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Interpretation of the low frequency response of aqueous solutions: A molecular dynamics analysis

A. Idrissi *, P. Damay

Laboratoire de Spectroschimie Infrarouge et Raman (UMR CNRS A8516), Centre d'Etudes et de Recherches Lasers et Applications,
Université des Sciences et Technologies de Lille, 59655 Villeneuve d'Ascq cedex, France

Abstract

In the case of a mixture it is difficult to determine the nature and origin of the low-frequency response. The fundamental difficulty arises from the large number of different interaction mechanisms, and their corresponding cross terms, that contribute to the low-frequency response of the system. Molecular dynamics simulation is used to obtain qualitative information on the role of different contributions (translation, rotation, dipole–dipole-induced interactions) to the low-frequency response of aqueous solutions, as obtained by Raman spectroscopy and the time-resolved optical Kerr effect. On the basis of these results, three contributions to the low-frequency response of aqueous solutions are proposed. The first is associated with the vibrational motion of the solute or solvent molecule in a cage formed by the neighboring molecules. The second is associated with hydrogen bonding interactions between water molecules. The third contribution is associated with hydrogen bonds between solute and water and with the librational motion of urea molecules. This interpretation is applied to analyze the low-frequency response of the urea/water and acetone/water systems as a function of the concentration of the solute. The three criteria provided by the fitting procedure (the chi-square, the correlation matrix and the structure of the residue) are used to validate the three bands model proposed by the molecular dynamics simulation.

Keywords: Molecular dynamics; Time resolved measurements; Raman spectroscopy; Solution chemistry

1. Introduction

The analysis of the low-frequency response of aqueous solutions, as obtained by Raman spectroscopy and by the optical Kerr effect, is a powerful tool for evaluating the influence of solutes on the structure and dynamics of water. It provides information on both intermolecular interactions and molecular dynamics. A comprehensive discussion of the use of low-frequency Raman spectroscopy may be found in a recent review by Nielsen ([1] and references therein). Many investigations have been carried out to analyze the effect of solute molecules on the intermolecular vibrations of water [2–7]. The changes in the positions and widths of the two vibrational bands in the regions of 180 cm^{-1} and 50 cm^{-1} provide a basis for the quantitative analysis of the influence of the solute. The same approach was applied to the analysis of the low-frequency response obtained by the optical Kerr effect [8–10].

In the case of pure water [11], it was suggested that the lower peak $\bar{\nu}_1 \sim 50\ \text{cm}^{-1}$ observed in the low frequency response is associated with a vibration of water molecules in a cage formed by their neighboring molecules. The higher peak $\bar{\nu}_3 \sim 180\ \text{cm}^{-1}$ was assigned to a hydrogen bond interaction between the water molecules. In the case of a mixture it is difficult to determine the nature and origin of the low-frequency response. The fundamental difficulty arises from the large number of different interaction mechanisms, and their corresponding cross terms, that contribute to the low-frequency response of the system. Molecular dynamics simulation (MD) can yield qualitative information on the role of the different interactions in the low-frequency response. To analyze the low frequency response of a mixture in terms of intermolecular interactions, one must

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* Corresponding author.
E-mail address: idrissi@univ-lillel.fr (A. Idrissi).

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calculate the Fourier transform (FT) of the time correlation function of the dynamical property (the polarizability tensor in the case of the Raman spectroscopy and the susceptibility tensor in the case of the Kerr effect) to be able to compare it with the low-frequency response of the system.

The complication arises because the correlation function can be written as a sum of contributions: that of the solvent molecules and that of the solute molecules, as well as those due to the cross term. Each of these terms is made up of a part associated with the reorientation of the molecules a part associated with the dipole–dipole-induced interactions and the cross term between the two. It is difficult to determine the effect of these different contributions in the analysis of the experimental low-frequency response. Thus, molecular dynamics simulation is of great help, as it provides qualitative information on the various contributions to the low-frequency response of the system. The objectives of the present study are first, to analyze these various contributions to the low-frequency response of aqueous solutions (urea/water is chosen as model system) and second, to confront this analysis to intrinsic criteria of a curve fitting procedure.

2. Molecular dynamics

The preliminary study [11] of the various interaction potentials suggested the use of the DKJ [12] model of urea and the TIP4P [13] potential of water. The choice was made on the basis of the quit good agreement with the experimental results obtained on these substances for the density, energy and the coefficient of diffusion [11], as well as the structure factor [14]. The potential models are written in terms of a Lennard-Jones (LJ) pair potential between the atomic sites, plus a Coulomb interaction between the corresponding partial atomic charges.

The molecular dynamics simulations were performed on a system of 864 molecules (173 urea molecules and 691 water molecules). Periodic boundary conditions were applied. The Ewald summation method was employed to handle long-range electrostatic interactions. Simulations were carried at $T = 298$ K with an average pressure of about $P = 1$ MPa. A time step of 0.5 fs was used in integrating the equations of motion. The system was equilibrated for 500 ps followed by at least 200 ps of data collection.

