

## Multi-state multi-mode vibronic coupling effects in photoinduced molecular dynamics

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A short overview is given over our activities in studying multi-mode molecular quantum dynamics on intersecting (and thus strongly coupled) potential energy surfaces. Often such situations are treated in a two-state approximation, where only two strongly coupled surfaces are considered. Here we address the more general situation of three and more strongly interacting electronic states. A common situation consists in one of the potential energy surfaces being doubly degenerate by symmetry at a suitable nuclear conformation, and thus subject to the Jahn-Teller (JT) effect. The numerical treatment often relies on a low-order Taylor series for the coupling matrix, where in the simplest case only terms linear in the displacements are retained.

Examples are presented to highlight extensions to both the linear-coupling and the two-state approximations. Specific second-order terms (bilinear in the coordinates of JT-active and totally symmetric vibrational modes) are found to be crucial to correctly describe the photoelectron spectra of the methoxy anion [1] and of the isoelectronic (neutral) methyl fluoride [2]. - For the larger benzene radical cation several (degenerate and nondegenerate) electronic states are found to interact simultaneously, with complicated multidimensional (also mutually intersecting) seams of conical intersections [3]. The nuclear motion is thus subject to multiple nonadiabatic coupling effects, one of them being related to the JT effect, the other to so-called pseudo-JT effects [4,5]. This gives rise to highly complex spectral structures [4,5] and to stepwise ultrafast (i.e. femtosecond) internal conversion processes [6]. The relation to the fluorescence dynamics of the benzene radical cation is discussed, as well as the impact of halogenation on the vibronic dynamics [7].

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