The pre-reactive complex $H_2O\cdots ClF$ identified in mixtures of water vapour and chlorine monofluoride by rotational spectroscopy

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A pre-reactive complex $H_2O\cdots ClF$ of planar (C_{2v}) or effectively planar (C_s) geometry is characterised for the first time in mixtures of water vapour and chlorine monofluoride through its rotational spectrum, as observed with a fast-mixing nozzle/Fourier-transform microwave spectrometer.

The reaction between water and chlorine monofluoride is both vigorous and complex at room temperature. It was first investigated by Ruff *et al.* at the time of their original synthesis of ClF from its elements.[1] Among the products detected were HF, Cl_2 and O_2. Subsequent investigations[2] revealed that, by varying the relative proportions of the reactants, either ClO_2F or O_2 could be obtained as a concomitant of HF and Cl_2. Christe established in a more recent, very detailed examination of the reaction[3] that, depending on the conditions, the principal products are either $Cl_2/O_2/HF$ through reaction (1) or $ClO_2/Cl_2/O_2/HF$ [reaction (2)] or HF/Cl_2O [reaction (3)]

$$4ClF + 2H_2O = 4HF + 2Cl_2 + O_2 \tag{1}$$

$$10ClF + 5H_2O \overset{25\,°C}{=} 10HF + 2ClO_2 + 4Cl_2 + \tfrac{1}{2}O_2 \tag{2}$$

$$4ClF + 2H_2O \overset{\text{low}\,T}{=} 4HF + 2Cl_2O \tag{3}$$

The presence of Cl_2OF among the the products[2] is understood in terms of the quantitative fluorination of Cl_2O by ClF, which can occur even at −78 °C.[3]

Given the complexity of the H_2O–ClF reaction, the simplicity of the reactants and the proposal[3] that HOCl is a reactive intermediate of reaction (3), generated according to ClF + H_2O → HOCl + HF, it is of evident interest to characterise any pre-reactive complex of H_2O and ClF formed on the initial encounter of the components, prior to any chemistry. The question to answer first is: how can $H_2O\cdots ClF$ be isolated before the vigorous reaction alluded to occurs?

We report here evidence for the formation of a gas-phase complex of H_2O and ClF. By incorporating a fast-mixing nozzle[4,5] into a Balle–Flygare type Fourier-transform microwave spectrometer,[6] complexes $H_2O\cdots ClF$ could be isolated and lived for long enough to allow them to be characterised through their rotational spectrum. The fast-mixing nozzle consists of two concentric, nearly coterminal tubes attached to the bottom plate of a Series 9 solenoid valve (General Valve Corp.) so that they are concentric with the valve exit orifice. Water vapour was flowed continuously into the evacuated Fabry–Pérot cavity of the spectrometer through the inner (0.3 mm internal diameter, glass) tube to yield a pressure of 3×10^{-5} mbar. Simultaneously, a mixture containing 0.5% of ClF in argon was pulsed from a reservoir, *via* the solenoid valve, through the outer (Teflon) tube into the cavity. The water and ClF therefore remained separate until they emerged from the coterminal tubes. Complexes $H_2O\cdots ClF$ were formed in three-body collisions as the two fast-moving gas flows met. Although such collisions cease within *ca.* 1 nozzle diameter downstream, two-body collisions continue for *ca.* 10 nozzle diameters.[5] At the end of this phase of the expansion, the complexes present at the interface of the concentric gas flows are in states of low internal energy and suffer no subsequent collisions. No chemical reaction is then possible. The rotational spectrum of the complexes isolated in collisionless expansion was obtained following polarization of the gas with pulses of microwave radiation in the usual way.

The ground-state rotational spectrum observed when using isotopically normal components was readily attributed to $H_2{}^{16}O\cdots{}^{35}ClF$ and $H_2{}^{16}O\cdots{}^{37}ClF$. When either the flow of water vapour was stopped or the ClF was removed from the ClF/Ar mixture, the spectrum disappeared. It had the pattern expected for a nearly prolate asymmetric rotor molecule in which the *a*-component of the electric dipole moment is non-zero. The six *a*-type rotational transitions $2_{12} \leftarrow 1_{11}$, $2_{02} \leftarrow 1_{01}$, $2_{11} \leftarrow 1_{10}$, $3_{13} \leftarrow 2_{12}$, $3_{03} \leftarrow 2_{02}$ and $3_{12} \leftarrow 2_{11}$ fell within the frequency range 8–18 GHz and each carried a nuclear quadrupole hyperfine structure arising from a Cl nucleus. A detailed analysis (to be reported elsewhere) led to the rotational constants B_0 and C_0, the centrifugal distortion constants Δ_J and Δ_{JK} (Watson A reduction,[7] I^r representation) and the Cl-nuclear quadrupole coupling constants χ_{aa}(Cl) and [χ_{bb}(Cl) − χ_{cc}(Cl)] given in Table 1 for the two $H_2O\cdots ClF$ isotopomers. The rotational constant A_0 could not be determined from the observed frequencies and its value was in each case pre-set to that calculated from the geometry of $H_2O\cdots ClF$ deduced below when θ = 0 was assumed. Table 1 also includes the corresponding set of spectroscopic constants of $D_2{}^{16}O\cdots{}^{35}ClF$ and $D_2{}^{16}O\cdots{}^{37}ClF$ obtained by fitting frequencies of transitions observed when D_2O vapour was flowed through the fast-mixing nozzle.

