DIABATIC MODEL HAMILTONIAN TREATMENTS OF THE NITRATE RADICAL

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Spectral lines associated with the NO_3 molecule were first detected and reported by Chappuis in the period 1880-1882. Although the carrier of these lines was not determined without ambiguity, it still remains a fact that this may well have represented the first spectroscopic detection of a polyatomic radical. In the intervening century and a quarter, NO_3 has emerged as both an important species in the nighttime atmosphere as well as a major challenge for molecular spectroscopy. The difficulties in the spectroscopy lay in the exceedingly complex quantum mechanics that governs the molecule; there are five low-lying electronic states, and vibronic interactions mixing these states are ubiquitous. This talk focuses on the ground electronic state of NO_3, which is strongly coupled (*via* a pseudo-Jahn-Teller interaction) with an excited state having $^2E'$ symmetry that is positioned roughly 2 eV higher in energy. Through use of a model Hamitonian approach, the identity of most vibronic levels within 3000 cm^{-1} of the zero-point level is revealed, and a number of spectroscopic misassignments are corrected and other unassigned lines are properly accounted for. The question the molecular structure of NO_3 is discussed towards the end of the talk, where it will be argued that viewing the molecule as a symmetric D_{3h} species is appropriate to understand its spectroscopy, while viewing it as a C_{2v} species effectively rationalizes its remarkably high reactivity. The question of the symmetry associated with the minimum on the adiabatic potential energy surface is largely irrelevant in this regard.