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The Chlorine Nuclear Quadrupole Coupling Tensor in Chlorotrifluoroethylene

K. W. HILLIG II, E. R. BITTNER, AND R. L. KUCZKOWSKI

Department of Chemistry, University of Michigan, Ann Arbor, Michigan 48109

W. LEWIS-BEVAN

Department of Chemistry and Biochemistry, Southern Illinois University, Carbondale, Illinois 62901

AND

M. C. L. GERRY

Department of Chemistry, The University of British Columbia, 2036 Main Mall, Vancouver, British Columbia, Canada, V6T 1Y6

The 273 hyperfine components from 56 rotational transitions of chlorotrifluoroethylene were measured with a Fourier transform microwave spectrometer. A global least-squares fit was made to the rotational constants, quartic distortion constants, and ^{35}Cl quadrupole coupling constants; the RMS deviation of the fit was 1.6 kHz. It is shown that such high-resolution measurements enable χ_{ab} to be determined without the near degeneracies usually necessary with less precise data. The principle tensor quadrupole coupling constants are $\chi_{zz} = -77.46\ (10)$, $\chi_{xx} = 38.85\ (10)$, and $\chi_{yy} = \chi_{cc} = 38.614\ (3)$ MHz. The values are comparable to other vinyl chlorides, removing some anomalies from previous studies. © 1988 Academic Press, Inc.

INTRODUCTION

The microwave spectrum of chlorotrifluoroethylene, $CF_2{=}CFCl$, was first reported by Stone and Flygare (*1*). They measured several low-*J* *Q*- and *R*-branch transitions with a Stark-modulated spectrometer and used them to evaluate the rotational constants of the ^{35}Cl isotopic species, along with a structure consistent with the limited isotopic data. The ^{35}Cl quadrupole coupling constants in the inertial axis system (χ_{aa}, χ_{bb}, and χ_{cc}) were also determined. Using this structure and the assumption that the C–Cl bond is a principal axis of the quadrupole tensor, the inertial quadrupole tensor was rotated to obtain the principal value $\chi_{zz} = -89.1$ MHz. This value was much larger than those of other vinyl halides, and the result was rationalized in terms of the bonding of the molecule. A second MW study of this compound appeared subsequently and reported a quite different assignment and rotational constants and more normal quadrupole coupling (*2*).

We were motivated initially to explore the assignment ambiguity, and also to resolve the question of the anomalous quadrupole coupling. The latter could be achieved if the complete quadrupole tensor could be determined, in particular the off-diagonal

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element χ_{ab}. This constant would permit the quadrupole tensor to be diagonalized directly without any structural assumptions. To determine χ_{ab}, however, deviations from first-order quadrupole splitting patterns must be measured. For ^{35}Cl these deviations are usually so small that in the absence of accidental near degeneracies of the correct type (see, for example Ref. (*4*)) they cannot be determined with a Stark-modulated waveguide spectrometer.

EXPERIMENTAL DETAILS

The transitions were observed with the FTMW spectrometer at the University of Michigan. This is of the Balle-Flygare type and operates in the frequency range of 6–18 GHz (*3, 5*). Both a modified Bosch 0-280-150-045 fuel injector and a Newport Research Model BV-100 pulsed gas valve were used as molecular beam sources, with orifice diameters of 0.5 and 1.0 mm. A sample of 1% $CF_2{=}CFCl$ in argon was used at a backing pressure of 1–2 atm.

Most transitions could be seen by averaging 1–100 pulses, although 10^3–10^5 pulses were typically accumulated when determining final transition frequencies. Doppler splitting of the lines was minimized by careful adjustment of the timing of gas and MW pulses. Typical linewidths were ≈10 kHz (FWHM) and frequency measurements were usually reproducible to within 1 kHz. Transitions were detectable for states with rotational energies as high as 6.8 cm^{-1} (9.8 K). Such energies imply less efficient rotational cooling than with other species which have been studied with this instrument; no special efforts were made to generate states this high in energy or to detect them other than with long signal averaging times for the weakest transitions.

The program used to fit the transitions performs a simultaneous least-squares fit to the rotational, centrifugal distortion and quadrupole coupling constants including χ_{ab}. It has been previously applied to species such as BrNCO (*6*) and chloroketene (*4*).

