The Centimeter and Millimeter Microwave Spectrum of 1,1-Difluoro-2-Chloroethylene

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The rotational spectra of both ^{35}Cl and ^{37}Cl 1,1-difluoro-2-chloroethylene isotopomers have been measured in the frequency range 12–225 GHz. A first order quadrupole coupling analysis has been performed for both isotopic species. The calculated quadrupole coupling constants for the ^{37}Cl species not previously reported are $\chi_{aa} = -49.2$ (2), $\chi_{bb} = 14.2$ (1), and $\chi_{cc} = 28.7$ (1). Accurate rotational constants, quartic and some sextic centrifugal distortion constants have also been determined for both isotopomers from the fit to the observed central frequencies.

Introduction

The microwave spectrum of 1,1-difluoro-2-chloroethylene was first studied by Jenkins and Sugden [1] in the frequency range below 26.5 GHz. For the ^{35}Cl species they report the rotational and quadrupole coupling constants determined from the analysis of several R and Q-branch transitions. However for the ^{37}Cl isotopomer they could not resolve the quadrupole coupling structure and gave a set of rotational constants determined from a series of Q-branch lines and only one R-branch transition. A further investigation of the $F_2C=CH^{35}Cl$ spectrum in the centimeter wave range was performed by Stone and Flygare [2] to determine the off-diagonal element χ_{ab} of the nuclear quadrupole coupling tensor from the analysis of second order effects.

In the present work the centimeter and millimeter-wave spectra of both $F_2C=CH^{35}Cl$ and $F_2C=CH^{37}Cl$ have been investigated to determine accurate rotational and centrifugal distortion constants as well as the quadrupole coupling constants for the ^{37}Cl isotopomer.

Experimental Details

The sample of 1,1-difluoro-2-chloroethylene was obtained from Fluorochem Ltd. and was used without further purification. The spectra of the ^{35}Cl and ^{37}Cl isotopomers were observed in natural abundance at 260 K and room temperature. Lines in the frequency range 12–54 GHz were measured using centimeter and millimeter Stark modulation spectrometers described elsewhere [3, 4]. The source used for the 37.2 –54 GHz region was a 12.4–18 GHz BWO followed by a Spacek Labs. Q-3K Frequency tripler. Measurements in the 80–255 GHz were performed using a source modulated computed controlled millimeter-wave spectrometer [5]. The estimated accuracy of frequency measurements is better than 30 kHz.

Analysis of the Spectrum

1,1-difluoro-2-chloroethylene is a prolate asymmetric rotor ($\varkappa \approx -0.9$) with the dipole moment mainly oriented along *b* inertial axis [1]. The low-*J* ^{b}R and ^{b}Q rotational transitions of $F_2C=CH^{35}Cl$ were easily assigned and measured from a prediction of the spectrum using the rotational and ^{35}Cl quadrupole coupling constants previously reported [1, 2]. After these initial measurements the assignment of the spectrum for higher values of *J* was continued for the R, Q and P-branch on the basis of the Stark patterns and the predicted quadrupole coupling structure. Centrifugal distortion constants were allowed to vary in the intermediate fits as *J* was increased. A total of 178 transitions up to $J = 60$ with their corresponding quadrupole coupling components have been measured.

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Table 1. Qudrupole coupling constants for the ^{35}Cl and ^{37}Cl isotopomers of 1,1-difluoro-2-chloroethylene.

	^{35}Cl	^{37}Cl
χ_{aa}/MHz	−54.81 (8)[a]	−42.9 (2)
χ_{bb}/MHz	18.18 (4)	14.2 (1)
χ_{cc}/MHz	36.63 (6)	28.7 (1)
σ_s[b]/MHz	0.033	0.042

[a] Standard errors in parenthesis in units of the last digit.

[b] Standard deviation of the quadrupole fit.

Table 2. A selection of observed quadrupole coupling components (MHz) used in the quadrupole coupling analysis, and differences between observed and calculated values for $F_2C=CH^{35}Cl$.