Unambiguous characterisation of the complex is possible from the observations reported. The value of $\chi_{aa}(^{35}Cl)$ is slightly larger in magnitude than $\chi_0(^{35}Cl)$ = −145.87 MHz of free ClF.[8] Similar increases have been observed in other B···ClF complexes, *e.g.* HCN···ClF,[9] and result from the change in the electric field gradient at the Cl nucleus induced by the B

Table 1 Ground-state spectroscopic constants of four isotopomers of $H_2O\cdots ClF$

Spectroscopic constant	$H_2{}^{16}O\cdots{}^{35}ClF$	$H_2{}^{16}O\cdots{}^{37}ClF$	$D_2{}^{16}O\cdots{}^{35}ClF$	$D_2{}^{16}O\cdots{}^{37}ClF$
B_0/MHz	2920.2516(4)	2919.0626(4)	2696.3183(6)	2694.3036(7)
C_0/MHz	2901.9630(4)	2900.7976(4)	2667.9396(6)	2665.9906(7)
Δ_J/kHz	4.92(2)	4.99(2)	4.51(2)	4.64(3)
Δ_{JK}/kHz	−251.9(2)	−251.3(2)	−52.1(3)	−54.8(4)
χ_{aa}(Cl)/MHz	−146.987(3)	−115.847(4)	−146.884(5)	−115.776(6)
[χ_{bb}(Cl) − χ_{cc}(Cl)]/MHz	−1.174(8)	−0.951(8)	−1.044(11)	−0.850(14)

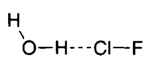
subunit. The near-equality $\chi_{aa}(\mathrm{Cl}) \approx \chi_0(\mathrm{Cl})$ for all observed isotopomers demonstrates that the ClF subunit must lie along, or nearly along, the a-axis of the complex. The small difference $[\chi_{bb}(\mathrm{Cl}) - \chi_{cc}(\mathrm{Cl})]$ indicates that the cyclindrical symmetry of ClF is only slightly perturbed in $H_2O\cdots ClF$.

The experimental rotational constants B_0 and C_0 given in Table 1 are consistent only with a geometry in which the order of the nuclei is $H_2O\cdots ClF$. The small changes in B_0 and C_0 attending isotopic substitution of ^{37}Cl into $H_2O\cdots{}^{35}ClF$ show that Cl lies closer to the centre of mass of the complex than does F. The relatively large changes in B_0 and C_0 on deuteriation of $H_2O\cdots ClF$ are consistent only with a geometry in which the H atoms are distant from the centre of mass. Hydrogen bonded structures **I** or **II** would lead to significantly smaller isotopic shifts. A geometry of the type shown in Fig. 1 is therefore suggested.

Further evidence about the $H_2O\cdots ClF$ geometry follows from the relative intensities of $K_{-1} = 1$ and $K_{-1} = 0$ transitions in, *e.g.*, the set $2_{12} \leftarrow 1_{11}$, $2_{02} \leftarrow 1_{01}$ and $2_{11} \leftarrow 1_{10}$. For the isotopomers $H_2{}^{16}O\cdots{}^{35}ClF$ and $H_2{}^{16}O\cdots{}^{37}ClF$, the two $K_{-1} = 1$ transitions each have a greater intensity than the $K_{-1} = 0$ transition, despite the fact that $K_{-1} = 1$ levels of a nearly prolate asymmetric rotor are higher in energy by *ca.* $h(A - B)$ than the $K_{-1} = 0$ level of a given J, and the $K_{-1} = 1$ transitions have a smaller line strength. This implies a nuclear spin statistical weight advantage, as well as a high effective rotational temperature, for the $K_{-1} = 1$ levels.

