Hydrogen Bonding in Gaseous Mixtures. Microwave Spectroscopic Detection of Simple Complexes

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Summary Microwave spectra of the simple hydrogen-bonded complexes $MeCN \cdots HF$ and $H_2O \cdots HF$ have been detected in gaseous mixtures; a preliminary analysis of the spectra for the former is reported.

THE study of hydrogen bonding in the gas phase offers the possibility of investigating the hydrogen bond in simple situations. I.r. detection of hydrogen bonding in gaseous mixtures[1] has been extended to the investigation of such spectra for numerous complexes, but the only microwave studies so far have been those for mixed carboxylic acids.[2] We now report the observation of microwave spectra of examples of simple complexes having a single hydrogen bond. The analysis of such spectra can provide information on structure, harmonic and anharmonic potential constants, dissociation energies and dipole moments.

The detection of a complex between MeCN and HF is readily demonstrated by reference to Figure 1. Traces (a) and (b), for MeCN and HF alone, show no absorption in the region 13·5—16·0 GHz, while trace (c) of a mixture having corresponding partial pressures shows a broad absorption band centred at *ca.* 15·1 GHz. Further investigation shows evidence of similar features at *ca.* 26·4, 30·2, 34·0, and 37·7 GHz which are assigned as $J = 7 \leftarrow 6$, $8 \leftarrow 7$, $9 \leftarrow 8$, and 10←9 for the symmetric rotor, hydrogen-bonded complex MeCN ··· HF. A similar study for mixtures of H_2O and HF shows bands centred at *ca.* 14·45 and 28·90 GHz which are assigned to $J = 1 \leftarrow 0$ and $2 \leftarrow 1$ transitions of the near symmetric rotor complex H_2O ··· HF.

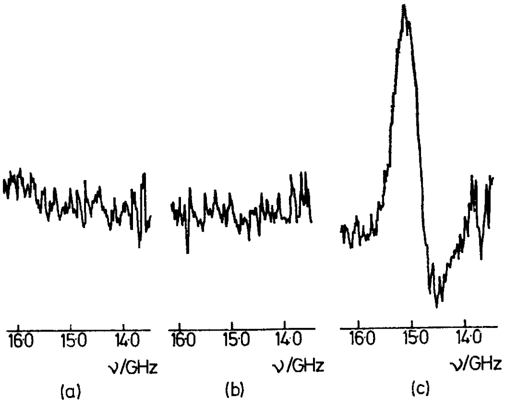

FIGURE 1. Microwave spectra of (a) MeCN; (b) HF; (c) mixture of MeCN and HF.

Each band in the spectrum of MeCN–HF mixtures shows extensive structure under higher resolution. For example the transition $J = 8 \leftarrow 7$ for the vibrational ground state is accompanied by a number of lines which are assigned as vibrational satellites in the Table, where v_s and v_b denote the number of quanta of the stretching and bending modes of the complex illustrated in Figure 2. Similar vibrational satellite series have been assigned for other rotational transitions, leading to a consistent set of rotational constants and in particular to a value for B_0 of 1852·86 MHz. A similar analysis for CD_3CN ··· HF leads to $B_0 = 1685·59$ MHz. Further isotopic substitution will be required for a complete structural determination, but from these two results a preliminary value of the NF distance is obtained as $r = 2·741$ Å. We have assumed only that the structure[3] of methyl cyanide remains unchanged on complex formation, since the result is sensibly independent of the hydrogen position. This value may be compared with 2·833 Å, a result recently obtained from a detailed quantum mechanical calculation for the closely related HCN ··· HF complex.[4]

TABLE

Assignment of $J = 8 \leftarrow 7$ transitions for MeCN ··· HF

v_b	v_s	ν/MHz	v_b	v_s	ν/MHz
0	1	29,521·3	5	0	30,791·2
0	0	29,645·2	6	0	31,048·6
1	0	29,861·3	7	0	31,315·5
2	0	30,089·0	8	0	31,578·7
3	0	30,318·1	9	0	31,861·9
4	0	30,555·1			

The assignment of the vibrational satellites given above is also consistent with the observed intensity pattern. The intensities of the series on the high frequency side of the ground-state transition pass through a maximum as expected for the doubly degenerate bending mode ν_b. Relative intensity measurements of such satellites provide a route to vibrational frequencies and hence to force fields of hydrogen-bonded complexes. Approximate intensity measurements in the present case lead to $\nu_s = 181 \pm 20$ cm^{-1} and $\nu_b = 45 \pm 15$ cm^{-1}. I.r. studies of complexes of MeCN with HCl[5] and HF[6] have already been made and the present values for ν_s and ν_b are entirely consistent with those obtained from the i.r. study of 168 ± 3 and 40 ± 14 cm^{-1} respectively.

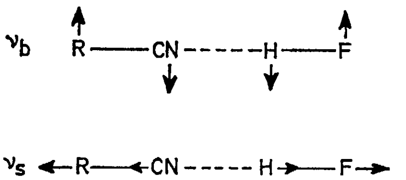

FIGURE 2. Diagrammatic representation of low-frequency bending and stretching modes.

The frequencies of the vibrational satellites lead to rotation–vibration constants $\alpha_b = -12·65 \pm 0·21$ and $\alpha_s = 7·61 \pm 0·16$ MHz. Evaluation of such constants, taken with a harmonic force field, offers a source of information on cubic potential constants for complexes. Further information on the potential function can be obtained from the dissociation energy of the complex. We are at present studying the equilibrium (1) in order to obtain the molar

$$\mathrm{MeCN} + \mathrm{HF} \rightleftharpoons \mathrm{MeCN} \cdots \mathrm{HF} \qquad (1)$$

enthalpy of formation and other thermodynamic quantities using microwave intensity measurements, which it has recently been pointed out[7] offer an advantageous method for study of this kind of equilibrium. Life-times of hydrogen bonded complexes are of considerable interest. We have observed that under certain conditions each line shows sub-structure of sufficiently small width to indicate that the complex is long lived.

We thank the S.R.C. for financial support.

(*Received*, 10*th December* 1974; *Com.* 1492.)

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