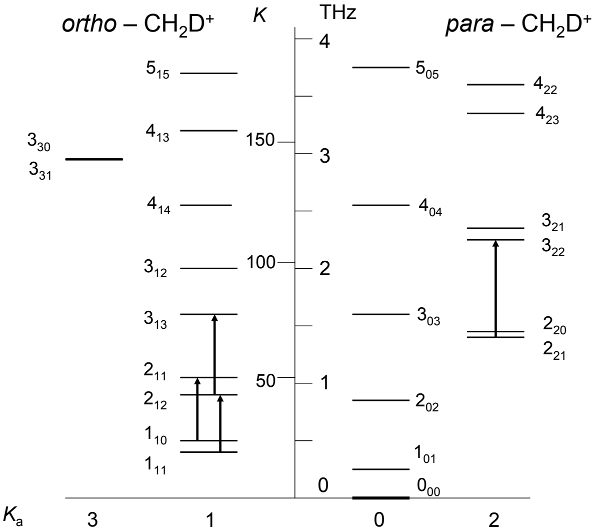

Fig. 2. The energy level diagram for the low lying states of CH_2D^+. The arrows indicate the transitions observed in this investigation.

Table 2. Molecular constants for CH_2D^+ in the ground state (in MHz).

Constant	present[a]	Rösslein et al. (1991)	Jagod et al. (1992)
A	280 866.25(99)	280 866.9(51)	280 847.1(30)
B	173 019.332(70)	173 019.2(30)	173 012.3(24)
C	105 686.839(44)	105 687.0(15)	105 684.0(12)
Δ_J	3.6289(33)	3.639(21)	3.592(15)
Δ_{JK}	10.9520(105)	10.852(78)	10.673(60)
Δ_K	8.043(52)	7.939(21)	7.825(60)
δ_J	1.38955(165)	1.4000(90)	1.3730(60)
δ_K	11.957(28)	11.845(57)	11.806(45)
Φ_J	0.000089(33)		
Φ_{KJ}	0.00524(52)		

Notes. [a] The values in parentheses indicate one standard deviation from the least-squares fit to the last quoted digits.

reactions in the plasma are complicated, and from the submillimeter observation alone we cannot identify specific processes to contribute to the formation of CH_2D^+. It is interesting that adding D_2 instead of CD_4 resulted in no signal. Although the signal was seen without H_2, it appears to play a subtle role in the formation, resulting in about a factor 2 increase in intensity.

As this ion is a light asymmetric molecule and the signal was only weakly observed, four transitions were detected so far in the 280–890 GHz region. Figure 1 shows a typical example of the observed signals. All observed transition frequencies agree within 1 MHz of the predicted frequencies given by Rösslein et al. (1991), as listed in Table 1. The energy level diagram for the low-*J* states is illustrated in Fig. 2. Two astronomical lines identified as due to CH_2D^+ by Lis et al. (2009) are consistent with the laboratory frequencies.

The accuracy of the submillimeter-wave lines is on the order of a few tens of kHz, while the accuracy of the rotational transition frequencies calculated with the molecular constants derived from the infrared measurements can be as high as about 30 MHz. So, although the frequencies measured in this work agree extremely well with the predicted frequencies from the infrared data by Rösslein et al. (1991), these submillimeter-wave lines should be very useful to obtain improved predictions of other frequencies by a combined reanalysis of the combination differences from the infrared bands and the submillimeter-wave lines. Thus a combined analysis was carried out by using the combination differences derived from the transition wavenumbers for both the ν_1 and ν_4 fundamental bands given in Jagod et al. (1992). We took 307 combination differences that involved the energy levels of less than $J = 10$, from which we excluded 83 combination differences from the fit. The excluded combination differences were obviously not as accurate, showing more than 0.005 cm^{-1} deviations. The standard deviation of the fit for the infrared combination differences was found to be about 45 MHz[1]. Table 2 lists the molecular constants determined from the least-squares fit together with those obtained by Rösslein et al. (1991) and Jagod et al. (1992) for comparison. The predicted rotational transition frequencies between the levels located below 4 THz (see Fig. 2) are shown in Table 3.

3. Discussion

The signals exhibited typical characteristics of positive ions in extended negative glow discharges; i.e. the lines were only observable with a magnetic field over approximately 100 Gauss, and the intensity decreased dramatically by warming the cell wall from liquid nitrogen temperature. All experimental evidence supports the identification of the species detected in this experiment to be CH_2D^+.