RESULTS AND ANALYSIS

Initially a search was made for four low-J ($J \leqslant 3$) lines of the ^{35}Cl species. It quickly became clear that the constants of Ref. (*1*) predicted the transition frequencies and splitting patterns fairly well while those of Ref. (*2*) did not. However, the splittings deviated from a simple rigid rotor plus quadrupole Hamiltonian with diagonal coupling constants by several tens of kiloHertz. Including χ_{ab} in the fit did not reproduce the frequencies to within experimental error and gave an unreasonable value of χ_{ab}. A second fit was tried, including the measurements of Stone and Flygare in the data set, and the cause of the earlier discrepancy became clear. The accuracy of the FTMW data is so high that unless the positions of the rotational energy levels are very well determined, including centrifugal distortion contributions, anomalous fits are obtained even at very low J. Thus, in order to determine accurate quadrupole constants, accurate distortion constants were needed. These could be obtained only by drastically increasing the number of measured transitions.

In the end, 273 components of 56 rotational transitions of $CF_2{=}CF^{35}Cl$ were measured with the FTMW spectrometer. These have included remeasurements of those reported earlier (*1*). A global least-squares fit was made to all rotational constants, quartic distortion constants (Watson's S-reduction in the I^r representation (*7*)), and

^{35}Cl quadrupole coupling constants. The results are presented in Table I. Several fits were attempted including in addition various sextic distortion constants; in all cases these were indeterminate and the goodness of the fit was unaffected. The very small observed linewidths and RMS deviations suggest that effects of magnetic spin–rotation coupling were also negligible.

It is clear from Table I that the precision of the derived constants is extremely high. The precision in χ_{ab} in particular is higher than has ever been previously reported (*4*). Table II presents the frequencies of all measured transitions along with a comparison of the obs – calc deviations obtained when χ_{ab} is included in the fitting process and when it is deleted. The differences represent the contributions from χ_{ab}.

Although the contributions of χ_{ab} to the frequencies are small in general (<0.1

TABLE I

Spectroscopic Constants of $CF_2{=}CF^{35}Cl$

		Present Work	
	Ref. (1)	Final values	Reduced Data Set[a]
Rotational constants (MHz)			
A	4506.05(2)[b]	4506.105428(88)[c]	4506.10546(10)[c]
B	2268.66(2)	2268.700337(50)	2268.700412(86)
C	1508.09(2)	1508.093176(51)	1508.093233(87)
Centrifugal distortion constants (kHz)			
D_J	d	0.21266(89)	0.2153(28)
D_{JK}	d	0.0626(32)	0.0637(38)
D_K	d	1.1152(72)	1.1094(85)
d_1	d	-0.09325(72)	-0.09338(89)
d_2	d	-0.01740(33)	-0.01734(41)
^{35}Cl quadrupole coupling constants (MHz)			
χ_{aa}	-50.10(10)	-49.84817(83)	-49.84815(86)
$\chi_{bb}-\chi_{cc}$	-27.38(22)	-27.3799(17)	-27.3799(18)
$\lvert\chi_{ab}\rvert$	d	49.489(34)	49.48(11)
r.m.s. deviation (MHz)			
	d	0.0016	0.0016

[a] Least squares fit did not include the four transitions with the biggest contributions to χ_{ab} (see text).

[b] For ref. (1), numbers in parentheses are the stated uncertainties in units of the last significant figures.

[c] For the present work, numbers in parentheses are one standard deviation in units of the last significant figures.