Transition	F_u	F_l	Obs. freq.	Obs.-calc.
1 (1, 1) − 0 (0, 0)	1/2 −	3/2	12 596.320	−0.002
	3/2 −	3/2	12 604.510	0.005
	5/2 −	3/2	12 599.970	0.011
2 (2, 0) − 2 (1, 1)	5/2 −	5/2	25 268.010	0.016
	7/2 −	7/2	25 249.660	0.012
4 (2, 2) − 4 (1, 3)	5/2 −	5/2	24 055.350	−0.013
	7/2 −	7/2	24 059.730	0.015
	9/2 −	9/2	24 061.270	0.029
5 (2, 4) − 5 (1, 5)	7/2 −	7/2	28 952.380	0.006
	9/2 −	9/2	28 958.880	0.020
	11/2 −	11/2	28 960.720	0.031
	13/2 −	13/2	28 954.210	0.007
5 (1, 5) − 4 (0, 4)	13/2 −	11/2	26 619.750	−0.007
	11/2 −	9/2	26 619.110	−0.017
	9/2 −	7/2	26 618.350	0.015
5 (0, 5) − 4 (1, 4)	7/2 −	5/2	13 893.000	0.004
	9/2 −	7/2	13 892.690	0.036
	11/2 −	9/2	13 893.570	0.050
	13/2 −	11/2	13 893.870	0.008
6 (1, 6) − 5 (0, 5)	15/2 −	13/2	29 762.210	0.009
	13/2 −	11/2	29 761.360	0.011
	11/2 −	9/2	29 760.910	0.016
	9/2 −	7/2	29 761.730	−0.016
8 (4, 4) − 7 (3, 5)	13/2 −	11/2	93 824.630	0.006
	15/2 −	13/2	93 827.130	0.000
	17/2 −	15/2	93 827.760	0.011
	19/2 −	17/2	93 825.260	0.017
13 (2, 12) − 13 (1, 13)	23/2 −	23/2	45 077.490	0.020
	25/2 −	25/2	45 080.560	0.028
	27/2 −	27/2	45 080.870	−0.004
	29/2 −	29/2	45 077.800	−0.012
13 (1, 13) − 12 (0, 12)	23/2 −	21/2	52 131.980	0.066
	27/2 −	25/2	52 131.710	0.023

Table 3. A selection of observed quadrupole coupling components (MHz) used in the quadrupole coupling analysis, and differences between observed and calculated values for $F_2C=CH^{37}Cl$.

Transition	F_u	F_l	Obs. freq.	Obs.-calc.
7 (2, 6) − 7 (1, 7)	11/2 −	11/2	31 558.370	0.010
	13/2 −	13/2	31 562.000	0.032
	15/2 −	15/2	31 562.780	0.077
	17/2 −	17/2	31 559.120	0.026
8 (2, 7) − 7 (1, 6)	13/2 −	11/2	53 269.230	0.066
	15/2 −	13/2	53 268.700	0.054
	17/2 −	15/2	53 268.700	−0.065
	19/2 −	17/2	53 269.230	−0.053
8 (4, 4) − 7 (3, 5)	13/2 −	11/2	93 330.950	0.022
	15/2 −	13/2	93 332.920	0.032
	17/2 −	15/2	93 333.440	0.068
	19/2 −	17/2	93 331.440	0.027
10 (3, 8) − 10 (2, 9)	17/2 −	17/2	44 963.050	0.035
	23/2 −	23/2	44 963.310	0.018
11 (3, 8) − 10 (2, 9)	19/2 −	17/2	90 822.490	0.059
	23/2 −	21/2	90 824.510	−0.058
	25/2 −	23/2	90 822.790	0.001
12 (1, 12) − 11 (0, 11)	21/2 −	19/2	47 765.310	0.022
	23/2 −	21/2	47 765.000	0.074
	25/2 −	23/2	47 765.000	−0.015
	27/2 −	25/2	47 765.310	−0.067
14 (3, 12) − 14 (2, 13)	27/2 −	27/2	48 644.240	0.083
	29/2 −	29/2	48 644.240	−0.075
	31/2 −	31/2	48 642.740	−0.052
15 (3, 13) − 15 (2, 14)	31/2 −	31/2	50 035.330	−0.039
	33/2 −	33/2	50 033.860	−0.016
18 (2, 16) − 17 (3, 15)	33/2 −	31/2	51 179.390	0.035
	35/2 −	33/2	51 180.050	0.032

Table 4. A selection of the observed central frequencies (MHz) for $F_2C=CH^{35}Cl$. Differences between the observed frequencies and those calculated from the constants of Table 8 are given together with the calculated quartic and sextic contributions.

