The Role of Nonadiabatic Couplings in Spectroscopic Calculations of Aromatic Molecules

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Theoretically "exact" and numerically "accurate" Beyond Born–Oppenheimer (BBO) treatment [1-3] is implemented to construct diabatic potential energy surfaces (PESs) for several aromatic species, namely $C_6H_6^+$ [4,5],1,3,5-$C_6H_3F_3^+$ [6,7] and $C_4N_2H_4$ [8] molecules over a series of two-dimensional (2D) nuclear planes to include all possible nonadiabatic interactions among the low-lying electronic states. While computing the adiabatic PESs and nonadiabatic coupling terms (NACTs), we employ MRCI and CP-MCSCF methodologies as implemented in MOLPRO quantum chemistry software. Once are *ab initio* quantities (adiabatic PESs and NACTs) are obtained, those are used to construct single-valued, smooth, symmetric and continuous diabatic surface matrices for carrying out multi-state multi-mode nuclear dynamics with the help of time-dependent discrete variable representation (TDDVR) methodology to compute the photoelectron (PE)/photoabsorption (PA) spectra of the titled systems. In every case, our theoretically calculated spectra using BBO treatment and TDDVR dynamics show peak by peak correspondence with the experimental results as well as better than the findings of the multi-configuration time-dependent Hartree (MCTDH) method.

References:

[1] B. Mukherjee, K. Naskar, S. Mukherjee, S. Ghosh, T. Sahoo and S. Adhikari, *Int. Rev. Phys. Chem*. **38**, 287 (2019).

[2] K. Naskar, S. Mukherjee, B. Mukherjee, S. Ravi, S. Mukherjee, S. Sardar and S. Adhikari, *J. Chem. Theory Comput*. **16**, 1666 (2020).

[3] J. Dutta, S. Mukherjee, K. Naskar, S. Ghosh, B. Mukherjee, S. Ravi and S. Adhikari, *Phys. Chem. Chem. Phys. (Perspective)* **22**, 27496 (2020).

[4] S. Mukherjee, B. Mukherjee and S. Adhikari, *J. Phys. Chem. A* **121**, 6314 (2017).

[5] S. Mukherjee, S. Ravi, K. Naskar, S. Sardar and S. Adhikari, *J. Chem. Phys.* **154**, 094306 (2021).

[6] S. Mukherjee, J. Dutta, B. Mukherjee, S. Sardar and S. Adhikari, *J. Chem. Phys.* **150**, 064308 (2019).

[7] S. Mukherjee, S. Ravi, J. Dutta, S. Sardar and S. Adhikari, *Phys. Chem. Chem. Phys*. **24**, 2185 (2022).

[8] S. Hazra, S. Mukherjee, S. Ravi, S. Sardar and S. Adhikari, *Chem. Phys. Chem*. **23**, e202200482 (2022).