

MULTI-MODE DYNAMICAL JAHN-TELLER EFFECTS IN MOLECULAR ELECTRONIC SPECTRA AND INTERNAL CONVERSION DYNAMICS

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An overview is given over the basic theory of the Jahn-Teller (JT) effect in molecular electronic spectra, with an emphasis on doubly degenerate electronic states. While in the weak-coupling limit the nuclear motion is generally nonadiabatic, i.e. proceeds on both JT-split potential energy surfaces simultaneously, for strong coupling adiabatic and nonadiabatic energy regimes can be distinguished. Then, also the phenomenon of the geometric phase becomes of relevance. When another (degenerate or nondegenerate) electronic state is not too far in energy it may also interact with the degenerate electronic state in question (pseudo-JT coupling). In fact, this interaction can be important for an energetic separation as large as 2-3 eV. Pertinent examples of JT systems treated by us theoretically in the past several years, partly in collaboration with other groups, include electronic spectra of triatomic hydrogen^a, the methoxy radical^b and the benzene radical cation^c. The salient features of the various interaction mechanisms in these cases are elucidated based on ab initio calculated JT coupling parameters. - Additional strong pseudo-JT coupling effects are identified in the radical cations of the tetraphosphorous molecule^d, of allene^e and again benzene^f. Their profound impact on the internal conversion dynamics is established by wave-packet dynamical simulations.

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