

## Note

# Microwave spectra of the $^{35}\text{Cl}$ and $^{37}\text{Cl}$ isotopomers of dichloromethylene: Nuclear quadrupole-, spin–rotation-, and nuclear shielding constants from the hyperfine structures of rotational lines

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## Abstract

The rotational spectra of the isotopomers  $\text{C}^{35}\text{Cl}^{37}\text{Cl}$  and  $\text{C}^{37}\text{Cl}_2$  of dichloromethylene in the ground vibronic state were recorded in the range 10–33 GHz using a molecular beam Fourier transform microwave spectrometer.  $\text{CCl}_2$  was generated by flash pyrolysis using different precursors. The observed spectra were analyzed to yield rotational and centrifugal distortion constants, as well as the complete Cl nuclear quadrupole coupling tensors and the spin–rotation interaction constants from the hyperfine structure of the rotational lines. With inclusion of data from previous work on the most abundant species  $\text{C}^{35}\text{Cl}_2$  [N. Hansen, H. Mäder, F. Temps, *Phys. Chem. Chem. Phys.* (3) (2001) 50–55.] a refined  $r_0$  structure was determined. The spin–rotation interaction constants of all three isotopomers were used to derive  $^{35}\text{Cl}$  and  $^{37}\text{Cl}$  principal inertial axis nuclear magnetic shielding components which have not yet been determined by NMR spectroscopy.

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## 1. Introduction

The purpose of this note is to report the results of an investigation of the rotational spectra of the isotopomers  $\text{C}^{35}\text{Cl}^{37}\text{Cl}$  and  $\text{C}^{37}\text{Cl}_2$  of dichloromethylene in the ground vibronic state. This study extends previous microwave spectroscopic investigations on the most abundant species,  $\text{C}^{35}\text{Cl}_2$ , which have yielded structural information and  $^{35}\text{Cl}$  nuclear quadrupole coupling constants [1,2]. Thanks to the high resolution and precision

of the molecular-beam Fourier transform microwave (MB-FTMW) technique, spin–rotation interaction parameters could be determined [2] and were found to be unusually large compared to other molecules with  $C_{2v}$  symmetry and two identical Cl atoms. A similar finding has also been reported for  $\text{CF}_2$  [3] which may indicate that low-lying excited electronic states of these dihalocarbenes play an important role for the magnetic hyperfine interaction.

Dichloromethylene has been the subject of numerous theoretical and spectroscopic investigations (see [2] and references cited therein), emphasizing its importance as a highly reactive intermediate in chemical reactions such as decomposition processes of chloroalkanes. In this context, the low energy gap between the singlet ground

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and the first excited triplet electronic states which exhibit quite different chemical properties has been of particular interest. Recent results from dispersed fluorescence spectra of  $\text{CCl}_2$  vibronic bands [4] allow to estimate this singlet-triplet gap to about  $14 \text{ kcal mol}^{-1}$  which is in fair agreement with the most recent theoretical calculation [5].

Theoretical calculations of rovibrational and structural parameters of  $\text{C}^{35}\text{Cl}_2$  have also been reported lately [6]. Excellent agreement was found between the calculated equilibrium structure and the semi-experimental equilibrium structure derived from the experimental rotational constants by Hansen et al. [2] and the ab initio rovibrational interaction parameters. These data may also be used for a reliable prediction of the hitherto unknown spectra of less abundant isotopomers of  $\text{CCl}_2$  reported in this note.

## 2. Experimental

The spectra of  $\text{CCl}_2$  were recorded using a molecular beam Fourier transform microwave (MB-FTMW) spectrometer which has been described in some detail previously [2,7]. For the investigations on  $\text{C}^{35}\text{Cl}^{37}\text{Cl}$ , we employed the flash pyrolysis method as described in [3] for the generation of  $\text{C}^{35}\text{Cl}_2$ , using dibromodichloromethane ( $\text{CBr}_2\text{Cl}_2$ ) or dichloroacetylchloride ( $\text{CHCl}_2\text{COCl}$ ) as precursors. As observed previously for  $\text{C}^{35}\text{Cl}_2$  (relative abundance ca. 57%), the latter precursor yielded somewhat stronger spectra for  $\text{C}^{35}\text{Cl}^{37}\text{Cl}$  (relative abundance ca. 37%) as well, and the resulting spectrum could be readily assigned.

