The Microwave Spectrum and Structure of Hypochlorous Acid

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Summary The structure of hypochlorous acid has been calculated from microwave spectral data

The $1_{01} \leftarrow 0_{00}$ transitions of four isotopic species of hypochlorous acid have been observed using conventional Stark modulation spectrometers operating with samples at approximately −20°. The hypochlorous acid was prepared directly in the wave-guide through the equilibrium between water and dichlorine monoxide.

$$H_2O + Cl_2O \rightleftharpoons 2HOCl$$

$$D_2O + Cl_2O \rightleftharpoons 2DOCl$$

The hypochlorous acid lines were identified amongst the very rich dichlorine monoxide spectrum[1] by their characteristic Stark effects and nuclear quadrupole fine structure patterns and their diminished intensities at low temperatures owing to the small vapour pressure of water. The measured line frequencies, line centres, and quadrupole coupling constants (χ_{aa}) are given in Table 1.

TABLE 1

	$\Delta F = 0$	$\Delta F = +1$ (in MHz)	$\Delta F = -1$	B + C	χ_{aa}
$HO^{35}Cl$	29817·99	29848·63	29872·84	29842·42	—121·7
$HO^{37}Cl$	29303·86	29328·01	29347·80	29323·17	— 96·5
$DO^{35}Cl$	27949·41	27979·79	28004·05	27973·70	−121·4
$DO^{37}Cl$	27453·87	27477·98	27497·21	27473·14	− 96·3

The structure of hypochlorous acid has been calculated in a number of ways and the results together with the structure obtained by Ashby[2] from the high-resolution i.r. spectrum are shown in Table 2. If centrifugal distortion effects are neglected the $1_{01} \leftarrow 0_{00}$ transitions occur at a frequency of B + C. Structures 1 were calculated by least-squares fits to the four observed line centres. The moments of inertia I_a are well determined in the i r. work, and making certain assumptions regarding the inertial defects these were combined with the values of B + C to give the remaining moments of inertia. The *a* and *b* co-ordinates of the hydrogen atom and the *a* co-ordinate of the chlorine atom were calculated using Kraitchman's equations as recommended by Costain.[3] The remaining co-ordinates were then determined from the two first moment and the product of inertia conditions. Structures 2 and 3 were calculated using $HO^{35}Cl$ and $HO^{37}Cl$ as the parent molecule, respectively. The OH bond length and the HOCl angle are not well determined in Structures 1 but otherwise the agreement amongst the various structures is reasonable. The parameters $r_{O-Cl} = 1{\cdot}693 \pm 0{\cdot}005$ Å, $r_{O-H} = 0{\cdot}97 \pm 0{\cdot}01$ Å and ∠HOCl = 103 ± 3° may be taken as a preliminary structure for hypochlorous acid.

In $HO^{35}Cl$ the *a* inertial axis makes an angle of nearly 2° with the direction of the O–Cl bond and χ_{aa} is therefore a good estimate of the nuclear quadrupole coupling constant along this bond. This may be compared with the ^{35}Cl coupling constants along the O–Cl bond in methyl hypochlorite[5] (−114·0 MHz) and in dichlorine monoxide[6] (−141·06 MHz).

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TABLE 2

		r_{O-Cl} (Å)	r_{O-H} (Å)	∠HOCl (°)
Ashby		1·689	0·97	105
Structure 1	a	1·696	1·03	100
	b	1·695	0·99	100
Structure 2	a	1·692	0·967	103·5
	b	1·693	0·967	103·5
Structure 3	a	1·693	0·960	102·5
	b	1·693	0·960	102·5

[a] Calculated assuming the inertial defect ($\Delta = I_c - I_b - I_a$) equal to zero.

[b] Calculated using the inertial defects predicted by Oka and Morino.[4]

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