Stability of halides at the air/water interface using the generalized multipole polarizability-QM/MM model

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The stability of halides at the air/water (a/w) interface has been actively studied [1,2] in order to gain a fundamental understanding of solvation interactions. Whether polarization of the ion is the factor that may drive halides to the bulk or to the a/w interface is a subject of great debate. These ionic systems provide also a ground for the benchmarking of new methods. In this work we assess the performance of the generalized multipole polarizability (GMP)-QM/MM method [3,4] that has been developed as an ultrafast QM/MM approach to capture efficiently the electrostatic interactions ((ES)QM/MM) between the QM and MM subsystems, the calculation of which is the bottleneck in QM/MM methods.

Here, we present calculations of the free energy of halide anions in water clusters using the GMP-QM/MM Monte Carlo method. We compare the results with those obtained with full QM/MM (exact-QM/MM) and approximate MMpol/MM treatments outlined below.

(1) exact-QM/MM: the total energy of the system consists of the energy of MM subsystem, the Van der Waals interaction energy between the QM and MM subsystems, and the energy of QM subsystem. The latter term includes the electrostatic interaction energy between the QM and MM subsystems, and we express it as $E_{\mathrm{QM+(ES)QM/MM}}$. $E_{\mathrm{QM+(ES)QM/MM}}$ is not separable into QM and (ES)QM/MM parts as the electronic wave function of the QM subsystem depends on electric field of MM subsystem:

$$(\hat{H}_{\mathrm{QM}} + \hat{H}_{\mathrm{(ES)QM/MM}})\psi = E_{\mathrm{QM+(ES)QM/MM}}\psi$$

(2) GMP-QM/MM: The GMP-QM/MM MC is based on a second order perturbation theory treatment of the total Hamiltonian with $\hat{H}_{\mathrm{(ES)QM/MM}}$ as the perturbation Hamiltonian. The zeroth-order perturbation energy is equivalent to the eigenvalue of $\hat{H}_{\mathrm{QM}}$, i.e. of the isolated QM subsystem. The first and second order terms are responsible for the (ES)QM/MM part, but the first order term doesn't include the polarization of QM wave function. The response to the electric field of MM comes in higher terms than first order. The second order term is primary responsible for polarization. The third order and higher terms, if included, are responsible for energies that are due to hyper-polarizabilities. Accordingly, the quality of the GMP-QM/MM model is comparable to the quality of the exact QM/MM model as long as the nonlinear response is negligible.

(3)MMpol/MM: this model includes a representation of the solute as (distributed) charges plus induced dipole moments. This model has been used frequently in theoretical studies of halides at a/w interfaces.

In this work we compare the MMpol/MM model with the QM/MM and GP-QM/MM models. We discuss the effect from multipoles higher than dipole possibly included in MMpol. We also examine the effect of the 2nd hyperpolarizability and discuss the nonlinear response.

[References]

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