[d] Not determined or stated

TABLE II

Measured Rotational Transitions (in MHz) of CF_2CFCl

Transition F' - F"	Normalised[1] Weight	Observed Frequency	Residuals[2] Without χ_{ab}	With χ_{ab}
a-type transitions				
$2_{0\,2} - 1_{0\,1}$				
1/2 - 3/2	1.000	7413.466	0.071	0.0
3/2 - 3/2	1.000	7400.434	0.077	-0.001
7/2 - 5/2	1.000	7391.615	0.005	0.001
5/2 - 3/2	1.000	7391.076	0.055	0.001
1/2 - 1/2	1.000	7391.054	0.094	0.0
3/2 - 5/2	1.000	7387.939	0.040	-0.002
5/2 - 5/2	1.000	7378.581	0.017	-0.001
3/2 - 1/2	1.000	7378.023	0.101	0.0
$2_{1\,2} - 1_{1\,1}$				
1/2 - 1/2	1.000	6805.402	-0.067	-0.001
1/2 - 3/2	1.000	6800.374	-0.038	0.0
7/2 - 5/2	1.000	6796.303	0.002	0.002
3/2 - 1/2	1.000	6795.756	-0.049	0.001
3/2 - 5/2	1.000	6793.575	0.021	-0.003
3/2 - 3/2	1.000	6790.726	-0.022	-0.001
5/2 - 5/2	1.000	6786.659	0.002	-0.002
5/2 - 3/2	1.000	6783.811	-0.041	0.001
$2_{1\,1} - 1_{1\,0}$				
7/2 - 5/2	1.000	8316.929	0.007	0.001
5/2 - 3/2	1.000	8304.491	0.019	0.002
3/2 - 1/2	1.000	8323.888	0.028	0.006
5/2 - 5/2	1.000	8314.130	0.005	-0.001
3/2 - 3/2	1.000	8306.498	0.014	-0.001
1/2 - 1/2	1.000	8326.700	0.023	0.0
$3_{0\,3} - 2_{0\,2}$				
3/2 - 3/2	1.000	10732.775	-0.007	0.0
5/2 - 5/2	1.000	10728.283	0.003	-0.003
9/2 - 7/2	1.000	10722.594	0.004	0.002
7/2 - 5/2	1.000	10721.828	0.004	0.002
3/2 - 1/2	1.000	10719.743	-0.001	-0.001
5/2 - 3/2	1.000	10718.927	-0.017	0.0
7/2 - 7/2	1.000	10708.792	0.015	-0.001
$3_{1\,3} - 2_{1\,2}$				
3/2 - 3/2	1.000	10106.814	0.050	0.0
5/2 - 5/2	1.000	10100.754	0.032	0.0
9/2 - 7/2	1.000	10097.972	0.003	0.002
3/2 - 1/2	1.000	10097.167	0.067	0.0
7/2 - 5/2	1.000	10094.719	0.035	0.002
5/2 - 3/2	1.000	10093.838	0.013	0.001
7/2 - 7/2	1.000	10085.078	0.038	0.001
$3_{1\,2} - 2_{1\,1}$				
3/2 - 3/2	1.000	12360.652	0.032	0.001
3/2 - 1/2	1.000	12357.834	0.031	0.0
9/2 - 7/2	1.000	12356.960	0.004	0.0

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[1] Measurements were weighted according to $1/\sigma^2$, where σ is the uncertainty in the measurements. Unit weight corresponded to an uncertainty of 0.001 MHz.

[2] Observed frequency minus the frequency calculated using the constants in Table I.

