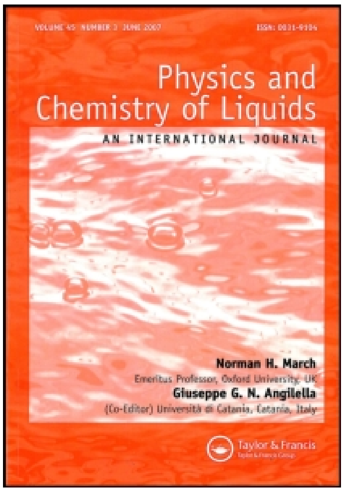

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Modelling the structure of the water molecule under both local environmental constraints and explosive conditions

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LETTER

Modelling the structure of the water molecule under both local environmental constraints and explosive conditions

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A model proposed by Gabbay and March allowed the geometry of the water molecule to be studied as the OH bond length was compressed from its equilibrium value; the corresponding H–O–H bond angle opened up from 104° and under extreme compression a limiting angle of 180° was predicted. Local environmental changes were later found to increase the bond angle of 104° by some degrees. Such structural changes are compared here and contrasted with molecular dynamics results of Schwegler *et al.* (Schwegler, Galli and Gygi, Phys. Rev. Lett. **84**, 2429 (2000)) on water under pressure, and with subsequent simulations by Wu *et al.* (Wu, Fried, Yang, Goldman and Bastea, Nat. Chem. **1**, 57 (2009)) involving the high-explosive pentaerythritol tetranitrate. Extreme conditions of both pressure and temperature lead to a homolytic dissociation reaction involving free atoms and radicals: $H_2O \rightleftharpoons H + OH$, in marked contrast to ambient conditions that favour the heterolytic self-ionisation. The X-ray induced homolytic dissociation of water and formation of an $O_2 + H_2$ crystalline alloy at high pressure as observed by Mao *et al.* (Mao, Mago, Meng, Eng, Hu, Chow, Cai, Shu and Hemley, Science **314**, 636 (2006)) are also noted.

Keywords: water under pressure; H_2O geometry; bond splitting

In early work, Gabbay and March [1] considered a model of the H_2O molecule in which the geometry was studied as a function of the OH distance. It was found that as the bond length was greatly reduced, the modelling led to the equilibrium H–O–H bond angle of about 104° increasing, albeit under extreme model compression of the OH bond length, to yield a limiting linear form of the water molecule. It is also relevant to mention that a very different 'form of constraints' on the H_2O molecule, namely either (i) the proximity to a ruthenium metal surface [2,3] or (ii) its interaction with a single beryllium atom [4], led to quite similar increases of some degrees in the H–O–H bond angle.

There has been an upsurge of interest in this general area over the last decade, due to advances in both first-principle molecular dynamics under pressure, and experimental techniques resulting in dissociation of H_2O.

Thus in 2000, Schwegler *et al.* [5] investigated water under pressure. After noting that at that time most studies of the effect of compression on the microscopic structure of liquid water had been performed at below 0.1 GPa pressure and only a few experiments had

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achieved pressures of the order of 2 GPa, these workers presented first-principle molecular dynamic simulations of H_2O under pressure, before dissociation occurred. At 10 GPa pressure and a temperature of 600 K, no appreciable molecular dissociation was observed in the simulations. However, the structure of water was substantially changed from that under ambient conditions. In particular, there was a pronounced collapse of the hydrogen bonding, as was also stressed by Soper and Ricci [6] in the experimental neutron diffraction measurements of the three partial structure factors for water as a function of pressure and at a temperature of 268 K.

We next turn to consider the structure and dissociation of water under explosive conditions produced by modelling the detonation of the high-explosive pentaerythritol tetranitrate (PETN). Such work goes back to the study of Ree [7]. He developed a multiphase, multicomponent equation of state model from first-principles statistical mechanical theory. Then, as a test case of this model, he chose PETN and calculated its detonation properties. His model yielded satisfactory agreement with available experimental facts. Very recent atomistic simulations by Wu *et al.* [8] have now uncovered the nature of dissociation of water under such explosive conditions produced by again modelling the detonation of the above-mentioned high-explosive PETN. Under such conditions, the ambient heterolytic dissociation of water, discussed for instance by Giguere [9], namely

$$2H_2O \rightleftharpoons H_3O^+ + HO^- \tag{1}$$

is to be replaced, according to [8], by

$$H_2O \rightleftharpoons H + HO. \tag{2}$$

In the context of the homolytic dissociation reaction (2) under extreme conditions of pressure and temperature, it is noteworthy to cite earlier experimental work by Mao *et al.* [10]. In their study, the X-ray- and pressure-induced cleaving of H_2O was observed, leading to the formation of $O_2 + H_2$ crystalline material.

In summary, we have confronted some early model predictions on the structure of a water molecule as the OH bond length is shortened, plus quantum-chemical calculations on the effect of local environment on the H–O–H bond angle, in which this angle was opened up, with simulations carried out since 2000. These calculations stressed especially the effect of pressure on the structure and dissociation of water. It emerged that the dissociation for water changed from the heterolytic reaction (1) under ambient conditions to the homolytic (2) under explosion of PETN. Finally, the cleaving of the water molecule under admittedly unusual circumstances being induced by X-rays, with the formation of a crystalline solid $O_2 + H_2$ under high pressure is referred.

Note

Two recent relevant works have come to our notice: F. Paesani and G. A. Voth [J. Phys. Chem. B **113**, 5702 (2009)] performed quantum simulations on the structure of water in different environments. A. F. Goncharov *et al.* [J. Chem. Phys. **130**, 124514 (2009)], using a diamond anvil cell and X-ray diffraction for water at temperatures up to 1500 K, found that the enthalpy of fusion increases enormously along the melting line (from 6 kJ/mole at 0 GPa to 120 kJ/mole at 57 GPa) and concluded from molecular dynamics computations that extensive dissociation occurs upon melting, arguing that (i) the dissociated species are largely partially charged H and OH (with assigned charges mostly in the range from +0.4 to −0.4); (ii) that the H_2O, H, and OH all become transient, on the scale of >1 ps; and (iii), as we have also argued, that $H_3O^{+\delta}$ is much more marginal.

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