



Combined use of Sequential QM/MM and Free Energy Gradient methods in the study of electronic and conformational structure of molecules with acceptor-donor groups

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INTRODUCTION

The combined use of the Sequential QM/MM method with a mean field approximation (ASEC) [1] and the Free Energy Gradient method [2] has been very successful in describing the electronic structure of molecules in solution [3]. In this work, we will show the results we recently obtained in applying that combination to study the structure of DMACA and Phenol Blue (PB) in several solvents, such as cyclohexane, acetonitrile, water and other protic and aprotic solvents covering a range of polarity. We studied the solvent effect in the geometry, the electronic absorption spectrum and the first hyperpolarizability.

METHODS

The methodology consists in an iterative process. In each step of the process we perform: (i) a Monte Carlo simulation with empirical Lennard-Jones-Coulomb potential to generate few hundreds of uncorrelated configurations; (ii) calculation of the ensemble average of the solvent potential to include in the solute's Hamiltonian; (iii) calculation of the atomic forces and the hessian matrix so that a new geometry can be obtained using a Newton-Raphson scheme; (iv) lastly, a calculation of the charge distribution of the molecules in the presence of the solvent in the new geometry. With the new geometry and atomic charges, the next step of the simulation is initiated. The geometry optimization and hyperpolarizability calculations were performed using the MP2 method. The electronic excitation calculations were obtained with TD-DFT.

RESULTS AND DISCUSSION

Covering a reasonable variety of solvents, we found that for low polarity solvents like cyclohexane, there are no significant changes in geometry, excitation energy and electrical properties in relation to the gaseous phase.

In aqueous solution, where the most significant changes are observed, PB has the typical conjugation of single and double N–C bonds between the rings slightly inverted. Also, the well characterized aromatic and quinonoidal rings of the molecule in vacuo are both deformed to something in between these two situations. In DMACA, the changes are less abrupt. The C=C bonds increase and the C–C bonds decrease, but they lie in the halfway to equalize themselves. But, in both solutes, the pyramidal angle of the dimethylamino group decreases almost 30 degrees in comparison with the vacuum, leading to a planar conformation of the amino group. Furthermore, our results are in accordance with the experimentally observed behavior of DMACA and PB in solution for solvatochromic shifts and hyperpolarizabilities.

CONCLUSIONS

The simulations performed in this work show that the ASEC-FEG method is able to capture efficiently the major solvent effects in the geometry of the molecules, giving results in good agreement with experiment for molecules with acceptor-donor groups connected by large conjugated or aromatic chains.

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