# ENERGY LEVELS OF THE NITRATE RADICAL BELOW 2000 CM$^{-1}$

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Highly sophisticated quantum chemistry techniques have been employed to build a three-state diabatic Hamiltonian for the nitrate radical ($NO_3$). Eigenvalues of this Hamiltonian (which includes effects beyond the Born-Oppenheimer approximation) are consistent with the known "vibrational" levels of $NO_3$ up to *ca.* 2100 cm$^{-1}$ above the zero-point level; with a small empirical adjustment of the diabatic coupling strength, calculated levels are within 20 cm$^{-1}$ of the measured level positions for those that have been observed experimentally. Of the eleven states with $e'$ symmetry calculated below 2000 cm$^{-1}$, nine of these have been observed either in the gas phase by Hirota and collaborators as well as Neumark and Johnston, or in frozen argon by Jacox. However, the Hamiltonian produces two levels that have not been seen experimentally: one calculated to lie at 1075 cm$^{-1}$ (which is the third $e'$ state, above $\nu_4$ and $2\nu_4$) and another at 1640 cm$^{-1}$ which is best assigned as one of the two $e'$ sublevels of $4\nu_4$. A significant result is that the state predicted at 1075 cm$^{-1}$ is not far enough above the predicted $2\nu_4$ level (777 cm$^{-1}$ *v. ca.* 760 cm$^{-1}$ from experiment) to be plausibly assigned as $3\nu_4$ (which is at 1155 cm$^{-1}$: experimental position: 1173 cm$^{-1}$), nor is its nodal structure consistent with such an idea. Rather, it is quite unambiguously the $\nu_3$ level. Given the fidelity of the results generated by this model Hamiltonian as compared to experiment, it can safely be concluded that the prominent infrared band seen at 1492 cm$^{-1}$ (corresponding to a calculated level at 1500 cm$^{-1}$) is *not* $\nu_3$, but rather a multiquantum state best viewed as a sublevel of the $\nu_3 + \nu_4$ combination.