The Rotational Spectrum and Nuclear Quadrupole Coupling of $CH^{35}ClF_2$

Susana Blanco[a], Alberto Lesarri[a], Juan C. López[a], José L. Alonso, and Antonio Guarnieri[b]

[a] Departamento de Química Física, Facultad de Ciencias, Universidad de Valladolid, E-47005 Valladolid
[b] Institut für Physikalische Chemie der Universität Kiel, Olshausenstr. 40, D-25098 Kiel

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The rotational spectrum of $CH^{35}ClF_2$ in the ground vibrational state has been measured in the frequency range 8–18 GHz using a waveguide Fourier transform microwave (FTMW) spectrometer in order to determine accurate nuclear quadrupole coupling constants. The spectra of the excited vibrational states $v_5 = 1$, $v_6 = 1$ and $v_9 = 1$ have been also observed and analyzed in the frequency region 8–250 GHz using FTMW, Stark, and source modulation spectrometers. Quadrupole coupling constants are also reported for these states.

Introduction

Chlorodifluoromethane ($CHClF_2$, CDFM) is an hydrochlorocarbon (HCFC-22) which is used as replacement for CFC-11 (CCl_3F) and CFC-12 (CCl_2F_2) in refrigeration and in the production of fluoropolymers. Due to its atmospheric lifetime, CDFM may take part in the ozone layer depletion. For this reason the laboratory study of this compound is of great interest for monitoring it in the atmosphere. In the past two years several European laboratories have been working on the analysis of the rotation and vibration-rotation spectra of CDFM within the frame of the SCAMP network. The results presented in this paper are part of this effort.

The rotational spectrum of CDFM has been studied by several authors [1–6]. Cramb et al. [3] studied the spectra of $CH^{35}ClF_2$, $CH^{37}ClF_2$, $CD^{35}ClF_2$ and $CD^{37}ClF_2$ in the frequency range 8–60 GHz and reported the rotational, quartic centrifugal distortion, and quadrupole coupling constants for these species. The spectra of $CH^{35}ClF_2$ in the millimeter-wave range was later measured by Spiehl et al. [4] and in the submillimeter-wave region by Cazzoli et al. [5], resulting in an accurate set of rotational, quartic and sextic centrifugal distortion constants for this isotopomer. High resolution infrared studies have resulted in the determination of the rotational constants of several vibrationally excited states [7–9]. Very recently, and as a result of the work on CDFM within the SCAMP network, two studies on the millimeter-wave [6] and infrared spectra [9] have reported the analysis of a Coriolis interaction between the two lowest excited vibrational states of $CH^{35}ClF_2$. The spectra of the states $v_9 = 1$ and $v_6 = 1$ were assigned in our laboratory using the Stark modulation spectrometer at the same time as they were assigned in the millimeter-wave region by Kisiel et al. [6].

In this work we have investigated the microwave spectra of $CH^{35}ClF_2$ in the ground and low-lying vibrational excited states by means of Fourier transform microwave spectroscopy in order to obtain precise quadrupole coupling constants of these states.

1. Experimental

The sample of CDFM was obtained from Aldrich and was used without further purification. Three different spectrometers have been used depending on the frequency range investigated. A computer-controlled Stark modulation spectrometer [10–11] was used to measure transitions between 26.5 and 72 GHz with sample pressures below 30 mTorr at about 260 K. Measurements in the range 80–250 GHz were carried out using a computer-controlled source modulation spectrometer [12]. With this spectrometer experiments were made at room temperature and pressures below 30 mTorr. A waveguide Fourier transform microwave spectrometer (FTMW) recently constructed [13] was used to measure the quadrupole hyperfine structure of transitions in the frequency range between 8 and

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Reprint requests to Prof. Dr. A. Guarnieri.

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18 GHz. Sample pressures down to 0.1 mTorr and temperatures of about 230 K were used for the FTMW experiments. The estimated accuracy of the frequency measurements is 10 kHz for the FTMW spectrometer and 50 kHz for the CW spectrometers. In cases of non resolved hyperfine components the accuracy is lower and in the worst cases may reach values of 100 kHz. Lists of the observed frequencies have been deposited by the University Library in Kiel under the number TNA 35 and can be obtained from the authors (JLA, AG) on request.

