VIBRONIC COUPLING MECHANISMS IN THE NITRATE RADICAL

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An argument can be made that the nitrate radical (NO₃) is the most complicated tetraatomic molecule in nature, an assertion that becomes undoubtedly correct when its quantum mechanical complexity is convolved with its environmental importance. The three lowest electronic states of this molecule $(X^2A'_2, A^2E'')$ and B^2E') are separated by less than 2 eV, and considerable vibronic mixing between these states leads to the complicated spectral patterns observed experimentally for NO₃. This talk reviews the various (qualitative) coupling mechanisms responsible for the abundance of various Franck-Condon forbidden features in electronic spectra of this species, with particular emphasis given to: photodetachment of the (well-behaved) nitrate anion; the A-X absorption spectrum; and the B-X absorption and dispersed fluorescence spectra. Apart from the A-X absorption spectrum, all of the above can be qualitatively reproduced by an extremely simple vibronic Hamiltonian, and semi-quantitative agreement is achieved with a more elaborate but conceptually identical form. As time permits, a progress report will be given on the interpretation of the A-X spectrum, some features of which remain poorly understood.