TABLE II—*Continued*

Transition F' - F"	Normalised Weight	Observed Frequency	Residuals Without χ_{ab}	Residuals With χ_{ab}
5/2 - 5/2	1.000	12356.497	0.007	-0.001
5/2 - 3/2	1.000	12354.488	0.009	0.0
7/2 - 5/2	1.000	12353.641	0.019	0.0
7/2 - 7/2	1.000	12350.842	0.017	-0.002
$3_{2\,2}$ - $2_{2\,1}$				
9/2 - 7/2	1.000	11333.954	0.020	0.001
7/2 - 5/2	1.000	11321.476	0.003	0.001
5/2 - 3/2	1.000	11330.431	0.044	0.001
3/2 - 1/2	1.000	11342.810	-0.023	0.002
$3_{2\,1}$ - $2_{2\,0}$				
3/2 - 1/2	1.000	11950.953	-0.022	0.001
7/2 - 7/2	1.000	11943.661	0.004	-0.003
9/2 - 7/2	1.000	11942.282	0.002	0.0
5/2 - 3/2	1.000	11939.297	0.010	0.001
3/2 - 3/2	1.000	11937.953	0.017	-0.001
7/2 - 5/2	1.000	11930.595	-0.008	0.0
5/2 - 5/2	1.000	11929.944	-0.016	-0.002
$4_{0\,4}$ - $3_{0\,3}$				
11/2 - 9/2	1.000	13791.514	0.003	0.001
9/2 - 7/2	1.000	13790.702	-0.002	0.0
5/2 - 3/2	1.000	13790.161	-0.004	0.001
7/2 - 5/2	1.000	13789.377	-0.003	0.0
$4_{1\,4}$ - $3_{1\,3}$				
11/2 - 9/2	1.000	13316.996	0.002	0.001
5/2 - 3/2	1.000	13315.965	-0.037	0.0
9/2 - 7/2	1.000	13315.510	-0.019	-0.001
7/2 - 5/2	1.000	13314.526	-0.015	0.001
$4_{1\,3}$ - $3_{1\,2}$				
5/2 - 5/2	1.000	16234.535	0.016	-0.006
7/2 - 7/2	1.000	16229.625	-0.015	-0.005
11/2 - 9/2	1.000	16228.532	0.001	-0.001
5/2 - 3/2	1.000	16228.378	0.0	0.0
9/2 - 7/2	1.000	16226.922	0.002	-0.001
7/2 - 5/2	1.000	16226.773	0.001	0.0
9/2 - 9/2	1.000	16220.802	0.012	-0.004
$4_{2\,3}$ - $3_{2\,2}$				
5/2 - 3/2	1.000	14982.411	0.027	-0.002
11/2 - 9/2	1.000	14980.599	0.005	0.0
7/2 - 5/2	1.000	14977.282	0.014	0.001
9/2 - 7/2	1.000	14975.484	0.018	-0.002
$4_{2\,2}$ - $3_{2\,1}$				
5/2 - 3/2	1.000	16295.698	0.015	0.001
11/2 - 9/2	1.000	16294.015	0.003	0.002
7/2 - 5/2	1.000	16291.359	0.002	-0.002
7/2 - 7/2	1.000	16290.709	-0.005	-0.003
9/2 - 7/2	1.000	16289.683	0.008	-0.001
$4_{3\,2}$ - $3_{3\,1}$				
5/2 - 3/2	1.000	15386.179	-0.012	-0.001
11/2 - 9/2	1.000	15380.509	0.011	0.003
7/2 - 5/2	1.000	15375.204	0.019	0.001
9/2 - 7/2	1.000	15369.500	-0.005	-0.001

TABLE II—*Continued*

Transition F' - F"	Normalised Weight	Observed Frequency	Residuals Without χ_{ab}	Residuals With χ_{ab}
$4_{31} - 3_{30}$				
5/2 - 3/2	1.000	15516.770	-0.011	0.0
11/2 - 9/2	0.063	15511.136	0.001	-0.002
7/2 - 5/2	1.000	15505.929	0.007	-0.002
9/2 - 7/2	1.000	15500.282	-0.004	0.002
$4_{13} - 4_{14}$				
9/2 - 9/2	1.000	7457.029	-0.008	0.001
7/2 - 7/2	1.000	7454.686	-0.019	0.001
11/2 - 11/2	1.000	7450.379	-0.005	0.0
5/2 - 5/2	1.000	7448.037	-0.017	0.001
$2_{21} - 2_{02}$				
5/2 - 5/2	1.000	10652.225	-0.012	0.0
3/2 - 5/2	1.000	10643.245	-0.070	-0.001
5/2 - 3/2	1.000	10642.867	-0.035	0.001
3/2 - 3/2	1.000	10633.887	-0.092	0.0
7/2 - 7/2	1.000	10626.691	-0.027	0.001
$3_{22} - 3_{03}$				
7/2 - 7/2	1.000	11251.873	-0.013	-0.002
5/2 - 5/2	1.000	11245.389	-0.033	0.0
9/2 - 9/2	1.000	11238.051	-0.011	0.001
3/2 - 3/2	1.000	11231.586	-0.016	0.002
$4_{23} - 4_{04}$				
11/2 - 11/2	1.000	12427.138	-0.007	0.002
5/2 - 5/2	0.063	12423.834	0.013	-0.002
b-type transitions				
$1_{11} - 0_{00}$				
3/2 - 3/2	1.000	6016.495	0.054	0.0
5/2 - 3/2	1.000	6013.644	0.008	0.0
1/2 - 3/2	1.000	6011.465	0.081	-0.001
$2_{12} - 1_{01}$				
7/2 - 5/2	1.000	9030.653	0.007	0.001
5/2 - 3/2	1.000	9033.506	0.046	0.0
3/2 - 1/2	1.000	9018.013	0.091	0.002
5/2 - 5/2	1.000	9021.011	0.009	-0.001
3/2 - 3/2	1.000	9040.422	0.066	-0.001
1/2 - 1/2	1.000	9027.659	0.074	0.0
$3_{13} - 2_{02}$				
9/2 - 7/2	1.000	11737.009	0.005	0.001
7/2 - 5/2	1.000	11737.150	0.028	0.002
5/2 - 3/2	1.000	11733.824	-0.001	-0.001
3/2 - 1/2	1.000	11733.772	0.047	0.001
$4_{14} - 3_{03}$				
11/2 - 9/2	1.000	14331.411	0.003	0.001
9/2 - 7/2	1.000	14330.833	0.006	0.0
7/2 - 5/2	1.000	14329.423	0.0	0.0
5/2 - 3/2	1.000	14329.992	0.009	0.0
$3_{03} - 2_{12}$				
9/2 - 7/2	1.000	9083.556	0.002	0.002
7/2 - 5/2	1.000	9079.395	0.009	0.0

