LARGE TORSIONAL EFFECTS IN THE PARALLEL BAND ($v_5 = 1 \leftarrow 0$) OF CH$_3$SiF$_3$

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The lowest frequency parallel fundamental band ν_5 of CH$_3$SiF$_3$ near 388 cm^{-1} has been measured at a resolution of 0.00125 cm^{-1} with Fourier transform spectroscopy. Internal rotation plays a surprisingly important role in determining the form of the spectrum. The C_{3v}-type parallel band normally expected for a near-spherical top was strongly distorted by the Fermi-like interactions between the torsional stack of levels ($v_6 = 0, 1, 2..$) in the ground vibrational state and the corresponding stack with ($v_5 = 1$). The torsional fine structure in the spectrum was increased from ~ 0.0008 to ~ 1.1 cm^{-1} due to resonant interaction between ($v_5 = 0, v_6 = 4$) and ($v_5 = 1, v_6 = 0$) states. A detailed analysis was carried out of a data set consisting of 1194 infrared frequencies determined in the current work along with 134 mw, mmw and molecular beam measurements previously reported for the two torsional states $v_6 = 0$ and 1 of the ground vibrational state. A fit has been obtained to within experimental accuracy for all the data blocks using a vibration-torsion-rotation Hamiltonian with 31 parameters, including 3 parameters that characterize the Fermi-like interactions. The standard deviation for the infrared data is ~ 0.00016 cm^{-1}.

The Fermi-like terms in the Hamiltonian have two important general implications. First, the coefficients that characterize the Fourier expansion of the torsional barrier in the ground vibrational state undergo significant changes, which can be explained in terms of the contact transformation commonly used to remove intervibrational interactions. This is relevant when the torsional barrier height of CH$_3$SiF$_3$ is predicted with quantum chemical calculations. Second, due to the strong mixing with the ($v_5 = 0$, $v_6 = 4$) state, the probability density as a function of the torsional angle for the ($v_5 = 1$, $v_6 = 0$) state shows dramatic changes from that predicted with the classical model. This severe mixing with large $|\Delta v_6|$ has serious implications for vibration-rotation relaxation in molecules with low frequency, highly anharmonic vibrational modes.