**Showcasing research from Prof. David van der Spoel's laboratory, Uppsala University, Sweden.**

Thermodynamics of hydronium and hydroxide surface solvation

The surface composition of droplets is important in atmospheric chemistry but difficult to probe by direct experiments. Accurate theoretical free energy calculations yield the surface affinity of hydronium and hydroxide ions. The hydronium ions are prone to localization on the surface while hydroxide ions reside predominantly in the bulk phase.

As featured in:
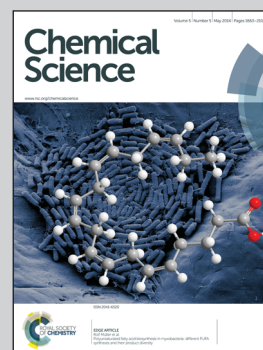
Chemical Science

See David van der Spoel *et al.*, *Chem. Sci.*, 2014, **5**, 1745.

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/chemicalscience

Chemical Science

EDGE ARTICLE

Thermodynamics of hydronium and hydroxide surface solvation†

Jochen S. Hub,‡[a] Maarten G. Wolf,‡[b] Carl Caleman,[cd] Paul J. van Maaren,[e] Gerrit Groenhof[f] and David van der Spoel*[e]

The concentration of hydronium and hydroxide at the water–air interface has been debated for a long time. Recent evidence from a range of experiments and theoretical calculations strongly suggests the water surface to be somewhat acidic. Using novel polarizable models we have performed potential of mean force calculations of a hydronium ion, a hydroxide ion and a water molecule in a water droplet and a water slab and we were able to rationalize that hydronium, but not hydroxide, is slightly enriched at the surface for two reasons. First, because the hydrogen bond acceptance capacity of hydronium is weaker than water and it is more favorable to have the hydronium oxygen on the surface. Second, hydroxide ions are expelled from the surface of the droplets, due to the entropy being lower when a hydroxide ion is hydrated on the surface. As a result, the water dissociation constant pK_w increases slightly near the surface. The results are corroborated by calculations of surface tension of NaOH solutions that are in reasonable agreement with the experiment. The structural and thermodynamic interpretation of hydronium and hydroxide hydration provided by these calculations opens the route to a better understanding of atmospheric and surface chemistry.

1   Introduction

Atmospheric chemistry is different from bulk chemistry because reactions can take place in the gas phase or in contact with aerosols. For instance, the air–water interface increases reaction rates for processes in the ozone cycle, like oxidation of halide ions by OH radicals or O_3.[1] Due to the multitude of different constituents, both natural (*e.g.* from seawater, volcanic sources, or dust from deserts) and anthropogenic (*e.g.* from industrial sources) detailed models of the atmospheric composition are very complex.[2] Recent *in situ* measurements of

[a]*Institute for Microbiology and Genetics, Georg-August-University Göttingen, Justus-von-Liebig-Weg 11, D-37077 Göttingen, Germany*

[b]*Computational Biomolecular Chemistry, Max Planck Institute for Biophysical Chemistry, Am Fassberg 11, D-37077 Göttingen, Germany*

[c]*Department of Physics and Astronomy, Uppsala University, Box 516, SE-75120 Uppsala, Sweden*

[d]*Center for Free-Electron Laser Science, DESY, Notkestraße 85, D-22607 Hamburg, Germany*

[e]*Uppsala Center for Computational Chemistry, Science for Life Laboratory, Department of Cell and Molecular Biology, Uppsala University, Husargatan 3, Box 596, SE-75124 Uppsala, Sweden. E-mail: david.vanderspoel@icm.uu.se; Tel: +46 184714205*

[f]*Department of Chemistry and Nanoscience Center, University of Jyväskylä, P.O. Box 35, FI-40014 Jyväskylä, Finland*

† Electronic supplementary information (ESI) available: Additional methods describing model development and validation and additional results. See DOI: 10.1039/c3sc52862f

‡ These authors contributed equally to this work.

