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High-resolution millimeter-wave spectroscopy of CH$_2$DCl: paving the way for future astronomical observations of chloromethane isotopologues

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Abstract

Chloromethane is the only organochloride detected in space to date. Its recent observation towards the low-mass protostar IRAS 16293-2422 with ALMA offers a prompt for new laboratory studies of CH$_3$Cl and its isotopologues. Here, we report the investigation of the rotational spectrum of monodeuterated chloromethane CH$_2$DCl in the frequency region between 90 and 300 GHz. The measurements have been carried out with a frequency-modulation millimeter-wave spectrometer, arranged to perform saturation spectroscopy. From the analysis of hyperfine-resolved spectra of the two chlorine isotopologues CH$_2$D^{35}Cl and CH$_2$D^{37}Cl, consistent sets of accurate spectroscopic parameters have been obtained. This work provides reliable spectral predictions which can be used to guide radio-astronomical searches of CH$_2$DCl in the interstellar medium and represents a solid base for future analyses of high-resolution infrared spectra of monodeuterated chloromethane.

Keywords: Rotational Spectroscopy, Lamb-dip, Hyperfine structure, Halocarbon, Chloromethane

1. Introduction

In the family of halocarbons, chloromethane (CH$_3$Cl) represents the smallest member of the chlorine-bearing species. This organochloride is massively-employed in industry as a methylating and chlorinating agent, while its use as refrigerant (R-40) ceased because of its ozone depletion potential and global

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warming power [1]. Indeed, large amounts of CH_3Cl are known to be present in the Earth's atmosphere: its atmospheric abundance has been demonstrated to be due to both anthropogenic (accidental releases or burning processes) and natural causes (produced by plants, bacteria, phytoplankton) [2]. Atmospheric CH_3Cl, previously revealed by *in situ* measurements [3, 4], has been spectroscopically identified for the first time in the solar absorption spectrum of our troposphere through its strong infrared (IR) features around $2967\,cm^{-1}$ [5], corresponding to the Q branch of the ν_1 vibrational mode. Because of its tendency to accumulate in the upper levels of the atmosphere, chloromethane has been suggested as an optimal biosignature gas to be searched for in potentially habitable exoplanets [6, 7].

The presence of chloromethane in environments other than our Solar system has been recently identified at a pre-planetary stage, thanks to the observation of CH_3Cl emission towards the low-mass protostar IRAS 16293-2422 with the Atacama Large Millimeter/submillimeter Array (ALMA) [8]. In particular, this detection relied on the observation at submillimeter-wavelengths of some $J = 13 \leftarrow 12$ rotational transitions of the two stable chlorine isotopologues, $CH_3{}^{35}Cl$ and $CH_3{}^{37}Cl$.

The protostar IRAS 16293-2422 is also a rich source of interstellar deuterated species [9]. During the last 25 years, a plethora of deuterium-bearing molecules have been identified in this source, including multiply-deuterated forms of water (HDO and D_2O) [10], ammonia (up to ND_3) [11], methanol (up to CD_3OH) [12], and methyl cyanide (CH_2DCN and CHD_2CN) [13]. High abundances of many other deuterated species are predicted by astrochemical models, which unfortunately have not yet taken into account deuterium enrichment in CH_3Cl. However, given its chemical similarity with CH_3CN and CH_3OH, CH_3Cl can likely exhibit a strong deuterium fractionation (or D/H ratio) in IRAS 16293-2422, thus producing significant amounts of monodeuterated chloromethane CH_2DCl. A vast spectroscopic literature is available for the parent species CH_3Cl about its vibrational and rotational spectra (see Refs. [14, 15] and references therein). Extended line lists [16] and molecular database [17] are available for both the $CH_3{}^{35}Cl$ and $CH_3{}^{37}Cl$ species. Also the rare ^{13}C isotopologues have been spectroscopically characterized widely, from the millimeter-wave to the infrared domains (see, e.g., Refs. [18, 19] and references therein). On the other hand, deuterated forms of CH_3Cl have been poorly characterized from a spectroscopic point-of-view.

