ALGEBRAIC APPROACH FOR THE CALCULATION OF POLYATOMIC FRANCK-CONDON FACTORS: APPLICATION TO THE VIBRONICALLY-RESOLVED EMISSION SPECTRUM OF S_2O

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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 S_2O molecules. The fluorescence accompanying selective excitation of single rovibronic lines in the $2_0^2 3_0^1$ and 2_o^v (v=0-3) bands of the intense $\tilde{C}\ ^1\mathrm{A}' \leftarrow \tilde{X}\ ^1\mathrm{A}'$ ($\pi^* \leftarrow \pi$) absorption system were dispersed under moderate spectral resolution (5-10 cm^{-1}). Ground state vibrational levels possessing as much as 20 quanta of excitation in the ν_2 S-S stretching mode and residing up to $\sim$13000 cm^{-1} above the vibrationless $\tilde{X}\ ^1\mathrm{A}'$ zero-point energy have been observed and assigned.

Detailed analyses of S_2O vibrational energies within the $\tilde{X}$ and $\tilde{C}$ 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 S_2O vibrational dynamics suggests that the $\tilde{X}\ ^1\mathrm{A}'$ surface is substantially more "local" in nature than the $\tilde{C}\ ^1\mathrm{A}'$ state, with the latter exhibiting significant mixing of vibrational character among the ν_1 (S-O stretching), ν_2 (S-S stretching) and (to a lesser extent) ν_3 (bending) degrees of freedom. Structural parameters deduced from algebraic analyses largely confirm the $\tilde{C}\ ^1\mathrm{A}'$ equilibrium geometry inferred from previous studies under the assumption of an unchanged S-O bond length upon $\tilde{C} \leftarrow \tilde{X}$ excitation.

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