TABLE II—*Continued*

Transition F'	- F"	Normalised Weight	Observed Frequency	Residuals Without χ_{ab}	With χ_{ab}
5/2	- 3/2	1.000	9078.939	-0.005	0.0
3/2	- 1/2	1.000	9083.140	0.021	0.001
4_{04}	- 3_{13}				
11/2	- 9/2	1.000	12777.100	0.003	0.003
9/2	- 7/2	1.000	12775.382	-0.024	0.002
7/2	- 5/2	1.000	12774.483	-0.016	0.004
5/2	- 3/2	1.000	12776.134	-0.050	0.001
2_{20}	- 1_{11}				
5/2	- 5/2	1.000	15960.102	0.012	0.0
5/2	- 3/2	1.000	15957.248	-0.037	-0.003
3/2	- 1/2	0.063	15952.930	-0.084	0.0
3/2	- 3/2	0.063	15947.900	-0.057	-0.001
7/2	- 5/2	1.000	15947.030	-0.006	-0.002
1/2	- 1/2	1.000	15939.931	-0.045	0.0
2_{21}	- 1_{10}				
5/2	- 5/2	1.000	15037.231	0.014	-0.001
3/2	- 1/2	1.000	15035.997	-0.021	0.002
5/2	- 3/2	1.000	15027.593	0.029	0.002
7/2	- 5/2	1.000	15024.731	-0.013	0.002
1/2	- 1/2	1.000	15023.658	0.067	0.0
3/2	- 3/2	1.000	15018.609	-0.033	-0.003
3_{12}	- 2_{21}				
7/2	- 5/2	1.000	5630.540	0.010	0.0
4_{13}	- 3_{22}				
5/2	- 3/2	1.000	10546.446	0.011	0.001
11/2	- 9/2	1.000	10543.739	0.008	0.0
7/2	- 5/2	1.000	10538.719	0.013	0.0
9/2	- 7/2	1.000	10535.986	0.009	-0.001
7_{34}	- 6_{43}				
17/2	- 15/2	1.000	11978.406	0.002	-0.001
15/2	- 13/2	1.000	11972.217	0.680	-0.001
13/2	- 11/2	1.000	11973.061	0.045	0.0
11/2	- 9/2	1.000	11980.480	0.607	0.001
7_{35}	- 6_{42}				
17/2	- 15/2	1.000	8513.626	-0.001	0.001
15/2	- 13/2	1.000	8505.080	-0.228	0.0
13/2	- 11/2	1.000	8507.052	-0.031	0.001
11/2	- 9/2	1.000	8514.996	-0.399	0.0
3_{12}	- 3_{03}				
7/2	- 7/2	1.000	5560.939	-0.004	0.0
5/2	- 5/2	1.000	5557.337	-0.019	0.002
9/2	- 9/2	1.000	5553.257	-0.005	0.001
3/2	- 3/2	1.000	5549.651	-0.008	0.0
4_{13}	- 4_{04}				
11/2	- 9/2	1.000	8004.890	-0.011	0.003
5/2	- 7/2	1.000	8002.497	0.002	-0.002
7/2	- 9/2	1.000	7999.865	-0.015	-0.002
9/2	- 9/2	1.000	7997.160	0.0	0.0
7/2	- 7/2	1.000	7994.732	-0.016	0.0
9/2	- 7/2	1.000	7992.026	-0.002	0.002
11/2	- 11/2	1.000	7990.276	-0.005	0.0

