A Combined QM/MM Molecular Dynamics Simulations Study of Nitrate Anion (NO_3^-) in Aqueous Solution

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The structural and dynamical properties of NO_3^- in dilute aqueous solution have been investigated by means of two combined quantum mechanics/molecular mechanics (QM/MM) molecular dynamics simulations, namely HF/MM and B3LYP/MM, in which the ion and its surrounding water molecules were treated at HF and B3LYP levels of accuracy, respectively, using the DZV+ basis set. On the basis of both HF and B3LYP methods, a well-defined first hydration shell of NO_3^- is obtainable, but the shell is quite flexible and the hydrogen-bond interactions between NO_3^- and water are rather weak. With respect to the detailed analysis of the geometrical arrangement and vibrations of NO_3^-, the experimentally observed solvent-induced symmetry breaking of the ion is well reflected. In addition, the dynamical information, i.e., the bond distortions and shifts in the corresponding bending and stretching frequencies as well as the mean residence time of water molecules surrounding the NO_3^- ion, clearly indicates the "structure-breaking" ability of this ion in aqueous solution. From a methodical point of view it seems that both the HF and B3LYP methods are not too different in describing this hydrated ion by means of a QM/MM simulation. However, the detailed analysis of the dynamics properties indicates a better suitability of the HF method compared to the B3LYP-DFT approach.