Albeit the fundamental $J_{K_a, K_c} = 1_{0,1} \leftarrow 0_{0,0}$ rotational transition of CH_2DCl was recorded in 1950 by Stark modulation microwave spectroscopy [20] and in the early 1970s with a molecular-beam maser spectrometer [21, 22], the rotational spectrum of CH_2DCl remains substantially unstudied so far. Since most of the molecules observed in space are detected through rotational lines emission [23], the lack of such spectral data poses substantial limitations to the identification of monodeuterated chloromethane in the interstellar medium (ISM). As far as the infrared spectrum of CH_2DCl is concerned, the analysis of six fundamental and some of their hot-bands has been recently reported for the ^{35}Cl isotopologue [24, 25, 26], while no data are available for the ^{37}Cl one.

Here, we report the investigation of the rotational spectra of $CH_2D^{35}Cl$ and $CH_2D^{37}Cl$, observed at millimeter-wavelengths with a frequency-modulation (FM) absorption spectrometer. This work is aimed at (i) providing reliable spectral predictions that will assist radio-astronomical searches of CH_2DCl and (ii) obtaining a set of accurate spectroscopic parameters for both the chlorine isotopologues, which constitutes a solid base to further investigate the infrared spectrum of monodeuterated chloromethane.

2. Experimental details

A pure sample of CH_2DCl was synthesized in our laboratory by reacting monodeuterated methanol (CH_2DOH; CND Isotopes, 99.2% D-enriched) with sodium chloride (NaCl) in acid aqueous solution, following the procedure described in Ref. [24].

Rotational spectra of CH_2DCl were recorded in the frequency ranges 90–125 GHz and 240–300 GHz using a FM millimeter-/submillimeter-wave spectrometer, used in past for the study of other deuterated species [27, 28, 29].

Two Gunn diodes from J. E. Carlstrom Co. and Radiometer Physics GmbH, emitting between 80–115 GHz and 116–125 GHz, respectively, are used as primary radiation source of the instrument. Spectral coverage at higher frequencies is obtained by coupling the Gunn diodes to passive frequency multipliers, namely doublers and triplers in cascade. A 75 MHz sine-wave modulated wave is used as reference signal in a Phase-Lock Loop through which the Gunn's radiation is locked to a harmonic of a digital synthesizer (HP8672A, 2–18 GHz); in this way, the frequency modulation f is transferred to the output radiation. The frequency accuracy of the radiation is guaranteed by locking the radio-frequency synthesizers to a rubidium atomic clock.

The millimeter-wave is fed to a 3.25 m long glass absorption cell, closed at the two ends by high-density polyethylene windows and connected to a pumping system. Doppler-limited spectra were recorded by filling the cell with CH_2DCl vapors at the stagnation pressure of 6 Pa, in order to minimise pressure-broadening effects; higher pressures (up to 25 Pa) were used to record the very weak b-type transitions (see §3).

Two Schottky barrier diodes were used as detector, from Millitech Co. up to 125 GHz and the WR3.4ZBD from Virginia Diodes between 240 and 300 GHz. The detected signal is pre-amplified, filtered and demodulated at $2f$ by an analog Lock-in, digitally-converted, and finally sent to a computer.

Additional measurements in the 240–300 GHz frequency range were performed exploiting the Lamb-dip technique [30]. In this case, the optics of the spectrometer were appropriately set up in a double-pass configuration, as described in Ref. [31]. Also, a low-pressure (~1 Pa) of CH_2DCl, and f and modulation-depth values as low as 1 kHz and 15 kHz, respectively, were used. With such experimental conditions, chlorine hyperfine splittings could be well-resolved even at high frequencies.

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3. Spectral analysis

From a spectroscopic point of view, CH$_2$DCl is a nearly-prolate asymmetric-top rotor belonging to the C_s point group. Therefore, its nine vibrational modes are either of A' or A'' symmetry, as illustrated for CH$_2$D^{35}Cl in Table 1.

Table 1: Vibrational modes and their energy for CH$_2$D^{35}Cl.

