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(Article begins on next page)

High-resolution millimeter-wave spectroscopy of CH₂DCl: 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 CH₃Cl and its isotopologues. Here, we report the investigation of the rotational spectrum of monodeuterated chloromethane CH₂DCl 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 CH₂D³⁵Cl and CH₂D³⁷Cl, 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 CH₂DCl 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

2 In the family of halocarbons, chloromethane (CH₃Cl) represents the small-
3 est member of the chlorine-bearing species. This organochloride is massively-
4 employed in industry as a methylating and chlorinating agent, while its use as
5 refrigerant (R-40) ceased because of its ozone depletion potential and global

[∗]Supplementary material available.

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6 warming power [1]. Indeed, large amounts of CH₃Cl are known to be present
7 in the Earth’s atmosphere: its atmospheric abundance has been demonstrated
8 to be due to both anthropogenic (accidental releases or burning processes) and
9 natural causes (produced by plants, bacteria, phytoplankton) [2].
10 Atmospheric CH₃Cl, previously revealed by *in situ* measurements [3, 4], has
11 been spectroscopically identified for the first time in the solar absorption spec-
12 trum of our troposphere through its strong infrared (IR) features around 2967 cm⁻¹
13 [5], corresponding to the *Q* branch of the ν_1 vibrational mode. Because of its
14 tendency to accumulate in the upper levels of the atmosphere, chloromethane
15 has been suggested as an optimal biosignature gas to be searched for in poten-
16 tially habitable exoplanets [6, 7].
17 The presence of chloromethane in environments other than our Solar system
18 has been recently identified at a pre-planetary stage, thanks to the observation
19 of CH₃Cl emission towards the low-mass protostar IRAS 16293-2422 with the
20 Atacama Large Millimeter/submillimeter Array (ALMA) [8]. In particular, this
21 detection relied on the observation at submillimeter-wavelengths of some $J =$
22 $13 \leftarrow 12$ rotational transitions of the two stable chlorine isotopologues, CH₃³⁵Cl
23 and CH₃³⁷Cl.
24 The protostar IRAS 16293-2422 is also a rich source of interstellar deuterated
25 species [9]. During the last 25 years, a plethora of deuterium-bearing molecules
26 have been identified in this source, including multiply-deuterated forms of water
27 (HDO and D₂O) [10], ammonia (up to ND₃) [11], methanol (up to CD₃OH) [12],
28 and methyl cyanide (CH₂DCN and CHD₂CN) [13]. High abundances of many
29 other deuterated species are predicted by astrochemical models, which unfortu-
30 nately have not yet taken into account deuterium enrichment in CH₃Cl. How-
31 ever, given its chemical similarity with CH₃CN and CH₃OH, CH₃Cl can likely
32 exhibit a strong deuterium fractionation (or D/H ratio) in IRAS 16293-2422,
33 thus producing significant amounts of monodeuterated chloromethane CH₂DCl.
34 A vast spectroscopic literature is available for the parent species CH₃Cl about
35 its vibrational and rotational spectra (see Refs. [14, 15] and references therein).
36 Extended line lists [16] and molecular database [17] are available for both the
37 CH₃³⁵Cl and CH₃³⁷Cl species. Also the rare ¹³C isotopologues have been spec-
38 troscopically characterized widely, from the millimeter-wave to the infrared do-
39 mains (see, e.g., Refs. [18, 19] and references therein). On the other hand,
40 deuterated forms of CH₃Cl have been poorly characterized from a spectroscopic
41 point-of-view.
42 Albeit the fundamental $J_{K_a, K_c} = 1_{0,1} \leftarrow 0_{0,0}$ rotational transition of CH₂DCl
43 was recorded in 1950 by Stark modulation microwave spectroscopy [20] and in
44 the early 1970s with a molecular-beam maser spectrometer [21, 22], the rota-
45 tional spectrum of CH₂DCl remains substantially unstudied so far. Since most
46 of the molecules observed in space are detected through rotational lines emission
47 [23], the lack of such spectral data poses substantial limitations to the identifi-
48 cation of monodeuterated chloromethane in the interstellar medium (ISM). As
49 far as the infrared spectrum of CH₂DCl is concerned, the analysis of six fun-
50 damental and some of their hot-bands has been recently reported for the ³⁵Cl
51 isotopologue [24, 25, 26], while no data are available for the ³⁷Cl one.