In case of  $\text{C}^{37}\text{Cl}_2$ , these precursors were also used in an initial step of the investigation. However, probably because of the much smaller relative abundance (ca. 6%), no clear assignment was obtained for this isotopomer, even after long and tedious scans over the expected range of transition frequencies. We have thus recently modified the experimental setup and have also used a different precursor to improve the yield of  $\text{CCl}_2$  by the pyrolysis technique. In the new setup, the heating current is fed into the SiC tube through the movable aluminum mirror of the microwave resonator extending the heating zone to the end of the SiC tube. Therefore, the molecular beam expansion begins immediately after the heating zone which minimizes the possibility of recombination or other reactions of the reactive species in an unheated part of the SiC tube.

Instead of using the aforementioned precursors, the radicals were formed leading Ar at a pressure of about 5 bar over solid trimethyl(trichloromethyl)silane ( $(\text{CH}_3)_3\text{SiCCl}_3$ ) contained in a stainless steel reservoir at room temperature. This precursor was previously used by Clouthier and Karolczak [8,9] for the pyrolytic generation of dichloromethylene for the studies of rota-

tionally resolved electronic spectra. The gas mixture was then expanded into the SiC tube through a pulsed molecular beam valve (General Valve Series 9). The heating current of the SiC tube was optimized for the observed S/N ratio and was found to yield best results for a temperature which was estimated to be approx.  $700^\circ\text{C}$ . The resulting molecular beam enters the high vacuum in the microwave cavity through a hole in the center of the spherical mirror. This setup allows for a repetition rate of the molecular beam valve of ca. 2 Hz with a typical opening time of 1 ms. The molecular ensemble was then excited by a microwave pulse of  $1.0 \mu\text{s}$  duration with a power of about 3 mW. After a time of typical  $10 \mu\text{s}$  which allowed the excitation pulse to decay, the transient emission signal was recorded for  $160 \mu\text{s}$  at a sample interval of 10 ns. To improve the S/N ratio, up to 20,000 of these records (for the weakest components of  $\text{C}^{37}\text{Cl}_2$ ) were averaged and subsequently Fourier transformed to yield the corresponding spectra. This led to a linewidth of approx. 4 kHz which allowed a resolution of ca. 2 kHz for the stronger components.

## 3. Spectral assignment and analysis

In the initial step of the investigation, the rotational constants derived from the  $r_0$ -structure and the centrifugal distortion constants of the parent species  $\text{C}^{35}\text{Cl}_2$  [2] were used for a prediction of the range of expected rotational transitions of  $\text{C}^{35}\text{Cl}^{37}\text{Cl}$  and  $\text{C}^{37}\text{Cl}_2$ , respectively. Because of the aforementioned assignment problems for the less abundant species  $\text{C}^{37}\text{Cl}_2$ , the recent semi-experimental equilibrium structure and ab initio rovibrational interaction parameters given by Demaison et al. [6] were used and found to more closely predict the expected transition frequencies. The hyperfine splittings of the lines due to Cl nuclear quadrupole coupling and spin-rotation interaction were predicted using the data given in [2], which however, requires a scaling of the quadrupole coupling constants  $\chi_{gg}$  and the spin-rotation interaction parameters  $C_{gg}$  for  $^{37}\text{Cl}$  according to the ratios

$$\frac{\chi_{gg'}(^{35}\text{Cl})}{\chi_{gg'}(^{37}\text{Cl})} = \frac{Q(^{35}\text{Cl})}{Q(^{37}\text{Cl})} = 1.26878, \quad (1)$$

where the  $Q$ -values denote the electric nuclear quadrupole moments, and

$$\frac{C_{gg}(^{35}\text{Cl})}{C_{gg}(^{37}\text{Cl})} = \frac{\mu(^{35}\text{Cl})}{\mu(^{37}\text{Cl})} = 1.20131, \quad (2)$$

where  $\mu$  denotes the nuclear magnetic moments. The ratios of the electric quadrupole and magnetic moments were taken from [10].