2. Results and Discussion

2.1 Ground State Spectrum

Measurements of the ground state spectrum of $^{12}CH^{35}ClF_2$ were carried out in the frequency range 8–18 GHz using a FTMW spectroscopy. ^cQ and ^cR type transitions up to $J = 60$ were observed. Predictions for these lines were based on the rotational and quadrupole coupling parameters previously obtained [3–5]. The central frequencies were first analyzed together with those previously reported [3–5] to the A reduced semirigid rotor Hamiltonian of Watson [14] in the I^r representation. The resulting rotational, quartic and sextic centrifugal distortion constants are collected in Table 1. Subsequently all the observed quadrupole hyperfine components were analyzed by direct diagonalization using the program CALPGM written by Pickett [15]. In this analysis the rotational and centrifugal distortion constants were held fixed to the previously determined values in order to obtain the quadrupole coupling constants. Due to the C_s-symmetry of $CHClF_2$ there is only one non zero off diagonal quadrupole coupling constant χ_{ac}, and it was included in the fit. The resulting quadrupole coupling parameters are shown in Table 2. No transitions strongly perturbed by $|\chi_{ac}|$ have been observed, and this off-diagonal element is poorly determined. To transform the coupling tensor in its own principal axis system, a rotation of an angle $\theta_{z,a}$ around the b principal axis had to be performed. The coupling constant χ_{bb} is the equal of one of the diagonal values, say χ_{yy}. The χ_{zz} and χ_{xx} elements can not be calculated to great accuracy, and the value of the asymmetry parameter, η, is not determined (see Table 2). However, the calculated angle of the rotation in the transformation of the coupling tensor to its principal axis system ($\theta_{z,a} = 13.4(25)^\circ$) is very close to the angle between the a axis and the C–Cl bond ($\theta_a = 14.4$) [3], which indicates that the value of χ_{ac} is reliable. The magnitude of the coupling constants is typical for ^{35}Cl coupling in molecules with single bonds [16]. The values are also comparable with our recent results obtained on chlorofluoromethane [17] and 1-chloro-1-fluoroethane [18].

Table 1. Results of the fit of the central frequencies (this work and [3–5]) for the ground state of $CH^{35}ClF_2$ to the A-reduced semirigid rotor Hamiltonian of Watson [14] in the I^r axis representation.

A	/MHz	10234.70311 (28)[a]
B	/MHz	4861.25340 (13)
C	/MHz	3507.43791 (10)
Δ_J	/kHz	1.566355 (72)
Δ_{JK}	/kHz	4.59131 (25)
Δ_K	/kHz	4.92139 (21)
δ_J	/kHz	0.44098 (18)
δ_K	/kHz	5.01468 (26)
Φ_J	/Hz	0.0007021 (50)
Φ_{JK}	/Hz	0.010030 (78)
Φ_{KJ}	/Hz	−0.001026 (25)
Φ_K	/Hz	0.002956 (20)
ϕ_J	/Hz	0.003278 (18)
ϕ_{JK}	/Hz	0.005418 (46)
ϕ_K	/Hz	0.09155 (32)
N[b]		362
RMS		0.136

[a] Estimated errors in parentheses are given in units of the last digit.
[b] Number of central frequencies fitted.

Table 2. Quadrupole coupling constants for the ground state of $CH^{35}ClF_2$.

χ_{aa}	/MHz	−65.0239 (65)[a]
$\chi_{bb} - \chi_{cc}$	/MHz	5.911 (15)
χ_{ac}	/MHz	24.0 (5)
N[b]		369
RMS		0.016
χ_{bb}	/MHz	35.467 (14)
χ_{cc}	/MHz	29.556 (14)
χ_{zz}	/MHz	−70.8 (25)
χ_{xx}	/MHz	35.3 (25)
χ_{yy}	/MHz	35.467 (14)
η[c]		0.0024 (390)
$\theta_{z,a}$[d]		13.4 (25)
θ_a[e]		14.4

[a] Estimated errors in parentheses are given in units of the last digit.
[b] Number of analyzed quadrupole components.
[c] $\eta = (\chi_{xx} - \chi_{yy})/\chi_{zz}$ is the asymmetry parameter of the quadrupole coupling tensor.
[d] $\theta_{z,a}$ is the angle between the a and z axis.
[e] θ_a is the angle between the a axis and the C-Cl bond [3].

2.2 *Excited States Spectra*

The spectra of the excited states $v_9 = 1$ (366.2 cm^{-1} [9]) and $v_6 = 1$ (412.9 cm^{-1} [9]) which present the effects of a Coriolis coupling between them [6, 9] and of $v_5 = 1$ (596.4 cm^{-1} [7]) of $^{12}CH^{35}ClF_2$ have also been investigated. For the two former states we have measured *c*-type spectra up to $J = 42$. In order to determine the quadrupole coupling constants for these states we have analyzed the measured data in several steps. In a first stage we have fitted the central frequencies to the same two-state Hamiltonian as used in [6] and [9] using Pickett's program [15]. We have used as initial values for the fit the parameters given in [6] and [9]. When these parameters were fixed, the high-*J* transitions measured in this work showed significant deviations which were still larger when the parameter of [9] were used. For this reason it was decided to allow the variation of all the parameters in the fit within the errors quoted in these papers [6, 9]. This way good fits were obtained. As an example, the results of the fit obtained using the parameters of [6] are collected in Table 3. The diagonal elements of the quadrupole coupling tensor were then obtained by direct diagonalization from a fit of all the resolved hyperfine components to a Hamiltonian including the corresponding quadrupole coupling operators. The results are also shown in Table 3. Considering three times the estimated errors, the quadrupole coupling constants χ_{aa} and χ_{bb} result to be different for both states, and compared with those obtained for the ground state (see Table 2) appear to be shifted in opposite senses.

