

## ALGEBRAIC APPROACH FOR THE EVALUATION AND ANALYSIS OF POLYATOMIC FRANCK–CONDON FACTORS: A DETAILED STUDY OF THE $S_2O \tilde{C} - \tilde{X}$ SYSTEM

T. MÜLLER and P. H. VACCARO, *Department of Chemistry, Yale University, P.O. Box 208107, New Haven, CT 06520-8107 USA*; F. IACHELLO and F. PÉREZ-BERNAL, *Center for Theoretical Physics, Yale University, New Haven, CT 06520-8120 USA*.

A new scheme for evaluating multidimensional Franck-Condon factors and related (non-Condon) transition moment matrix elements has been exploited to extract detailed structural and dynamical information directly from spectral intensity patterns. The underlying methodology builds upon a robust Lie algebraic framework that has the distinct advantage of incorporating anharmonicity effects explicitly from the onset, thereby leading to economical parameterization and rapid convergence of expansions employed for the description of polyatomic eigenvalues and eigenfunctions. This "vibron" approach has been applied to the analysis of extensive, vibronically-resolved absorption (CRDS) and emission (LIF, DLIF) spectra acquired under rotationally-cold slit-jet expansion conditions for the  $S_2O \tilde{C}^1A' - \tilde{X}^1A' (\pi^* - \pi)$  system. A unified interpretation for all available spectroscopic data, including vibrational energy levels supported by the pertinent electronic manifolds as well as relative transition intensities, has been achieved with quantitative agreement realized between experimental measurements and theoretical predictions. Aside from elucidating the substantial changes in geometry accompanying the  $S_2O \pi^* - \pi$  excitation process, this work has uncovered pronounced differences in vibrational dynamics between the  $\tilde{C}^1A'$  and  $\tilde{X}^1A'$  potential surfaces (with the latter being surprisingly more local in character than the former) and has documented a strong dependence of the  $\tilde{C} - \tilde{X}$  transition dipole moment on nuclear degrees of freedom.