IMPROVED DIABATIC MODEL FOR VIBRONIC COUPLING IN THE GROUND ELECTRONIC STATE OF NO_3

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While model Hamiltonian approaches have provided considerable qualitative understanding regarding the nature of vibronic coupling and, especially, its effect on the electronic spectra of the nitrate radical, the parametrizations heretofore applied have been rather simplistic. As a result, while patterns of energy levels and appearance of "forbidden" spectral features are satisfactorily reproduced, the absolute position of the levels has not been calculated accurately enough to allow meaningful comparisons with those based on experimental assignments. In recent years, the machinery has been developed and applied to rather routinely make quite accurate calculations of level positions in strongly coupled systems (to, say, 20 cm^{-1} per quantum of excitation). Such calculations, which have been carried out for systems such as BNB, the formyloxyl radical (HCO_2) and low-lying excited electronic states of propadienylidene ($H_2C{=}C{=}C{:}$), have now been completed for NO_3. The spectra obtained from the corresponding model Hamiltonian, which explicitly treat the coupling between the ground $\tilde{X}^2A_2'$ and $\tilde{B}^2E'$ electronic states, and use a fairly elaborate parametrization of the corresponding diabatic surfaces, are presented and discussed.