Table 3. Results of the fit of the central frequencies observed in this work for the $v_9 = 1$ and $v_6 = 1$ excited vibrational states of $CH^{35}ClF_2$ (see text). The lower part of the Table presents the results of the analysis of the hyperfine components.

		$v_9 = 1$	$v_6 = 1$
A	/MHz	10259.17253 (79)[a]	10233.91668 (80)
B	/MHz	4858.56190 (16)	4857.86390 (17)
C	/MHz	3500.608 (42)	3501.970 (41)
Δ_J	/kHz	1.559915 (70)	1.595508 (77)
Δ_{JK}	/kHz	4.46068 (56)	4.61030 (61)
Δ_K	/kHz	5.20321 (56)	4.90650 (56)
δ_J	/kHz	0.447887 (21)	0.446874 (26)
δ_K	/kHz	5.2696 (12)	4.8872 (12)
Φ_J	/Hz	0.0006691 (69)	0.0007849 (89)
Φ_{JK}	/Hz	0.019587 (76)	0.002117 (45)
Φ_{KJ}	/Hz	−0.00955 (25)	[0.][b]
Φ_K	/Hz	0.00518 (24)	0.0075100 (27)
ϕ_J	/Hz	0.0003250 (22)	0.000379 (20)
ϕ_{JK}	/Hz	0.009576 (46)	0.00184 (23)
ϕ_K	/Hz	0.11456 (25)	0.07709 (32)
ΔE	/MHz	14900971.38 (26)	
G[c]	/MHz	4755.0 (6)	
F[c]	/MHz	−12.486 (30)	
F[a]	/MHz	465.4 (11)	
N[c]		204	
RMS		0.035	
χ_{aa}	/MHz	−64.952 (11)	−65.129 (15)
$\chi_{bb} - \chi_{cc}$	/MHz	5.588 (20)	6.036 (26)
N[d]		331	
RMS		0.032	
χ_{bb}	/MHz	35.270 (25)	35.583 (31)
χ_{cc}	/MHz	29.682 (25)	29.547 (31)

[a] Estimated errors in parentheses are given in units of the last digit.
[b] Fixed.
[c] Number of fitted central frequencies.
[d] Number of analyzed quadrupole components.

Table 4. Results of the fit of the observed hyperfine components for the $v_5 = 1$ excited vibrational state of $CH^{35}ClF_2$.

A	/MHz	10206.49095 (62)[a]
B	/MHz	4860.92387 (29)
C	/MHz	3507.08263 (21)
Δ_J	/kHz	1.57191 (24)
Δ_{JK}	/kHz	4.58153 (90)
Δ_K	/kHz	4.84086 (56)
δ_J	/kHz	0.442422 (45)
δ_K	/kHz	4.99097 (13)
Φ_J	/Hz	0.0007021[b]
Φ_{JK}	/Hz	0.010030[b]
Φ_{KJ}	/Hz	−0.001026[b]
Φ_K	/Hz	0.002956[b]
ϕ_J	/Hz	0.0003278[b]
ϕ_{JK}	/Hz	0.005418[b]
ϕ_K	/Hz	0.09155[b]
χ_{aa}	/MHz	−64.995 (16)
$\chi_{bb} - \chi_{cc}$	/MHz	6.220 (28)
N[c]		482
RMS		0.047
χ_{bb}	/MHz	35.607 (36)
χ_{cc}	/MHz	29.389 (36)

[a] Estimated errors in parentheses are given in units of the last digit.
[b] Fixed to the ground state values.
[c] Number of analyzed quadrupole components.

The rotational spectrum of the $v_5 = 1$ state was assigned in the Stark modulation spectrometer using the spectroscopic constants reported by Gambi et al. [7] on the basis of quadrupole hyperfine structure and intensity patterns. *c*-type transitions up to $J = 60$ were measured for this state. The observed hyperfine components were fitted by direct diagonalization to the same Hamiltonian as used for the ground vibrational state but including only the diagonal elements of the quadrupole coupling tensor. The sextic centrifugal distortion constants were in this case fixed to the values obtained for the ground state. The results of the fit are collected in Table 4. For this state the obtained quadrupole coupling constants seem also to be slightly different from those found for the ground state.

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