

Alma Mater Studiorum Università di Bologna
Archivio istituzionale della ricerca

High-resolution millimeter-wave spectroscopy of CH₂DCI: Paving the way for future astronomical observations of chloromethane isotopologues

This is the final peer-reviewed author's accepted manuscript (postprint) of the following publication:

Published Version:

Melosso M., Achilli A., Tamassia F., Cane' E., Pietropolli Charmet A., Stoppa P., et al. (2020). High-resolution millimeter-wave spectroscopy of CH₂DCI: Paving the way for future astronomical observations of chloromethane isotopologues. JOURNAL OF QUANTITATIVE SPECTROSCOPY & RADIATIVE TRANSFER, 248, 1-7 [10.1016/j.jqsrt.2020.106982].

Availability:

This version is available at: <https://hdl.handle.net/11585/778767> since: 2024-06-03

Published:

DOI: <http://doi.org/10.1016/j.jqsrt.2020.106982>

Terms of use:

Some rights reserved. The terms and conditions for the reuse of this version of the manuscript are specified in the publishing policy. For all terms of use and more information see the publisher's website.

This item was downloaded from IRIS Università di Bologna (<https://cris.unibo.it/>).
When citing, please refer to the published version.

(Article begins on next page)

High-resolution millimeter-wave spectroscopy of CH₂DCl: paving the way for future astronomical observations of chloromethane isotopologues

Mattia Melosso^{a,*}, Andr  Achilli^a, Filippo Tamassia^b, Elisabetta Can ^b,
Andrea Pietropolli Charmet^c, Paolo Stoppa^c, Luca Dore^a

^a*Dipartimento di Chimica “Giacomo Ciamician”, Universit  di Bologna, Via F. Selmi 2, 40126 Bologna (Italy)*

^b*Dipartimento di Chimica Industriale “Toso Montanari”, Universit  di Bologna, Viale del Risorgimento 4, 40136 Bologna (Italy)*

^c*Dipartimento di Scienze Molecolari e Nanosistemi, Universit  Ca’ Foscari Venezia, Via Torino 155, 30172 Mestre (Italy)*

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

In the family of halocarbons, chloromethane (CH₃Cl) 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

[☆]Supplementary material available.

*Corresponding author

Email address: mattia.melosso2@unibo.it (Mattia Melosso)

6 warming power [1]. Indeed, large amounts of CH_3Cl 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 CH_3Cl , 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 CH_3Cl 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, $\text{CH}_3^{35}\text{Cl}$
 23 and $\text{CH}_3^{37}\text{Cl}$.
 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 D_2O) [10], ammonia (up to ND_3) [11], methanol (up to CD_3OH) [12],
 28 and methyl cyanide (CH_2DCN and CHD_2CN) [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 CH_3Cl . How-
 31 ever, given its chemical similarity with CH_3CN and CH_3OH , CH_3Cl can likely
 32 exhibit a strong deuterium fractionation (or D/H ratio) in IRAS 16293-2422,
 33 thus producing significant amounts of monodeuterated chloromethane CH_2DCl .
 34 A vast spectroscopic literature is available for the parent species CH_3Cl 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 $\text{CH}_3^{35}\text{Cl}$ and $\text{CH}_3^{37}\text{Cl}$ species. Also the rare ^{13}C 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 CH_3Cl 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 CH_2DCl
 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 CH_2DCl 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 CH_2DCl is concerned, the analysis of six fun-
 50 damental and some of their hot-bands has been recently reported for the ^{35}Cl
 51 isotopologue [24, 25, 26], while no data are available for the ^{37}Cl one.

Here, we report the investigation of the rotational spectra of $\text{CH}_2\text{D}^{35}\text{Cl}$ and $\text{CH}_2\text{D}^{37}\text{Cl}$, 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.

