Experimental determination of the electron density of liquid H$_2$O and D$_2$O

LETTER TO THE EDITOR

Experimental determination of the electron density of liquid H_2O and D_2O

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Abstract
X-diffraction experiments on liquids are most commonly analysed within the independent atom approximation (IAA), despite the fact that compounds of light elements may show deviations from this simple approximation. An analysis of high energy x-ray diffraction data on liquid water in terms of the electron density auto-correlation function is given. The analysis shows that some but not all deviations from the IAA can be accounted for by a charged atom model. This corroborates findings from Compton scattering experiments on solid water that the nature of hydrogen bonding is at least partly covalent. The electron densities in H_2O and D_2O are found to be indistinguishable within the limits of the present experiments. This is in agreement with the interpretation of the differences in the intermolecular structure of H_2O and D_2O as being quantum mechanical in origin, and not the effect of a differing interaction potential.

Neutrons diffract from nuclei while x-rays are sensitive to the electron distribution around the nuclei. While for crystalline samples it is not uncommon to determine the electron distribution from a combination of both techniques, the results of liquid diffraction experiments are most commonly interpreted within the independent atom approximation (IAA). Within the IAA, the electron density of a molecule is approximated as the sum of the electron densities of the atoms centred at the nuclear positions. Chemical bonding is thus completely neglected.

Liquid water is a promising target for an experimental charge density study as 80% of its electrons are valence electrons and thus participate in chemical bonding. Two recent studies [1, 2] use *ad hoc* modifications of the atomic form factors to account for the modifications of the electron density in water induced by chemical bonding. Here, we present an approach based on the determination of the electron density auto-correlation function (ACF) and its interpretation in terms of a model used in crystallographic work and referred to as 'spherical atom kappa formalism' in [3]. On the other hand the discussion of the nature of

the hydrogen bonds is an interesting aspect in this context, which is still controversial [4–6]. Hydrogen bonding largely determines the intermolecular structure of liquid water and hence its physical properties. Most simulation studies mimic the hydrogen bond as a two-body electrostatic potential—the SPC, PPC, TIP4P or TIP5P models are typical examples—while on the other hand there is the picture of the hydrogen bond as one of a covalent three-centre, four-electron bond [4]. Evidence from Compton scattering has shown that, while electrostatic forces play an important role [5, 6], there is a significant covalent contribution to hydrogen bonding in ice I. The electron density ACF of water determined from a high energy x-ray diffraction measurement [7] and neutron data [8] indicate that some but not all deviations from the IAA in liquid water can be accounted for by a charged atom model.

The intensity $I(Q)$ of x-rays scattered from a liquid sample is related to the electron density ACF $g_{el}(r)$:

$$I(Q) = N\left(\int 4\pi \overline{\rho_{el}} r^2 g_{el}(r) j_0(Qr)\, dr + C(Q) \right), \tag{1}$$

where $Q = 4\pi/\lambda \sin(\theta)$, λ is the wavelength of the radiation, 2θ the scattering angle, N is a constant which depends on instrumental parameters, $\overline{\rho_{el}}$ the average electron density, $j_0(x) = \sin(x)/x$ is the zeroth order Bessel function and $C(Q)$ accounts for Compton scattering contributions. While it is in general quite sufficient to treat Compton scattering intensities within the IAA, here the $C(Q)$ from [9] have been used. These are Compton intensities for monomeric water molecules, calculated at the configuration interaction level, thus taking electron correlations explicitly into account. The maximum deviation from the IAA-$C(Q)$ is 0.8 electron units at $Q \sim 3.1$ Å^{-1}.

The normalization constant N is a scale factor which has to be determined at high Q values, where the scattered intensity is dominated by Compton scattering (91.0% at $Q = 20$ Å^{-1} for water) and core electron scattering (8.2% at $Q = 20$ Å^{-1} for water) and, thus, known without prior assumptions about the structure of the valence electrons. No Q dependence of this normalization 'constant' has been observed for the data set used in this study [7], indicating that systematic effects like detector dead-times, absorption and degree of polarization have been properly accounted for. The normalization constant is determined with a statistical accuracy of 0.3%.

The electron density ACF of a single water molecule can be calculated within the IAA by

$$g_{el}^{mol} = \frac{1}{(2\pi)^3 \overline{\rho_{el}}} \int 4\pi Q^2 F_M^2 j_0(Qr)\, dQ. \tag{2}$$

F_M is a molecular form factor, which for water within the IAA is

$$F_M^{IAA} = \sqrt{f_O^2 + 2f_H^2 + 4f_H f_O j_0(Qr_{OH})\exp(-Q^2\gamma_{OH}^2) + 2f_H^2 j_0(Qr_{HH})\exp(-Q^2\gamma_{HH}^2)} \tag{3}$$

where the r_{ij} are the equilibrium distances of the atoms, γ_{ij} the mean square displacement [12] and the atomic form factors f_i related to the radial electron densities $4\pi r^2 \rho_{el}(r)$ of the unperturbed atoms via

$$f_i = \int 4\pi r^2 \rho_{el}(r) j_0(Qr)\, dr. \tag{4}$$

The electron densities of the atoms have been calculated from the Roothaan–Hartree–Fock wavefunctions of [10].