Transition						Obs.	Obs.-calc.	P4 term	P6 term
49	15	35	50	14	36	36 215.090	−0.043	−144.228	−0.393
50	15	36	51	14	37	31 721.190	0.005	−144.035	−0.417
51	15	37	52	14	38	27 209.910	0.001	−143.589	−0.442
54	7	47	54	6	48	91 718.310	−0.036	−270.124	0.306
53	16	38	54	15	39	36 220.020	−0.001	−176.145	−0.566
54	16	39	55	15	40	31 718.340	0.000	−175.794	−0.598
56	13	44	56	12	45	208 249.980	−0.023	−382.416	−0.525
56	13	43	56	12	44	208 237.340	−0.043	−382.189	−0.526
55	16	40	56	15	41	27 200.210	0.003	−175.165	−0.629
57	12	46	56	13	43	33 504.960	0.002	63.065	0.371
57	12	45	56	13	44	33 526.170	0.009	62.670	0.372
58	13	46	58	12	47	207 151.600	−0.003	−402.401	−0.570
58	13	45	58	12	46	207 123.550	0.060	−401.886	−0.572
57	17	41	58	16	42	36 216.320	0.011	−212.378	−0.795
59	8	51	59	7	52	90 975.910	0.019	−304.325	0.389
58	17	42	59	16	43	31 707.730	0.004	−211.847	−0.836
60	8	53	59	9	50	94 421.760	0.012	199.962	−0.777
60	13	48	59	14	45	28 612.810	−0.001	87.822	0.518
60	13	47	59	14	46	28 618.090	−0.012	87.700	0.518
59	17	43	60	16	44	27 183.490	−0.001	−211.013	−0.876

Initial predictions of the microwave spectrum of $F_2C=CH^{37}Cl$ were performed using the rotational constants reported by Jenkins and Sugden [1] for this isotopomer. We also used the ^{35}Cl quadrupole coupling constants corrected by a factor equal to the quadrupole coupling ratio (^{35}Cl/^{37}Cl) [6] which is approximately obeyed by the quadrupole coupling tensor elements in related molecules [7]. The ^{b}Q transi-

Table 5. A selection of the observed central frequencies (MHz) for $F_2C=CH^{37}Cl$. Differences between the observed frequencies and those calculated from the constants of Table 8 are given together with the calculated quartic and sextic contributions.

Transition						Obs.	Obs.-calc.	P4 term	P6 term
48	14	35	49	13	36	30 004.970	−0.013	−116.028	−0.351
51	13	39	51	12	40	212 350.620	0.003	−324.819	−0.441
51	14	38	52	13	39	16 764.400	0.023	−113.150	−0.408
58	9	49	58	8	50	102 956.740	0.009	−106.174	−0.351
58	13	46	58	12	47	209 402.170	−0.009	−392.790	−0.594
58	13	45	58	12	46	209 387.680	0.049	−392.512	−0.595
58	12	47	57	13	44	29 506.950	0.005	61.361	0.415
58	12	46	57	13	45	29 523.210	0.005	61.044	0.416
57	16	42	58	15	43	26 766.980	−0.005	−174.040	−0.757
59	13	47	58	14	44	14 884.910	0.011	95.100	0.541
59	13	46	58	14	45	14 886.580	0.016	95.061	0.541
60	8	52	60	7	53	88 894.740	−0.008	−287.882	0.342
59	16	44	60	15	45	17 909.550	−0.003	−170.914	−0.823
59	17	43	60	16	44	36 137.350	−0.001	−211.982	−0.961

Table 6. Results of the fit considering the observed central frequencies of $F_2C=CH^{35}Cl$ for transitions up to $J=40$ after the *A* reduced Hamiltonian of Watson [9] up to quartic terms for the three possible representations

	I^r	II^r	III^r
A/MHz	10 710.737 (1)[a]	10 710.738 (1)	10 710.737 (1)
B/MHz	2 297.1873 (3)	2 297.1742 (3)	2 297.1900 (3)
C/MHz	1 890.1462 (3)	1 890.1586 (3)	1 890.1435 (3)
Δ_J/kHz	0.3485 (2)	6.271 (5)	6.391 (4)
Δ_{JK}/kHz	4.0781 (9)	−13.69 (1)	−14.05 (1)
Δ_K/kHz	7.882 (9)	7.889 (9)	7.888 (9)
δ_J/kHz	0.05990 (4)	−3.021 (2)	2.961 (2)
δ_K/kHz	2.597 (2)	3.643 (4)	−4.009 (5)
N[b]	115.	115.	115.
J_{max}	40.	40.	40.
σ[c]/MHz	0.030	0.031	0.030

[a] Standard errors in parenthesis in units of the last digit.
[b] Number of fitted transitions.
[c] Standard deviation of the fit.

