

Supporting Information to the "The quadrupole moment of water molecules and the permittivity of water near a charged surface"

E. Gongadze, A. Velikonja, T. Slivnik, V. Kralj-Iglič, and A. Iglič*

E-mail: ales.iglic@fe.uni-lj.si

Energy of a single water molecule

The energy of a single water molecule can be written as:

$$\begin{aligned}
 W(x) = -2q\phi\left(x - \frac{d}{2} \cos \omega\right) + q\phi\left(x - \frac{d}{2} \cos \omega + a \cos(\omega + \varphi)\right) \\
 + q\phi\left(x - \frac{d}{2} \cos \omega + a \cos(\omega - \varphi)\right), \quad (1)
 \end{aligned}$$

where $+q$ and $-q$ are point charges and d and a the distances as denoted in Fig.1 (see also Fig.1 in the main text). For small d and a we can expand the energy $W(x)$ in Eq.1 into a Taylor series up to the quadratic terms:

$$\begin{aligned}
 W(x) = -2q \left[\phi(x) - \frac{d}{2} \cos \omega \phi'(x) + \frac{d^2}{8} \cos^2 \omega \phi''(x) \right] \\
 + q \left[\phi(x) + \left(-\frac{d}{2} \cos \omega + a \cos(\varphi + \omega) \right) \phi'(x) + \frac{1}{2} \left(-\frac{d}{2} \cos \omega + a \cos(\varphi + \omega) \right)^2 \phi''(x) \right] \\
 + q \left[\phi(x) - \left(-\frac{d}{2} \cos \omega + a \cos(\varphi - \omega) \right) \phi'(x) + \frac{1}{2} \left(-\frac{d}{2} \cos \omega + a \cos(\varphi - \omega) \right)^2 \phi''(x) \right]. \quad (2)
 \end{aligned}$$

*To whom correspondence should be addressed

Rearrangement of the above Eq.2 yields:

$$W(x) = 2qd \cos \omega \phi'(x) + qr^2 \sin^2 \Phi \sin^2 \omega \phi''(x) \quad , \quad (3)$$

where we took into account $d = a \cos \varphi$ and $a \sin \varphi = r \sin \Phi$ (see Fig.1). For $d = 0$ and omitted $\sin^2 \Phi$ the above Eq.3 gives the energy of the "pure" rod-like quadrupole as a function of its inclination with respect to the x-axis described by the angle $\vartheta = \pi/2 - \omega$ (see also^{1,2}).

The derived energy expression of single water molecule (Eq.3) depends on the rotation angle Φ around the molecule symmetry axis (see also Fig.1). Close to the charged surface, where the magnitude of the electric field $|E|$ is high, the water molecules are predominantly oriented with their symmetry axes in the direction perpendicular to the charged surface (see also Fig.2 in the main text), if the magnitude of $\phi''(x)$ is not too high. Consequently, the energy of a single water molecule do not vary substantially as a function of the rotation angle Φ (i.e. the rotation around the molecule symmetry axis) which allow us to approximate the term $\sin^2 \Phi$ in Eq.3 with 1/2 to get :

$$W(x) = 2qd \cos \omega \phi'(x) + \frac{1}{2} qr^2 \sin^2 \omega \phi''(x) \quad . \quad (4)$$

Using the definition of dipole $p = 2qd$ and quadrupole $\mathcal{Q} = qr^2/2$ and electric field $E = -\phi'(x)$ it follows from the above equation:

$$W(\omega) = |E| p \cos \omega - \mathcal{Q} \left| \frac{dE}{dx} \right| \sin^2 \omega \quad , \quad (5)$$

where we took into account that in our case the surface charge density $\sigma < 0$ and therefore $-E(x) = \phi'(x) > 0$ and $\phi''(x) < 0$. The adopted approximate relation $\langle \sin^2 \Phi \rangle = 1/2$ enable us to derive an analytical expression for the average orientation of water molecules, the space dependence of dielectric permittivity and the corresponding Poisson equation (see the main text). In electric double layer the region of high $|E(x)|$ also coincide with the region