Deconvoluting the intra-molecular electron distribution from the electron density ACF gives the molecular radial distribution function [11]:

$$g_{mol}^{IAA,X} = \frac{1}{(2\pi)^3 \rho_{mol}} \int 4\pi Q^2 \frac{I(Q)/N - C(Q) - (F_M^{IAA})^2}{(F_M^{IAA})^2} j_0(Qr)\, dQ, \tag{5}$$

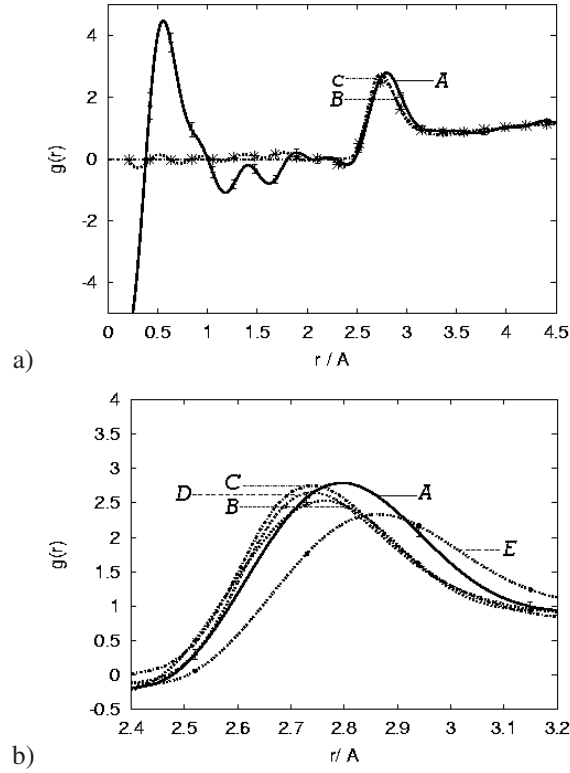with ρ_{mol} the molecular density.

Figure 1. (a) Error bars [13] and solid curve (A): $g_{mol}^{IAA,X}$ for D_2O (equation (5), data [7]); the horizontal distance of the error bar corresponds to the real space resolution ($Q_{max} = 14.97$ Å^{-1}) of the data and is not influenced by termination ripples. Stars and dashed curve (B): $g_{mol}^{IAA,n}$ (equation (6), data: [8]) at the same real space resolution as the x-ray data. Dashed–dotted curve (C): the oxygen–oxygen partial pair distribution function g_{OO} derived from neutron data [8]. (b) Zoom to the region 2.4–3.2 Å. The curves and symbols are the same as in (a). In addition: double-dashed curve (D): $g_{mol}^{IAA,n}$ ($Q_{max} = 40$ Å^{-1}, data [8]), circles and triple-dashed curve (E) $g_{mol}^{IAA,X}$ ($Q_{max} = 14.97$ Å^{-1}, data [11]).

The site–site pair distribution functions g_{ij} and their Fourier transforms the site–site partial structure factors s_{ij} are known from neutron diffraction [8], and the g_{mol} to be expected if the water molecule were adequately described by the IAA can be calculated via

$$g_{mol}^{IAA,n} = \frac{1}{(2\pi)^3 \rho_{mol}} \int 4\pi Q^2 \frac{f_O^2 s_{OO} + 4 f_O f_H s_{OH} + 4 f_H^2 s_{HH} - (F_M^{IAA})^2}{(F_M^{IAA})^2} j_0(Qr) \, dQ. \qquad (6)$$