All predictions and spectra analyses were based on the effective Hamiltonian given in [2], which contains a rotational part including centrifugal distortion (up to

fourth-order terms) as well contributions from Cl nuclear quadrupole coupling and spin–rotation interaction. For the prediction of the  $\chi$ - and  $C$ -tensor elements of  $C^{35}\text{Cl}^{37}\text{Cl}$  with respect to the principal inertial axes, the influence of the small rotation angle about the  $c$ -axis (ca.  $0.18^\circ$ ) due to the unsymmetric substitution of the  $^{37}\text{Cl}$  nucleus was neglected. The numerical treatment of the Hamiltonian for predictions and analyses were carried out with the programs SPCAT and SPFIT, respectively, written by Pickett [11].

For  $C^{35}\text{Cl}^{37}\text{Cl}$ , a total of 47 hyperfine components of five  $b$ -type rotational transitions could be assigned ( $J$  ranging from 1 to 8). Due to the less favourable line intensities, only four rotational  $b$ -type transitions ( $J$  ranging from 1 to 5) and a total of 18 hyperfine components could be unambiguously assigned for  $C^{37}\text{Cl}_2$ . All measured transitions are listed in the [supplementary material for this article](#).

A least-squares analysis of the measured transitions frequencies yielded the spectroscopic constants for both isotopomers, summarized in Table 1. For comparison, the table also shows the previous results on the parent species [2] which were obtained from a total of 169 lines (43 lines in the cm-wavelength range and 126 higher  $J$ -lines in the mm-wavelength range [1]), thus yielding reliable values for the centrifugal distortion constants. Because of the limited number of (low- $J$ ) transitions in the present study, those constants were kept fixed in the fit. Similarly, some of the hyperfine constants were also held constant. For  $C^{35}\text{Cl}^{37}\text{Cl}$ , the off-diagonal element  $\chi_{ab}(^{37}\text{Cl})$  was fixed with the constant scaling factor of Eq. (1) to the fit value of  $\chi_{ab}(^{35}\text{Cl})$ . No reliable fit result was obtained for the spin–rotation interaction constants  $C_{cc}(^{35}\text{Cl})$  and  $C_{cc}(^{37}\text{Cl})$  of both isotopomers, which were subsequently fixed to the value for  $C^{35}\text{Cl}_2$ , scaled for the  $^{37}\text{Cl}$  nucleus according to Eq. (2). In addition, the values for  $C_{aa}(^{37}\text{Cl})$  and  $C_{bb}(^{37}\text{Cl})$  of  $C^{35}\text{Cl}^{37}\text{Cl}$  were also fixed, with the ratio of Eq. (2), to the fit result of  $C_{aa}(^{35}\text{Cl})$  and  $C_{bb}(^{35}\text{Cl})$ , respectively.

## 4. Results and discussion

### 4.1. Structure determination

The  $r_0$ -structure was redetermined with the additional data on rotational constants of all dichloromethylene isotopomers in the ground vibrational state, given in Table 1. A least squares analysis resulted in the values  $r_0(\text{C–Cl}) = 1.7141(1) \text{ \AA}$  and  $\angle(\text{Cl–C–Cl}) = 109.349(1)$ , in agreement with [2] but with smaller standard deviations (given in parentheses as  $1\sigma$ ). These standard errors are rather meaningless, however, since they do not reflect systematic errors like neglect of vibration–rotation interaction, made in the assumptions for an  $r_0$ -structure analysis. Part of the effects from vibration–rotation

Table 1

Spectroscopic constants for  $\text{CCl}_2$  isotopomers from the fit to the observed transition frequencies using Watson's A-reduction and representation  $I'$

