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

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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, $\phi$, 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 $H_2O\cdots ICF_3$.