Symmetry	Mode	Description	Wavenumber[a]	Reference
A'	ν_1	CH$_2$ sym. stretching	2989.9(3)	[24]
	ν_2	C−D stretching	2223.7(3)	[24]
	ν_3	CH$_2$ scissoring	1433.839(3)	[25]
	ν_4	CH$_2$ wagging	1268.3335(1)	[26]
	ν_5	C−D in plane bending	827.02343(8)	[24]
	ν_6	C−Cl stretching	714.11267(9)	[24]
A"	ν_7	CH$_2$ asym. stretching	3035.3(3)	[24]
	ν_8	C−D/CH$_2$ out of plane bending	1267.6775(1)	[26]
	ν_9	C−D/CH$_2$ out of plane bending	986.69013(6)	[25]

[a] Units are cm^{-1}. Numbers in parenthesis represent quoted uncertainties.

Differently from the parent species CH$_3$Cl (C_{3v} group), in which the carbon-halogen bond lies on the symmetry axis, the a-axis of the principal inertia system of CH$_2$DCl is slightly rotated with the respect to the C−Cl bond because of the different center of mass. Replacing one hydrogen atom with deuterium causes the permanent dipole moment ($\mu = 1.870$ D for CH$_3$Cl [32]) to be distributed along two components; based on geometric considerations [33], and assuming that the total dipole moment does not change among the isotopologues, one can estimate $\mu_a = 1.868$ D and $\mu_b = 0.076$ D for CH$_2$DCl.

The rotational energy of CH$_2$DCl can be modeled by using the standard semi-rigid Hamiltonian for an asymmetric rotor with a non-vanishing nuclear spin:

$$\mathscr{H} = \mathscr{H}_{\mathrm{rot}} + \mathscr{H}_{\mathrm{cd}} + \mathscr{H}_{\mathrm{hfs}}, \tag{1}$$

where $\mathscr{H}_{\mathrm{rot}}$ contains the rotational constants in the A-Watson reduced form [34]:

$$\mathscr{H}_{\mathrm{rot}} = \tfrac{1}{2}\left(B + C\right)\hat{P}^2 + \left[A - \tfrac{1}{2}\left(B + C\right)\right]\hat{P}_a^2 + \tfrac{1}{2}\left(B - C\right)\left(\hat{P}_b^2 - \hat{P}_c^2\right), \tag{2}$$

the $\mathscr{H}_{\mathrm{cd}}$ part accounts for centrifugal distortion terms with increasing power of the angular momentum

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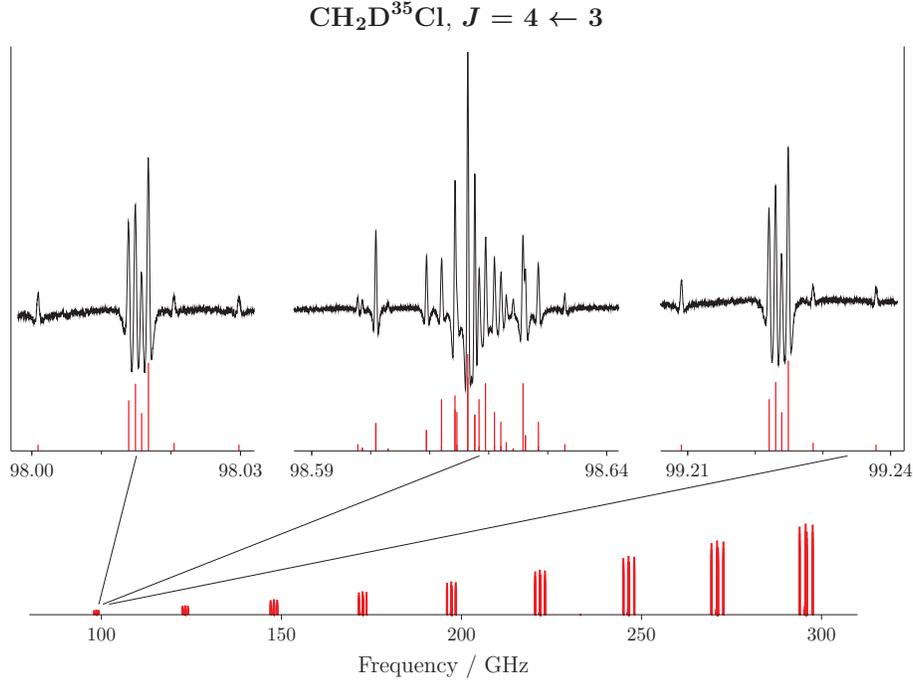
Figure 1: The hyperfine structure of the $J = 4 \leftarrow 3$ transition of $CH_2D^{35}Cl$. The black trace is the experimental spectrum, red sticks symbolise hyperfine components as predicted from the final fit. The $K_a = 1$ doublet is shown in the side spectra, whereas the central spectrum contains the $K_a = 0$, 2 and 3 components.