Various efforts to improve the signal intensity were unsuccessful, and only one *para* line was observed. The lowest *para* transition, 1_{01}–0_{00}, at 278 691.7 MHz is located at the lowest frequency edge covered by our BWO oscillator. In

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[1] A complete list of the fitted results is available from the author.

Table 3. Predicted rotational transition frequencies between the low-lying rotational levels of CH$_2$D$^+$ in the ground state (in MHz).

para-CH$_2$D$^+$		*ortho*-CH$_2$D$^+$	
Transition	Frequency[a]	Transition	Frequency[a]
$1_{01}-0_{00}$	278 691.656(26)	$2_{11}-1_{10}$	624 492.647(21)
$2_{02}-1_{01}$	534 280.362(153)	$2_{12}-1_{11}$	490 012.249(31)
$3_{03}-2_{02}$	757 259.34(30)	$3_{12}-2_{11}$	918 639.68(25)
$4_{04}-3_{03}$	963 382.45(25)	$3_{13}-2_{12}$	722 354.621(26)
$5_{05}-4_{04}$	1 169 125.70(66)	$4_{13}-3_{12}$	1 185 028.50(69)
		$4_{14}-3_{13}$	945 398.62(19)
$3_{21}-2_{20}$	913 931.77(46)	$5_{14}-4_{13}$	1 414 577.97(116)
$3_{22}-2_{21}$	835 464.379(51)	$5_{15}-4_{14}$	1 161 990.60(70)
$4_{22}-3_{21}$	1 244 857.02(71)		
$4_{23}-3_{22}$	1 095 330.70(32)	$4_{31}-3_{30}$	1 176 104.86(86)
$5_{23}-4_{22}$	1 556 427.93(128)	$4_{32}-3_{31}$	1 147 307.54(43)
$5_{24}-4_{23}$	1 341 292.62(76)		
$2_{20}-2_{21}$	23 015.873(169)	$1_{10}-1_{11}$	67 273.548(45)
$3_{21}-3_{22}$	101 483.26(62)	$2_{11}-2_{12}$	201 753.947(70)
$4_{22}-4_{23}$	251 009.58(129)	$3_{12}-3_{13}$	398 039.01(23)
		$4_{13}-4_{14}$	637 668.89(103)
$3_{22}-3_{03}$	666 882.54(289)	$5_{14}-5_{15}$	890 256.25(269)
$4_{23}-4_{04}$	798 830.79(279)		

Notes. (a) The values in parentheses indicate one standard deviation to the last quoted digits.

the helium discharge, plasma interaction tends to be more severe, especially in the lower frequency region, so the severe baseline distortion hampers the detection of this line even with the double modulation scheme with the on-off magnetic field modulation. Two other lines, $2_{02}-1_{01}$ at 534 280 MHz and $3_{03}-2_{02}$ at 757 259 MHz, should have a similar intensity as the $3_{22}-2_{21}$ line at 100 K. However, these frequencies fall into the frequency gaps of the spectrometer by a very unfortunate coincidence, and cannot be measured with the current setup.

As shown in Tables 2 and 3, an inclusion of the submillimeter-wave lines, albeit only four lines, results in a substantial improvement in determination of the molecular constants and the rotational line frequencies. The notable improvement of the accuracy is evident for B and C. Although the accuracy for the A rotational constant is significantly improved, the degree of the improvement is not as dramatic as for B and C, because the lines observed here do not strongly depend on A. In the fit, other higher-order centrifugal distortion constants were not significantly determined. These parameters and the predictions should prove to be useful in further astronomical searches and laboratory investigations. The predicted frequencies listed in the Cologne database (CDMS)[2] agree mostly with the values in Table 3 within their given uncertainties.

4. Conclusions

Four submillimeter-wave lines of CH$_2$D$^+$ have been definitely identified, and the rest frequencies are obtained to uncertainties of 20−50 kHz. These rest frequencies should be instrumental in the identification of interstellar CH$_2$D$^+$. A combined least-squares fit with the submillimeter-wave lines and the combination differences yielded significantly improved molecular constants and the predictions of the rotational line frequencies related to the relatively low-lying energy levels.

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[2] http://www.astro.uni-koeln.de/cdms/