52 Here, we report the investigation of the rotational spectra of $\text{CH}_2\text{D}^{35}\text{Cl}$ and
53 $\text{CH}_2\text{D}^{37}\text{Cl}$, observed at millimeter-wavelengths with a frequency-modulation
54 (FM) absorption spectrometer. This work is aimed at (i) providing reliable
55 spectral predictions that will assist radio-astronomical searches of CH_2DCl and
56 (ii) obtaining a set of accurate spectroscopic parameters for both the chlorine
57 isotopologues, which constitutes a solid base to further investigate the infrared
58 spectrum of monodeuterated chloromethane.

59 2. Experimental details

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

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

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

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

83 Two Schottky barrier diodes were used as detector, from Millitech Co. up to
84 125 GHz and the WR3.4ZBD from Virginia Diodes between 240 and 300 GHz.
85 The detected signal is pre-amplified, filtered and demodulated at $2f$ by an
86 analog Lock-in, digitally-converted, and finally sent to a computer.

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

94 **3. Spectral analysis**

95 From a spectroscopic point of view, CH₂DCl is a nearly-prolate asymmetric-top
 96 rotor belonging to the C_s point group. Therefore, its nine vibrational modes
 97 are either of A' or A'' symmetry, as illustrated for CH₂D³⁵Cl in Table 1.

Table 1: Vibrational modes and their energy for CH₂D³⁵Cl.

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.

98 Differently from the parent species CH₃Cl (C_{3v} group), in which the carbon-
 99 halogen bond lies on the symmetry axis, the a -axis of the principal inertia system
 100 of CH₂DCl is slightly rotated with the respect to the C–Cl bond because of the
 101 different center of mass. Replacing one hydrogen atom with deuterium causes
 102 the permanent dipole moment ($\mu = 1.870$ D for CH₃Cl [32]) to be distributed
 103 along two components; based on geometric considerations [33], and assuming
 104 that the total dipole moment does not change among the isotopologues, one can
 105 estimate $\mu_a = 1.868$ D and $\mu_b = 0.076$ D for CH₂DCl.

106 The rotational energy of CH₂DCl can be modeled by using the standard semi-
 107 rigid Hamiltonian for an asymmetric rotor with a non-vanishing nuclear spin:

$$\mathcal{H} = \mathcal{H}_{\text{rot}} + \mathcal{H}_{\text{cd}} + \mathcal{H}_{\text{hfs}}, \quad (1)$$

108 where \mathcal{H}_{rot} contains the rotational constants in the A -Watson reduced form
 109 [34]:

$$\mathcal{H}_{\text{rot}} = \frac{1}{2} (B + C) \hat{P}^2 + \left[A - \frac{1}{2} (B + C) \right] \hat{P}_a^2 + \frac{1}{2} (B - C) \left(\hat{P}_b^2 - \hat{P}_c^2 \right), \quad (2)$$

110 the \mathcal{H}_{cd} part accounts for centrifugal distortion terms with increasing power of
 111 the angular momentum