of high $|dE(x)/dx|$ where the quadrupole part of the energy (Eq.5) can not be neglected. As it can be seen in Fig.2 (in the main text of the article) the nonzero quadrupole moment diminish the average orientation of the water molecules in the direction perpendicular to the charged surface. Therefore the assumption $\langle \sin^2 \Phi \rangle = 1/2$ is valid only for small enough values of $|dE(x)/dx|$ (i.e. small enough magnitudes of surface charge density σ) so that the predominant average orientation of the water molecules at the charged surface in the direction perpendicular to the charged surface is still preserved. On the other hand, at larger distance from the charged surfaces, where the water molecules are not oriented the magnitude of $|dE(x)/dx|$ is very small, therefore the quadrupole part of Eq.5 becomes negligible and the approximation $\langle \sin^2 \Phi \rangle = 1/2$ is not important anyway.

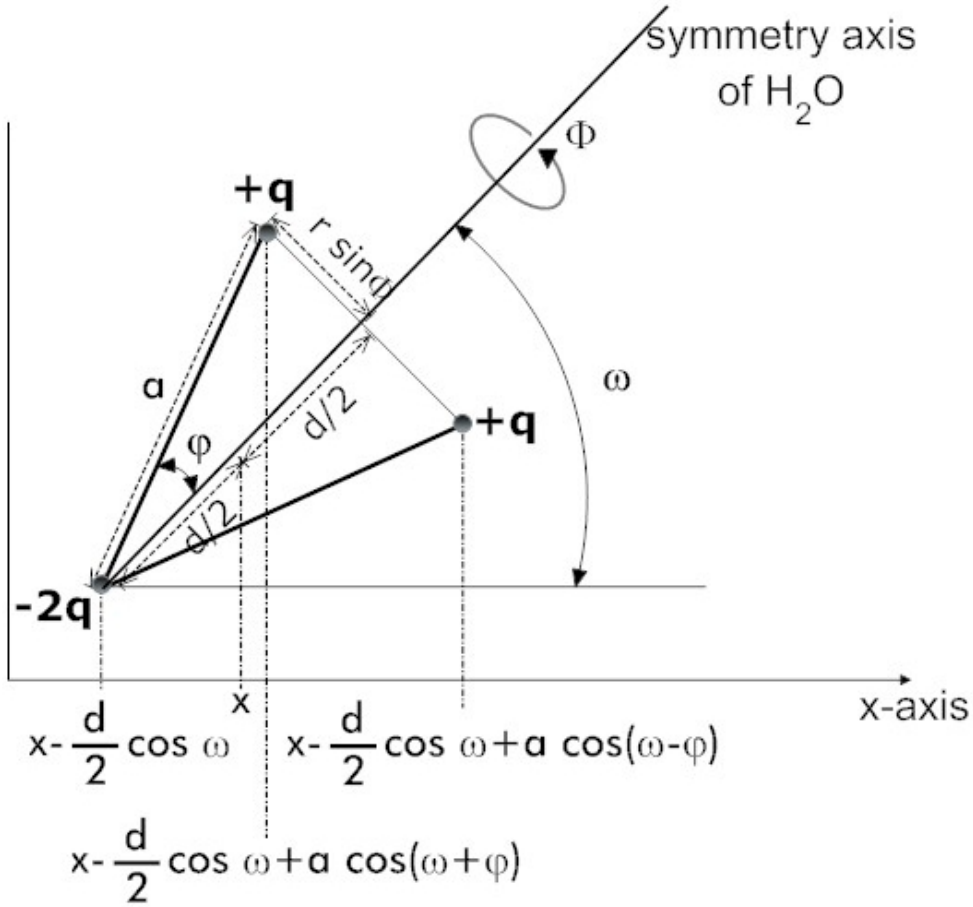


Figure 1: The geometrical parameters of the triangular atomic model of the water molecule. The principal symmetry axis of water molecule is the rotational axis for angle Φ .

References

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