Largest correlation coefficient 0.94 between B/C and B/Δ_J for the I^r-representation. For the representations II^r and III^r correlation coefficients near 1 for Δ_J, Δ_{JK}, Δ_K, δ_J each with Δ_{JK}, Δ_K, δ_J, δ_K.

tions were identified but it was not possible to assign the R-branch spectrum. With the available data the rotational constants were calculated using only one R-branch transition, the $7_{0.7} \leftarrow 6_{1.6}$ for which the reported mean was 22 561.1 MHz [1]. A misassignment of this line could have caused erroneous values for the rotational constants. From our measured Q-branch lines values of $A-C = 8864.70$ MHz and $\varkappa = -0.9128$ were calculated. Giving the orientation of the *a* inertial axis [2] a very small change in the *A* rotational constants would be expected upon isotopic substitution on the Cl atom. Thus using the value of this constant determined for the ^{35}Cl isotopomer and the constants $A-C$ and $\varkappa$, B and C were calculated. Using these new constants we were able to assign the R-branch on the basis of the Stark and quadrupole coupling patterns. The calculated mean frequency for the $7_{0.7} \leftarrow 6_{1.6}$ transition gets a value of 22 552.17 MHz, a value which is 9 MHz lower than the frequency reported by Jenkins and Sudgen [1]. Using the same procedure as for the ^{35}Cl isotopomer, the assignment of the spectrum for higher values of J in the R, Q and P-branch was performed up to $J = 60$. A total of 170 transitions and their quadrupole coupling components have been measured.

The first order quadrupole coupling analysis has been followed for both the ^{35}Cl and ^{37}Cl isotopomers [8]. A total of 100 quadrupole coupling components have been fitted for both cases. The resulting quadrupole coupling constants are given in Table 1. A selection of the measured quadrupole coupling component frequencies included in the analysis as well as the differences with the calculated values are collected in Table 2 for ^{35}Cl, and Table 3 for ^{37}Cl. A complete set of measured frequencies can be obtained from the authors (JLA) on request.

The centrifugal distortion analysis has been performed using the calculated central frequencies. Selection of some of them for the observed transitions with high values of J, for both isotopomers, are collected on Tables 4 and 5. As a first step in the centrifugal distortion analysis the spectra of both isotopomers up to $J = 40$ have been fitted to the *A* and *S* reduced Watson semirigid rotor Hamiltonians [9] using only quartic terms in the three right handed representations. These fits have been performed in order to see if there is any dependence of the standard deviation of the fit on the representation and reduction used, and which is the best Hamiltonian to determine the quartic centrifugal distortion constants [10]. The conclusions of this first analysis are the same for both isotopomers, so we present here the results for ^{35}Cl only. Table 6 gives the results obtained for the *A* reduced Hamiltonian, and Table 7 those for the *S* reduced Hamiltonian. It can be observed that the quality of the fit is the same in all cases. The planarity relations for the quartic centrifugal distortion constants give values close to 0.03 MHz^2. For the *A* reduction the value of the constant Δ_K is the same in all representations, and the absolute values of the δ_J and d_1 constants for each

Table 7. Results of the fit considering the observed central frequencies of $F_2C{=}CH^{35}Cl$ for transitions up to $J = 40$ after the S reduced Hamiltonian of Watson [9] up to quartic terms.

	I^r	II^r	III^r
A/MHz	10 710 738 (1)[a]	10 710.741 (1)	10 710.741 (1)
B/MHz	2 297.1820 (3)	2 297.1842 (3)	2 297.1784 (3)
C/MHz	1 890.1514 (3)	1 890.1473 (3)	1 890.1526 (3)
D_J/kHz	0.3179 (2)	4.264 (2)	4.563 (2)
D_{JK}/kHz	4.2636 (9)	−1.653 (1)	−3.0834 (7)
D_K/kHz	7.724 (9)	−2.143 (3)	−1.251 (2)
d_1/kHz	−0.05990 (4)	3.021 (2)	−2.961 (2)
d_2/kHz	−0.01533 (1)	−1.003 (1)	−0.914 (1)
N[b]	115.	115.	115.
J_{max}	40.	40.	40.
σ[c]/MHz	0.030	0.030	0.030

[a] Standard errors in parenthesis in units of the last digit.
[b] Number of fitted transitions.
[c] Standard deviation of the fit.

Largest correlation coefficient 0.94 between B/C and B/D_J for the I^r-representation. For the representations II^r and III^r correlation coefficients near 1 for D_J, D_{JK}, D_K, d_1 each with D_{JK}, D_K, d_1, d_2.

Table 8. Final results of the fit considering the observed central frequencies of $F_2C{=}CH^{35}Cl$ and $F_2C{=}CH^{37}Cl$ after the A reduced Hamiltonian of Watson [9].