TABLE II—*Continued*

Transition			Normalised	Observed	Residuals	
F'	-	F"	Weight	Frequency	Without χ_{ab}	With χ_{ab}
5/2	-	5/2	1.000	7987.869	-0.003	0.001
9/2	-	11/2	1.000	7982.545	0.005	-0.004
7/2	-	5/2	1.000	7980.103	-0.021	0.003
$2_{2\,0}$	-	$2_{1\,1}$				
5/2	-	5/2	1.000	6886.747	0.021	0.0
5/2	-	3/2	1.000	6884.739	0.024	0.001
5/2	-	7/2	1.000	6883.948	0.018	-0.002
3/2	-	5/2	1.000	6877.396	-0.003	-0.002
3/2	-	3/2	1.000	6875.388	0.001	0.0
7/2	-	5/2	1.000	6873.680	0.008	0.002
3/2	-	1/2	1.000	6872.571	0.0	0.001
7/2	-	7/2	1.000	6870.881	0.005	0.0
1/2	-	3/2	1.000	6862.388	0.039	-0.001
1/2	-	1/2	1.000	6859.571	0.039	0.0
$2_{2\,1}$	-	$2_{1\,2}$				
7/2	-	7/2	1.000	8987.646	-0.036	-0.005
5/2	-	5/2	1.000	9009.790	-0.009	-0.004
3/2	-	3/2	1.000	8993.895	-0.084	-0.004
1/2	-	1/2	1.000	8971.917	0.029	0.002
$3_{2\,2}$	-	$3_{1\,3}$				
7/2	-	7/2	1.000	10236.554	-0.034	0.002
5/2	-	5/2	1.000	10230.491	-0.050	0.0
9/2	-	9/2	1.000	10223.634	-0.013	0.0
3/2	-	3/2	1.000	10217.556	-0.065	0.0
$3_{2\,1}$	-	$3_{1\,2}$				
7/2	-	7/2	1.000	6463.702	-0.005	0.001
5/2	-	5/2	1.000	6460.196	0.0	0.0
9/2	-	9/2	1.000	6456.203	0.003	0.001
3/2	-	3/2	1.000	6452.690	-0.014	0.0
$4_{2\,2}$	-	$4_{1\,3}$				
11/2	-	9/2	1.000	6529.412	-0.010	0.003
5/2	-	7/2	1.000	6527.775	0.019	-0.002
7/2	-	9/2	1.000	6527.489	-0.012	-0.002
9/2	-	9/2	1.000	6526.463	0.001	0.0
7/2	-	7/2	1.000	6524.783	0.001	0.0
9/2	-	7/2	1.000	6523.758	0.016	0.003
11/2	-	11/2	1.000	6521.683	0.002	0.001
5/2	-	5/2	1.000	6520.010	0.001	0.0
9/2	-	11/2	1.000	6518.733	0.013	-0.003
7/2	-	5/2	1.000	6517.018	-0.016	0.002
$4_{2\,3}$	-	$4_{1\,4}$				
5/2	-	7/2	1.000	11898.422	0.020	0.001
7/2	-	9/2	1.000	11898.297	-0.022	-0.001
9/2	-	9/2	1.000	11896.527	0.001	-0.001
7/2	-	7/2	1.000	11893.247	-0.020	-0.001
9/2	-	7/2	1.000	11891.480	0.005	0.003
11/2	-	11/2	1.000	11887.239	-0.009	0.0
5/2	-	5/2	1.000	11884.004	0.001	0.0
$6_{2\,4}$	-	$6_{1\,5}$				
15/2	-	15/2	1.000	9042.412	0.002	0.001
13/2	-	13/2	1.000	9046.084	0.002	0.002
11/2	-	11/2	1.000	9045.214	0.0	0.0
9/2	-	9/2	1.000	9041.543	0.001	0.002

