WEAK C-H--O AND C-H--F HYDROGEN BONDS IN THE TRIFLUOROMETHANE--OXIRANE AND DIFLUOROMETHANE--OXIRANE COMPLEXES

SUSANA BLANCO, JUAN C. LÓPEZ, ALBERTO LESARRI, SONIA ANTOLÍNEZ, EMILIO J. COCINERO and JOSÉ L. ALONSO, Grupo de Espectroscopía Molecular, Departamento de Química Física, Facultad de Ciencias, Universidad de Valladolid, 47005 Valladolid, Spain; WALTHER CAMINATI, Dipartimento di Chimica "G.Ciamici" Universita' degli Studi di Bologna, 40126 Bologna, Italy.

Alkanes appear capable of forming hydrogen bonds when sufficiently activated by neighboring electronegative substituents. In this context, the C-H--O interaction between the substituted alkanes trifluoromethane and difluoromethane with oxirane has been analyzed by molecular beam Fourier transform microwave spectroscopy. The ground state rotational spectra of $\text{C}_2\text{H}_4\text{O}--\text{HCF}_3$, $^{13}\text{CCH}_4\text{O}--\text{HCF}_3$, $\text{C}_2\text{H}_4\text{O}--\text{H}^{18}\text{CF}_3$, $\text{C}_2\text{H}_4\text{O}--\text{H}_2\text{CF}_2$, $\text{C}_2\text{H}_4\text{O}--\text{H}^{18}_2\text{CF}_2$ and $^{13}\text{CCH}_4\text{O}--\text{H}_2\text{CF}_2$ isotopomers have been studied, in their natural abundances, in the frequency range 6-18 GHz. A $C_s$ symmetry has been established for the oxirane--trifluoromethane complex with the C-H bond of trifluoromethane pointing to the domain of the nonbonding electron pairs of the O atom. The cooperative effect of two C-F--H-C interactions increases the stability of the complex. The barrier to internal rotation of the CF$_3$ group has been determined from the observed A-E splittings. In the oxirane--difluoromethane complex the determined structural data reveals the existence of two bifurcated hydrogen bonds: one between the CH$_2$ group of difluoromethane with the O atom of oxirane and the other between the methylene C-H groups of oxirane with the closest fluorine atom of difluoromethane. To our knowledge this is the first experimental evidence of this behaviour. The C-H--S interaction has been also analyzed in the trifluoromethane--tirane complex. The rotational spectra of $\text{C}_2\text{H}_4\text{S}--\text{HCF}_3$, $\text{C}_2\text{H}_2^{18}\text{S}--\text{HCF}_3$, $^{13}\text{CCH}_4\text{S}--\text{HCF}_3$ and $\text{C}_2\text{H}_4\text{S}--\text{H}^{18}\text{CF}_3$ isotopic species have been studied in their natural abundance.