Supplementary Information

N. Arul Murugan[†], Jacob Kongsted[‡], Z. Rinkevicius[†], Hans Ågren[†]

† Department of theoretical Chemistry, Royal Institute of Technology, Stockholm,

Sweden

‡ Department of Physics and Chemistry, University of Southern Denmark, Campusvej 55, DK-5230 Odense M, Denmark.

1 Computational details

1.1 Finite temperature structure of SM in trichloromethane and water solutions

We have employed the Car-Parrinello mixed quantum mechanics/molecular mechanics technique (CP-QM/MM)[1, 2, 3] to obtain the finite temperature structures of stilbazolium merocyanine (SM) in trichloromethane and water solutions. The CP-QM/MM calculations were initiated from the equilibrated SM/trichloromethane and SM/water structures obtained from classical molecular dynamics (MD) simulations. The MD simulations were carried out for SM with the molecular geometry optimized using the Gaussian 03[4] software at the level of HF/6-31G^{*}. The atomic charges were calculated using the CHELPG^[5] method in which the charges are fitted to reproduce the molecular electrostatic potential at a number of points around the molecule. The optimized structure along with the GAFF[6] force-field and atomic charges obtained from the CHELPG procedure has been used to describe the SM molecule in the classical MD calculations. The SM molecule was solvated in 10633 water molecules in an orthorhombic box with a size of approximately, 72.6, 69.9, and 63.8 Å. The water molecules were described using the TIP3P force-field^[7] and were allowed to equilibrate under ambient condition using MD simulations in an isothermal-isobaric ensemble for a total simulation time of 100 ps. The classical MD simulations were carried out using the SANDER module of the Amber8 software[8]. The final configuration was used as the input configuration for the CP-QM/MM calculations. A similar procedure has been adopted in order to obtain the equilibrated start structure for SM in trichloromethane. We have here employed the GAFF force field for trichloromethane as solvent. The simulation box contains the single SM molecule and 2332 solvent molecules in an orthorhombic box of size approximately, 71.9, 69.8, and 63.2 Å. Subsequently, with the final configuration obtained from this MD run, we have carried out CP-QM/MM simulations for SM in trichloromethane. In the CP-QM/MM simulations for SM in water and trichloromethane, the SM molecule is treated at the density-functional theory level and the solvents were described using molecular mechanics force-fields[1, 2, 3]. We have used the Becke, Lee, Yang and Parr (BLYP) gradient corrected functional[9, 10] and the Troullier-Martins norm conserving pseudopotentials[11]. Here, the electronic wave function is expanded in a plane wave basis set with an energy cut off of 80 Ry. We have used 5 au as the time step for the integration of the equation of motion and 600 amu as the fictitious electronic mass. The total time scale for the production run is 26 and 34 ps in case of SM in trichloromethane and water as solvents, respectively.

2 Property calculations

2.1 UV/Vis absorption spectra calculations for SM in trichloromethane and in water

The UV/Vis absorption spectra calculations were performed using time-dependent density functional theory based on 80 snapshots extracted from the entire trajectory corresponding to SM in trichloromethane or in water. Two sets of calculations were performed for these two systems namely SM/trichloromethane and SM/water; (i) In one set of calculations, the properties were computed for the SM molecular structures alone obtained from the trajectory corresponding to SM in trichloromethane and in water. This set of calculations will be referred to as QM/MM-0. In this set of calculations, the solvent is not included explicitly or implicitly and the obtained property correspond to neutral or zwitter ionic structures of SM. (ii) In the second set of calculations, the properties were computed using the QM/MM response technique[12] as implemented in the developmental version of Dalton 2.0[13] which allows explicit treatment of solvent environment during the property calculations. The QM/MM response framework includes explicit mutual solute-solvent polarization. This set of calculations will be referred as QM/MM-1. For the QM/MM-0 and QM/MM-1 sets of calculations, we have employed the CAM-B3LYP/Turbomole-TZVP level of theory[14, 15]. There are reports of benchmark calculations on UV/Vis absorption spectra using the Turbomole-TZVP basis set[16, 17] and so we employ CAM-B3LYP/Turbomole-TZVP level of theory in our calculations. In the QM/MM-1 calculations, solvents are treated explicitly using molecular mechanics forcefields. For water we have employed a modified Ahlström water model[18] replacing the original single-centered polarizability by a distributed polarizability (expansion points at the atomic nuclei) calculated at the B3LYP/aug-cc-pVTZ level using the LoProp approach [19]. For trichloromethane we followed a similar strategy for the derivation of the distributed polarizabilities, but the charges were calculated using the CHELPG procedure at the B3LYP/aug-cc-pVTZ level of theory. The use of charges and distributed polarizabilities in these force-fields allows for an explicit inclusion of mutual solute-solvent polarizabilities.