cloud seeding agents have shown that effective ice-nucleation particles are primarily dust or metallic particles.[3] Reactions under atmospheric conditions as well as models of the atmosphere as a whole are influenced by the inherent properties of water droplets with dissolved molecules. We have previously shown that the concentration of organic materials and ions may be reduced or enhanced at the water droplet–air interface.[4–6] In this work we revisit the surface p[H] and p[OH] (hydronium and hydroxide concentrations respectively) of atmospheric water droplets and, for comparison, water slabs, which are influenced by the presence of organic components, carbon dioxide, ions and dust particles.[2] The composition and pH of aerosols vary with the seasons and location on earth; they have been characterized in many places and are most often acidic.[7–9] This variation has been shown to be important for modeling of clouds.[10]

During the last few years a number of experimental[11–15] and theoretical[12,16–20] studies have shown that there is an enhancement of H_3O^+ on water surfaces. The answer to why this is the case has not yet been fully addressed. Here, we address the bulk/surface solvation of hydronium and hydroxide using a highly reduced system, which is a single ion in a water droplet (Fig. 1A), and describe why the outermost surface (the first few Ångströms) is slightly positively charged in droplets.

2   Results and discussion

Existing molecular models are not able to reproduce the structure of hydroxide in water correctly, as they yield too large
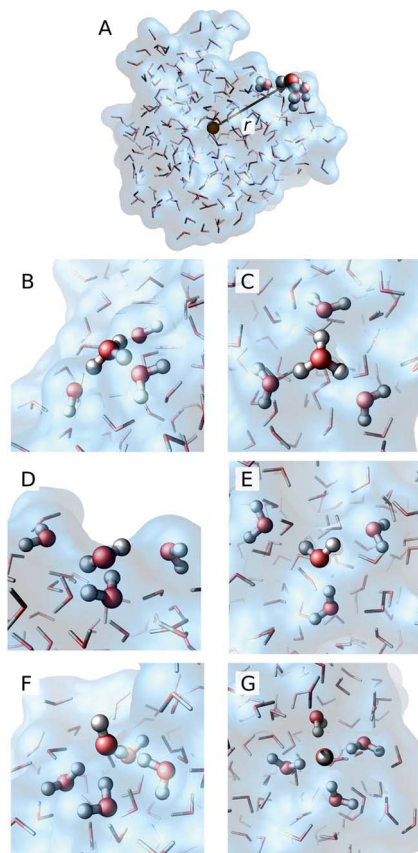
Fig. 1 (A) Simulation snapshot of a water droplet with a hydronium ion on the surface. Orientation on the droplet surface in side view and top view for (B and C) hydronium, (D and E) water and (F and G) hydroxide. Water molecules that form a hydrogen bond to the solute are shown as ball-and-stick models, visualizing the coordination number of the solute at the surface.

coordination numbers or inaccurate radial distribution functions.[21–24] *Ab initio* simulations, in contrast, yield the correct solvation but they do not provide converged free energies and enthalpies due to a higher computational cost. To obtain the appropriate solvation structure with a reduced computational cost, we developed novel polarizable models for hydroxide and hydronium that work in conjunction with the SWM4-NDP water model.[25] Details on the new models are given in the ESI.†

The hydroxide ion predominantly forms a hypercoordinated structure in dilute aqueous solutions[21,26–35] (Fig. 2). The hydroxide oxygen (O*) accepts four hydrogen bonds in a square planar configuration. In addition, the hydroxide hydrogen (H*) can donate a weak hydrogen bond.[21,26–31,36] Occasionally, the O* coordination changes to 3-fold[21,22,27,28,30,34,35,37] or 5-fold.[22,34] For hydronium, the dominant structure in the bulk is a dynamically distorted Eigen complex.[38–46] The coordination of hydroxide observed in bulk simulations using our model is very similar to what was obtained with Car–Parinello MD (CPMD) simulations (Table 1). Further validation of the hydronium and hydroxide models showed excellent agreement with *ab initio*, Fourier transform infrared (FTIR), neutron diffraction and X-ray structural data (see ESI†).
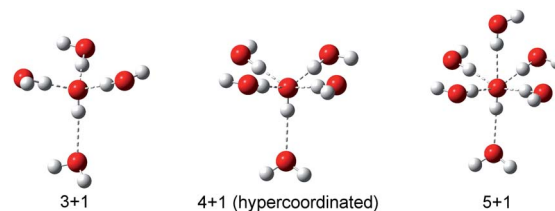

Fig. 2 Hydroxide complexed by 3, 4, or 5 water molecules. The numbers ($X + Y$) refer to the number of hydrogen bonds with O* and H*, respectively.

