An algebraic theory, based upon expansion of the molecular Hamiltonian in terms of bosonic creation and annihilation operators, has been used to extract detailed vibrational information from vibronically-resolved emission spectra of jet-cooled \( \text{S}_2\text{O} \) molecules. The fluorescence accompanying selective excitation of single rovibronic lines in the \( 2^3 \text{S}_{\text{II}} \) and \( 2^3 \text{S}_{\text{II}} \) \((v=0-3)\) bands of the intense \( \text{C} \ 1\text{A}' \leftarrow \text{X} \ 1\text{A}' (\pi^* \leftarrow \pi) \) absorption system were dispersed under moderate spectral resolution \((5-10 \text{ cm}^{-1})\). Ground state vibrational levels possessing as much as 20 quanta of excitation in the \( \nu_2 \) S-S stretching mode and residing up to \( \sim 13000 \text{ cm}^{-1} \) above the vibrationless \( \text{X} \ 1\text{A}' \) zero-point energy have been observed and assigned.

Detailed analyses of \( \text{S}_2\text{O} \) vibrational energies within the \( \text{X} \) and \( \text{C} \) manifolds, as well as their interconnecting vibronic resonances, have been performed through a \( U(2) \) based algebraic treatment. Although computationally no more intensive than a Dunham-like expansion, this approach offers the ability to extract multidimensional wavefunctions and related vibrational information. In particular, Franck-Condon factors and vibronic transition amplitudes can be evaluated efficiently without recourse to arduous numerical calculations. The emerging picture of \( \text{S}_2\text{O} \) vibrational dynamics suggests that the \( \text{X} \ 1\text{A}' \) surface is substantially more “local” in nature than the \( \text{C} \ 1\text{A}' \) state, with the latter exhibiting significant mixing of vibrational character among the \( \nu_1 \) (S-O stretching), \( \nu_2 \) (S-S stretching) and (to a lesser extent) \( \nu_3 \) (bending) degrees of freedom. Structural parameters deduced from algebraic analyses largely confirm the \( \text{C} \ 1\text{A}' \) equilibrium geometry inferred from previous studies under the assumption of an unchanged S-O bond length upon \( \text{C} \leftarrow \text{X} \) excitation.

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