nature chemistry

SUPPLEMENTARY INFORMATION

DOI: 10.1038/NCHEM.2161

Coulomb explosion during the early stages of the reaction of alkali metals with water

Philip E. Mason,[1] Frank Uhlig,[1] Václav Vaněk,[1] Tillmann Buttersack,[2] Sigurd Bauerecker,[2] and Pavel Jungwirth[1*]

[1]*Institute of Organic Chemistry and Biochemistry, Academy of Sciences of the Czech Republic, Flemingovo nám. 2, 16610 Prague 6, Czech Republic and* [2]*Institut für Physikalische und Theoretische Chemie, Technische Universität Braunschweig, Hans-Sommer-Strasse 10, D-38106 Braunschweig, Germany.*

Index:

1. Computational: Additional details concerning the simulations

Both ab initio molecular dynamic (AIMD) simulations and force-field based molecular dynamics (FFMD) of a sodium cluster surrounded by water molecules were performed for an isolated system (i.e., employing no periodic boundary conditions). For AIMD all snapshots depicting isosurfaces of densities of dissolving electrons were generated along a particular trajectory as a difference density of the full electron density

© 2015 Macmillan Publishers Limited. All rights reserved

minus the densities of the sodium cations and the water molecules along the same trajectory.

To benchmark the applied BLYP-D functional we have recalculated points along the ab initio MD trajectory using the van der Waals DFT functional.[1] Both methods show quantitatively the same behaviour, as demonstrated on energy benchmarking along part of the trajectory presented in Figure S1.

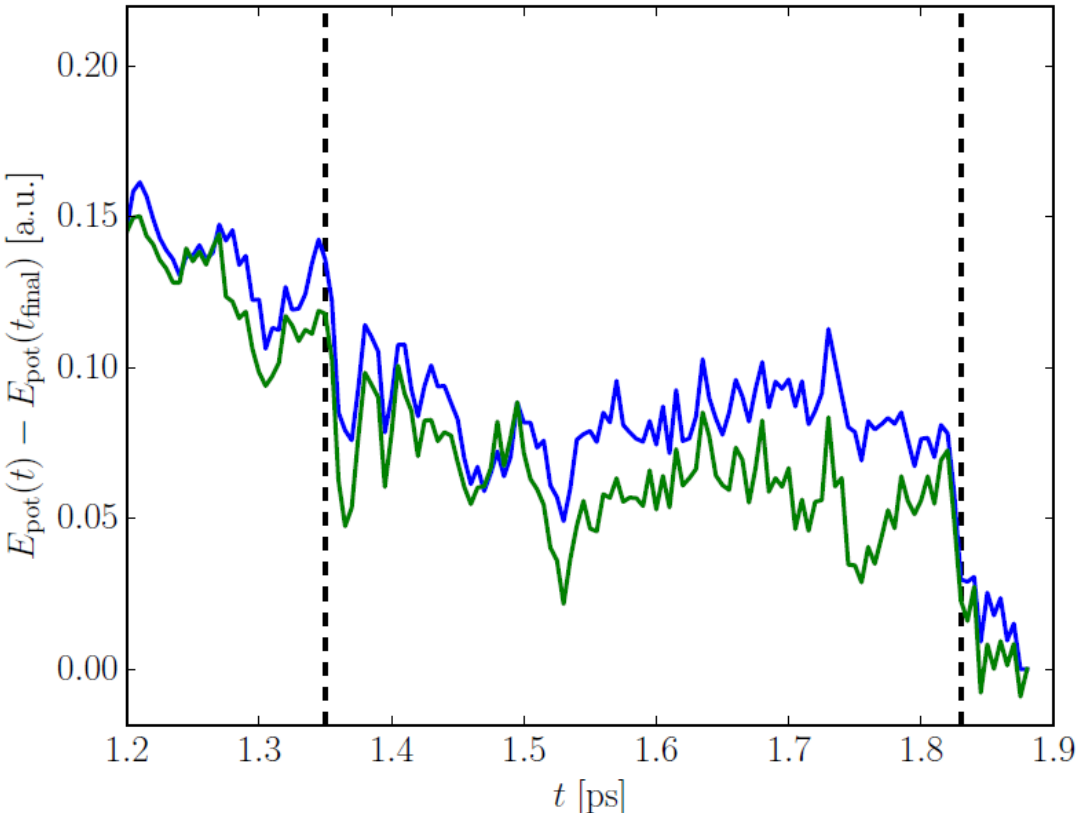

Figure S1: Time evolution of BLYP-D (blue) vs. van der Waals (green) DFT functional potential energies (relative to the values at the end of the trajectory) for a part of the trajectory involving move of electrons from sodium to water and formation of hydrogen molecules and hydroxide ions (these reactive events are highlighted by the vertical dashed lines).

© 2015 Macmillan Publishers Limited. All rights reserved

For FFMD, initial conditions were obtained by first creating a sphere consisting of 4000 sodium atoms cut out from a body-centered cubic structure of sodium metal with a lattice constant of 3.72 Å. This structure was then solvated spherically using the Gromacs tool "genbox" with a structure of 34717 equilibrated water molecules. The energy of the whole system was minimized with respect to its geometry and subsequently the cluster was equilibrated using canonical sampling through velocity rescaling[2] at 300 K. The numerical integration of Newton's equation of motion employed a timestep of 0.5 fs throughout all simulations. A cutoff of 5 nm for electrostatic and van der Waals interactions was used throughout. The last snapshot of the equilibration was then used as initial configuration for the production simulations after removal of evaporated water molecules.