$$\mathscr{H}_{\mathrm{cd}} = -\Delta_J \hat{P}^4 - \Delta_{JK} \hat{P}^2 \hat{P}_a^2 - \Delta_K \hat{P}_a^4$$
$$- \delta_J \hat{P}^2 \left(\hat{P}_b^2 - \hat{P}_c^2 \right) - \delta_K \left[\hat{P}^2 \left(\hat{P}_b^2 - \hat{P}_c^2 \right) + \left(\hat{P}_b^2 - \hat{P}_c^2 \right) \hat{P}^2 \right] + \dots, \quad (3)$$

while $\mathscr{H}_{\mathrm{hfs}}$ contains the nuclear quadrupole coupling (NQC) χ_{ii} and spin-rotation (SR) C_{ii} constants of the chlorine nuclear spins ($I_{\mathrm{Cl}} = 3/2$). Deuterium is a quadrupolar nucleus too ($I_{\mathrm{D}} = 1$), but its contribution to the rotational energy levels is negligible in the millimeter region and, thus, is not considered in this work.

Both chlorine isotopologues of CH_2DCl show a strong a-type spectrum, with groups of $(J + 1) \leftarrow J$ transitions spaced by nearly $(B + C) \simeq 24\,\mathrm{GHz}$. The structure of each transition is typical of an asymmetric rotor very close to the prolate limit: most of the K_a components are grouped in the proximity of the $K_a = 0$, whereas the high and low components of the $K_a = 1$ doublet are found $ca.\ \frac{1}{2}(B - C)(J + 1)$ above or below, respectively. Moreover, because the chlorine quadrupolar interactions split each rotational level into four sub-levels with $F = J + 3/2;\ J + 1/2;\ J - 1/2;\ J - 3/2$, a hyperfine structure (HFS) is

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produced in the spectrum. Considering the selection rules $\Delta F = 0; \pm 1$, up to nine hyperfine components are allowed for each $J'_{K'_a, K'_c} \leftarrow J_{K_a, K_c}$ transition, the strongest components being those with $\Delta F = \Delta J$. As an example, the complexity of the $J = 4 \leftarrow 3$ transition, including its HFS, is highlighted in Figure 1.

4. Results and Discussion

Spectral predictions for $CH_2D^{35}Cl$ were initially performed by using the ground state spectroscopic constants reported in Ref. [24] together with the NQC constants from Ref. [21]. As far as $CH_2D^{37}Cl$ is concerned, rotational and centrifugal distortion constants were evaluated from the chloromethane equilibrium geometry of Ref. [33] and the NQC constants taken from Ref. [22].

First, we recorded five complete a-type $(J + 1) \leftarrow J$ transitions for both isotopologues, with $4 \leq J \leq 11$. Once the sets of spectroscopic parameters had been refined and the uncertainty of the A constants reduced, we have searched for the extremely weak b-type transitions. They were expected to be about 600 times weaker than the a-type ones, but thanks to the high-sensitivity of the spectrometer we were able to detect them with a good signal-to-noise ratio (SNR) in the spectrum.

Also, most transitions in the frequency range 240–300 GHz have been recorded with the Lamb-dip technique, thus allowing the resolution of small hyperfine splittings even at high J values. Some Lamb-dip spectra are shown in Figure 2, in which the splitting evolution for different K_a transitions can be noticed.