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

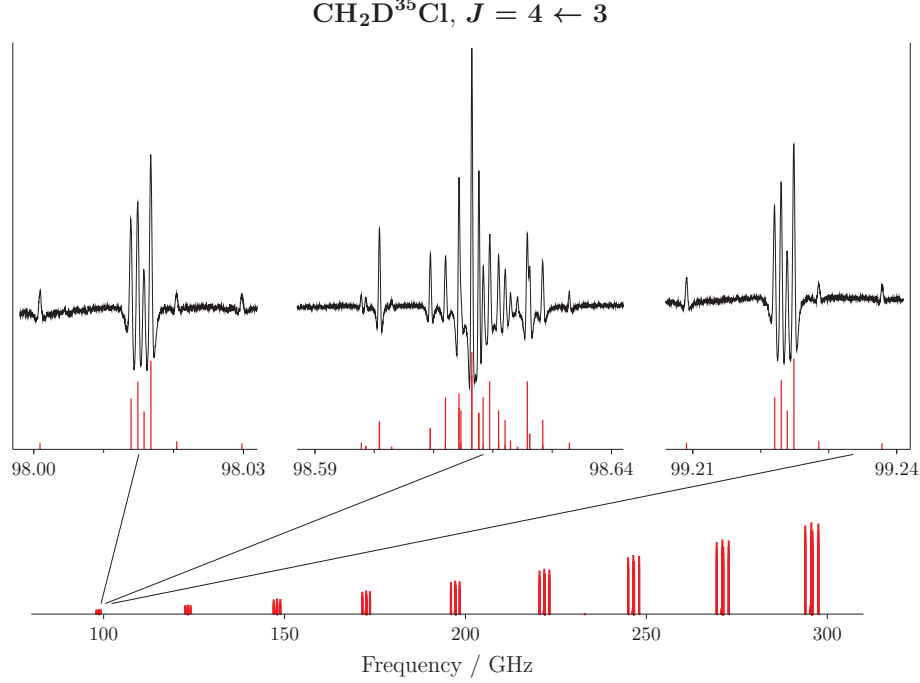


Figure 1: The hyperfine structure of the $J = 4 \leftarrow 3$ transition of $\text{CH}_2\text{D}^{35}\text{Cl}$. The black trace is the experimental spectrum, red sticks symbolise hyperfine components as predicted from the final fit. The $K_a = 1$ doublet is shown in the side spectra, whereas the central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

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

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 $v_5 = 1$ and $v_6 = 1$ 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,

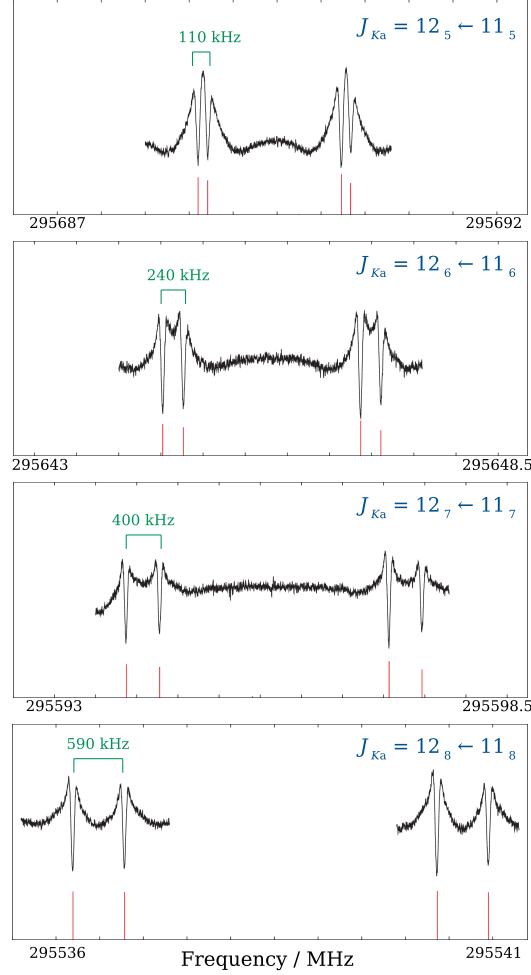


Figure 2: Splitting evolution in $\text{CH}_2\text{D}^{35}\text{Cl}$ Lamb-dip spectra. The black trace is the experimental spectrum, red sticks symbolise hyperfine components as predicted from the final fit. The HF components in each panel are, from lower to higher frequency: $F' \leftarrow F = 12.5 \leftarrow 11.5, 11.5 \leftarrow 10.5, 13.5 \leftarrow 12.5, 10.5 \leftarrow 9.5$. 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.

