A NEW TYPE OF VIBRONIC INTERACTION IN THE NITRATE FREE RADICAL NO_3

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A new type of vibronic interaction is proposed to replace the traditional explanation for the observation of the nu4 progression in the photoelectron spectra of the nitrate anion. The proposal is based upon the high-resolution infrared spectroscopic results that the first-order Coriolis coupling constant is found to include the contributions not only from the degenerate vibrational mode, but also from the angular momentum of the unpaired electron. In sharp contrast with the traditional model, which requires a large off-diagonal vibronic interaction matrix element between the ground and excited electronic states, the new model points out that the fundamental state of a degenerate vibrational mode in the ground electronic state manifold intrinsically bears the character of the excited degenerate electronic state, thereby eliminating structural distortions of the NO_3 neutral molecule caused by a huge Herzberg-Teller effect, as predicted by the traditional treatment.