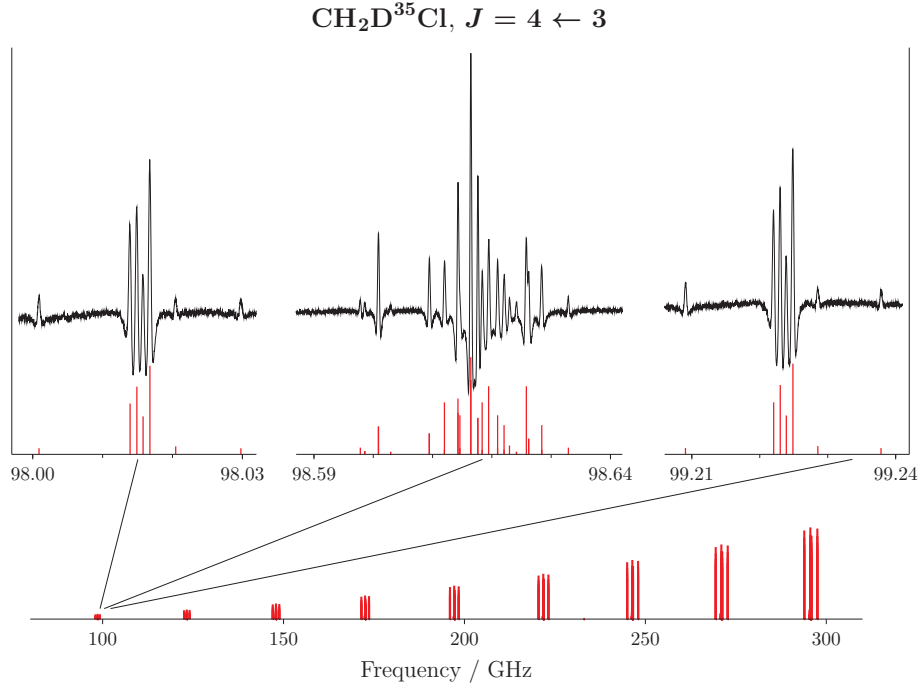


Figure 1: The hyperfine structure of the $J = 4 \leftarrow 3$ transition of $\text{CH}_2\text{D}^{35}\text{Cl}$. The black trace is the experimental spectrum, red sticks symbolise hyperfine components as predicted from the final fit. The $K_a = 1$ doublet is shown in the side spectra, whereas the central spectrum contains the $K_a = 0, 2$ and 3 components.

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

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

117 Both chlorine isotopologues of CH_2DCl show a strong a -type spectrum, with
 118 groups of $(J + 1) \leftarrow J$ transitions spaced by nearly $(B + C) \simeq 24$ GHz. The
 119 structure of each transition is typical of an asymmetric rotor very close to the
 120 prolate limit: most of the K_a components are grouped in the proximity of the
 121 $K_a = 0$, whereas the high and low components of the $K_a = 1$ doublet are
 122 found *ca.* $\frac{1}{2}(B - C)(J + 1)$ above or below, respectively. Moreover, because the
 123 chlorine quadrupolar interactions split each rotational level into four sub-levels
 124 with $F = J + 3/2; J + 1/2; J - 1/2; J - 3/2$, a hyperfine structure (HFS) is

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

130 4. Results and Discussion

131 Spectral predictions for $\text{CH}_2\text{D}^{35}\text{Cl}$ were initially performed by using the ground
 132 state spectroscopic constants reported in Ref. [24] together with the NQC con-
 133 stants from Ref. [21]. As far as $\text{CH}_2\text{D}^{37}\text{Cl}$ is concerned, rotational and cen-
 134 trifugal distortion constants were evaluated from the chloromethane equilibrium
 135 geometry of Ref. [33] and the NQC constants taken from Ref. [22].

136 First, we recorded five complete a -type $(J + 1) \leftarrow J$ transitions for both iso-
 137 topologues, with $4 \leq J \leq 11$. Once the sets of spectroscopic parameters had
 138 been refined and the uncertainty of the A constants reduced, we have searched
 139 for the extremely weak b -type transitions. They were expected to be about
 140 600 times weaker than the a -type ones, but thanks to the high-sensitivity of
 141 the spectrometer we were able to detect them with a good signal-to-noise ratio
 142 (SNR) in the spectrum.

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

147 In addition to the measurements of the ground state spectra of CH_2DCl , three
 148 R branch a -type rotational transitions have been observed for $\text{CH}_2\text{D}^{35}\text{Cl}$ in the
 149 $\nu_5 = 1$ and $\nu_6 = 1$ vibrational excited states, previously investigated in the
 150 infrared region [24].

151 The data analysis has been carried out with the SPFIT subprogram of the
 152 CALPGM suite [35]. For the $\text{CH}_2\text{D}^{35}\text{Cl}$ isotopologue, the newly measured
 153 ground and excited states transitions have been fitted in a weighted least-square
 154 procedure together with ro-vibrational data from the literature [24]. Each da-
 155 tum has a weight proportional to the inverse square of its uncertainty. Infrared
 156 data were used with half the uncertainties quoted in the original paper, as sug-
 157 gested by their fit standard deviation [24]. The experimental error of our tran-
 158 sition frequencies, instead, was estimated to be between 15 and 50 kHz, mostly
 159 depending on the SNR of the observed absorption line, and around 3 kHz for
 160 Lamb-dip measurements. The same criteria were applied to evaluate the experi-
 161 mental error associated to each transition of the $\text{CH}_2\text{D}^{37}\text{Cl}$ isotopologue, whose
 162 analysis is based on our measurements only.

