The Microwave Spectrum and Structure of Chlorine Thiocyanate

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Summary From its microwave spectrum, chlorine thiocyanate has been shown to be ClSCN, rather than the isothiocyanate ClNCS, in the gas phase.

THE preparation of chlorine thiocyanate has recently been reported.[1] It is one of a series of simple compounds, some of which have the thiocyanate structure RSCN (*e.g.* CH_3-SCN,[2] NCSCN[3]), and others the isothiocyanate structure RNCS (*e.g.* HNCS,[4] CH_3NCS,[2] SiH_3NCS[5]) with the other isomers unknown (*e.g.* HSCN, SiH_3SCN). Since it is thus difficult to predict *a priori* whether its structure should be ClSCN or ClNCS, we have begun a study of its microwave spectrum to determine its gas-phase configuration, and to measure its structural parameters.

The rotational spectrum of the molecule in its ground vibrational state is that of a slightly asymmetric prolate rotor with non-zero components of its dipole moment along the *a*- and *b*-principal inertial axes. In general the lines are broad, chiefly because of unresolved chlorine and nitrogen quadrupole hyperfine structure; for a few transitions some quadrupole structure due to chlorine has been partially resolved. To obtain accurate rotational constants we have done a preliminary analysis accounting for centrifugal distortion. Though we have thus far insufficient data to obtain accurate values for all the distortion constants, the rotational constants are accurate enough to permit useful structural deductions.[6] The rotational constants are given in the Table for two isotopic species, along with corresponding principal moments of inertia and inertial defects.

Because the inertial defects are small positive numbers, invariant with isotopic species, we conclude that the molecule is planar. The Table contains, furthermore, rotational constants calculated using assumed model structures for ^{35}ClSCN and ^{35}ClNCS. For ClSCN the molecule was taken to be a hybrid of SCl_2[7] and $S(CN)_2$[3], with the angle at S the average of the angles of these two mole-

TABLE Rotational constants, principal moments of inertia, and inertial defects of chlorine thiocyanate

	Experimental		Calculated[a]	
	^{35}ClSCN	^{37}ClSCN	^{35}ClSCN	^{35}ClNCS
A/MHz	12 109 28(10)[b]	11 975 76(28)	12 408	50 230
B/MHz	2902 943(14)	2836 427(15)	2849	1773
C/MHz	2337 285(12)	2289 116(15)	2317	1712
I_a/u Å^2	41 735	42 200		
I_b/u Å^2	174 092	178 175		
I_c/u Å^2	216 225	220 775		
Δ/u Å^2 [c]	0 398	0 400		

[a] Calculated using assumed model structures [b] Numbers in parentheses are standard deviations in units of the last significant figures [c] $\Delta = I_c - I_b - I_a$

cules For ClNCS the NCS chain was assumed to be that of HNCS,[4] the ClN length that of ClNCO,[8] and the ClNC angle 7° wider than that of ClNCO, as with other isothiocyanates [2,4] Clearly ClSCN is the correct model (in contrast with the corresponding isocyanate, ClNCO[8]), and the close similarity of the observed and calculated rotational constants indicates that the molecule is very nearly an exact hybrid of SCl_2 and $S(CN)_2$ A fit to I_a and I_b of both isotopic species assuming the SCN angle as in $S(CN)_2$ gave r(Cl–S) = 2 022, r(S–C) = 1·693 Å, and ∠Cl–S–C = 99 8°, in good agreement with the model Finally, the approximate Cl quadrupole coupling constants [$\chi_{aa} = -$ 36(4) MHz, $\chi_{bb} - \chi_{cc} = -$ 65(1) (MHz] are also very close to those of SCl_2[7] (the ClS bond and inertial axes have similar relative orientations in both cases), again confirming the structure

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