

MILLIMETER-WAVE SPECTROSCOPY OF THE EXCITED VIBRATIONAL STATES OF THIOPHENE (C₄H₄S)

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Thiophene is a five-membered, aromatic heterocycle with C_{2v} symmetry and a moderate dipole (C₄H₄S, $\mu_a = 0.55$ D). A number of fundamental states of thiophene had previously been investigated through ro-vibrational studies in the infrared, but pure rotational spectroscopy had not extended beyond the ground state. We have measured and assigned transitions for 19 excited states by rotational spectroscopy, three of which are the IR inactive, A_2 symmetry states, and several of which are overtones or combination states. The new mm-wave data (40 - 360 GHz) and the previously published high resolution IR data are combined in a global least-squares fit. The interactions between the states permit the determination of several precise fundamental frequencies beyond those previously directly measured by high-resolution IR. The vibrationally excited states treated here are connected by a Fermi interaction and complex set of multiple Coriolis couplings, many of which are determined by the global fit. Several of these states may be treated as isolated vibrational states, but other states are involved in a pentad, a triad, and at least three dyads.