

ROTATIONAL SPECTRUM OF SO_3 AND THEORETICAL EVIDENCE FOR THE FORMATION OF ROTATIONAL ENERGY LEVEL CLUSTERS IN ITS VIBRATIONAL GROUND STATE

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The structure of the purely rotational spectrum of sulphur trioxide SO_3 is investigated using a new synthetic line list. The list combines line positions from an empirical model with line intensities determined, in the form of Einstein coefficients, from variationally computed ro-vibrational wavefunctions in conjunction with an *ab initio* dipole moment surface. The empirical model providing the line positions involves an effective, Watsonian-type rotational Hamiltonian with literature parameter values resulting from least-squares fittings to observed transition frequencies. The formation of so-called rotational energy clusters at high rotational excitation are investigated. The SO_3 molecule is planar at equilibrium and exhibits a unique type of rotational-energy clustering associated with unusual stabilization axes perpendicular to the S–O bonds. This behaviour is characterized theoretically in the J range from 100 through 250. The wavefunctions for these cluster states are analysed, and the results are compared to those of a classical analysis in terms of the rotational-energy-surface formalism.