	$C^{35}\text{Cl}_2$ <sup>a</sup>	$C^{35}\text{Cl}^{37}\text{Cl}$	$C^{37}\text{Cl}_2$
$A$ (MHz)	50229.403(1) <sup>b</sup>	50030.425(7)	49830.685(5)
$B$ (MHz)	3695.3459(2)	3595.1710(6)	3495.8519(4)
$C$ (MHz)	3438.3643(4)	3350.5444(17)	3263.2496(19)
$\Delta_J$ (kHz)	1.505(1)	1.505 <sup>c</sup>	1.505 <sup>c</sup>
$\Delta_{JK}$ (kHz)	−33.17(5)	−33.17 <sup>c</sup>	−33.17 <sup>c</sup>
$\Delta_K$ (MHz)	1.557(1)	1.557 <sup>c</sup>	1.557 <sup>c</sup>
$\delta_J$ (kHz)	0.1558(1)	0.1558 <sup>c</sup>	0.1558 <sup>c</sup>
$\delta_K$ (kHz)	9.3(1)	9.3 <sup>c</sup>	9.3 <sup>c</sup>
$\chi_{bb}(^{35}\text{Cl})$ (MHz)	17.319(1)	17.055(14)	—
$\chi_{cc}(^{35}\text{Cl})$ (MHz)	5.540(1)	5.539(23)	—
$ \chi_{ab} (^{35}\text{Cl})$ (MHz)	46.2(2)	47.7(11)	—
$\chi_{zz}(^{35}\text{Cl})$ (MHz)	−53.1(1)	−54.4(10)	—
$\chi_{xx}(^{35}\text{Cl})$ (MHz)	47.6(1)	48.9(10)	—
$\chi_{yy}(^{35}\text{Cl})$ (MHz)	5.540(1)	5.539(23)	—
$\chi_{bb}(^{37}\text{Cl})$ (MHz)	—	13.845(17)	13.653(1)
$\chi_{cc}(^{37}\text{Cl})$ (MHz)	—	4.393(28)	4.361(3)
$ \chi_{ab} (^{37}\text{Cl})$ (MHz)	—	37.6(9) <sup>d</sup>	37.2(3)
$\chi_{zz}(^{37}\text{Cl})$ (MHz)	—	−43.1(8)	−42.6(1)
$\chi_{xx}(^{37}\text{Cl})$ (MHz)	—	38.7(8)	38.2(1)
$\chi_{yy}(^{37}\text{Cl})$ (MHz)	—	4.392(28)	4.361(3)
$C_{aa}(^{35}\text{Cl})$ (kHz)	58.2(3)	59.9(19)	—
$C_{bb}(^{35}\text{Cl})$ (kHz)	2.8(1)	3.5(5)	—
$C_{cc}(^{35}\text{Cl})$ (kHz)	1.4(1)	1.4 <sup>c</sup>	—
$C_{aa}(^{37}\text{Cl})$ (kHz)	—	49.8(16) <sup>c</sup>	43.9(9)
$C_{bb}(^{37}\text{Cl})$ (kHz)	—	2.9(4) <sup>c</sup>	1.7(3)
$C_{cc}(^{37}\text{Cl})$ (kHz)	—	1.2 <sup>f</sup>	1.2 <sup>f</sup>
Number of lines	43 <sup>g</sup>	47	18
$\sigma$ (kHz) <sup>h</sup>	1.6	3.0	1.0

Uncertainties in parentheses correspond to  $1\sigma$  standard deviation.

<sup>a</sup> Ref. [2].

<sup>b</sup> Misprint in [2].

<sup>c</sup> Fixed to values from  $C^{35}\text{Cl}_2$ .

<sup>d</sup> Fixed with constant ratio ( $^{35}\text{Cl}/^{37}\text{Cl}$ ) = 1.26878 to fit parameter  $|\chi_{ab}|(^{35}\text{Cl})$ .

<sup>e</sup> Fixed with constant ratio ( $^{35}\text{Cl}/^{37}\text{Cl}$ ) = 1.20131 to corresponding fit parameter for  $^{35}\text{Cl}$ .

<sup>f</sup> Fixed to scaled value from  $C^{35}\text{Cl}_2$ .

<sup>g</sup> Kiel data [2].

<sup>h</sup> Standard deviation of the fit (only lines in cm-wavelength range).

interaction may be eliminated by an  $r_s$ -structure analysis [12] which did, however, yield no reliable results in the present study because the Cl atoms are too close to the  $a$ -axis of the molecule which imposes a rather large uncertainty of the respective  $b$ -coordinates [13]. Thus, we may conclude that the combination of the experimentally determined  $r_0$ -structure together with ab initio results of rotation–vibration interaction parameters as performed in [6] give more reliable data on a “semi-experimental”  $r_e$ -structure of dichloromethylene.