and the $C_{ii}(\text{Cl})$ SR constants. The final parameters are collected in Tables 2 and 3, where they are compared with those of Ref. [24].
 Tables 2 and 3 show a great improvement in the precision of all the spectroscopic parameters of $\text{CH}_2\text{D}^{35}\text{Cl}$. In particular, due to the first observation of b -type transitions, the constants A and Δ_K are confidently determined with errors that are three orders of magnitude smaller than those reported in Ref. [24]. Also, all the remaining parameters are one or two orders of magnitude more precise.
 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 |
| 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) |
| $\chi_{aa}(\text{Cl})$ | 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 $(J, K_a)_{\text{max}}$ | | 57, 14 | 57, 14 | |
| IR rms | cm ⁻¹ | 4.4×10^{-4} | 4.9×10^{-4} | |
| MW data | | 272 | | 210 |
| MW $(J, K_a)_{\text{max}}$ | | 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 CH₂D³⁷Cl 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 CH₂D³⁵Cl 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 $\text{CH}_2\text{D}^{35}\text{Cl}$ 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 $\text{CH}_2\text{D}^{35}\text{Cl}$ and $\text{CH}_2\text{D}^{37}\text{Cl}$ 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 $\text{CH}_2\text{D}^{35}\text{Cl}$ and $\text{CH}_2\text{D}^{37}\text{Cl}$, 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 $\text{CH}_2\text{D}^{35}\text{Cl}$ 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.

227 6. Acknowledgement

228 This study was supported by Bologna University (RFO funds), MIUR (Project
 229 PRIN 2015: STARS in the CAOS, Grant Number 2015F59J3R), and Ca' Foscari
 230 University, Venice (AdiR funds). The authors gratefully remember Mr. A. Bal-
 231 dan for the preparation of the sample of CH_2DCl .

232 References

- 233 [1] M. S. Emani, R. Roy, B. K. Mandal, Development of refrigerants: a brief
 234 review, Indian J. Sci. Res. 14 (2) (2017) 175–181.
- 235 [2] F. Keppler, D. Harper, T. Röckmann, R. Moore, J. Hamilton, New insight
 236 into the atmospheric chloromethane budget gained using stable carbon iso-
 237 tope ratios, Atmos. Chem. Phys. 5 (9) (2005) 2403–2411.

- [3] J. Lovelock, Natural halocarbons in the air and in the sea, *Nature* 256 (5514) (1975) 193–194.
- [4] E. Grimsrud, R. Rasmussen, Survey and analysis of halocarbons in the atmosphere by gas chromatography-mass spectrometry, *Atmos. Environ.* 9 (11) (1975) 1014–1017.
- [5] J. Park, R. Zander, C. Farmer, C. Rinsland, J. Russell III, R. Norton, et al., Spectroscopic detection of CH_3Cl in the upper troposphere and lower stratosphere, *Geophys. Res. Lett.* 13 (8) (1986) 765–768.
- [6] S. Seager, W. Bains, J. Petkowski, Toward a list of molecules as potential biosignature gases for the search for life on exoplanets and applications to terrestrial biochemistry, *Astrobiology* 16 (6) (2016) 465–485.
- [7] E. W. Schwieterman, N. Y. Kiang, M. N. Parenteau, C. E. Harman, S. Das-Sarma, T. M. Fisher, et al., Exoplanet biosignatures: a review of remotely detectable signs of life, *Astrobiology* 18 (6) (2018) 663–708.
- [8] E. C. Fayolle, K. I. Öberg, J. K. Jørgensen, K. Altwegg, H. Calcutt, H. S. Müller, et al., Protostellar and cometary detections of organohalogens, *Nat. Astron.* 1 (10) (2017) 703.
- [9] E. F. van Dishoeck, G. A. Blake, D. J. Jansen, T. Groesbeck, Molecular abundances and low mass star formation II. Organic and deuterated species towards IRAS 16293-2422, *Astrophys. J* 447 (1995) 760–782.
- [10] A. Coutens, C. Vastel, E. Caux, C. Ceccarelli, S. Bottinelli, L. Wiesenfeld, et al., A study of deuterated water in the low-mass protostar IRAS 16293-2422, *Astron. Astrophys.* 539 (2012) A132.
- [11] E. Roueff, D. C. Lis, F. Van der Tak, M. Gerin, P. Goldsmith, Interstellar deuterated ammonia: from NH_3 to ND_3 , *Astron. Astrophys.* 438 (2) (2005) 585–598.
- [12] B. Parise, A. Castets, E. Herbst, E. Caux, C. Ceccarelli, I. Mukhopadhyay, et al., First detection of triply-deuterated methanol, *Astron. Astrophys.* 416 (1) (2004) 159–163.
- [13] H. Calcutt, J. Jørgensen, H. Müller, L. Kristensen, A. Coutens, T. Bourke, et al., The ALMA-PILS survey: complex nitriles towards IRAS 16293–2422, *Astron. Astrophys.* 616 (2018) A90.
- [14] A. Nikitin, T. Dmitrieva, I. Gordon, Improved spectroscopic line list of methyl chloride in the $1900\text{--}2600\text{ cm}^{-1}$ spectral region, *J. Quant. Spectrosc. Ra.* 177 (2016) 49–58.
- [15] L. N. Štríteská, M. Šimečková, P. Kania, P. Musil, L. Kolesníková, J. Kouček, et al., Precise ground state molecular parameters of chloromethane, *J. Mol. Struct.* 919 (1-3) (2009) 89–93.

