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Note

# Microwave spectra of the $^{35}Cl$ and $^{37}Cl$ 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 $C^{35}Cl^{37}Cl$ and $C^{37}Cl_2$ of dichloromethylene in the ground vibronic state were recorded in the range 10–33 GHz using a molecular beam Fourier transform microwave spectrometer. $CCl_2$ 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 $C^{35}Cl_2$ [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 $^{35}Cl$ and $^{37}Cl$ principal inertial axis nuclear magnetic shielding components which have not yet been determined by NMR spectroscopy.


*Keywords:* Dichloromethylene; $CCl_2$; Rotational spectra; MB-FTMW spectroscopy; Cl nuclear quadrupole and spin–rotation coupling; Cl magnetic shielding

## 1. Introduction

The purpose of this note is to report the results of an investigation of the rotational spectra of the isotopomers $C^{35}Cl^{37}Cl$ and $C^{37}Cl_2$ of dichloromethylene in the ground vibronic state. This study extends previous microwave spectroscopic investigations on the most abundant species, $C^{35}Cl_2$, which have yielded structural information and $^{35}Cl$ 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 $CF_2$ [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 $CCl_2$ vibronic bands [4] allow to estimate this singlet-triplet gap to about 14 kcal mol$^{-1}$ which is in fair agreement with the most recent theoretical calculation [5].

Theoretical calculations of rovibrational and structural parameters of $C^{35}Cl_2$ 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 $CCl_2$ reported in this note.

## 2. Experimental

The spectra of $CCl_2$ 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 $C^{35}Cl^{37}Cl$, we employed the flash pyrolysis method as described in [3] for the generation of $C^{35}Cl_2$, using dibromodichloromethane ($CBr_2Cl_2$) or dichloroacetylchloride ($CHCl_2COCl$) as precursors. As observed previously for $C^{35}Cl_2$ (relative abundance ca. 57%), the latter precursor yielded somewhat stronger spectra for $C^{35}Cl^{37}Cl$ (relative abundance ca. 37%) as well, and the resulting spectrum could be readily assigned.

In case of $C^{37}Cl_2$, 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 $CCl_2$ 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 ($(CH_3)_3SiCCl_3$) 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 rotationally 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 °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 μs duration with a power of about 3 mW. After a time of typical 10 μs which allowed the excitation pulse to decay, the transient emission signal was recorded for 160 μs 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 $C^{37}Cl_2$) 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 $C^{35}Cl_2$ [2] were used for a prediction of the range of expected rotational transitions of $C^{35}Cl^{37}Cl$ and $C^{37}Cl_2$, respectively. Because of the aforementioned assignment problems for the less abundant species $C^{37}Cl_2$, 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 $^{37}Cl$ according to the ratios

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

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

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

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