All the production simulations were run in the microcanonical ensemble. Periodically every 5 fs the simulation was stopped. If at that time a sodium atom was in a close contact with at least three water molecules, this sodium atom was alchemically transformed into a sodium cation. Counter-charges in form of hydroxide anions were generated by removing a proton of a water molecule with a preset minimum distance from the newly created sodium cation. Accordingly, the ionization process produces a roughly spherical shell of hydroxide anions around the initial sodium configuration. Charges on the newly created sodium cations were gradually increased according to an exponential fit to the time evolution of the average charge of sodium atoms located on the surface of the sodium cluster from the AIMD simulations with a time constant of 1.8 ps. In the same manner counter charges on the oxygen atoms of the hydroxide anions were adjusted to maintain charge neutrality of the whole system. Initial ionization took place for most of the sodium atoms on the surface of the sodium cluster. The ionization thus leads to a capacitor-like distribution of sodium cations and hydroxide anions with a tunable distance between the two respective spherical shells. Hence this is a microscopic version of the capacitor model described in the following section.

© 2015 Macmillan Publishers Limited. All rights reserved

2. Theoretical: Estimate of the Rayleigh instability limit

This Rayleigh instability limit is reached when the fissility parameter $X = E_{Coulomb}/2E_{Surface}$ exceeds unity.[3, 4] The surface energy $E_{Surface}$ of the Na/K droplet of a radius r is given as $4\pi r^2\gamma$, where γ is the surface tension amounting at ambient conditions for 90% wt of potassium to ~100 mN/m.[5, 6] By moving one electron from each surface alkali atom into water an effective capacitor is formed. The Coulomb self-energy of a capacitor $E_{Coulomb}$ equals to $Q^2/2C$, where Q is the charge built on the plate of a capacitor and C is its capacitance. The charge is given as $Q = 4\pi r^2 q$, where the charge density q can be estimated from the value of the closest separation between potassium atoms in the metal[7] of 4.6 Å to be about 0.75 C/m^2. The capacitance is given as $C = \varepsilon_0\varepsilon_r 4\pi r^2/d$, where $\varepsilon_0 = 8.85 \times 10^{-12}$ F/m is the permittivity of vacuum, $\varepsilon_r = 80$ is the dielectric constant of water, and d is the effective separation between the positive and negative charges. With the above parameters one directly gets that the instability limit $X > 1$ is reached for $d > 5$ Å.

3. Experimental: Safety Note

Use of very small and uniform quantities of the liquid Na/K alloy makes the experimental procedure a relatively safe method of studying its explosive behaviour in water. Due to potential hazards upon oxidation, the alloy must not be kept in an oxygen containing environment for extended periods.[8] Also, the argon atmosphere under which the experiments are performed significantly reduces the violence of the explosions by preventing ingnition of the produced hydrogen gas. The use of a clean surface of the liquid Na/K drop ensures that the explosion happens almost immediately after impact with water in a controlled time window (in contrast with the very erratic explosive behavior of solid sodium or potassium in water). Last, but not least, use of a face shield is a must.

© 2015 Macmillan Publishers Limited. All rights reserved

4. Supplementary videos

We provide three videos as supplementary material:

Supplementary video S1. Explosion of a sodium/potassium drop in water. This video provides footage from high speed cameras place of the explosion of a sodium/potassium alloy drop in water compared to a water drop hitting a water surface. Footages from cameras aiming both from above and below the water surface are provided.

Supplementary video S2. Ab initio molecular dynamics of sodium in water. This video shows an ab initio molecular dynamics simulation of a cluster of 19 sodium atoms immersed in a water cluster.

Supplementary video S3: Classical molecular dynamics of Coulomb explosion. This video shows a force field molecular dynamics simulation of a Coulomb explosion of a 4000 atom sodium cluster, which becomes positively charged upon contact with surrounding water molecules. Negatively charged hydroxides are places about 5 Å from the surface of the cluster.

5. References

1. Lee, K., Murray, E. D., Kong, L., Lundqvist, B. I. & Langreth, D. C. Higher-accuracy van der Waals density functional. *Phys. Rev. B* **82**, 246401 (2010).

2. Bussi, G., Donadio, D. & Parrinello, M. Canonical sampling through velocity rescaling. *J. Chem. Phys.* **126**, 014101 (2007).

3. Rayleigh, L. On the Equilibrium of Liquid Conducting Masses Charged with Electricity. *Philos. Mag. A* **14,** 184-186 (1882).

4. Echt, O., Scheier, P. & Mark, T.D. Multiply charged clusters. *Comptes Rendus Physique* **3**, 353-364 (2002).

© 2015 Macmillan Publishers Limited. All rights reserved

5. Lebedev, R. V. Measurements of interphase surface-tension of sodium-potassium alloys. *Izvestiya Vysshikh Uchebnykh Zavedenii Fizika* **15**, 155-158 (1972).

6. Alchagirov, B. B., Afaunova, L. K, Dyshekova, F.F., Kegadueva, Z. A., Mozgovoi, A. G., Arkhestov, R. K. *et al.* Surface Tension and Adsorption of Components in the Sodium–Potassium Alloy Systems: Effective Liquid Metal Coolants Promising in Nuclear and Space Power Engineering. *Inorg. Materials: Appl. Res.* **2**, 461-467 (2011).

7. Liu L. G. Compression and polymorphism of potassium to 400 kbar. *J. Phys. Chem. Solids* **47**, 1067-1072 (1986).

8. Desreumaux, J., Calais, M., Adriano, R., Trambaud, S., Kappenstein, C. & Nguefack, M. Reactions of sodium-potassium alloys with inert gas impurities - Potential hazards after oxidation. *Eur. J. Inorg. Chem.* **2000**, 2031-2045 (2000).

© 2015 Macmillan Publishers Limited. All rights reserved