- [16] A. Owens, A. Yachmenev, W. Thiel, A. Fateev, J. Tennyson, S. N. Yurchenko, ExoMol line lists–XXIX. The rotation-vibration spectrum of methyl chloride up to 1200 K, *Mon. Not. R. Astron. Soc.* 479 (3) (2018) 3002–3010.
- [17] I. E. Gordon, L. S. Rothman, C. Hill, R. V. Kochanov, Y. Tan, P. F. Bernath, et al., The HITRAN2016 molecular spectroscopic database, *J. Quant. Spectrosc. Ra.* 203 (2017) 3–69.
- [18] M. Litz, H. Bürger, L. Féjard, F. Constantin, L. Margulès, J. Demaison, Infrared and millimeter-wave studies of $^{13}\text{CH}_3\text{Cl}$ in the ground, 3^1 , and 6^1 states, *J. Mol. Spectrosc.* 219 (2) (2003) 238–247.
- [19] P. Kania, L. N. Stríteská, M. Šimečková, P. Musil, L. Kolesníková, J. Koubek, et al., Rotational spectrum of ^{13}C chloromethanes, *J. Mol. Spectrosc.* 252 (1) (2008) 90–92.
- [20] G. Matlack, G. Glockler, D. Bianco, A. Roberts, The microwave spectra of isotopic methyl chloride, *J. Chem. Phys.* 18 (3) (1950) 332–334.
- [21] S. G. Kukolich, High-resolution measurements of ^{35}Cl and D quadrupole coupling in CH_2DCl and CD_3Cl , *J. Chem. Phys.* 55 (9) (1971) 4488–4493.
- [22] S. G. Kukolich, A. C. Nelson, Variation of Cl quadrupole coupling with isotopic substitution in CH_3Cl , *J. Chem. Phys.* 57 (9) (1972) 4052–4054.
- [23] B. A. McGuire, 2018 Census of Interstellar, Circumstellar, Extragalactic, Protoplanetary Disk, and Exoplanetary Molecules, *Astrophys. J. Suppl. S.* 239 (2018) 17.
- [24] A. Baldacci, P. Stoppa, A. Pietropolli Charmet, S. Giorgianni, G. Nivellini, High resolution FTIR study of the ν_5 and ν_6 bands of $\text{CH}_2\text{D}^{35}\text{Cl}$: analysis of resonances and determination of ground and upper state constants, *Mol. Phys.* 103 (20) (2005) 2803–2811.
- [25] A. Baldacci, R. Visinoni, S. Giorgianni, G. Nivellini, High-resolution FTIR spectroscopy of $\text{CH}_2\text{D}^{35}\text{Cl}$: rovibrational analysis of the ν_3 , ν_9 fundamentals and the $2\nu_6$ - ν_6 , ν_5 + ν_6 - ν_5 hot bands, *Mol. Phys.* 106 (9-10) (2008) 1233–1240.
- [26] A. Baldacci, R. Visinoni, G. Nivellini, High-resolution FTIR spectroscopy of $\text{CH}_2\text{D}^{35}\text{Cl}$: analysis of the nearly degenerate ν_4 and ν_8 levels, *Mol. Phys.* 108 (18) (2010) 2395–2401.
- [27] M. Melosso, B. Conversazioni, C. Degli Esposti, L. Dore, E. Cané, F. Tamassia, et al., The pure rotational spectrum of $^{15}\text{ND}_2$ observed by millimetre and submillimetre-wave spectroscopy, *J. Quant. Spectrosc. Ra.* 222 (2019) 186–189.

