SIMULATIONS OF VIBRONIC LEVELS IN DEGENERATE ELECTRONIC STATES IN THE PRESENCE OF JAHN-TELLER COUPLING - EXPANSION OF PES THROUGH THIRD ORDER.

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Accurate measurements of vibronic levels in molecules exhibiting Jahn-Teller (JT) activity necessitate the inclusion of JT terms in the full vibronic Hamiltonian. JT terms of up to the second order have long been demonstrated to be important in the analysis of symmetric top molecules[a]. Recently it was pointed out that the inclusion of the interaction of symmetric and degenerate vibrational modes may be necessary to explain peculiarities of the vibronic structure of methoxy [b]. We have extended this approach to include terms off-diagonal in the projection of the electronic orbital angular momentum (JT terms) and diagonal in its projection (Fermi coupling terms). The resulting potential energy surface (PES) of the JT distorted degenerate electronic state is treated accurately up to third order in the nuclear coordinates, using a fast, interactive graphical interface software package. The C++/Fortran hybrid was designed to simulate vibronic spectra of JT distorted molecules in the presence of spin-orbit coupling. The multimode calculations include the interaction of up to 3 degenerate vibrational modes and up to 3 symmetric modes. The Franck-Condon approximation is used for the intensity analysis of experimental spectra. The Levenberg-Marquardt least squares fit in conjuncture with a numerical derivatives approach is successfully implemented to optimize the parameters of the Hamiltonian. The new computational package is used in a study of PES parameters of the methoxy (CH_3O) radical.

[a] T. A. Barckholtz, T. A. Miller, Int. Rev. Phys. Chem., **17**, 435, 1998
[b] J. Schmidt-Klugmann, H. Koppel, S. Schmatz, P. Botschwina, Chem. Phys. Letters **369**, 21-30, 2003