3. Analysis

The analysis by MD of the low-frequency response of the system was made by calculation of the FT of the correlation function of the anisotropic component of the total polarizability tensor, $\Pi^{ab}_{\text{tot}}(t)$, where $a = X, Y, Z$ and $b = X, Y, Z$) of the solution and X, Y, Z are the axes in the laboratory frame. In an isotropic liquid, all of the combinations a, b are equivalent.

The total polarizability $\Pi^{ab}_{\text{tot}}(t)$ can be expressed as a first approximation in terms of the molecular polarizability $\Pi^{ab}_{\text{mol}}(t)$ and the dipole–dipole-induced polarizability $\Pi^{ab}_{\text{ind}}(t)$, according to the expression [15]:

$$\Pi^{ab}_{\text{tot}}(t) = \Pi^{ab}_{\text{mol}}(t) + \Pi^{ab}_{\text{ind}}(t) \tag{1}$$

$$= \sum_{i=1}^{N} \alpha_i^{ab}(t) + \sum_{i=1}^{N} \sum_{j \neq i}^{N} \alpha_i^{ab}(t) T_{ij}(t) \alpha_j^{ab}(t). \tag{2}$$

Here, N is the number of the molecules, α_i^{ab} is the polarizability of molecule i and Π^{ab}_{mol} and Π^{ab}_{ind} are the total molecular and the interaction-induced polarizability tensors, respectively. The interaction tensor between molecules i and j is expressed in tensor notation by:

$$T_{ij} = \frac{3\mathbf{r}_{ij}\mathbf{r}_{ij} - r_{ij}^2 \mathbf{I}}{r_{ij}^5}, \tag{3}$$

where $\mathbf{r}_{ij}$ is the vector between centers of mass of molecules i and j, r_{ij} is the corresponding distance and $\mathbf{I}$ is a unit 3x3 matrix.

The variation in time of the molecular term is due to the reorientation of the molecules, whereas for the induced term it is due to the reorientation, as well as the relative translation of the molecules. The FT of the correlation function, $\langle \Pi^{ab}_{\text{tot}}(t) \Pi^{ab}_{\text{tot}}(0) \rangle$ (where $\langle \cdots \rangle$ denotes the statistical average), yields the spectral density, $\Xi^{ab}_{\text{tot}}(\omega)$, which can be compared with the low-frequency response of the system. In the case of the Kerr effect, the low-frequency response is obtained by the FT of the signal, $R(t)$, whose expression is given by [16]:

$$R(t) = -\frac{H(t)}{k_B T} \frac{\partial}{\partial t} \langle \Pi^{ab}(t) \Pi^{ab}(0) \rangle, \tag{4}$$

where $H(t)$ is the Heaviside function, defined by:

$$H(t) = 0 \quad \text{for } T \leqslant 0,$$
$$H(t) = 1 \quad \text{for } T > 0;$$

k_B is the Boltzmann constant, and T is the temperature. In the case of the urea/water mixture, the decomposition of $\Xi^{ab}_{\text{tot}}(\omega)$ in terms of contributions of the molecular, $\Xi^{ab}_{\text{mol}}(\omega)$, and induced parts $\Xi^{ab}_{\text{ind}}(\omega)$ of the total polarizability tensor are given in Figs. 1a, 1b and 1c, respectively. The weak intermediate peaks visible along the calculated spectral densities are due to statistic noise. As in Eq. (1), the quantity $\Pi^{ab}_{\text{tot}}(t)$ is divided into two terms; thus,

$$\Pi^{ab}_{\text{tot}}(t) = \Pi^{ab}_{\text{urea}}(t) + \Pi^{ab}_{\text{water}}(t), \tag{5}$$

each of these terms can be split into molecular and dipole–dipole-induced contribution as,

$\Pi^{ab}_{\text{X}}(t) = \Pi^{ab}_{\text{X,mol}}(t) + \Pi^{ab}_{\text{X,ind}}(t)$, where X represents the urea or the water molecule.

The following correlation functions have been calculated:

$\langle \Pi^{ab}_{\text{X}}(t) \Pi^{ab}_{\text{X}}(0) \rangle$, $\langle \Pi^{ab}_{\text{X,mol}}(t) \Pi^{ab}_{\text{X,mol}}(0) \rangle$ and $\langle \Pi^{ab}_{\text{X,ind}}(t) \Pi^{ab}_{\text{X,ind}}$ - $(0) \rangle$. The corresponding spectral densities, $\Xi^{ab}_{\text{X}}(\omega)$, $\Xi^{ab}_{\text{X,mol}}(\omega)$ and $\Xi^{ab}_{\text{X,ind}}(\omega)$ were then evaluated, and are