2.2 Ground-state and excited-state dipole moments for SM

We report that the molecular structure of SM in water is zwitter ionic which changes to a neutral molecular structure in trichloromethane as solvent. In order to understand the influence of this structural change on the absorption spectra, we have computed the ground- and excited-state dipole moments for the neutral and zwitter ionic structures of SM. The excited-state dipole moment was computed from a double residue of the quadratic response function[20, 21] as implemented in Dalton 02[13]. In fact, the calculations performed here are similar to the QM/MM-0 set as described in subsection 2.1 where the properties are computed for gas-phase structures without including solvents. The dipole moment was computed for 80 snapshots of SM obtained from the CP-QM/MM calculations on SM/trichloromethane and SM/water systems.

3 Charge distribution of SM in trichloromethane and water

It is generally believed that the SM molecule exists as a resonance mixture of neutral and zwitter ionic canonical mesomeric forms in solvents and the average molecular structure is decided by the solvent polarity. The nature of the molecular structure can be inferred from the average bond lengths along the conjugation pathway since there is a remarkable difference in bond lengths depending upon the nature of molecular structure. Particularly for the SM molecule, the C_7 - C_8 and $C_{1'}$ -O bond lengths (See Figure 1 of the article) decides the nature of molecular structure. In trichloromethane solvent, the single-bond character of C_7 - C_8 and the double-bond character of $C_{1'}$ -O (See Table 1) suggest a neutral molecular structure for SM. In contrary, the double-bond character of the C_7-C_8 and the single-bond character of $C_{1'}-O$ (Table 1) for SM in water suggests a change of structure towards the zwitter ionic form. Another way to look into the nature of the molecular structure in solvents is to compute the group charges for the donor and acceptor groups. Particularly for solvatochromic molecules, the solvent-induced change in the charge distribution is remarkable and can be used to characterize the nature of the molecular structure [22, 23, 24]. So, we have computed the D-resp[1] charges for the phenolic (referred as D-pi group) and N-methyl pyridinium (referred as A-pi group) groups of SM in both trichloroethane and water as solvents. The D-resp charges are dynamic quantities in CP-QM/MM calculations and take into account the instantaneous electric field due to dynamic solvent environment.

The distribution of D-resp charges for D-pi and A-pi groups of SM in trichloromethane and water as solvents are shown in Figure 1S. For comparison, the group charges are shown also for SM in the gas phase. In the gas phase, the molecular structure should correspond to the neutral canonical form since the zwitter ionic form cannot be stabilized in vacuum. The group charges for D-pi and A-pi groups of SM in the gas phase are, respectively, -0.24 and 0.24 q/e, while in trichloromethane as solvent the values are, respectively, -0.30 and 0.30 q/e. The group charges in water as solvent are much larger and amount to -0.72 and 0.72 q/e. These results show that SM has a neutral molecular structure in trichloromethane as solvent similar to the gas phase structure. In water as solvent, we see an increased charge accumulation on D-pi and A-pi groups of SM (by almost 2.4 times larger when compared to that in trichloroethane as solvent), which shows that indeed the molecular structure corresponds to a zwitter ionic or charge-separated structure. Overall, both the results on average molecular structure and average D-pi and A-pi group charges suggest that indeed the molecular structure changes from the neutral to the zwitter ionic form when the solvent environment changes from trichloromethane to water.



