EFFECTIVE C_{2v} SYMMETRY IN THE DIMETHYL ETHER–ACETYLENE DIMER

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Rotational spectra for five isotopomers of the dimethyl ether–acetylene complex have been measured by Fourier-transform microwave spectroscopy and the rotational constants and planar moments are consistent with a structure of effective C_{2v} symmetry in which the HCCH lies along the C_2 axis of the dimethyl ether (DME). The C–H...O intermolecular distance is determined to be 2.08(3) Å. Measurement of the dipole moment gives a value of $\mu_a = \mu_{total} = 1.79(4)$D, also consistent with a C_{2v} symmetry geometry.

Ab initio calculations at the MP2/6-311++G(2d,2p) level reveal a very flat potential energy surface around the C_{2v} geometry; basis set superposition error and zero point energy corrections are found to be crucial in predicting the correct order of stabilities of the minima located on the potential energy surface. Less than 24 cm^{-1} separates the structure in which the HCCH is coordinated to the lone pair of electrons on the DME from the structure with the HCCH lying along the C_2 axis of the DME. The structure and binding of the DME–HCCH complex will be described and compared to similar complexes.