

NO₃ STATES ACCESSED BY PHOTODETACHMENT AND DARK-STATE SPECTROSCOPY: WHAT DO WE KNOW?

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A good argument can be made that the atmospherically relevant NO₃ radical is the most complicated tetraatomic molecule. Five electronic states (the ground \tilde{X}^2A_2 state, and the two degenerate \tilde{A}^2E'' and \tilde{B}^2E' states) lie within 2 eV, and are coupled by several strong interactions. Amongst these is a strong linear and quadratic Jahn-Teller effect in the \tilde{A}^2E'' state, and a profound pseudo-Jahn-Teller interaction which couples the \tilde{X}^2A_2 ground state with the second excited state. The latter is almost strong enough to break the D_{3h} equilibrium symmetry of the ground state, and severely perturbs vibrational levels associated with the two in-plane modes of e' symmetry. This talk will report *ab initio* calculations based on the equation-of-motion coupled cluster model, its application to parametrize various vibronic model Hamiltonians, and simulations of the photodetachment spectrum of NO₃⁻ as well as the recent experiments of Okumura and coworkers in which the (dipole forbidden) \tilde{A}^2E'' state is accessed by direct absorption from the ground state.