In addition to the measurements of the ground state spectra of CH_2DCl, three R branch a-type rotational transitions have been observed for $CH_2D^{35}Cl$ in the $v_5 = 1$ and $v_6 = 1$ vibrational excited states, previously investigated in the infrared region [24].

The data analysis has been carried out with the SPFIT subprogram of the CALPGM suite [35]. For the $CH_2D^{35}Cl$ isotopologue, the newly measured ground and excited states transitions have been fitted in a weighted least-square procedure together with ro-vibrational data from the literature [24]. Each datum has a weight proportional to the inverse square of its uncertainty. Infrared data were used with half the uncertainties quoted in the original paper, as suggested by their fit standard deviation [24]. The experimental error of our transition frequencies, instead, was estimated to be between 15 and 50 kHz, mostly depending on the SNR of the observed absorption line, and around 3 kHz for Lamb-dip measurements. The same criteria were applied to evaluate the experimental error associated to each transition of the $CH_2D^{37}Cl$ isotopologue, whose analysis is based on our measurements only.

Thanks to the observation of both a- and b-type transitions, chlorine-resolved hyperfine components, and Lamb-dip measurements, an accurate set of spectroscopic parameters has been attained for each CH_2DCl isotopologue. They include the rotational constants, the complete set of quartic and some sextic centrifugal distortion terms, the diagonal $\chi_{ii}(Cl)$ constants of the NQC tensor,
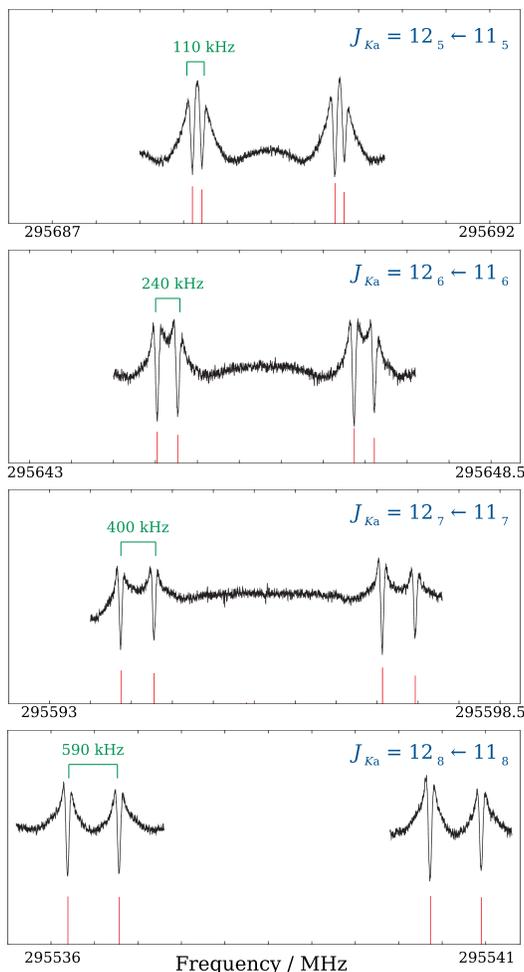
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Figure 2: Splitting evolution in $CH_2D^{35}Cl$ Lamb-dip spectra. The black trace is the experimental spectrum, red sticks symbolise hyperfine components as predicted from the final fit. The HF components in each panel are, from lower to higher frequency: $F' \leftarrow F = 12.5 \leftarrow 11.5, 11.5 \leftarrow 10.5, 13.5 \leftarrow 12.5, 10.5 \leftarrow 9.5$. The magnitude of some hyperfine splittings is indicated in green. The quantum numbers K_c have been omitted in the labelling of each transition, because asymmetry splittings are not resolved.

