Microwave Spectrum, Structure, and Nuclear Quadrupole Coupling Constants of Chloryl Fluoride

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Summary The structure and nuclear quadrupole coupling constants of chloryl fluoride have been determined from its microwave spectrum.

CHLORYL FLUORIDE, $FClO_2$, is one of several molecules in which a halogen atom is bonded to a stable paramagnetic species. The internuclear parameters of these molecules are of interest because in general the bond from the halogen atom to the remainder of the molecule is very long, usually much longer than the sum of the single bond radii, and because the structural parameters of the paramagnetic species usually change little on bonding with the halogen atom.[1,2] Several attempts to account theoretically for these features have been made.[2,3] We have studied the microwave spectrum of chloryl fluoride to determine its internuclear parameters and thus decide whether it too has the same structural properties.

Spectra have been assigned for the two most abundant isotopic species, $^{19}F^{35}Cl^{16}O_2$ and $^{19}F^{37}Cl^{16}O_2$, in the ground vibrational state. The spectra are those of a rather asymmetric oblate rotor having components of its dipole moment along the *a*- and *c*-inertial axes. Each transition was clearly resolved by nuclear quadrupole coupling with chlorine, and values of all the coupling constants have been obtained. To obtain accurate rotational constants an analysis for centrifugal distortion using the first-order equation of Watson[4] was carried out. Though we have thus far insufficient data to obtain accurate values for all the distortion constants this procedure has been shown to yield good values for the rotational constants.[5] These are given in Table 1 along with the principal moments of inertia and the nuclear quadrupole coupling constants.

TABLE 1

Rotational constants, principal moments of inertia and nuclear quadrupole coupling constants of chloryl fluoride

	$^{19}F^{35}Cl^{16}O_2$	$^{19}F^{37}Cl^{16}O_2$
A (MHz)	9636·04	9597·97
B (MHz)	8275·69	8239·12
C (MHz)	5019·14	5016·67
I_a (Amu Å^2)	52·448	52·656
I_b (Amu Å^2)	61·069	61·340
I_c (Amu Å^2)	100·693	100·742
$I_a + I_c - I_b$	92·071	92·058
χ_{cc} (MHz)	52·0 ± 0·4	40·9 ± 0·5
$\chi_{bb} - \chi_{aa}$ (MHz) ..	18·0 ± 0·4	14·1 ± 0·7

TABLE 2

Structural parameters of chloryl fluoride and related compounds

	$FClO_2$	FCl[10]	ClF_3[11]	ClO_2[12]
r(F–Cl) (Å)	1·664 ± 0·030	1·6281	1·698 1·598[a]	
r(Cl–O) (Å)	1·434 ∓ 0·015			1·471
∠ (O–Cl–O)	113·5 ± 2·0°			117° 35′
∠ (F–Cl–O)	103·2 ∓ 1·5°			

[a] The Cl–F bond on the axis of symmetry.

The overall spectrum, with *a*- and *c*-type transitions, is consistent with a pyramidal configuration with chlorine at the apex of the pyramid, and thus C_s molecular symmetry. Such a deduction is supported by (i) the near identity of $I_a + I_c - I_b$ for the two isotopic species, which indicates that the chlorine *b*-co-ordinate is zero; (ii) the very small changes in the moments of inertia, particularly I_c, on isotopic substitution; (iii) the quadrupole coupling constant χ_{cc}, whose value is similar to that of the isoelectronic chlorate ion.[6] From the equation $4m_0b_0^2 = I_a + I_c - I_b$ an r_0 value for the O–O distance is found to be 2·399 Å. The co-ordinates of chlorine were determined using the substitution procedure,[7] and the remaining co-ordinates of fluorine and oxygen were calculated using the centre of mass conditions, and by reproducing I_a and I_c. The resulting internuclear parameters are given in Table 2, together for comparison with those of related molecules. The uncertainties listed arise chiefly from the uncertainty in the rather small *a*-co-ordinate of chlorine. The difference in the value of $I_a + I_c - I_b$ of the two isotopic species, which may reflect different contributions of vibrational averaging to the effective moments of inertia in the two species, suggests such large uncertainties. The parameters obtained using other methods of calculation, notably using the product of inertia condition to calculate the *a*-coordinate of chlorine, are within the limits given.

It is seen from Table 2 that the Cl–F bond is evidently somewhat longer than that in ClF, *i.e.* longer than the sum of the single bond radii,[8] as expected. On the other hand, the Cl–O bond length and (O–Cl–O) angle are somewhat different from those of ClO_2, in contrast to the features found for other molecules of this assumed type. The changes observed in the ClO_2 frame can be rationalized within the $(p\text{-}\pi^*)\sigma$ bonding formalism developed by Jackson[2] and Spratley and Pimentel.[3] The unpaired electron in ClO_2 is in a b_1 orbital, antibonding between chlorine and oxygen.[13] The F–Cl bond can be thought as arising from overlap of this orbital with a *p*-orbital of fluorine. In contrast to other molecules treated in this way there is evidently withdrawal of antibonding electron density from the b_1 orbital of ClO_2 to the *p*-orbital of fluorine. This should result in a shortening of the Cl–O bond from that of ClO_2, as found. Only a small increase in the F–Cl bond length over the sum of the single bond radii can be expected, again as found. These deductions are tentative, however, and more definite conclusions must await a more refined determination of structural parameters using further isotopic substitutions.

We thank Dr. F. Aubke for his advice and facilities for preparation of this molecule. We acknowledge gratefully the support of the National Research Council of Canada in the form of research grants and a bursary (to C.R.P.).

(*Received*, 30*th December* 1971; *Com.* 2211.)

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[1] A. C. Legon and D. L. Millen, *J. Chem. Soc.* (*A*), 1968, 1736; K. S. Buckton, A. C. Legon, and D. J. Millen, *Trans. Faraday Soc.*, 1969, **65**, 439.
[2] R. H. Jackson, *J. Chem. Soc.*, 1962, 4585.
[3] R. D. Spratley and G. C. Pimentel, *J. Amer. Chem. Soc.*, 1966, **88**, 2394.
[4] J. K. G. Watson, *J. Chem. Phys.*, 1967, **46**, 1935.
[5] G. E. Herberich, R. H. Jackson, and D. J. Millen, *J. Chem. Soc.* (*A*), 1966, 336.
[6] R. W. Moshier, *Inorg. Chem.*, 1966, **3**, 199.
[7] C. C. Costain, *J. Chem. Phys.*, 1958, **29**, 864.
[8] L. Pauling, 'The Chemical Bond', Cornell University Press, Ithaca, New York, 1960.
[9] D. F. Smith, G. M. Begun, and W. H. Fletcher, *Spectrochim. Acta*, 1964, **20**, 1763.
[10] D. A. Gilbert, A. Roberts, and P. A. Griswold, *Phys. Rev.*, 1949, **76**, 1723.
[11] D. F. Smith, *J. Chem. Phys.*, 1953, **21**, 609.
[12] R. F. Curl, R. F. Heidelberg, and J. L. Kinsey, *Phys. Rev.*, 1962, **125**, 1993.
[13] A. D. Walsh, *J. Chem. Soc.*, 1953, 2266.