MULTI-STATE VIBRONIC INTERACTIONS IN FLUORINATED BENZENE RADICAL CATIONS.

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Conical intersections of potential energy surfaces have emerged as paradigms for signalling strong nonadiabatic coupling effects [a]. An important class of systems where some of these effects have been analyzed in the literature, are the benzene and benzenoid cations, where the electronic structure, spectroscopy, and dynamics have received great attention in the literature. In the present work a brief overview is given over our theoretical treatments of multi-mode and multi-state vibronic interactions in the benzene radical cation and some of its fluorinated derivatives. The fluorobenzene derivatives are of systematic interest for at least two different reasons. (1) The reduction of symmetry by incomplete fluorination leads to a disappearance of the Jahn-Teller effect present in the parent cation. (2) A specific, more *chemical* effect of fluorination consists in the energetic increase of the lowest σ-type electronic states of the radical cations.

The multi-mode multi-state vibronic interactions between the five lowest electronic states of the fluorobenzene radical cations are investigated theoretically, based on *ab initio* electronic structure data, and employing the well-established linear vibronic coupling model, augmented by quadratic coupling terms for the totally symmetric vibrational modes. Low-energy conical intersections, and strong vibronic couplings are found to prevail within the set of $\tilde{X}$–$\tilde{A}$ and $\tilde{B}$–$\tilde{C}$–$\tilde{D}$ cationic states, while the interactions between these two sets of states are found to be weaker and depend on the particular isomer. This is attributed to the different location of the minima of the various conical intersections occurring in these systems.

Wave-packet dynamical simulations for these coupled potential energy surfaces, utilizing the powerful multi-configuration time-dependent Hartree method [b] are performed. Ultrafast internal conversion processes and the analysis of the MATI and photo-electron spectra shed new light on the spectroscopy and fluorescence dynamics of these species[c].

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[b] M. H. Beck and A. Jäckle and G. A. Worth and H. -D. Meyer, Phys. Rep. **324**, 1 (2000).

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