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Ab initio simulations of sulfuric acid solutions

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ABSTRACT

Ab initio molecular dynamics simulations are presented for a solution consisting of a single H_2SO_4 molecule in a periodic box with 63 water molecules. Three trajectories lasting 35–55 ps were calculated at temperatures in the 320–326 K range, for two functionals, and double- and triple-zeta quality basis sets. All three trajectories displayed prompt ionization of the first proton. The HSO_4^- ion displayed varying extents of ionization in the different trajectories. Proton hopping was observed between the HSO_4^- oxygen atoms. Moreover, hopping of the solvating water molecules also occurred between the different oxygen atoms of the anions, with bidentate water, hydrogen bonding to two different oxygen atoms, serving as an intermediate.

1. Introduction

Since the introduction of the Car–Parrinello (CP) simulation method [1], on-the-fly *ab initio* molecular dynamics (AIMD) simulations are becoming a staple tool of computational chemistry. In particular, the technique allows modeling proton-transfer systems such as acid and base solutions, while treating all possible solvation states within a unified computational scheme. A recent review by Marx [2] summarizes the achievements of the method in studies of proton-transfer processes in hydrogen-bonded networks. However, the method is not a black box tool.

The electronic state of the system is calculated at each trajectory time step in order to obtain the Born–Oppenheimer potential energy surfaces and the forces acting on the nuclei. This fact imparts the method its ‘first principles’ flavor, avoiding the need for calibration of empirical potentials. However, the heavy computational cost limits both the level of feasible electronic structure calculations and the duration of the trajectories. Typically, density functional theory (DFT) is used in conjunction with computationally efficient exchange-correlation functionals such as Becke–Lee–Yang–Parr (BLYP) [3,4], Perdew–Burke–Eruzerhot (PBE) [5], or Hamprecht–Cohen–Tozer–Handy (HCTH) [6]. The range of applications is constantly increasing with advances in computer technology and in computational algorithms. Thus, while initially trajectories of a few picoseconds (ps) duration required access to supercomputers, currently 1–2 orders of magnitude longer trajectories are feasible on modern personal computers.

Recently, it has been realized that meaningful liquid phase simulations require longer equilibration and simulation times than thought initially [7–12]. Moreover, AIMD simulations of water in the vicinity of room temperature tend to underestimate the diffusion constant (*D*) by about an order of magnitude. The diffusion constant itself is difficult to estimate near this temperature, as the slope of the mean square displacement (MSD) was reported to change with time [7]. In two investigations of water, a transition was observed into a state of low diffusivity after a ~10 ps long AIMD simulation employing BLYP at 315 K [9] and PBE at 325 K [10]. The problem may be related to the use of a first principle (rather than an empirical) potential in conjunction with classical mechanics [8,10]. Nuclear zero-point energy and quantum delocalization effects are neglected making classical water overbound. It has been suggested [8] that ‘including proton quantum effects is approximately equivalent to a temperature increase of 50 and 100 K, when using a rigid or a flexible water model, respectively’. Additional critiques of the performance of AIMD can be found in Ref. [13].

One may summarize the current status by stating that the AIMD method has great promise, but careful analysis of the performance is needed for different systems and computational schemes. Of particular interest are solutions in which proton transfer is taking place; since there AIMD is one of the two principal computational tools available (the other being the empirical valence bond method [13,14]). Since the first AIMD studies of a protonated water solution [15] more than 10 years ago, a number of AIMD simulations of acid and base aqueous solutions have been published. For representative recent studies, see, Refs. [16,17] (OH^- solution), [18] (H^+), [19] (HBr), [20,21] (HCl), [22] (HF), [23] (HCl–HF mixture), and [24] (sulfuric acid). To exemplify the problematic aspects of AIMD in this context, and the potential gains, one may note a recent AIMD

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study of proton-transfer in base solutions [16]. Three different functionals were used to study the hydroxide solvation shell and the transport mechanism, each yielding different results. The results employing BLYP, which gave the most physically reasonable diffusion coefficient (intermediate between water and proton diffusivity) were used to elucidate the molecular diffusion mechanism for the system. In modeling ionic solutions, one may expect other problems in addition to a dependence on the exchange-correlation functional. Ion–water bonds are much stronger than normal hydrogen bonds, and thus an adequate sampling of system configurations may not be attained even for trajectories of tens of picoseconds duration. Long range interactions between ions in a small periodic box may also introduce artifacts. The simulation model does not reproduce a true liquid of a given concentration, but rather an infinite ‘super-crystal’ in which ions and molecules in the different periodic boxes are obliged to follow the same dynamics. Moreover, the model solution density (typically adopted from experiment) may correspond to pressures vastly differing from 1 bar [35]. The phase diagram of such models may differ considerably from the true liquid.

