MICROWAVE SPECTRA, MOLECULAR STRUCTURES AND INTERNAL DYNAMICS OF $H_2S \cdots ICF_3$ and $H_2O \cdots ICF_3$ REVEALED BY BROADBAND ROTATIONAL SPECTROSCOPY

N. R. WALKER, S. L. STEPHENS AND A. C. LEGON, *School of Chemistry, University of Bristol, Bristol, BS8 1TS, U.K..*

The rotational spectra of three isotopologues of $H_2S \cdots ICF_3$ and four isotopologues of $H_2O \cdots ICF_3$ have been measured between 7 and 18.5 GHz by chirped-pulse Fourier transform microwave spectroscopy. The rotational constant, B_0, the centrifugal distortion constants, D_J and D_{JK}, and the nuclear quadrupole coupling constant of ^{127}I, $\chi_{aa}(I)$, are precisely determined for $H_2S \cdots ICF_3$ and $H_2O \cdots ICF_3$ by fitting observed transitions to the Hamiltonians appropriate to *symmetric* tops. The measured rotational constants allow determination of the molecular geometries. The C_2 axis of H_2O / H_2S intersects the C_3 axis of the CF_3I sub-unit at the oxygen atom. The r_0 lengths of halogen bonds identified between iodine and sulphur, $r(S \cdots I)$, and iodine and oxygen, $r(O \cdots I)$, are determined to be 3.5589(2) Å and 3.0517(18) Å respectively. The angle, ϕ, between the local C_2 axis of the H_2S / H_2O sub-unit and the C_3 axis of CF_3I is found to be $93.7(2)^\circ$ in $H_2S \cdots ICF_3$ and $34.4(20)^\circ$ in $H_2O \cdots ICF_3$. The observed symmetric top spectra imply nearly free internal precession of the C_2 axis of the hydrogen sulphide/water unit about the C_3 axis of CF_3I in each of these complexes. Additional transitions of $H_2^{16}O \cdots ICF_3$, $D_2^{16}O \cdots ICF_3$ and $H_2^{18}O \cdots ICF_3$ can only be assigned using Hamiltonians appropriate to asymmetric tops, suggesting that the effective rigid-rotor fits employed do not completely represent the internal dynamics of $H_2O \cdots ICF_3$.