TABLE II—*Continued*

Transition F' - F"	Normalised Weight	Observed Frequency	Residuals Without χ_{ab}	 With χ_{ab}
$3_{31} - 3_{22}$				
7/2 - 7/2	1.000	13192.004	0.007	-0.001
5/2 - 5/2	1.000	13184.644	-0.009	0.0
9/2 - 9/2	1.000	13176.261	-0.001	0.0
3/2 - 3/2	1.000	13168.911	0.010	-0.001
$3_{30} - 3_{21}$				
7/2 - 7/2	1.000	12441.778	0.010	0.001
9/2 - 9/2	1.000	12427.349	-0.001	-0.001
3/2 - 3/2	1.000	12420.621	0.016	0.002
$4_{32} - 4_{23}$				
9/2 - 9/2	1.000	13586.021	-0.015	0.001
7/2 - 7/2	1.000	13582.565	-0.005	0.0
11/2 - 11/2	1.000	13576.167	0.001	0.0
5/2 - 5/2	1.000	13572.679	-0.028	0.0
$4_{31} - 4_{22}$				
11/2 - 11/2	1.000	11644.477	0.005	0.003
9/2 - 9/2	1.000	11652.371	-0.008	-0.002
7/2 - 7/2	1.000	11649.603	0.003	0.002
5/2 - 5/2	1.000	11641.691	-0.012	-0.001
$5_{32} - 5_{23}$				
13/2 - 13/2	1.000	10677.491	0.003	0.001
11/2 - 11/2	1.000	10682.242	0.009	0.001
9/2 - 9/2	1.000	10680.894	0.004	0.0
7/2 - 7/2	1.000	10676.166	0.013	0.0
$5_{33} - 5_{24}$				
13/2 - 13/2	1.000	14304.756	0.001	-0.001
11/2 - 11/2	1.000	14311.853	0.012	0.0
9/2 - 9/2	1.000	14309.841	0.002	0.0
7/2 - 7/2	1.000	14302.775	0.015	-0.001
$6_{33} - 6_{24}$				
15/2 - 15/2	1.000	9912.085	0.003	0.001
13/2 - 13/2	1.000	9915.282	0.001	-0.001
11/2 - 11/2	1.000	9914.524	0.002	-0.001
9/2 - 9/2	1.000	9911.330	0.002	-0.001
$7_{34} - 7_{25}$				
17/2 - 17/2	1.000	9757.729	0.0	-0.001
15/2 - 15/2	1.000	9760.257	-0.001	-0.002
13/2 - 13/2	1.000	9759.745	0.003	0.002
11/2 - 11/2	1.000	9757.215	0.0	-0.001
$9_{36} - 9_{27}$				
21/2 - 21/2	1.000	12322.973	0.001	0.0
19/2 - 19/2	1.000	12325.362	0.0	-0.001
17/2 - 17/2	1.000	12324.980	0.0	0.0
15/2 - 15/2	1.000	12322.592	0.001	0.001
$4_{40} - 4_{31}$				
9/2 - 9/2	0.250	17946.666	0.005	0.001
7/2 - 7/2	0.250	17942.210	-0.017	-0.001
11/2 - 11/2	0.250	17934.006	-0.008	0.001
5/2 - 5/2	0.250	17929.572	0.005	-0.001

