

How much do, and can, we ``understand'' about the ground state of NO₃

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The ground electronic state of the nitrate radical has been of great interest to theoreticians for decades. Historically, questions centered on the geometrical structure of this strange molecule, with significant debate centering on the question of whether it is threefold symmetric (point group D_{3h}) or distorted to C_{2v}, an issue that led to significant confusion both with regards to the consistency of computational results and indeed, even the proper interpretation of the question. Another, and more recent, focus of study has been the vibrational energy level structure in the ground electronic state, both in the position of the levels and the designation of the states by the usual harmonic oscillator numbering system. The issue of the vibrational levels, especially the large (> 400 cm⁻¹) discrepancy between calculated and assigned positions for the ν_3 degenerate stretching fundamental, has been quite controversial in the past several years. This talk will review some recent results for this molecule, specifically the construction of an elaborate quasidiabatic Hamiltonian using equation-of-motion coupled-cluster theory, and its application to the calculation of energy levels and spectra involving the ground electronic state of NO₃. The degree to which one can describe the spectacularly rich infrared spectrum of this molecule (which has many characteristics of an electronic spectrum) will be emphasized, especially the limitations of trying to understand it in the conventional manner based on harmonic oscillator mode numbering and standard expectations about mode intensities.