Figure 1S

References

- [1] A. Laio, J. VandeVondele, U. Röthlisberger, J. Phys. Chem. B., 106, 7300(2002).
- [2] A. Laio, J. VandeVondele, U. Röthlisberger, J. Chem. Phys., 116, 6941(2002).
- [3] J. Hutter, M. Parrinello, D. Marx, P. Focher, P.; M. Tuckerman, W. Andreoni, A. Curioni, E. Fois, U. Röthlisberger, P. Giannozzi, T. Deutsch, A. Alavi, D. Sebastiani, A. Laio, J. VandeVondele, A. Seitsonen, S. Billeter, *Computer code CPMD, version 3.11*, Copyright IBM Corp. and MPI-FKF, Stuttgart, 1990–2002.

- [4] M.J. Frisch, et al., Gaussian 03, Rev. B.05. 2003, Gaussian, Inc. Pittsburgh, PA.
- [5] C.M. Breneman, K.B. Wiberg, J. Comp. Chem., 11, 361(1990).
- [6] J. Wang, R.M. Wolf, J.W. Caldwell, P.A. Kollman, D.A Case, J. Comp. Chem., 25(9), 1157(2004).
- [7] W.L. Jørgensen, J. Am. Chem. Soc., **103**, 55(1981).
- [8] D.A. Case, et al., AMBER8, 2004. University of California, San Francisco, CA.
- [9] A.D. Becke, *Phys. Rev. A.*, **38**, 3098(1988).
- [10] C. Lee, W. Yang, R.C. Parr, *Phys. Rev. B.*, **37**, 785(1988).
- [11] N. Trouiller, J.L. Martins, *Phys. Rev. B.*, **43**, 1993(1991).
- [12] C. B. Nielsen, O. Christiansen, K. V. Mikkelsen, J. Kongsted, J. Chem. Phys., 126, 154112 (2007).
- [13] "DALTON, a molecular electronic structure program, Release 2.0 (2005), see http://www.kjemi.uio.no/software/dalton/dalton.html"
- [14] T. Yanai, D. P. Tew, N. C. Handy, *Chem. Phys. Lett.*, **393**, 51 (2004).
- [15] M. J. G. Peach, T. Helgaker, P. Salek, T. W. Keal, O. B. Lutns, D. J. Tozer, N. C. Handy, Phys. Chem. Chem. Phys., 5, 558 (2006).
- [16] A. Schafer, C. Huber, R. Ahlrichs, J. Chem. Phys., 100, 5829 (1994).
- [17] M. R. Silva Junior, M. Schreiber, S. P. A. Sauer, W. Thiel, J. Chem. Phys., 129, 104103 (2008).
- [18] P. Ahlström, A. Wallqvist, S. Engström, B. Jönsson, Mol. Phys., 68, 563(1989).
- [19] L. Gagliardi, R. Lindh, and G. Karlström, J. Chem. Phys., **121**, 4494 (2004).
- [20] J. Olsen, P. Jørgensen, J. Chem. Phys., 82, 3235 (1985).
- [21] P. Salek, O. Vahtras, T. Helgaker, H. Ågren, J. Chem. Phys., 117, 9630 (2002).
- [22] T.L. Fonseca, K. Coutinho, S. Canuto, *Chem. Phys.*, **349**, 109(2008).
- [23] N. Arul Murugan, Hans Ågren, J. Phys. Chem. A, 113 (11), 2572(2009).
- [24] N. Arul Murugan, Z. Rinkevicius, Hans Agren, J. Phys. Chem. B, 113 (17), 4833(2009).