

## Existence and Molecular Properties of a Gas-phase, Hydrogen-bonded Complex between Hydrogen Fluoride and Water established from Microwave Spectroscopy

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**Summary** The rotational spectrum of the hydrogen-bonded complex  $\text{H}_2\text{O} \cdots \text{HF}$  has been analysed to give rotational constants, approximate  $v = 1 \leftarrow 0$  separations for the three lowest-lying vibrational modes, the  $\text{O} \cdots \text{F}$  internuclear distance  $2.68 \pm 0.01 \text{ \AA}$ , and a value for the dipole moment component  $\mu_a$  of  $3.82 \pm 0.02 \text{ D}$ .

THE hydrogen-bonded complex between hydrogen fluoride and water has been the subject of much theoretical interest.<sup>1</sup> Its structure and molecular properties have been predicted from *ab initio* calculations<sup>2</sup> but so far no experimental information about the gas-phase complex has been available. We now report the identification and some experimental properties of such a complex from a study of its microwave rotational spectrum.

The existence of the complex is established through rotational transitions observed near to 14.4 and 28.8 GHz in an approximately 1:1 mixture of hydrogen fluoride and water vapour having total pressure 0.8 Torr. At similar pressures the monomer species exhibit no spectra near these regions. The vibrational ground state transitions (Table 1) consist of a single  $J = 1 \leftarrow 0$  transition at  $B + C$  and an almost symmetric triplet centred at  $2(B + C)$  which characterise a very nearly prolate asymmetric top. Although such a spectrum is expected of all models for the 1:1 complex, the observed  $B + C$  value is consistent only with structure (I) of Table 2, which shows some physical

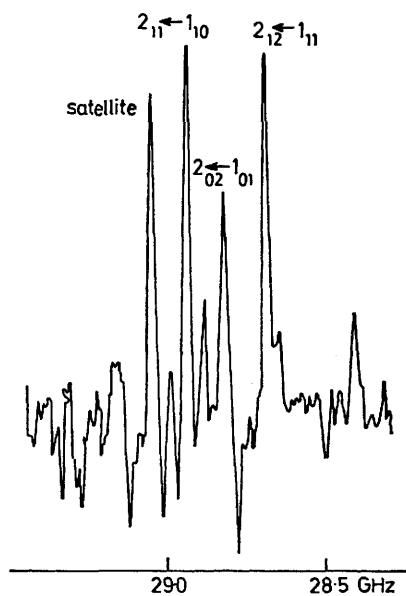


FIGURE 1. Nuclear spin statistical weight effects in the  $J = 2 \leftarrow 1$  vibrational ground state transitions of  $\text{H}_2^{16}\text{O} \cdots \text{HF}$ .

properties predicted from *ab initio* investigations<sup>2</sup> of three (planar) models for the complex. Structure (I) is also

predicted to have the most favourable stabilisation energy  $\Delta E$ , and gives best agreement with experiment for the  $v = 1 \leftarrow 0$  separation for the hydrogen-bond stretching mode (Table 2).

It is not possible, on the basis of rotational constants alone, to distinguish between the planar equilibrium structure (I) ( $C_{2v}$  symmetry) and the corresponding non-planar equilibrium ( $C_s$ ) structure because of the small contribution of the hydrogen atoms to the rotational constants B and C. We have assumed the former in using experimental B values of 7263.4 MHz and 6916.3 MHz for  $\text{H}_2\text{O} \cdots \text{HF}$  and  $\text{H}_2^{18}\text{O} \cdots \text{HF}$  to obtain  $r(\text{O} \cdots \text{F}) = 2.679 \pm 0.013 \text{ \AA}$ . Additionally, monomer structures<sup>3</sup> are assumed unchanged on complex formation (*ab initio* calculations for  $\text{HCN} \cdots \text{HF}$  suggest<sup>4</sup> this is reasonable and in any case the result is insensitive to any reasonable changes in the hydrogen atom positions).

TABLE 1

Rotational transitions in the vibrational ground state of  $\text{H}_2\text{O} \cdots \text{HF}$

| Transition                  | Frequency/MHz     |
|-----------------------------|-------------------|
| $1_{01} \rightarrow 0_{00}$ | $14403 \pm 1.0$   |
| $2_{11} \rightarrow 1_{10}$ | $28920.7 \pm 0.5$ |
| $2_{02} \rightarrow 1_{01}$ | $28804.7 \pm 0.5$ |
| $2_{12} \rightarrow 1_{11}$ | $28673.4 \pm 0.5$ |

The effects of nuclear spin statistics are evident in the spectra and are important in discussing the geometrical structure and the vibrational satellites. Figure 1 shows a trace of the  $J = 2 \leftarrow 1$  triplet for  $\text{H}_2^{16}\text{O} \cdots \text{HF}$  in the