With these new models we studied the hydronium and hydroxide ions in a water droplet, and, for comparison, a water molecule in a droplet (Fig. 1). Earlier studies of pure water droplets[47] and water droplets containing alkali or halide ions[4,5] have shown that the simulated properties of such systems critically depend on the model used. Using state of the art polarizable models,[25,48] we recently disentangled the complex energetics underlying surface solvation preferences of the halide ions.[5]

The potential of mean force (PMF) in a water droplet is shown in Fig. 3 along with a breakdown of enthalpy $\Delta H(r)$ and entropy $-T\Delta S(r)$. Here, the distance r between the center-of-mass (COM) of the droplet and the COM of the solute was taken as the reaction coordinate (Fig. 1A). The inside (bulk) of the droplet is taken as the reference point where the energy was defined to zero. Fig. 3A confirms earlier experimental[11–15] and theoretical[12,16–20] work showing that hydronium is preferentially solvated at the water surface. The enthalpic contribution to the PMF for hydronium solvation is stronger than the unfavorable entropic contribution (Fig. 3B and C), demonstrating that the surface preference of hydronium is an enthalpic effect. Hence, the thermodynamics for hydronium solvation is different from small hydrophobic molecules, which are expelled from bulk water mainly by an entropic effect at room temperature.[6,49] For hydroxide the enthalpic contribution is almost flat, whereas entropy favors the bulk, similar to the case of a fluoride ion.[5] As expected, the PMF curve for water is approximately zero until it gets outside the droplet, and it therefore lies in between the hydroxide and hydronium curves. A similar plot of the free energy profile for a hydronium and a hydroxide ion in a water slab is given in Fig. S6 of the ESI.†

By decomposing the enthalpy into water–water and water–ion interaction energies we are able to further rationalize the causes underlying surface solvation. The diffusion of hydronium from the surface to bulk leads to a rupture of favorable water–water interactions (Fig. 4A), which remarkably is not

Table 1 Population (in %) of various hydroxide complexes in bulk water using our new model. $X + Y$ refer to the number of hydrogen bonds with O* and H*, respectively. CPMD data are from ref. 22

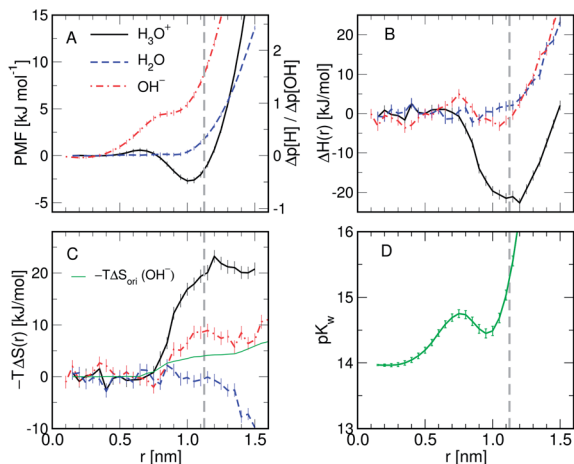| Model	3 + 0	3 + 1	4 + 0	4 + 1	5 + 0	5 + 1
Our model	<1	<1	50	43	3	3
CPMD	6	9	30	45	4	5

Fig. 3 (A) Potential of mean force (PMF), (B) enthalpy and (C) entropy as a function of position r in a water droplet (visualized in Fig. 1) for hydronium (black/solid line), water (blue/dashed) and hydroxide (red/dot-dashed). (C, green) Orientational entropy of hydroxide. (D) pK_w as a function of position in the droplet. The grey dashed line indicates the Gibbs dividing surface.

