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# Electronic and structural properties of supercritical fluids. Evaluation of force fields for the description of the absorption spectrum of paranitroanilina in supercritical $CO_2$

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**Abstract:** In this work we study the structural and electronic properties of supercritical $CO_2$ starting with the evaluation of force fields based on previous ab initio Born-Oppenheimer molecular dynamics (BOMD) [1]. The main application is the description of the absorption spectrum of paranitroanilina (pNA) [2,3] in supercritical $CO_2$. The supercritical $CO_2$ is considered a ``green alternative" to conventional organic solvents and the search for safer solvents, along with the increasing awareness of environmental issues has led to the interest in ``green chemistry" [4,5], seeking sustainable solutions. At first we studied three traditional force fields for $CO_2$, applied in the supercritical region. These force fields can be validated by first principles simulation. We considered the supercritical condition for $CO_2$ as T=315K, $\rho$=0.81g/cm³ and the classical force field of Zhang and Duan [6]. We also did an analysis consisting of a change of the atomic point charges and the geometry of $CO_2$, including a non-linear case in which an angle (O-C-O)=176° was considered [1]. The study of the solvatochromism of pNA in supercritical $CO_2$ was made considering all these situations, evaluating the theoretical outcome and the experimental results. The simulation generates structures using Monte Carlo and are used in quantum mechanics calculations using DFT (CAM-B3LYP [7]). To verify the importance of a proper description of the structural property, we considered another geometry for the pNA geometry different from that we used initially in the simulations with supercritical $CO_2$. This ``modified geometry" of pNA was obtained from a previous Born-Oppenheimer simulation [1] and was used in a Monte Carlo simulation with the nonlinear $CO_2$ for the supercritical condition. The results of all simulations indicated that the changes of atomic charges and thus in the polarization due to the solvent, has no great significance in the absorption spectrum of the pNA. When considering the nonlinear $CO_2$, we obtained slightly better results. But the most significant results are obtained for the situation in which we use the modified geometry of pNA. Part of the shift in the absorption spectrum of the pNA comes with the electrostatic contribution of solute-solvent interaction and the other part comes from the structural change.

**Key-words**: S-QM/MM, solvatochromism, absorption spectrum, supercritical fluids.

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