Two equilibrium geometries of the type shown in Fig. 1 are consistent with an enhanced nuclear spin statistical weight for $K_{-1} = 1$ transitions, namely either that with $\theta = 0$ (planar C_{2v}) or that with $\theta \neq 0$ (C_s) but with a potential energy barrier to the planar (C_{2v}) conformation low enough that the vibrational wavefunctions have C_{2v} symmetry. The second of these is referred to as effectively planar. In either case, the operation C_2^a exchanges a pair of equivalent protons and Fermi–Dirac statistics then require[10] that the $K_{-1} = 1$ levels in the vibrational ground state have a nuclear spin statistical weight of 3 while that of the $K_{-1} = 0$ level is 1. Conversely, in $D_2O\cdots ClF$, similar arguments applied to exchange of equivalent D($I = 1$) nuclei lead to a weight ratio of 1 : 2 for these levels. This reversal of intensity ratio was indeed exhibited by $D_2O\cdots ClF$, in which the $K_{-1} = 0$ transitions were observed to be significantly more intense than the $K_{-1} = 1$ transitions.

As discussed elsewhere,[11] for complexes such as $H_2S\cdots HF$, which is permanently pyramidal and exhibits no tunnelling splitting in the zero-point state, the $K_{-1} = 1$, a-type transitions are dramatically depopulated after the supersonic expansion in which they are formed. Hence, the observation of significantly populated $K_{-1} = 1$ rotational energy levels coupled with a nuclear spin statistical weight enhancement in $H_2O\cdots ClF$ isotopomers is strong evidence in favour of a planar or



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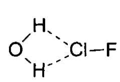

II

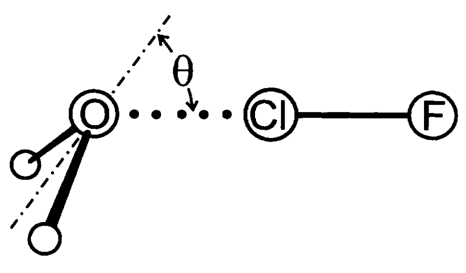

Fig. 1 Possible angular geometries of $H_2O\cdots ClF$. Those with $\theta = 0$ (planar, C_{2v}) or $\theta \neq 0$ but with low potential energy barrier to the planar form (effectively planar, C_s) are consistent with experimental observations.

effectively planar geometry. We cannot confidently distinguish between these possibilities on the basis of the data available, although it is worth noting that the planar model ($\theta = 0$) for $H_2O\cdots{}^{35}ClF$ predicts $B - C = 19.8$ MHz, which should be compared with the observed value $B_0 - C_0 = 18.3$ MHz. By contrast, $H_2O\cdots HCN$, which almost certainly has a vanishingly small potential energy barrier to the planar form, has an observed $B - C$ value larger than the planar model predicts.[12] This difference of behaviour, taken with a change of sign for Δ_{JK}, suggests that, although effectively planar in the zero-point state, $H_2O\cdots ClF$ has a pyramidal equilibrium geometry.

If a planar geometry ($\theta = 0$, Fig. 1) is assumed and the H_2O and ClF geometries are unperturbed[13,14] on complex formation, the rotational constants B_0 and C_0 for $H_2{}^{16}O\cdots{}^{35}ClF$ and $H_2{}^{16}O\cdots{}^{37}ClF$ can be fitted to give $r(O\cdots Cl) = 2.575(1)$ Å. When the isotopomers $D_2{}^{16}O\cdots{}^{35}ClF$ and $D_2{}^{16}O\cdots{}^{37}ClF$ are used instead, the result is $r(O\cdots Cl) = 2.547(1)$ Å. If, on the other hand, the configuration at O is allowed to become pyramidal ($\theta \neq 0$, Fig. 1), a least-squares fit of B_0 and C_0 for the two H_2O-based isotopomers leads to $\theta = 22(3)°$ and $r(O\cdots Cl) = 2.580(2)$ Å while the result from the two D_2O isotopomers is $\theta = 35(2)°$ and $r(O\cdots Cl) = 2.570(2)$ Å. The $r(O\cdots Cl)$ are now more nearly equal and the small extent of non-planar character, increasing in the deuteriated species, is not unreasonable. However, these results must be treated cautiously in view of the well known internal inconsistency of ground-state constants in such complexes caused by changes in the zero-point motion on substitution of H by D.

Finally, we note that the intermolecular stretching force constant k_σ, as calculated from the centrifugal distortion constant Δ_J under the assumption of rigid, unperturbed subunits,[15] has the value 14.2 N m^{-1} for $H_2{}^{16}O\cdots{}^{35}ClF$. This places $H_2O\cdots ClF$ as intermediate in binding strength between $H_2O\cdots HF$ and $H_2O\cdots HCl$, on the one hand,[16] and between $H_3N\cdots ClF$[17] and $HCN\cdots ClF$,[9] on the other.

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