counterbalanced by any increased hydronium–water interaction (Fig. 4B). The mechanistic reason for this is that hydronium is a weaker hydrogen bond acceptor than water. This behavior contrasts that of positive alkali ions which are solvated inside droplets[5] due to strong ion–water interactions. The energetics of hydronium solvation is qualitatively similar to what was found for the *negative* halide ions, Cl^-, Br^- and I^- (but not F^-). For hydroxide, the weakening of ion–water and strengthening of water–water interactions near the interface exactly cancel each other, demonstrating that the bulk preference is a purely entropic effect. The enthalpy components for solvation of water in a water droplet also cancel each other. It is important to note, however, that the energetics of bulk/surface
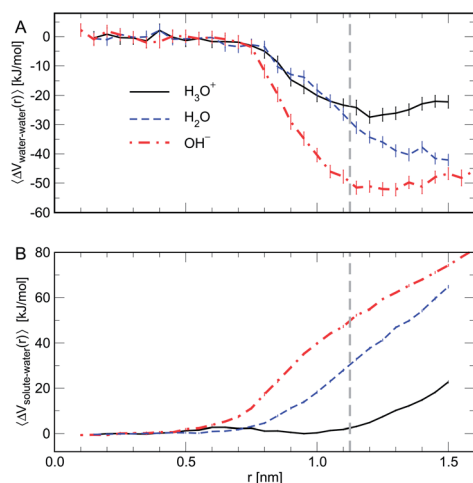

Fig. 4 Decomposition of enthalpy (Fig. 3B) into interaction energies for each of the three solutes as a function of distance r from the droplet center (visualized in Fig. 1). The grey dashed line indicates the Gibbs dividing surface.

solvation may alter at a high salt concentration due to interactions with nearby counterions.

Gray-Weale and Beattie suggested that hydroxide ions are surface-bound (or rather located slightly below the surface) based on surface tension data and Poisson–Boltzmann calculations.[50–52] They estimated that the hydroxide surface affinity should be in the order of 20 k_BT, or 50 kJ mol^{-1}, at room temperature. These values are an order of magnitude larger than the effects seen here, in previous experiments[11,13–15] and calculations.[16–20] Mundy *et al.* have performed *ab initio* MD simulations[53] and found a surface preference of OH^- of just 1 k_BT. While *ab initio* simulations are in principle more general than classical simulations, they cannot provide the same rigorous sampling. We have computed the surface tension for sodium hydroxide solutions at five concentrations (Table S3†). The increase in surface tension upon addition of salt is about 0.88 mN m^{-1} (Fig. S7†), which is smaller than the experimental value of 2 mN m^{-1}.[54] However, in line with the PMFs, the density profile (Fig. S7C†) shows that hydroxide and sodium ions predominantly reside in the bulk, suggesting that an increased surface tension is not an indicator for surface affinity. In summary, we find that the surface affinity is approximately +4 kJ mol^{-1} for hydroxide – hence preferring the bulk – whereas it is −3 kJ mol^{-1} for hydronium – preferring the surface (Fig. 3). These findings are in agreement with a large body of evidence.[11–20] This surface enrichment of H_3O^+ in a neat water droplet corresponds to a slightly lower surface p[H], which coincides with an increased surface p[OH] (Fig. 3A, right y-axis). As a net result, the autodissociation constant pK_w is slightly increased near the surface, which might affect the protonation state of pH indicator dyes (Fig. 3D, details in the ESI†). The concentration of H_3O^+ in atmospheric water droplets will be further enhanced by the hydrolysis of carbon dioxide to carbonic acid, or due to the presence of dust particles.[2]

Can our present results be generalized to other ions in order to predict their bulk/surface preference? There are both positive as well as negative ions that are preferentially solvated on the droplet surface (*e.g.*, H_3O^+, Cl^-, Br^- and I^-) while there are other positive as well as negative ions that are solvated in the bulk (*e.g.*, OH^-, F^-, alkali ions and the ammonium ion[4]). In addition, inverting the charge of the large halide ions *in silico* eliminates their surface preference.[5] Neither the sign, nor the polarizability of the ion is sufficient to explain the surface preference and it is therefore unlikely that the surface/bulk preference can be rationalized using continuum descriptions of water such as Poisson–Boltzmann calculations, since (a) water is an inherently asymmetric molecule and (b) entropic effects play a significant role. Experiments that do not probe the molecular scale are therefore unlikely to give conclusive evidence about surface acidity.[55] Ideally, a theoretical model should be able to reconcile the available measurements. Developing models that find the right balance between accuracy and computational tractability was one of the goals of this work.