### 4.2. Nuclear quadrupole coupling

The precision of the experimental data allowed to determine not only the diagonal elements  $\chi_{gg}$  ( $g = a, b, c$ ) of the nuclear quadrupole coupling tensor

with respect to the principal inertial axes but also the off-diagonal element  $\chi_{ab}$  with high precision (see Table 1). Thus, it was also possible to determine the principal moments of the  $\chi$ -tensor by diagonalization (Table 1), as well as the angle between the  $z$ -axis of the  $\chi$ -tensor and the C–Cl bond axis. Inspection of Table 1 shows that the principal  $\chi$ -tensor elements are in excellent agreement for the  $^{35}\text{Cl}$ - as the  $^{37}\text{Cl}$ -nuclei in the investigated isotopomers and also scale according to the ratio given in Eq. (1). As for  $\text{C}^{35}\text{Cl}^{37}\text{Cl}$  [2], a significant deviation of the  $z$ -axis of the quadrupole coupling tensor from the C–Cl internuclear axis (to larger angles with respect to the bisector of the Cl–C–Cl angle) was also found in the present study. Based on the  $r_0$ -structure, these deviations are all determined to about  $(1.9 \pm 0.2)^\circ$  which is considered to be significant in view of the precision of the Cl–C–Cl bond angle. Thus, the general assumption of coincidence between the principal axis  $z$  of the  $\chi$ -tensor and the internuclear axis for terminally bonded atoms with a quadrupole nucleus no longer holds strictly in the present case.

#### 4.3. Nuclear spin–rotation coupling and nuclear magnetic shielding

Although the effects of nuclear spin–rotation coupling are about two orders of magnitude smaller than those of nuclear quadrupole coupling, they could also be determined from the significant line shifts (up to about 60 kHz) of the quadrupole components (see Table 1). In particular, compared to other molecules with terminal Cl atoms like  $\text{SOCl}_2$  [14] and  $\text{SCl}_2$  [15], the  $C_{aa}$

constant for all  $\text{CCl}_2$  isotopomers is significantly larger (about one order of magnitude). Similar findings for the fluorine spin–rotation coupling constant of  $\text{CF}_2$  [3] may indicate that low-lying electronic states in these carbenes play an important role for this magnetic hyperfine interaction.

According to Flygare [16], the spin–rotation coupling constants can be written as the sum of an electronic and a nuclear contribution,  $C_{gg} = C_{gg}(\text{el}) + C_{gg}(\text{nuc})$ , the latter being determined from the molecular geometry. Thus, using the  $r_0$ -structural data, the values of  $C_{gg}(\text{nuc})$  could be determined to high precision and were subsequently used together with the experimental results for  $C_{gg}$  to determine the electronic contributions  $C_{gg}(\text{el})$ . The results are summarized in Table 2.

The electronic contributions  $C_{gg}(\text{el})$  are directly related to the diagonal elements of the paramagnetic shielding tensor  $\sigma(\text{p})$  of the chlorine nucleus [16] since they have the same dependence on the molecular geometry and electronic states. The resulting values are also given in Table 2, including the average paramagnetic shielding  $\sigma_{\text{av}}(\text{p}) = (1/3) \sum_g \sigma_{gg}(\text{p})$ . It should be interesting to obtain chlorine magnetic shielding tensor elements  $\sigma_{gg}$  which contain also a diamagnetic contribution  $\sigma_{gg}(\text{d})$  ( $\sigma_{gg} = \sigma_{gg}(\text{p}) + \sigma_{gg}(\text{d})$ ). These values are directly related to the chemical shifts of Cl NMR signals for dichloromethylene which, to our knowledge, have not been measured so far. The components of  $\sigma(\text{d})$  were evaluated theoretically using the atom dipole model of Gierke and Flygare [17] which, in addition to the molecular geometry, requires data on the chlorine free atom diamagnetic shielding constant  $\sigma(\text{d}; \text{free})$ .

