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A first principles approach to the electronic properties of liquid and supercritical CO_2

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ABSTRACT

The electronic absorption spectra of liquid and supercritical CO_2 ($scCO_2$) are investigated by coupling a many-body energy decomposition scheme to configurations generated by Born-Oppenheimer molecular dynamics. A Frenkel exciton Hamiltonian formalism was adopted and the excitation energies were calculated with time dependent density functional theory. A red-shift of ~ 0.2 eV relative to the gas-phase monomer is observed for the first electronic absorption maximum in liquid and $scCO_2$. The origin of this shift, which is not very dependent on deviations from the linearity of the CO_2 molecule, is mainly related to polarization effects. However, the geometry changes of the CO_2 monomer induced by thermal effects and intermolecular interactions in condensed phase lead to the appearance of an average monomeric electric dipole moment $\langle\mu\rangle$ = 0.26 ± 0.04 D that is practically the same at liquid and supercritical conditions. The predicted average quadrupole moment for both liquid and $scCO_2$ is $\langle\Theta\rangle$ = – 5.5 D Å, which is increased by ~ –0.9 D Å relative to its gas-phase value. The importance of investigating the electronic properties for a better understanding of the role played by CO_2 in supercritical solvation is stressed.

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