Structural insight into the bulk/surface hydration is given in Fig. 5 which presents the probability for the orientational angle θ between the molecular dipole and the axis between the droplet center and the center-of-mass of the solute. The probabilities

are normalized by the PMF for the respective solute, thus presenting the two-dimensional probability $P(r, \cos(\theta))$. All three solutes are isotropically distributed inside the droplets ($r < 0.5$ nm). On the surface ($r \approx 1$ nm), in contrast, hydronium is strongly oriented with the dipole pointing to the droplet center (with the oxygen on the outside, Fig. 1B and C). Water molecules at the surface display only a weak preference with the oxygen pointing slightly inwards (Fig. 1D and E). The second orientational vector of the water molecule connecting the two hydrogen atoms is nearly randomly oriented at the surface (not shown). The hydroxide ion, if located at the surface, is oriented parallel to the distance axis, but in this case with the oxygen on the inside (Fig. 1F and G). Analysis of the Shannon entropy of $P(r, \cos(\theta))$ shows that only 50% of the reduced entropy for OH^- being at the surface (Fig. 3C, red) is due to the reduced rotational freedom (Fig. 3C, green), suggesting that alterations in the water entropy are important as well. These structures are consistent with the notion that hydronium is a weak hydrogen bond acceptor whereas hydroxide is a weak hydrogen bond donor.

3 Conclusions

The results presented here, in conjunction with earlier results on alkali- and halide-ions,[5] show that water is a complex material, which cannot be described by macroscopic models if effects on the molecular scale are of importance.[56,57] The hydroxide model devised in this work is probably the first simulation model to have the correct solvation structure and henceforth yields a significant improvement in the ability to model subtle phenomena. It is demonstrated here that hydronium is surface-bound and hydroxide is not. Much of the debate in the literature on whether the surface of water is basic or acidic involves ionic solutions or water at non-neutral pH, and we do not want to extrapolate our work to systems we have not tested explicitly. Nevertheless, it seems valid to infer that the surface of water may be characterized by a slight hydronium enrichment at neutral pH and low ionic strength, where the concentration of hydronium and hydroxide is very low. Beyond that, only direct experimental evidence, for instance in the fashion demonstrated by Petersen et al.,[11,13] probing the water surface at the molecular scale, should be regarded as definite proof in this matter.

The presence of H_3O^+ at the surfaces of aerosol particles might influence the production of bromine atoms, which in turn are involved in the depletion of stratospheric ozone.[58,59] By rationalizing the hydronium and hydroxide concentration at the water droplet surface using PMF calculations, and previous work on droplet composition,[4–6] we hope to contribute to improving models of the atmosphere[2] which in turn can contribute to more accurate climate models.

Acknowledgements

References

1 B. J. Finlayson-Pitts, *Phys. Chem. Chem. Phys.*, 2009, **11**, 7760–7779.

2 R. Sommariva and R. von Glasow, *Environ. Sci. Technol.*, 2012, **46**, 10429–10437.

3 D. J. Cziczo, K. D. Froyd, C. Hoose, E. J. Jensen, M. Diao, M. A. Zondlo, J. B. Smith, C. H. Twohy and D. M. Murphy, *Science*, 2013, **340**, 1320–1324.

4 C. Caleman and D. van der Spoel, *Phys. Chem. Chem. Phys.*, 2007, **9**, 5105–5111.

5 C. Caleman, J. S. Hub, P. J. van Maaren and D. van der Spoel, *Proc. Natl. Acad. Sci. U. S. A.*, 2011, **108**, 6838–6842.

6 J. S. Hub, C. Caleman and D. van der Spoel, *Phys. Chem. Chem. Phys.*, 2012, **14**, 9537–9545.

7 A. Pszenny, J. Moldanov, W. Keene, R. Sander, J. Maben, M. Martinez, P. Crutzen, D. Perner and R. Prinn, *Atmos. Chem. Phys.*, 2004, **4**, 147–168.

8 L. Zongxing, H. Yuanqing, W. H. Theakstone, J. Wenxiong, X. Huijuan, Z. Wei, L. Jing and W. Shuxin, *J. Earth Sci.*, 2010, **21**, 157–165.

9 K. B. Benedict, T. Lee and J. L. Collett, Jr, *Atmos. Environ.*, 2012, **46**, 104–114.

10 S. Banzhaf, M. Schaap, A. Kerschbaumer, E. Reimer, R. Stern, E. van der Swaluw and P. Builtjes, *Atmos. Environ.*, 2012, **49**, 378–390.