Table 2

Chlorine nuclear spin–rotation interaction constants and derived nuclear magnetic shielding constants for  $\text{CCl}_2$  isotopomers

	$\text{C}^{35}\text{Cl}_2$	$\text{C}^{35}\text{Cl}^{37}\text{Cl}$ ( $^{35}\text{Cl}$ )	$\text{C}^{35}\text{Cl}^{37}\text{Cl}$ ( $^{37}\text{Cl}$ )	$\text{C}^{37}\text{Cl}_2$
$C_{aa}$ (kHz)	58.2(3)	59.9(19)	49.9(16)	43.9(9)
$C_{bb}$ (kHz)	2.8(1)	3.5(5)	2.9(4)	1.7(3)
$C_{cc}$ (kHz)	1.4(1)	1.4(1)	1.2(1)	1.2(1)
$C_{aa}(\text{nuc})$ (kHz)	−0.49	−0.50	−0.41	−0.41
$C_{bb}(\text{nuc})$ (kHz)	−0.26	−0.25	−0.21	−0.21
$C_{cc}(\text{nuc})$ (kHz)	−0.28	−0.27	−0.22	−0.22
$C_{aa}(\text{el})$ (kHz)	58.7(3)	60.4(19)	50.3(16)	44.3(9)
$C_{bb}(\text{el})$ (kHz)	3.1(1)	3.8(5)	3.1(4)	1.9(3)
$C_{cc}(\text{el})$ (kHz)	1.7(1)	1.7(1)	1.4(1)	1.4(1)
$\sigma_{aa}(\text{p})$ (ppm)	−1958(10)	−2023(64)	−2024(64)	−1790(36)
$\sigma_{bb}(\text{p})$ (ppm)	−1388(45)	−1750(233)	−1742(224)	−1109(173)
$\sigma_{cc}(\text{p})$ (ppm)	−817(49)	−835(150)	−856(120)	−857(123)
$\sigma_{\text{av}}(\text{p})$ (ppm)	−1388(22)	−1536(95)	−1541(87)	−1252(72)
$\sigma_{aa}(\text{d})$ (ppm)	1162	1162	1162	1162
$\sigma_{bb}(\text{d})$ (ppm)	1255	1255	1255	1255
$\sigma_{cc}(\text{d})$ (ppm)	1268	1268	1268	1268
$\sigma_{\text{av}}(\text{d})$ (ppm)	1228	1228	1228	1228
$\sigma_{aa}$ (ppm)	−796(10)	−861(64)	−862(64)	−628(36)
$\sigma_{bb}$ (ppm)	−133(45)	−494(233)	−487(224)	146(173)
$\sigma_{cc}$ (ppm)	451(49)	433(150)	412(120)	411(123)
$\sigma_{\text{av}}$ (ppm)	−159(22)	−307(95)	−312(87)	−23(72)

Uncertainties in parentheses correspond to  $1\sigma$  standard deviation.

atom) as well as on the average squared electronic distance  $\langle \rho^2 \rangle_n$  from each nucleus  $n$  in the molecule. A theoretical value for the free atom contribution ( $\sigma(\text{d}; \text{chlorine free atom}) = 1138 \text{ ppm}$ ) was taken from Hartree–Fock calculations of Malli and Fraga [18], and the values for  $\langle \rho^2 \rangle_{\text{C}}$  ( $= 1.288 \times 10^{-16} \text{ cm}^2$ ) and  $\langle \rho^2 \rangle_{\text{Cl}}$  ( $= 2.581 \times 10^{-16} \text{ cm}^2$ ) were derived from theoretical values for the corresponding diamagnetic susceptibilities of the neutral atoms given in [19]. No errors have been given for the resulting diamagnetic shielding constants in Table 2, which includes also the average diamagnetic shielding,  $\sigma_{\text{av}}(\text{d}) = (1/3) \sum_g \sigma_{gg}(\text{d})$ , since it is difficult to estimate the errors made in the theoretical calculations. Accordingly, the resulting chlorine shielding constants are only given with errors resulting from the uncertainties of the experimentally determined spin–rotation interaction constants. In view of these rather large errors, the results for the shielding tensor elements of the different isotopomers of dichloromethylene are in fair agreement.

#### Appendix A. Supplementary data

Supplementary data for this article are available on ScienceDirect ([www.sciencedirect.com](http://www.sciencedirect.com)) and as part of the Ohio State University Molecular Spectroscopy Archives ([http://msa.lib.ohio-state.edu/jmsa\\_hp.htm](http://msa.lib.ohio-state.edu/jmsa_hp.htm)).

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