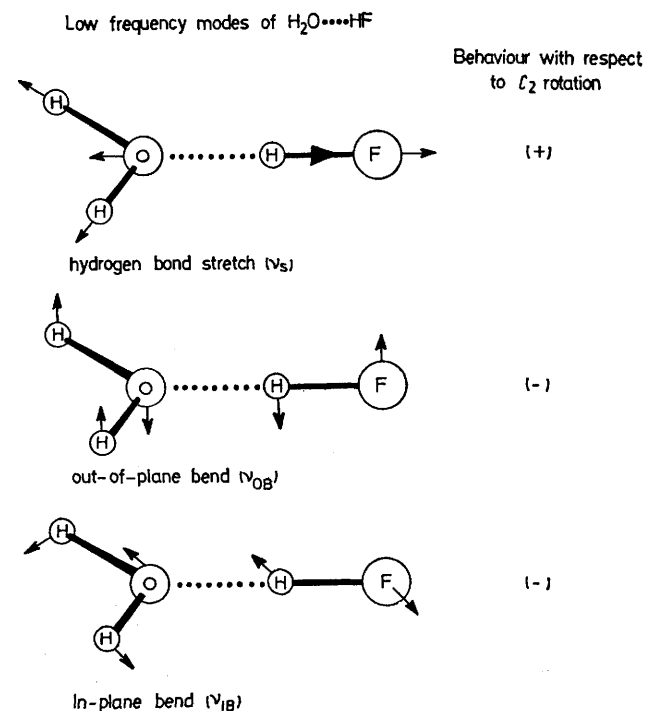


FIGURE 2

vibrational ground state. In order to explain this intensity pattern we need to use a nuclear statistical weight of 3 for rotational states of  $K_{-1}$  odd and 1 for  $K_{-1}$  even. Such a pattern can result from a pair of equivalent protons either in a planar ( $C_{2v}$ ) equilibrium structure or in a non-planar ( $C_s$ ) equilibrium structure with a low barrier to inversion in the centre of mass.

The three lowest energy vibrational modes of the complex are of the type shown in Figure 2, where for simplicity a planar  $C_{2v}$  equilibrium structure is used. The vibrational satellites with  $\nu_{IB}$  and  $\nu_{OB}$  even plus all satellites associated with  $\nu_s$ , will exhibit the same nuclear spin statistics as the ground state while those having  $\nu_{OB}$  and  $\nu_{IB}$  odd will be reversed. We have observed (centred at 28288.2 MHz) a  $J = 2 \leftarrow 1$  triplet with ground state-like statistics which has accordingly been assigned to  $\nu_s = 1$ . At 29033.7 and 28872.6 MHz we observe the central  $2_{02} \leftarrow 1_{01}$  components of satellites having the reversed statistics and these are assigned to the  $\nu_{OB} = 1$  and the  $\nu_{IB} = 1$  states respectively. Preliminary relative intensity measurements give the approximate  $v = 1 \leftarrow 0$  separations as *ca.* 94, *ca.* 180 and *ca.* 198  $\text{cm}^{-1}$  for the  $\nu_{OB}$ ,  $\nu_{IB}$  and  $\nu_s$  modes respectively.<sup>5</sup> The large separation of  $\nu_{OB} = 1$  from the ground state suggests that the equilibrium structure of the complex is either planar or that there is a very low barrier to the planar structure. The latter seems more probable on chemical grounds but we are currently investigating the species  $\text{D}_2\text{O} \cdots \text{DF}$  to clarify the position.

TABLE 2. *ab initio* Calculations for the water-hydrogen fluoride dimer<sup>a</sup>

| Structure                        | (I)   | (II)  | (III) |
|----------------------------------|-------|-------|-------|
| $(B+C)_{\text{calc}}/\text{MHz}$ | 13832 | 11077 | 11900 |
| $(B+C)_{\text{obs}}/\text{MHz}$  | 14402 | —     | —     |
| $\Delta E/\text{kJ mol}^{-1}$    | 39    | 13    | 13    |
| $\bar{\nu}_s/\text{cm}^{-1}$     |       |       |       |
| Calc <sup>b</sup> :              | 184   | 119   | —     |
| Obs <sup>c</sup> :               | 198   | —     | —     |

<sup>a</sup> P. A. Kollman and L. C. Allen, *J. Chem. Phys.*, 1970, **52**, 5085.  
<sup>b</sup> Pseudo-diatomic model. <sup>c</sup> From microwave relative intensity measurements.

The electric dipole moment component  $\mu_a = 3.82 \pm 0.02 \text{ D}$  for the  $\nu_{OB} = 1$  state has been estimated from the Stark effect of the  $1_{01} \leftarrow 0_{00}$  transition. Experience shows that the corresponding value for the vibrational ground state will be little different<sup>6</sup> and for present purposes may be taken as identical. If the molecule is taken as

planar and the dipole moment taken as the vector sum of the known monomer components,<sup>7</sup> the calculated value is 3.68 D. As the two equivalent protons are taken out of the molecular plane the predicted value of  $\mu_a$  becomes smaller than this. There is some evidence here, therefore, for an

enhancement of the dipole moment for a gas phase complex over the vector sum of monomer components.

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<sup>1</sup> See, for example, P. A. Kollman and L. C. Allen, *Chem. Rev.*, 1972, **72**, 283.

<sup>2</sup> P. A. Kollman and L. C. Allen, *J. Chem. Phys.*, 1970, **52**, 5085; P. A. Kollman, A. Johansson, and S. Rothenberg, *Chem. Phys. Letters*, 1974, **24**, 199.

<sup>3</sup> F. C. de Lucia, P. Helminger, and W. Gordy, *Phys. Rev. A*, 1971, **3**, 1849; W. S. Benedict, N. Gailar, and E. K. Plyler, *J. Chem. Phys.*, 1956, **24**, 1139.

<sup>4</sup> L. A. Curtiss and J. A. Pople, *J. Mol. Spectroscopy*, 1973, **48**, 413.

<sup>5</sup> These values are in reasonable agreement with those estimated from the near i.r. spectrum of the complex; R. K. Thomas, personal communication.

<sup>6</sup> See, for example, values for the ground state O<sup>+</sup> and the O<sup>-</sup> state for cyanamide; J. K. Tyler, J. Sheridan, and C. C. Costain, *J. Mol. Spectroscopy*, 1972, **43**, 248.

<sup>7</sup> J. S. Muentzer and W. Klemperer, *J. Chem. Phys.*, 1970, **52**, 6033; T. R. Dyke and J. S. Muentzer, *ibid.*, 1973, **59**, 3125.