In this study, 40–60 ps AIMD simulations are presented for sulfuric acid, using the BLYP and HCTH functionals. The computational tool is Quickstep, a Gaussian based *ab initio* molecular dynamics code which is a part of the Cp2k package [36]. The objective is to examine the performance of the method on an ionic acid solution, on extended time scales, and if the performance proves reasonable, to derive information on molecular structure and dynamics of the system. Results are presented for a system composed of a single H_2SO_4 dissolved in 63 water molecules. Investigation of sulfuric acid introduces an interesting aspect into AIMD simulations of acid solutions, since H_2SO_4 is diprotic. It will be shown that during most of the trajectory duration, the model solutions display qualitatively reasonable behavior, with H_2SO_4 acting as a very strong acid and HSO_4^- as a weaker one. The only other AIMD study focusing on H_2SO_4 in solution of which we are aware is Ref. [24] which employed shorter simulations and the PBE functional; the emphasis of that study was on different system properties, and moreover, in contrast to the present investigation, second ionization of the acid was not observed at the same concentration. Earlier, AIMD simulations lasting a few ps were used to study sulfuric acid formation from water and SO_3 and a reaction of water with formaldehyde in H_2SO_4 [37]. A considerable body of research was devoted to mixed sulfuric acid–water clusters employing electronic structure [25–32] and Monte Carlo [33,34] methods. Many of these studies found that the dominant ionic species existing in small clusters was a hydrogen sulfate–hydronium contact ion pair. Depending upon the model employed, other types of ion pairing were reported with 50 water molecules [29], full sulfuric acid deprotonation was found in a cluster with nine waters [30], and bulk behavior predicted to occur with $3H_2SO_4$ in 240 water molecules [33].

The technical details of the simulation are given in Section 2. The results are described in Section 3 and summarized in Section 4.

2. Computational details

The simulations were obtained with the publicly available Cp2k/Quickstep suite of programs (Cp2k website: http://cp2k.berlios.de) which enables *ab initio* Born–Oppenheimer molecular dynamics within the Kohn–Sham framework of density functional theory. The *ab initio* molecular dynamics approach combines an atom-centered Gaussian basis set representation of the wavefunction with an auxiliary plane wave basis for the electron density [36]. Core electrons are replaced by Goedecker–Teter–Hutter atomic pseudopotentials [38] optimized for each density functional used. Elements of the Kohn–Sham and overlap matrices less than 10^{-12} are neglected while a 280 Ry density grid is employed. Convergence of the SCF wavefunction was subject to a criterion of 10^{-6} placed upon the electronic gradient. The nuclear equations of motion were integrated using the velocity Verlet algorithm with a 0.5 fs time step.

The simulations employed periodic boundary conditions imposed upon a cubic box of length 12.4138 Å. All simulations were derived from an equilibrated trajectory of 64 protiated water molecules employing DFT/BLYP and the double-zeta valence polarization (DZVP) basis set. One water molecule was replaced with a geometry-optimized molecule of sulfuric acid, all the H atoms were replaced by D atoms, and three new simulations were initiated; one with the widely used BLYP functional and two with the HCTH/120 functional, that was fitted on a training set containing hydrogen-bonded dimers. The simulation parameters for the three trajectories are given in Table 1.

One of the problems in simulating a liquid is the choice of temperature. As noted in the introduction for neat H_2O, past studies [8–10] suggest that the liquid range in AIMD model systems is shifted upward by 50–100 K, with respect to experiment, due to quantum effects (and possibly also other approximations of the scheme). Nevertheless, at this stage, the solution simulations were chosen to be closer to room temperature, in the 320–326 K range.

The drift in temperature was 0.5 K/ps for trajectory a, 0.3 K/ps for trajectory b, and 0.4 K/ps for trajectory c. The drift in energy was $\sim 6 \times 10^{-6}$ au/ps/atom. (Frequently drifts in temperature and energy were not reported for applications of AIMD simulations and rarely were such simulations extended beyond 25 ps.)

2.1. The problem of equilibration

As noted in the introduction, one can hardly expect to carry out a fully equilibrated AIMD simulation for an ionic solution on a feasible time scale (which here is several tens of picoseconds). The relaxation time scale of hydrogen bonds between water molecules is on that order of magnitude [7,9,10,12]; and ion-water bonds are far stronger and are thus expected to relax on a much longer time scale.

Fig. 1 gives the time dependence of the MSD, with the center of mass motion removed, for the water oxygen atoms for the three trajectories. The plots are approximately linear for most of the duration of the trajectories, suggesting at least stable liquid-like dynamics in that time regime. The diffusion constant calculated from the Einstein relation ranges from a factor of about 5–25 times smaller than the room temperature experimental value for neat water. This finding is not unexpected in view of the underestimation of D found in past numerical tests for neat water [7–12]. Also the presence of the ions can be reasonably expected to affect the value of the diffusion constant.

An unexpected feature of plots a and c is the change of the MSD slopes, and the relatively fast MSD increase at the end of the two trajectories. Similar phenomena were observed in simulations of HCl solutions; there, the changes of the MSD slopes took place earlier in the simulations over relatively short time scales, after which the slope adopted a new value. These results will be reported in detail elsewhere. Changes in the MSD slope were noted previously for neat water [7,9,10], and ascribed to inadequate relaxation of the trajectory. However, Fig. 3 of Ref. [10] reports large changes in the slope (corresponding to ‘freezing’ near $t = 9$ ps followed by ‘unfreezing’ near $t = 16$ ps) which took place at a temperature as high as 400 K. At this temperature the diffusion rate in the liquid-like portions of the trajectory is close to the experimental room temperature value, so one can reasonably expect relaxation on a $\sim$10 ps time scale.