Figure 1(a) compares g_{mol}^{IAA} obtained via equations (5) and (6) and the neutron OO partial pair distribution function g_{OO}. The statistical accuracy of the radial distribution function has been calculated as described in [13]. It is noted that the neutron $g_{mol}^{IAA,n}$ is very close to the pure g_{OO} function, in disagreement with [1]. On the other hand the positions of the maxima of $g_{mol}^{IAA,n}$ and $g_{mol}^{IAA,X}$ differ by 33/1000 Å (2.764 and 2.797 Å with $Q_{max} = 14.97$ Å^{-1}). However, here it is more important to notice that the g_{mol}^{IAA} differ at small distances (<2.4 Å) far more than might be expected from the statistical accuracy of the data. This deviation is
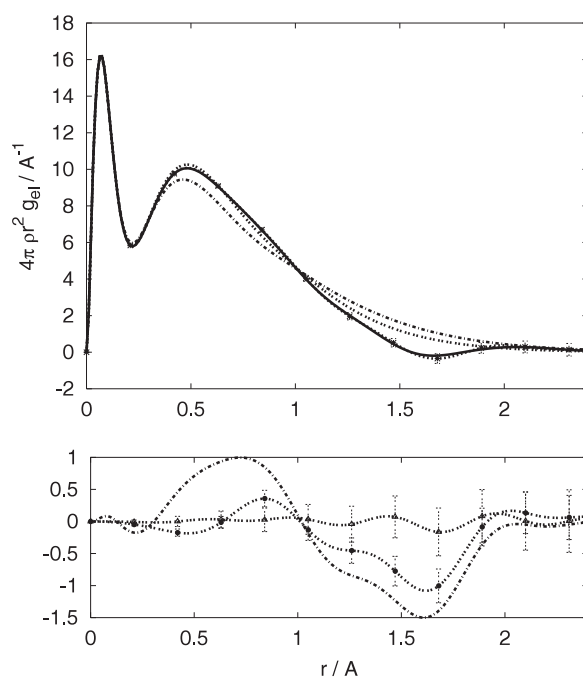
Figure 2. Top: the electron density ACF $4\pi r^2 g_{el}$ (equation (2)). Solid and dashed curves, experimental curves for H_2O and D_2O respectively (equation (7)); dashed–dotted, IAA; double dashed, CAA (equations (4) and (8)). Bottom: differences in $4\pi r^2 g_{el}$. Triple dashed, difference between D_2O and H_2O; dashed–dotted, difference experimental minus IAA; double dashed, experimental–charged atom model difference. The experimental curves all are all calculated from the data sets [7] (x-ray) and [8] (neutrons) via equations (7) and (2).

used to determine an experimental F_M^{exp} via

$$(F_M^{exp})^2 = (F_M^{IAA})^2 - \int^{r=2.4\,\text{Å}} 4\pi r^2 \rho_{mol} \left(g_{mol}^{IAA,n} - g_{mol}^{IAA,x} \right) j_0(Qr)\, \mathrm{d}r. \quad (7)$$

F_M^{exp} is related via equation (2) to the electron density ACF of an average molecule in liquid water. Figure 2 compares the experimental molecular electron–electron ACF with the IAA. Between 0.3 and 1 Å the deviation of the experimental density from the IAA is positive while it becomes negative further out. A very simple method to deal with deviations from the IAA used in crystallography is referred to as spherical atom κ formalism in [3]. In the κ formalism, the atomic density is formulated as

$$\rho'_{atom} = \rho_{core} + \rho'_{valence}(\kappa r) = \rho_{core} + P_v \kappa^3 \rho_{valence}(\kappa r), \quad (8)$$

where P_v is a population parameter effectively introducing a charge to the atom resulting in a contraction or expansion of the respective valence shells. We shall thus refer to this model as the charged atom approximation (CAA). The modified atomic electron density ρ'_{atom} calculated via equation (8) can be used to calculate modified form factors via equation (4). For Slater-type electronic wavefunctions, both the IAA and the CAA form factors can even be calculated analytically [14]. Equations (3) and (2) then give the electron ACF for the CAA.

Fitting this model to the experimental electron density ACF gives a minimum at a partial charge of $+0.53\,e$ at the hydrogen, in very good agreement with the study of Badyal *et al* [1] and recent *ab initio* simulations of liquid water [15]. The expansion of the oxygen atom function

gives a very good agreement with the experiment in the range 0–1 Å close to the statistical error level. Likewise, the contraction of the hydrogen improves at larger distances. However, at distances between 1.2 and 2 Å where the inter-molecular hydrogen–oxygen interaction, the hydrogen bond, becomes important, deviations from the experimental results for both the IAA and the CAA remain, indicating charge redistribution along the hydrogen bond in agreement with [6].

The difference between the electron distributions determined for H_2O and D_2O nowhere exceeds the error level. Very small differences occur at distances around 1.6 Å. These could have three reasons:

(1) differences in the inter-nuclear distances, as the neutron diffraction experiment determines the average H_2O/D_2O structure,
(2) differences in the electronic structure of the hydrogen bond,
(3) counting statistics of the measurement.

In short, the electronic structures of liquid D_2O and H_2O are indistinguishable within the limits of accuracy of these experiments. The inter-nuclear structure of D_2O and H_2O on the other hand is significantly different [7]. Classically the structure of two systems of particles interacting via the same potential should not depend on the mass of the particles. The present work does not indicate a difference in the electron distribution and hence a difference in the interaction potential of D_2O and H_2O. The results of this paper are thus consistent with the interpretation of the structural differences of D_2O and H_2O as quantum effects.

Liquid water exhibits significant deviations from the IAA which can be accounted for in part by a CAA. A formalism has been given to quantify these deviations and reveal an redistribution of chemical charge along the hydrogen bond, thus confirming that the partial covalent character found in the solid is observed also in the liquid state. The electron densities of liquid D_2O and H_2O are indistinguishable at the limit of present experimental results. The study described here indicates that, with modern experimental and analytical techniques, a new field is being opened up by detailed investigations into the electronic structure of simple molecules in liquids at room temperature.

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