168 and the $C_{ii}(Cl)$ SR constants. The final parameters are collected in Tables 2
169 and 3, where they are compared with those of Ref. [24].
170 Tables 2 and 3 show a great improvement in the precision of all the spectroscopic
171 parameters of $CH_2D^{35}Cl$. In particular, due to the first observation of b-type
172 transitions, the constants A and Δ_K are confidently determined with errors that
173 are three orders of magnitude smaller than those reported in Ref. [24]. Also, all
174 the remaining parameters are one or two orders of magnitude more precise.
175 In the analysis of the $v_5 = 1$ and $v_6 = 1$ states, coupled through a c-type Coriolis

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Table 2: Spectroscopic parameters determined for CH_2DCl in the ground vibrational state [a].

Parameter	Unit	This work $CH_2D^{35}Cl$	Previous IR [b]	This work $CH_2D^{37}Cl$
A	MHz	119836.774(23)	119890.(42)	119834.890(23)
B	MHz	12479.34832(74)	12479.392(39)	12278.10755(72)
C	MHz	12177.17067(76)	12177.117(39)	11985.46816(51)
Δ_J	MHz	0.01503113(40)	0.0150555(60)	0.01458138(72)
Δ_{JK}	MHz	0.1564373(24)	0.155233(90)	0.1520332(85)
Δ_K	MHz	1.64916(94)	2.04(33)	1.6526(18)
δ_J	kHz	0.36830(42)	0.3699(45)	0.34809(47)
δ_K	MHz	0.02440(28)	0.0330(90)	0.02227(30)
Φ_J	mHz	$-1.46(25)$		
Φ_{JK}	Hz	$-0.0461(64)$		0.316(33)
Φ_{KJ}	Hz	3.8555(18)		3.635(28)
$\chi_{aa}(Cl)$	MHz	$-74.471(12)$		$-58.703(14)$
$\chi_{bb}(Cl)$	MHz	37.116(24)		29.294(22)
$C_{aa}(Cl)$	kHz	3.9(10)		4.4(17)
$C_{bb}(Cl)$	kHz	3.46(76)		
$C_{cc}(Cl)$	kHz	1.25(76)		3.37(54)
IR data		2708	2708	
IR $(J, K_a)_{max}$		57, 14	57, 14	
IR rms	cm^{-1}	4.4×10^{-4}	4.9×10^{-4}	
MW data		272		210
MW $(J, K_a)_{max}$		30, 11		35, 11
MW rms	kHz	17.7		15.0
σ		0.83		0.77

Notes: [a] Numbers in parenthesis are one standard deviation and apply to the last significant digits. [b] Ref. [24].

interaction [24], the vibrational energies E and the resonance parameters G_c, G_c^{JK} and F_{ab} have been determined as well.

As far as the $CH_2D^{37}Cl$ species is concerned, this work represents the first detailed investigation of its rotational spectrum. Generally speaking, the spectral analysis is satisfactory; for instance, the standard deviation of the fit ($\sigma = 0.77$) indicates that the data set are adequately reproduced within their expected uncertainties. Additionally, the obtained spectroscopic parameters have errors similar to those of $CH_2D^{35}Cl$ and their values are consistent with the isotopic substitution. The only exception is represented by Φ_{JK}, whose values

Table 3: Spectroscopic parameters determined for $CH_2D^{35}Cl$ in the singly-excited vibrational states $v_5 = 1$ and $v_6 = 1$. [a]