	$F_2C{=}CH^{35}Cl$	$F_2C{=}CH^{37}Cl$
A/MHz	10 710.73661 (64)[a]	10 710.70390 (64)
B/MHz	2 297.18720 (14)	2 232.28255 (13)
C/MHz	1 890.14644 (15)	1 845.97821 (14)
Δ_J/kHz	0.348727 (26)	0.334897 (24)
Δ_{JK}/kHz	4.07532 (51)	3.93470 (48)
Δ_K/kHz	7.8803 (52)	8.0278 (54)
δ_J/kHz	0.059845 (8)	0.056140 (9)
δ_K/kHz	2.6008 (14)	2.5084 (18)
Φ_{KJ}/Hz	−0.0278 (24)	−0.0280 (26)
Φ_K/Hz	0.067 (15)	0.060 (18)
ϕ_{JK}/Hz	0.00225 (39)	0.00240 (50)
σ[b]/MHz	0.028	0.027
N[c]	178.	170.

[a] Standard error in parenthesis in units of the last digit.
[b] Standard deviation of the fit.
[c] Number of fitted transitions.

Largest correlation coefficient 0.97 between δ_K/ϕ_{JK} for ^{35}Cl isotopomer and 0.96 between the same constants for ^{37}Cl.

Table 9. Final results of the fit considering the observed central frequencies of $F_2C{=}CH^{35}Cl$ and $F_2C{=}CH^{37}Cl$ after the S reduced Hamiltonian of Watson [9].

	$F_2C{=}CH^{35}Cl$	$F_2C{=}CH^{37}Cl$
A/MHz	10 710.73789 (65)[a]	10 710.70517 (63)
B/MHz	2 297.18219 (15)	2 232.27770 (13)
C/MHz	1 890.15181 (15)	1 845.98339 (13)
D_J/kHz	0.318228 (26)	0.307153 (24)
D_{JK}/kHz	4.26160 (52)	4.10445 (47)
D_K/kHz	7.7280 (52)	7.8871 (52)
d_1/kHz	−0.059851 (8)	−0.056142 (9)
d_2/kHz	−0.015356 (8)	−0.013964 (10)
H_{KJ}/Hz	−0.0293 (25)	−0.0285 (25)
H_K/Hz	0.100 (16)	0.083 (18)
h_2/Hz	0.000019 (2)	0.000015 (3)
σ[b]/MHz	0.029	0.027

[a] Standard error in parenthesis in units of the last digit.
[b] Standard deviation of the fit.

Largest correlation coefficient 0.97 between d_2/h_2 for the ^{35}Cl isotopomer and 0.96 between the same constants for ^{37}Cl.

representation are the same within three times the quoted standard errors. The combinations of determinable parameters calculated from the obtained constants are independent of the Hamiltonian used. For both the A and S reductions the I^r representation yields acceptable values of the correlation coefficients. However, for the II^r and III^r representations the determined centrifugal distortion constants are highly correlated with coefficients very close to 1. Taking into account these results we used the I^r representation in the subsequent analysis of the spectra.

When the whole set of the measured mean frequencies up to $J = 60$ were included in the fit the standard deviation of the fit was increased. To obtain fits of the same quality as those shown in Tables 6 and 7 some sextic constants where allowed to vary. The final results for both isotopomers are shown in Tables 8 for the A reduction, and 9 for the S reduction. Tables 4 and 5 show the differences between the observed and calculated reported mean frequencies as well as the quartic and sextic contributions calculated from the constants given in Table 8. The transitions reported are those with the higher contributions of sextic terms. It can be observed that these contributions are very low, and this provides an explanation of why only some sextic centrifugal distortion constants can be determined.

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[1] D. R. Jenkins and T. M. Sugden, Trans. Faraday Soc. **55,** 1473 (1959).
[2] R. G. Stone and W. H. Flygare, J. Chem. Phys., **49,** 1943 (1968).
[3] A. G. Lesarri, M. E. Charro, R. Villamañan, D. G. Lister, J. C. López, and J. L. Alonso, J. Mol. Spectrosc., **149,** 317 (1991).
[4] A. G. Lesarri, J. C. López, and J. L. Alonso, J. Mol. Struct., in press (1992).
[5] A. G. Lesarri, J. C. López, and J. L. Alonso, to be published.
[6] W. Gordy and R. L. Cook, Microwave Molecular Spectra, Wiley-Interscience, New York 1985, p. 861.
[7] T. Ogata, Bull. Chem. Soc. Japan **55,** 9 (1982).
[8] W. Gordy and R. L. Cook, Microwave Molecular Spectra, Wiley-Interscience, New York 1985, Chap. IX, pp. 391–450.
[9] J. K. G. Watson, in: Vibrational Spectra and Structure, Vol. 6 (J. R. Durig, ed.), Elsevier, Amsterdam 1977, pp. 1–89.
[10] J. H. Carpenter, J. Mol. Spectrosc. **46,** 348 (1973).