The Microwave Spectrum and Molecular Structure of Monochloramine

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Summary A convenient method of preparing monochloramine for microwave spectroscopy is described; the molecular structure and chlorine and nitrogen quadrupole coupling constants (χ_{aa}) have been determined.

THE $1_{01} \leftarrow 0_{00}$ transitions of five isotopic species of monochloramine have been observed using a conventional 100 kHz Stark modulation spectrometer operating with samples at approximately −30°. The monochloramine was prepared in the waveguide cell by mixing dichlorine oxide vapour (*ca.* 1 volume) with the vapour from an aqueous solution of ammonia (*ca.* 5 volumes) at a total pressure of less than 1 cm Hg. Monochloramine appears to be the main product of reaction under these conditions and the microwave spectra of dichlorine oxide[1] and hypochlorous acid[2] have not been detected in the mixtures. The spectra of the deuteriomonochloramines were observed using a solution prepared by dissolving NH_3 gas in D_2O. The monochloramine lines were identified by their characteristic Stark effects and nuclear quadrupole hyperfine patterns. The theory of Bardeen and Townes[3] has been used to analyse the nuclear quadrupole effects. The line frequencies corrected for hyperfine structure, and the chlorine and nitrogen nuclear quadrupole coupling constants (χ_{aa}) are given in the Table.

TABLE

	$B+C$ MHz	χ_{aa} (chlorine) MHz	χ_{aa} (nitrogen) MHz
$NH_2{}^{35}Cl$	28063·51	−99·5	5·4
$NH_2{}^{37}Cl$	27602·14	−78·5	5·5
$NHD^{35}Cl$	26213·10	−99·2	5·4
$NHD^{37}Cl$	25768·27	−78·5	—
$ND_2{}^{35}Cl$	24599·80	−99·8	—

If centrifugal distortion effects are neglected, the $1_{01} \leftarrow 0_{00}$ transitions occur at $B+C$. The quantity $A - \frac{1}{2}(B+C)$ has been determined with useful accuracy for $NH_2{}^{35}Cl$ and $NHD^{35}Cl$ by high-resolution i.r. spectroscopy,[4] and combination with the microwave data gives A for these two isotopic species. A least-square fitting procedure to $1/A$ and $1/(B+C)$ has been adopted to give essentially an r_0 structure and the following parameters may be taken as a preliminary structure for monochloramine.

$r_{N-Cl} = 1{\cdot}750$ Å $\qquad r_{N-H} = 1{\cdot}025$ Å

$\angle NHCl = 104°$ $\qquad \angle HNH = 99°$

ϕ = angle between bisector of $\angle HNH$ and the extension of the N–Cl bond = 68°.

The N–Cl bond length is the most accurately determined feature of the structure and may be compared with that in dimethylmonochloramine[5,6] (N–Cl = 1·75 Å) and methyldichloramine[5] (N–Cl = 1·76 Å) as determined by electron diffraction. The N–H bond length is slightly longer and the HNH angle narrower than in ammonia[7] (r_0 N–H = 1·017 $\angle HNH = 107°47'$). The degree of non-planarity quantified by ϕ has been determined for a number of other NH_2X molecules, ammonia[7] (ϕ *ca.* 59°), methylamine[8] (ϕ *ca.* 52°), cyanamide[9] (ϕ *ca.* 38°), formamide[10] (ϕ *ca.* 17°), nitramide[11] (ϕ *ca.* 51°), aniline[12] (ϕ *ca.* 39°), and *p*-fluoroaniline[13] (ϕ *ca.* 46°). The low values for ϕ in many of these molecules is usually interpreted in terms of the planar $NH_2{}^+ = X^-$ structure contributing significantly to the overall state of the molecule, a situation that is not likely to occur in monochloramine.

We have found no inversion doubling in the microwave spectrum of monochloramine; this indicates that the rotational constants for the 0^+ and 0^- states are very similar and that the energy difference between these states is small. There is no evidence for inversion from the NH_2 wagging vibration in the i.r. spectrum.[4] This may be contrasted with the molecules listed above all of which have an 0^+–0^- separation larger, and a barrier to inversion smaller, than that for ammonia.

In monochloramine the *a* inertial axis is almost coincident with the N–Cl bond and χ_{aa} must be a good approximation to the quadrupole coupling constant along the bond. The chlorine coupling constants are smaller in magnitude than those of atomic chlorine (*e.g.*, $Q = -110$ MHz). This is consistent with either or both of some ionic character N^{+} Cl^{-} in the nitrogen chlorine bond or some *s*-character in the chlorine bonding orbital.[14] χ_{aa} for the nitrogen atom is appreciably larger than in the inertially similar molecules methylamine[8] ($\chi_{aa} = 2{\cdot}35$ MHz) and cyanamide[9] (amine-N $\chi_{aa} = 3{\cdot}05$ MHz), indicating a difference between the electron distributions in N–Cl and N–C bonds.

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