

Supporting Information for: Dynamics of Water Confined within Reverse Micelles

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May, 2006

Quantum Corrections to Classical Lineshapes

The absorbance spectrum of a quantum statistical ensemble at equilibrium can be shown to be:^{1,2}

$$\alpha(\omega)n(\omega) = \frac{\pi\omega}{3\hbar c V \epsilon_0} (1 - e^{-\beta\hbar\omega}) D(\omega) \frac{1}{2\pi} \int_{-\infty}^{+\infty} \langle \mathbf{M}(t) \cdot \mathbf{M}(0) \rangle e^{-i\omega t} dt \quad (\text{S1})$$

where $D(\omega)$ is a quantum correction factor which ensures that, when a classical time correlation function is used, the principle of detailed balance is satisfied.^{1,2} In the classical limit, the above quantum mechanically valid equation will generate the dielectric loss of the sample.³ Ahlborn and Space et al have previously shown that for liquid water the harmonic correction factor, $D(\omega) = \frac{\beta\hbar\omega}{(1 - e^{-\beta\hbar\omega})}$, is the best correction factor to use even though the Egelstaff y-time correction^{4,5,*} is commonly employed by other workers.^{1,2,6} We, too, find that the harmonic correction factor reproduces the lineshape better than the y-time correction.

Figure S1 presents the power absorption coefficient $\alpha(\omega)$ of bulk water as measured from experiment by Bertie and co-workers,⁷ calculated from Equation S1 using two different quantum correction factors, and calculated from the theory of Caillol and co-workers.⁸ Although the intensity for the spectra calculated by Equation S1 with the harmonic correction and Caillol's equation (Equation 11 in our paper) are both slightly too high, the difference in lineshape and intensity between the two is insignificant. We also note that the intensity for the calculation using Equation S1 with the harmonic correction factor is in quantitative agreement with the absorbance calculations for bulk water using INM and TCF methods by Ahlborn, Ji and Space.¹ In contrast, the spectrum calculated using the y-time correction is in significant disagreement with the experimental spectrum and the other two calculated spectra.

Inapplicability of Equation S1 to Reverse Micelles

The use of Equation S1 for reverse micelles presents three difficulties which are not present when using the classical approximation developed by Caillol and co-workers.⁸ 1. Equation S1 does not include the ionic properties of the solution. It uses only the net dipole correlation

* The y-time correction is performed by substituting the corrected time correlation function, $C(\sqrt{t^2 - i\hbar\beta t})$, for the classical time correlation function $C(t)$. To avoid the use of complex time, the transform is performed by time-shifting the classical correlation function $C(t)$ to $C(\sqrt{t^2 + (\hbar\beta/2)^2})$ which is multiplied by $\exp(\hbar\beta/2)$ after being Fourier transformed to generate the correct frequency domain function. The correct time domain function may be recovered by inverse Fourier transform. Refer to Reference 5 for specific details regarding this method.

