ANALYSIS OF THE ROTATIONALLY-RESOLVED SPECTRA OF THE VIBRONICALLY-ACTIVE MOLECULES

DMITRY G. MELNIK and TERRY A. MILLER, *Laser Spectroscopy Facility, Department of Chemistry, The Ohio State University, 120 W. 18th Avenue, Columbus, Ohio 43210.*

Rotational structure of the vibronically coupled, and specifically, Jahn-Teller active molecules in isolated vibronic states has been studied for the decades, and the corresponding Hamiltonian and relationship of its parameters to the molecular properties are well-established, at least for the e vibronic states. However, in many cases an isolated state approach, both for the ground and vibronically excited levels, does not produce satisfactory results either because the experimentally obtained parameters of such model are not physically transparent[a], or the model fails to predict the observed spectrum[b] to the experimental accuracy. To circumvent these problems, we develop, from the molecular symmetry standpoint, an effective coupled state rotational Hamiltonian directly accounting for the interactions within the appropriate subset of the interacting vibronic states. This approach is expected to be useful for the analysis of the rotational level structure of the closely-spaced vibronic levels such as those occurring in the vibrationally excited manifolds of the open-shell molecules. The application of this approach to the spectra of the nitrate radical, NO_3, in the Jahn-Teller active $\tilde{A}^2E''$ state, will be discussed.

[a] D. G. Melnik, T. A. Miller and J. Liu, **TI15**, 67th *Molecular Spectroscopy Symposium*, Columbus, 2012

[b] M. Roudjane, T. J. Codd and T. A. Miller, **TI03**, 67th *Molecular Spectroscopy Symposium*, Columbus, 2012