

Discrimination between protic and aprotic solvent effects on molecular and electronic structure of organic mixed-valence compounds by ab initio molecular dynamics simulations (CP2K)

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In Short

- Ab initio molecular dynamics simulations on organic mixed-valence systems in aprotic and protic solvents
- Snapshot cluster analyses of hyperfine couplings and optical excitation energies
- Analyses of the influence of hydrogen bonds on the structure of mixed-valence systems

The proper description of mixed-valence (MV) systems has been a topic of interest for several decades. It has been found that a solvent can be responsible for changing the classification of such a MV system. The classification scheme goes back to the work of Robin and Day.[1] A recently developed protocol showed that the description of the localized/delocalized character of MV systems, especially on the borderline of class II and III, is provided using the global hybrid functional BLYP35 (BLYP functional, with 35% Hartree-Fock exchange).[2] Calculation using a polarizable dielectric continuum solvent model (PCM) led to first good results in describing MV systems in solution. However, these calculations also revealed limits of PCM.[3] For example, the aprotic acetonitrile (MeCN) and the protic methanol (MeOH) have very similar dielectric constants and would thus be predicted to give very similar electron transfer behavior for a given MV system using a PCM. Experiments have shown that the protic solvent tends to cause much more pronounced charge localization. For example this can be found in case of the two organic MV systems, 1,4-dinitrobenzene and 1,3-dinitrobenzene. In the aprotic solvent (MeCN), the former has a delocalized (class III) charge while the latter has a localized charge (class II).[4–6] Calculations using PCM wrongly suggested that, in the case of 1,4-dinitrobenzene in MeOH, the charge is delocalized over the whole molecule (Compare Figs. 1,2), contradicting the experimental findings.

To get a deeper insight into the solvent-dependent dynamics of these MV systems we plan to perform Born-Oppenheimer (BO) molecular dynamics (MD) simulations using the CP2K program package.[7] The CP2K code will be used to carry out periodic liquid phase MD simulations. Subsequently, snapshots will be taken from these simulations in order

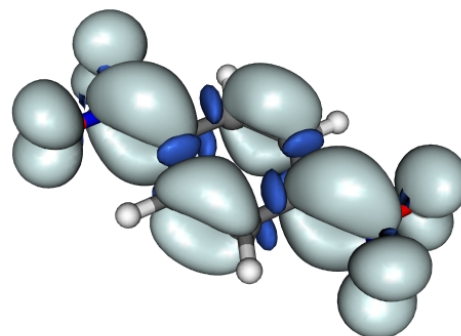


Figure 1: Spin density plots (iso surface ± 0.001 a.u.) of 1,4-dinitrobenzene radical anion in MeOH solution (COSMO).

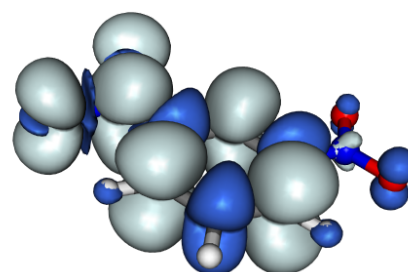


Figure 2: Spin density plots (iso surface ± 0.001 a.u.) of 1,3-dinitrobenzene radical anion in MeOH solution (COSMO).

to analyze the hyperfine couplings and optical excitation energies. In addition, we hope to obtain fundamental insights into the solvent dynamics of the abovementioned radical anions in different environments, in particular regarding the influence of hydrogen bonds on the structure of mixed-valence systems (MeOH). Therefore, time-dependent DFT (TDDFT) calculations will be performed to investigate the ET behavior of the MV systems using protic and aprotic solvents. The use of hybrid functionals is crucial in the proper description of MV systems. It was proven that CP2K is able to perform ab initio MD calculations using hybrid functionals despite their computational costs.[8]

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More Information

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