TABLE II—*Continued*

Transition F' - F"	Normalised Weight	Observed Frequency	Residuals Without χ_{ab}	Residuals With χ_{ab}
4_{41} - 4_{32}				
9/2 - 9/2	0.250	18097.417	0.004	0.0
7/2 - 7/2	0.250	18092.897	-0.017	0.003
11/2 - 11/2	0.250	18084.570	-0.007	0.004
5/2 - 5/2	0.250	18080.070	0.007	0.001
6_{42} - 6_{33}				
15/2 - 15/2	0.250	16735.773	-0.001	-0.001
13/2 - 13/2	0.250	16741.390	0.225	-0.003
11/2 - 11/2	0.250	16739.916	0.029	-0.002
9/2 - 9/2	0.250	16734.900	0.399	0.0
6_{43} - 6_{34}				
15/2 - 15/2	0.250	18193.903	0.003	0.002
13/2 - 13/2	0.250	18199.427	-0.685	0.0
11/2 - 11/2	0.250	18198.600	-0.041	0.002
9/2 - 9/2	0.250	18191.818	-0.616	-0.003
9_{45} - 9_{36}				
21/2 - 21/2	1.000	13158.899	0.001	0.0
19/2 - 19/2	1.000	13160.825	0.001	0.0
17/2 - 17/2	1.000	13160.519	0.003	0.002
15/2 - 15/2	1.000	13158.590	-0.001	-0.001
10_{46} - 10_{37}				
23/2 - 23/2	1.000	12833.416	0.002	0.001
21/2 - 21/2	1.000	12835.093	0.001	0.0
19/2 - 19/2	1.000	12834.851	0.001	0.0
17/2 - 17/2	1.000	12833.171	-0.002	-0.002
11_{47} - 11_{38}				
25/2 - 25/2	1.000	13558.512	0.0	-0.001
23/2 - 23/2	1.000	13560.172	0.002	0.001
21/2 - 21/2	1.000	13559.952	-0.001	-0.002
19/2 - 19/2	1.000	13558.296	0.003	0.002

MHz), they are nevertheless significant. However, for four transitions, namely $7_{34} \leftarrow 6_{43}$, $7_{35} \leftarrow 6_{42}$, $6_{43} \leftarrow 6_{34}$, and $6_{42} \leftarrow 6_{33}$, they are large enough to be detectable even with a Stark-modulated spectrometer. This is the result of the two near degeneracies 5_{51}–6_{43} and 6_{42}–5_{50}, both of which are less than 100 MHz. Since these transitions can be expected to have a large effect on the precision of χ_{ab}, and since one of the objectives was to see whether such transitions are necessary to obtain an accurate χ_{ab}, another fit was done omitting them. The results are also in Table I; it is clear that an excellent χ_{ab} was obtained, albeit at reduced precision. Thus, this coupling constant can be determined from frequency measurements of sufficiently high precision in the absence of perturbing near degeneracies. However, the effects of centrifugal distortion may be comparable to the contributions from χ_{ab} and must be properly taken into account. Of course, a large value of χ_{ab} is desirable, necessitating propitious values for θ_{za} and $\chi_{aa} - \chi_{bb}$ since $2\chi_{ab} = (\chi_{aa} - \chi_{bb})\tan 2\theta_{za}$.

DISCUSSION

Diagonalization of the quadrupole tensor gives the following principal values: $\chi_{zz} = -77.46 \pm 0.1$ MHz, $\chi_{xx} = 38.85 \pm 0.1$ MHz, and $\chi_{yy} = \chi_{cc} = 38.614 \pm 0.003$

MHz (the uncertainties are estimated outside error limits). The differences between our results and those of Stone and Flygare (*1*) are not due to improperly determined constants in either study. Table I gives a comparison, and it is clear that there is excellent agreement. The cause must thus lie in an incorrect assumed structure in Ref. (*1*) and a consequent incorrect angle θ_{za} between the z-principal axis and the a-inertial axis. We have found θ_{za} to be $29.16 \pm 0.03°$; in Ref. (*1*) it is 32.71°, a difference of 3.55°. A discrepancy this large when θ_{za} is ~25–45° should have a drastic effect on χ_{ab}. For $\theta_{za} = 32.71°$, $|\chi_{ab}| = 67.2$ MHz, considerably different from the experimental value of 49.489 MHz.

A simple Townes–Dailey calculation (*8*) gives the ionic and π-character of the C–Cl bond assuming this is the z-axis of the quadrupole tensor. Since $\chi_{xx} \simeq \chi_{yy}$, the π-character is effectively nil. This is smaller than in other vinyl chlorides where the chlorine double bonded structure ($^{+}\mathrm{Cl}{=}$) contributes from 2.4–5.3% (*1*). The ionic contribution, obtained assuming 15% s-character and no d-character of the σ-bonding orbital of Cl, is ~17%, so that the covalent character is ~83%. These values are much more in line with those of other vinyl chlorides (*1*).

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