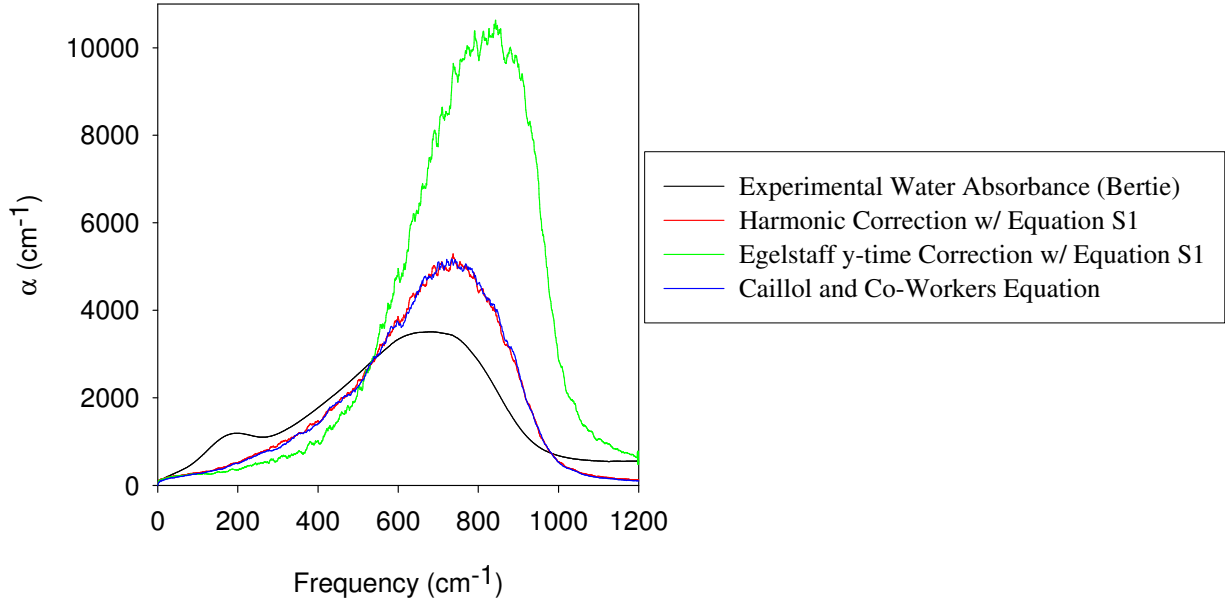


Figure S1. Absorbance spectra for bulk water from experiment and calculation. The Egelstaff y-time correction significantly overestimates the absorbance in the librational region.

function. 2. It only calculates the imaginary part of the complex permittivity (essentially the product of $\alpha(\omega)$ and $n(\omega)$). The Caillol treatment determines the complex-valued permittivity and conductivity. However, it should be noted that both $\alpha(\omega)$ and $n(\omega)$ can be obtained through a Kramers-Kronig analysis. 3. Most importantly, in contrast to the Caillol treatment, Equation S1 is not applicable for a system suspended in an infinite dielectric medium, making it inappropriate for reverse micelles. The effect of the dielectric continuum on the absorbance is significant, although it does not change the qualitative aspects of our results. Thus, for these three reasons, we use the theory developed by Caillol and co-workers rather than Equation S1.

Relationship of Caillol's Equation to Equation S1

The Caillol equation can be shown to be essentially equivalent to the harmonically corrected version of Equation S1 in the case of an infinite medium without ionic conductivity. Caillol's dielectric constant formula for a dipolar system in the case of Ewald sum boundary conditions (Equation 11 of our paper, expressed in SI units) is written as,⁸

$$\varepsilon(\omega) - 1 = \frac{\beta}{3V\varepsilon_0} \left[\langle \mathbf{M}^2 \rangle + i\omega \int_0^{+\infty} \langle \mathbf{M}(t) \cdot \mathbf{M}(0) \rangle e^{i\omega t} dt \right] \quad (\text{S2})$$

where \mathbf{M} is the total system dipole moment. Using the identity,

$$\alpha(\omega)n(\omega) = \frac{\omega}{c} \text{Im}[\varepsilon(\omega)] \quad (\text{S3})$$

it may be shown that,

$$\alpha(\omega)n(\omega) = \frac{\beta\omega^2}{3cV\epsilon_0} \int_0^{+\infty} \langle \mathbf{M}(t) \cdot \mathbf{M}(0) \rangle e^{i\omega t} dt. \quad (\text{S4})$$

In the case of $D(\omega) = \frac{\beta\hbar\omega}{(1 - e^{-\beta\hbar\omega})}$, Equation S1 may be written as,

$$\alpha(\omega)n(\omega) = \frac{1}{2} \frac{\beta\omega^2}{3cV\epsilon_0} \int_{-\infty}^{+\infty} \langle \mathbf{M}(t) \cdot \mathbf{M}(0) \rangle e^{-i\omega t} dt. \quad (\text{S5})$$

Equations S4 and S5 are not quite analytically equivalent, but for most functions the approximation

$$\int_{-\infty}^{+\infty} f(t) e^{-i\omega t} dt \approx 2 \int_0^{+\infty} f(t) e^{i\omega t} dt \quad (\text{S6})$$

is valid, thereby making them equivalent.

Summary

We therefore conclude that the Caillol method offers the same advantages as the harmonically corrected version of Equation S1. Furthermore, the Caillol method allows for the incorporation of different boundary conditions and the inclusion of effects due to mobile ions. These advantages make it preferable to Equation S1 for the case of molecular liquids with solvated ions in spherical geometries within a continuum dielectric, such as the reverse micelle simulations presented in the main paper.

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