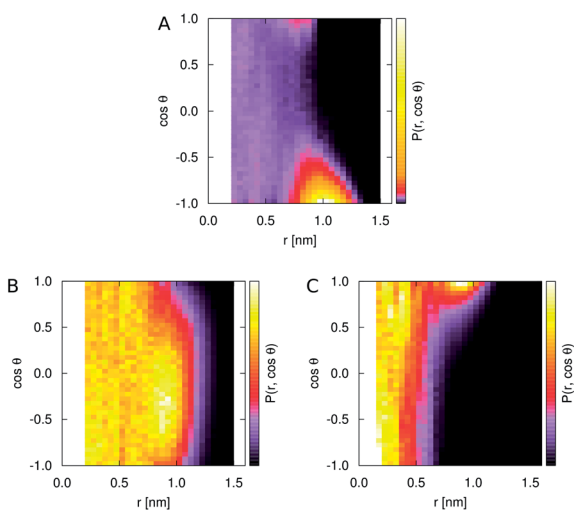11 P. Petersen and R. Saykally, *J. Phys. Chem. B*, 2005, **109**, 7976–7980.

Fig. 5 Orientation distribution of (A) hydronium, (B) water and (C) hydroxide in a water droplet as a function of distance from the center of the droplet r, as shown in Fig. 1A. θ is the angle between the dipole vector of the solute and the vector from the center of the droplet to the center of mass of the solute.

12 V. Buch, A. Milet, R. Vácha, P. Jungwirth and J. P. Devlin, *Proc. Natl. Acad. Sci. U. S. A.*, 2007, **104**, 7342–7347.

13 P. B. Petersen and R. J. Saykally, *Chem. Phys. Lett.*, 2008, **458**, 255–261.

14 B. Winter, M. Faubel, R. Vacha and P. Jungwirth, *Chem. Phys. Lett.*, 2009, **474**, 241–247.

15 S. Yamaguchi, A. Kundu, P. Sen and T. Tahara, *J. Chem. Phys.*, 2012, **137**, 151101.

16 R. Vácha, V. Buch, A. Milet, J. P. Devlin and P. Jungwirth, *Phys. Chem. Chem. Phys.*, 2007, **9**, 4736–4747.

17 R. Vácha, V. Buch, A. Milet, J. P. Devlin and P. Jungwirth, *Phys. Chem. Chem. Phys.*, 2008, **10**, 332–333.

18 S. Iuchi, H. Chen, F. Paesani and G. A. Voth, *J. Phys. Chem. B*, 2009, **113**, 4017–4030.

19 H.-S. Lee and M. E. Tuckerman, *J. Phys. Chem. A*, 2009, **113**, 2144–2151.

20 H. Takahashi, K. Maruyama, Y. Karino, A. Morita, M. Nakano, P. Jungwirth and N. Matubayasi, *J. Phys. Chem. B*, 2011, **115**, 4745–4751.

21 T. Megyes, S. Bálint, T. Grósz, T. Radnai, I. Bakó and P. Sipos, *J. Chem. Phys.*, 2008, **128**, 044501–044512.

22 D. Bucher, A. Gray-Weale and S. Kuyucak, *J. Chem.Theory Comput.*, 2010, **6**, 2888–2895.

23 I. Ufimtsev, A. Kalinichev, T. Martinez and R. Kirkpatrick, *Chem. Phys. Lett.*, 2007, **442**, 128–133.

24 P. Balbuena, K. Johnston and P. Rossky, *J. Phys. Chem.*, 1996, **100**, 2706–2715.

25 G. Lamoureux, E. Harder, I. V. Vorobyov, B. Roux and A. D. MacKerell, Jr, *Chem. Phys. Lett.*, 2006, **418**, 245–249.