Parameter	Unit	This work		Previous IR [b]	
		$v_6 = 1$	$v_5 = 1$	$v_6 = 1$	$v_5 = 1$
E	cm^{-1}	714.112221(24)	827.023678(23)	714.11267(9)	827.02343(8)
A	MHz	119734.935(32)	119936.977(37)	119787.68(6)	119990.67(9)
B	MHz	12390.1856(21)	12426.52318(83)	12390.16(1)	12426.56(1)
C	MHz	12086.4828(32)	12127.4790(26)	12086.64(2)	12127.24(3)
Δ_J	MHz	0.01529052(94)	0.01480945(63)	0.015295(2)	0.014827(3)
Δ_{JK}	MHz	0.1608453(90)	0.151884(10)	0.15841(9)	0.15247(9)
Δ_K	MHz	1.66109(95)	1.62429(96)	2.0506(4)	2.0159(5)
δ_J	kHz	0.43118(50)	0.26756(64)	0.428(2)	0.270(4)
δ_K	MHz	0.02948(90)	0.02440 [c]	0.032(2)	0.019(3)
χ_{aa}(Cl)	MHz	−74.632(61)	−74.629(80)		
χ_{bb}(Cl)	MHz	39.9(24)	37.116 [c]		
G_c	MHz	4821.13(86)		4904.(9)	
G_c^{JK}	kHz	-0.2087(32)			
F_{ab}	MHz	-2.3034(98)		-1.16(1)	
IR data		2708		2708	
IR $(J, K_a)_{max}$		57, 14		57, 14	
IR rms	cm^{-1}	4.4×10^{-4}		4.9×10^{-4}	
MW data		202			
MW $(J, K_a)_{max}$		12, 11			
MW rms	kHz	30.4			
σ		0.83			

Notes: [a] Numbers in parenthesis are one standard deviation and apply to the last significant digits. [b] Ref. [24]. [c] Fixed to the ground state value.

in $CH_2D^{35}Cl$ and $CH_2D^{37}Cl$ have opposite signs. This can be explained by the fact that different sets of sextic centrifugal distortion terms have been fitted and the analyses are based on different data-sets.

The complete list of all the observed transitions is deposited as supplementary material.

5. Conclusions

The rotational spectra of $CH_2D^{35}Cl$ and $CH_2D^{37}Cl$, the singly-deuterated forms of chloromethane, have been observed in the millimeter region for the first time. Exploiting the Lamb-dip technique, precise rest frequencies have been retrieved for a large range of J and K_a transitions. Besides the ground state spectra, about 200 transitions of $CH_2D^{35}Cl$ in its $v_5 = 1$ and $v_6 = 1$ excited states have been also recorded. The analysis of a conspicuous data-set led to accurate

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values of many spectroscopic parameters, including the rotational constants A, B, C, several centrifugal distortion terms, and quadrupole coupling constants $\chi_{ii}(Cl)$. Overall, the quality of all spectroscopic parameters of $CH_2D^{35}Cl$ has been improved with the respect to previous works [24]. As to $CH_2D^{37}Cl$, our set of constants is the first reported in literature.

The main aim of this work is to provide reliable spectral prediction to guide radio-astronomical searches of CH_2DCl, a species which might be present in the low-mass protostar IRAS 16293-2422. The recent detection of chloromethane in this source has revealed CH_3Cl to be fairly abundant and to possess a rotational temperature (T_{rot}) of $ca.$ 100 K [8]. Without astrochemical models, it is hard to guess a reasonable abundance of CH_2DCl. In similar molecules, e.g., methanol and methyl cyanide, deuterium fractionation can vary quite a lot, ranging from 90 % to 4 % for CH_2DOH and CH_2DCN, respectively [36, 13].

However, it is known that deuterium fractionation processes are very efficient at low temperature; therefore, one could expect CH_2DCl to possess a T_{rot} as low as 10 K. In that case, the spectrum of CH_2DCl will peak in the 2–3 mm region, where many radio-telescopes (such as IRAM 30m, APEX, and ALMA) offer wide spectral coverage and high-sensitivity. In case of a higher T_{rot}, however, CH_2DCl emission will peak at higher frequencies, e.g., around 400 GHz at 100 K. ALMA, whose capability has been already demonstrated by numerous detections [37, 38], represents the best ground-based facility covering such frequency region (thanks to its ALMA Band 8 window) that can be used to search for CH_2DCl signatures in the interstellar medium. Even in case of a non-detection, it would be instructive to derive an upper limit for its abundance in order to compare it with those of related species [39, 40] or use it within astrochemical models.

A second important accomplishment of this work is the determination of an accurate set of ground state spectroscopic constants for $CH_2D^{37}Cl$, which were not available to date. They will provide a good starting point for future analyses of the high-resolution ro-vibrational spectrum of $CH_2D^{37}Cl$, whose acquisition is in progress in our laboratory.

6. Acknowledgement

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