163 Thanks to the observation of both a - and b -type transitions, chlorine-resolved
 164 hyperfine components, and Lamb-dip measurements, an accurate set of spec-
 165 troscopic parameters has been attained for each CH_2DCl isotopologue. They
 166 include the rotational constants, the complete set of quartic and some sextic
 167 centrifugal distortion terms, the diagonal $\chi_{ii}(\text{Cl})$ constants of the NQC tensor,

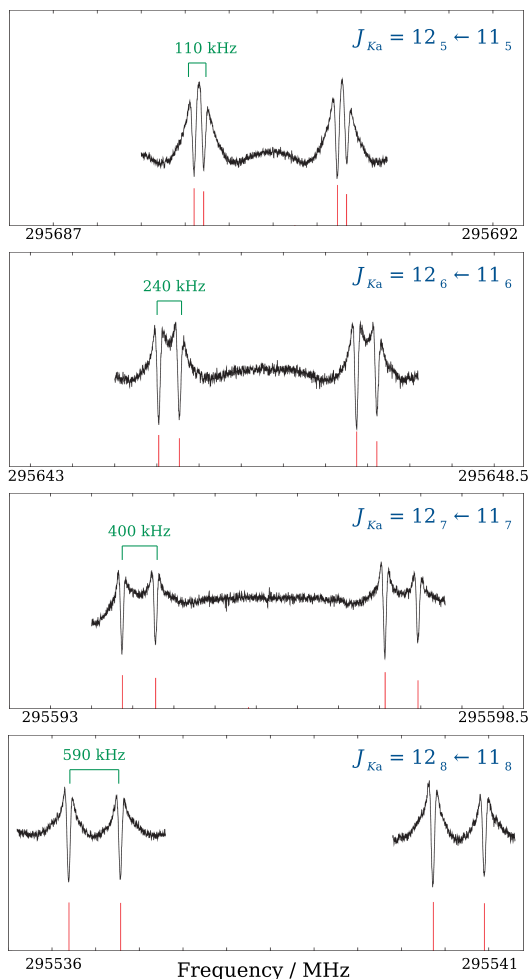


Figure 2: Splitting evolution in $\text{CH}_2\text{D}^{35}\text{Cl}$ Lamb-dip spectra. The black trace is the experimental spectrum, red sticks symbolise hyperfine components as predicted from the final fit. The HF components in each panel are, from lower to higher frequency: $F' \leftarrow F = 12.5 \leftarrow 11.5, 11.5 \leftarrow 10.5, 13.5 \leftarrow 12.5, 10.5 \leftarrow 9.5$. 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 $C_{ii}(\text{Cl})$ 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 $\text{CH}_2\text{D}^{35}\text{Cl}$. 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 $\nu_5 = 1$ and $\nu_6 = 1$ states, coupled through a c -type Coriolis

Table 2: Spectroscopic parameters determined for CH₂DCl in the ground vibrational state^[a].

Parameter	Unit	This work	Previous IR ^[b]	This work
		CH ₂ D ³⁵ Cl		CH ₂ D ³⁷ Cl
<i>A</i>	MHz	119836.774(23)	119890.(42)	119834.890(23)
<i>B</i>	MHz	12479.34832(74)	12479.392(39)	12278.10755(72)
<i>C</i>	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)
$\chi_{aa}(\text{Cl})$	MHz	-74.471(12)		-58.703(14)
$\chi_{bb}(\text{Cl})$	MHz	37.116(24)		29.294(22)
$C_{aa}(\text{Cl})$	kHz	3.9(10)		4.4(17)
$C_{bb}(\text{Cl})$	kHz	3.46(76)		
$C_{cc}(\text{Cl})$	kHz	1.25(76)		3.37(54)
IR data		2708	2708	
IR (<i>J, K_a</i>) _{max}		57, 14	57, 14	
IR <i>rms</i>	cm ⁻¹	4.4 × 10 ⁻⁴	4.9 × 10 ⁻⁴	
MW data		272		210
MW (<i>J, K_a</i>) _{max}		30, 11		35, 11
MW <i>rms</i>	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].