26 M. Tuckerman, K. Laasonen, M. Sprik and M. Parrinello, *J. Chem. Phys.*, 1995, **103**, 150.

27 M. Tuckerman, D. Marx and M. Parrinello, *Nature*, 2002, **417**, 925–929.

28 D. Marx, A. Chandra and M. Tuckerman, *Chem. Rev.*, 2010, **110**, 2174–2216.

29 A. Botti, F. Bruni, S. Imberti, M. Ricci and A. Soper, *J. Chem. Phys.*, 2003, **119**, 5001–5004.

30 M. Tuckerman, A. Chandra and D. Marx, *Acc. Chem. Res.*, 2006, **39**, 151–158.

31 M. Śmiechowski and J. Stangret, *J. Phys. Chem. A*, 2007, **111**, 2889–2897.

32 S. McLain, S. Imberti, A. Soper, A. Botti, F. Bruni and M. Ricci, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2006, **74**, 094201.

33 S. Imberti, A. Botti, F. Bruni, G. Cappa, M. Ricci and A. Soper, *J. Chem. Phys.*, 2005, **122**, 194509.

34 B. Chen, I. Ivanov, M. L. Klein and M. Parrinello, *Phys. Rev. Lett.*, 2003, **91**, 215503.

35 I. Heisler, K. Mazur and S. Meech, *J. Phys. Chem. Lett.*, 2011, **2**, 1155–1160.

36 E. Aziz, N. Ottosson, M. Faubel, I. Hertel and B. Winter, *Nature*, 2008, **455**, 89–91.

37 S. Roberts, K. Ramasesha, P. Petersen, A. Mandal and A. Tokmakoff, *J. Phys. Chem. A*, 2011, **115**, 3957–3972.

38 J. Heuft and H. Meijer, *Phys. Chem. Chem. Phys.*, 2006, **8**, 3116–3123.

39 O. Markovitcha and N. Agmon, *J. Chem. Phys.*, 2008, **129**, 084505.

40 J. Swanson and J. Simons, *J. Phys. Chem. B*, 2009, **113**, 5149–5161.

41 D. Marx, M. Tuckerman, J. Hutter and M. Parrinello, *Nature*, 1999, **397**, 601–604.

42 C. Ciobanu, L. Ojamäe, I. Shavitt and S. Singer, *J. Chem. Phys.*, 2000, **113**, 5321.

43 V. Buch, A. Dubrovski, F. Mohamed, M. Parrinello, J. Sadlej, A. Hammerich and J. Devlin, *J. Phys. Chem. A*, 2008, **112**, 2144–2161.

44 A. Botti, F. Bruni, M. Ricci and A. Soper, *J. Chem. Phys.*, 2006, **125**, 014508.

45 D. Asthagiri, L. Pratt and J. Kress, *Proc. Natl. Acad. Sci. U. S. A.*, 2005, **102**, 6704–6708.

46 M. Śmiechowski and J. Stangret, *J. Mol. Struct.*, 2008, **878**, 104–155.

47 C. Caleman and D. van der Spoel, *J. Chem. Phys.*, 2006, **125**, 154508.

48 G. Lamoureux, A. D. MacKerell and B. Roux, *J. Chem. Phys.*, 2003, **119**, 5185–5197.

49 D. Chandler, *Nature*, 2005, **437**, 640–647.

50 J. K. Beattie, *Phys. Chem. Chem. Phys.*, 2008, **10**, 330–331.

51 A. Gray-Weale and J. K. Beattie, *Phys. Chem. Chem. Phys.*, 2009, **11**, 10994–11005.

52 M. Liu, J. K. Beattie and A. Gray-Weale, *J. Phys. Chem. B*, 2012, **116**, 8981–8988.

53 C. J. Mundy, I.-F. W. Kuo, M. E. Tuckerman, H.-S. Leed and D. J. Tobias, *Chem. Phys. Lett.*, 2009, **481**, 2–8.

54 C. L. Henry, C. N. Dalton, L. Scruton and V. S. J. Craig, *J. Phys. Chem. C*, 2007, **111**, 1015–1023.

55 R. J. Saykally, *Nat. Chem.*, 2013, **5**, 82–84.

56 H. Zhang, T. Tan, W. Feng and D. van der Spoel, *J. Phys. Chem. B*, 2012, **116**, 12684–12693.

57 H. Zhang, T. Tan, C. Hetenyi and D. van der Spoel, *J. Chem. Theory Comput.*, 2013, **9**, 4542–4551.

58 R. Vogt, P. J. Crutzen and R. Sander, *Nature*, 1996, **383**, 327–330.

59 M. O. Andreae and P. J. Crutzen, *Science*, 1997, **276**, 1052–1058.