- [28] M. Melosso, L. Bizzocchi, F. Tamassia, C. Degli Esposti, E. Canè, L. Dore, The rotational spectrum of ^{15}ND . isotopic-independent Dunham-type analysis of the imidogen radical, *Phys. Chem. Chem. Phys.* 21 (2019) 3564–3573.
- [29] C. Degli Esposti, M. Melosso, L. Bizzocchi, F. Tamassia, L. Dore, Determination of a semi-experimental equilibrium structure of 1-phosphapropyne from millimeter-wave spectroscopy of CH_3CP and CD_3CP , *J. Mol. Struct.* 1203 (2020) 127429.
- [30] W. E. Lamb Jr, Theory of an optical maser, *Phys. Rev.* 134 (1964) A1429.
- [31] M. Melosso, L. Dore, J. Gauss, C. Puzzarini, Deuterium hyperfine splittings in the rotational spectrum of NH_2D as revealed by Lamb-dip spectroscopy, submitted to *J. Mol. Spectrosc.*
- [32] G. Wlodarczak, B. Segard, J. Legrand, J. Demaison, The dipole moment of $\text{CH}_3^{35}\text{Cl}$, *J. Mol. Spectrosc.* 111 (1985) 204–206.
- [33] G. Black, M. Law, The general harmonic force field of methyl chloride, *J. Mol. Spectrosc.* 205 (2) (2001) 280–285.
- [34] J. K. Watson, Determination of centrifugal distortion coefficients of asymmetric-top molecules, *J. Chem. Phys.* 46 (5) (1967) 1935–1949.
- [35] H. M. Pickett, The fitting and prediction of vibration-rotation spectra with spin interactions, *J. Mol. Spectrosc.* 148 (1991) 371–377.
- [36] B. Parise, C. Ceccarelli, A. Tielens, E. Herbst, B. Lefloch, E. Caux, et al., Detection of doubly-deuterated methanol in the solar-type protostar IRAS 16293-2422, *Astron. Astrophys.* 393 (3) (2002) L49–L53.
- [37] B. A. McGuire, C. L. Brogan, T. R. Hunter, A. J. Remijan, G. A. Blake, A. M. Burkhardt, et al., First results of an ALMA Band 10 spectral line survey of NGC 6334I: Detections of glycolaldehyde ($\text{HC(O)CH}_2\text{OH}$) and a new compact bipolar outflow in HDO and CS, *Astrophys. J. Lett.* 863 (2) (2018) L35.
- [38] M. Melosso, L. Dore, F. Tamassia, C. L. Brogan, T. R. Hunter, B. A. McGuire, The sub-millimeter rotational spectrum of ethylene glycol up to 890 GHz and application to ALMA Band 10 spectral line data of NGC 6334I, *J. Phys. Chem. A* 124 (2020) 240–246.
- [39] M. Melosso, A. Melli, C. Puzzarini, C. Codella, L. Spada, L. Dore, et al., Laboratory measurements and astronomical search for cyanomethanimine, *Astron. Astrophys.* 609 (2018) A121.
- [40] M. Melosso, B. A. McGuire, F. Tamassia, C. Degli Esposti, L. Dore, Astronomical search of vinyl alcohol assisted by submillimeter spectroscopy, *ACS Earth and Space Chemistry* 3 (7) (2019) 1189–1195.