176 interaction [24], the vibrational energies E and the resonance parameters G_c ,
177 G_c^{JK} and F_{ab} have been determined as well.
178 As far as the CH₂D³⁷Cl species is concerned, this work represents the first de-
179 tailed investigation of its rotational spectrum. Generally speaking, the spectral
180 analysis is satisfactory; for instance, the standard deviation of the fit ($\sigma = 0.77$)
181 indicates that the data set are adequately reproduced within their expected un-
182 certainties. Additionally, the obtained spectroscopic parameters have errors
183 similar to those of CH₂D³⁵Cl and their values are consistent with the iso-
184 topic substitution. The only exception is represented by Φ_{JK} , whose values

Table 3: Spectroscopic parameters determined for CH₂D³⁵Cl in the singly-excited vibrational states $\nu_5 = 1$ and $\nu_6 = 1$. ^[a]

Parameter	Unit	This work		Previous IR ^[b]	
		$\nu_6 = 1$	$\nu_5 = 1$	$\nu_6 = 1$	$\nu_5 = 1$
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)
$\chi_{aa}(\text{Cl})$	MHz	-74.632(61)	-74.629(80)		
$\chi_{bb}(\text{Cl})$	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 $(J, K_a)_{\text{max}}$			57, 14		57, 14
IR rms	cm ⁻¹		4.4×10^{-4}		4.9×10^{-4}
MW data			202		
MW $(J, K_a)_{\text{max}}$			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.

185 in CH₂D³⁵Cl and CH₂D³⁷Cl have opposite signs. This can be explained by the
186 fact that different sets of sextic centrifugal distortion terms have been fitted and
187 the analyses are based on different data-sets.

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

190 5. Conclusions

191 The rotational spectra of CH₂D³⁵Cl and CH₂D³⁷Cl, the singly-deuterated forms
192 of chloromethane, have been observed in the millimeter region for the first time.
193 Exploiting the Lamb-dip technique, precise rest frequencies have been retrieved
194 for a large range of J and K_a transitions. Besides the ground state spectra,
195 about 200 transitions of CH₂D³⁵Cl in its $\nu_5 = 1$ and $\nu_6 = 1$ excited states
196 have been also recorded. The analysis of a conspicuous data-set led to accurate

197 values of many spectroscopic parameters, including the rotational constants A ,
198 B , C , several centrifugal distortion terms, and quadrupole coupling constants
199 $\chi_{ii}(\text{Cl})$. Overall, the quality of all spectroscopic parameters of $\text{CH}_2\text{D}^{35}\text{Cl}$ has
200 been improved with the respect to previous works [24]. As to $\text{CH}_2\text{D}^{37}\text{Cl}$, our
201 set of constants is the first reported in literature.

202 The main aim of this work is to provide reliable spectral prediction to guide
203 radio-astronomical searches of CH_2DCl , a species which might be present in the
204 low-mass protostar IRAS 16293-2422. The recent detection of chloromethane in
205 this source has revealed CH_3Cl to be fairly abundant and to possess a rotational
206 temperature (T_{rot}) of *ca.* 100 K [8]. Without astrochemical models, it is hard to
207 guess a reasonable abundance of CH_2DCl . In similar molecules, e.g., methanol
208 and methyl cyanide, deuterium fractionation can vary quite a lot, ranging from
209 90 % to 4 % for CH_2DOH and CH_2DCN , respectively [36, 13].

210 However, it is known that deuterium fractionation processes are very efficient at
211 low temperature; therefore, one could expect CH_2DCl to possess a T_{rot} as low
212 as 10 K. In that case, the spectrum of CH_2DCl will peak in the 2–3 mm region,
213 where many radio-telescopes (such as IRAM 30m, APEX, and ALMA) offer
214 wide spectral coverage and high-sensitivity. In case of a higher T_{rot} , however,
215 CH_2DCl emission will peak at higher frequencies, e.g., around 400 GHz at 100 K.
216 ALMA, whose capability has been already demonstrated by numerous detections
217 [37, 38], represents the best ground-based facility covering such frequency region
218 (thanks to its ALMA Band 8 window) that can be used to search for CH_2DCl
219 signatures in the interstellar medium. Even in case of a non-detection, it would
220 be instructive to derive an upper limit for its abundance in order to compare it
221 with those of related species [39, 40] or use it within astrochemical models.

222 A second important accomplishment of this work is the determination of an
223 accurate set of ground state spectroscopic constants for $\text{CH}_2\text{D}^{37}\text{Cl}$, which were
224 not available to date. They will provide a good starting point for future analyses
225 of the high-resolution ro-vibrational spectrum of $\text{CH}_2\text{D}^{37}\text{Cl}$, whose acquisition
226 is in progress in our laboratory.

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