STRUCTURE AND INVERSION MOTIONS OF THE WEAKLY BOUND $CH_2F_2 \cdots CO_2$ DIMER

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The rotational spectrum of the $CH_2F_2 \cdots CO_2$ dimer has been measured using chirped-pulse and resonant cavity Fourier-transform microwave (FTMW) spectroscopy, with the broadband spectrum playing an essential role in allowing identification of the tunneling splittings. The observed a-type transitions were doubled by a few megahertz, while c-type transitions were split by around 200 MHz, suggesting a tunneling motion that inverts the μ_c dipole moment component. A Pickett-type coupled Hamiltonian has been used to analyze the spectra, giving an energy difference (ΔE) between the tunneling states for the normal isotopologue of $115.140(2)$ MHz, and rotational constants of $A_0 = 5567.8604(27)$ MHz, $B_0 = 1832.9676(5)$ MHz, $C_0 = 1828.6132(5)$ MHz, $A_1 = 5567.8540(26)$ MHz, $B_1 = 1831.7711(4)$ MHz, $C_1 = 1828.6106(4)$ MHz. It was also necessary to include a Coriolis coupling term ($G_b = 7.740(6)$ MHz) as well as fourth and sixth order centrifugal distortion constants to obtain a satisfactory spectroscopic fit. The rotational constants and planar moments are consistent with a C_s symmetry structure in which the C_2 axis of CH_2F_2 makes an angle of roughly 23° with the axis of the CO_2, with the fluorine atoms of CH_2F_2 straddling the CO_2 carbon atom. The spectra of five additional isotopologues were analyzed, providing detailed structural information, and all except the mixed $C^{18}O^{16}O$ species showed inversion splittings similar to the normal species. The observation of unsplit spectra for two distinct $C^{18}O^{16}O$ isotopologues confirms that the internal motion involves movement of the CH_2F_2 subunit between the two ends of the CO_2 molecule.