# Vibronic Coupling in the $NO_3$ Radical: Analysis of Negative-Ion Photoelectron and Dispersed Fluorescence Spectra

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The nitrate radical ($NO_3$) was first observed spectroscopically in 1880 and has been studied by infrared, electronic and negative-ion photodetachment spectroscopy. Interest in this radical is motivated by the fact that it is the most potent oxidizing agent in the nighttime atmosphere. Beyond that, $NO_3$ poses a great challenge to theory. For many years, a significant controversy surrounded its geometrical structure – did it or did it not have $D_{3h}$ symmetry? – as various high-level quantum chemical calculations gave conflicting answers to this question. In time, the difficulties with the ground $^2A_2$' electronic state of $NO_3$ have been traced to strong vibronic coupling with the second excited $^2E$' state, which greatly flattens the adiabatic potential of the former. The geometrical question ultimately comes down to $\omega_3$, the harmonic frequency that corresponds to the lowest e' vibrational mode of $NO_3$: an imaginary frequency implicates a lowering of symmetry from $D_{3h}$. A second question of more recent vintage surrounds the assignment of an infrared band at 1492 $cm^{-1}$ to the higher ($\nu_3$) degenerate stretching mode. This has been challenged both by vibronic coupling models and experiment, both of which point to reassignment of $\nu_3$ to a level near 1060 $cm^{-1}$. This talk provides an overview of the complexities posed by this radical and the various vibronic coupling mechanisms that are at play. It is shown that a vibronic Hamiltonian of the type advocated by Köppel, Domcke and Cederbaum provides excellent reproductions of the photoelectron and BX dispersed fluorescence spectrum of this species, suggesting that the low-lying vibronic level structure in the ground state is now well-established and secure.