

THz reflection spectroscopy of liquid water

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Abstract

We report an investigation of the temperature-dependent far-infrared spectrum of liquid water. We have employed a new experimental technique based on ultrashort electromagnetic pulses (THz pulses). This technique allows for fast and reliable data of both index of refraction and absorption coefficient for highly absorbing liquids. The temperature dependence reveals an enthalpy of activation corresponding to 2.5 kcal/mol, in agreement with recent Raman experiments, but lower than the enthalpy observed in dielectric relaxation experiments. This demonstrates that part of the orientational relaxation in liquid water takes place without breaking of hydrogen bonds with bonding energy of 5 kcal/mol, as suggested in recent theoretical model.

In this work we report an investigation of the temperature dependence of the far-infrared spectrum of liquid water in the range from 2 to 35 cm^{-1} . In this spectral region the spectrum is dominated by intermolecular interactions due to permanent and induced dipole moments in the hydrogen bonded network of water molecules.

The importance of liquid water is difficult to underestimate. In biological systems, liquid water defines the environment for the life supporting biochemical reactions and understanding the physical and chemical properties of liquid water is a prerequisite for understanding biology on a molecular level. Consequently, liquid water is perhaps one of the most studied chemical systems, with numerous experimental and theoretical studies over the last four decades [1]. Unfortunately, this has not yet led to a full understanding of the complex structural and dynamic properties of liquid water, as it theoretically

and experimentally is a very challenging system. In modelling the FIR-absorption of liquid water one has to take into account the dielectric relaxation of the individual dipoles, hydrogen bonding, quantum effects due to the light hydrogen atoms and many-body electrostatic interactions. Numerous molecular dynamics (MD) simulations addressing different aspects of liquid water dynamics have appeared since the first MD-simulation of water by Rahman and Stillinger [2]. Theoretical IR and Raman spectra can be calculated by evaluating the time correlation function of the macroscopic dipole moment or polarizability and subsequently Fourier transforming these. In a recent MD simulation of the FIR spectrum of liquid water by Guillot [3] good agreement was obtained with the experimental spectrum. In the region below 50 cm^{-1} , where quantum effects are assumed to be negligible ($kT = 208 \text{ cm}^{-1}$), the calculated absorption spectrum is dominated by reorien-

tation of permanent and induced dipole moments. The total dipole correlation function contains 70% contribution from the permanent dipole moment and 3% contribution from the dipole induced dipole moments (DID). The remaining 27% comes mainly from an interference term correlating the permanent dipole moment of one molecule with the induced moments of its neighbors. It is also interesting to note that over $\frac{2}{3}$ of the total dipole correlation function, and consequently the absorption spectrum, arises from collective contributions involving more than one water molecule. The different contributions resonate with the hydrogen bond network around 200 and 650 cm^{-1} , corresponding to the stretching mode of the O–H...O unit and the libration mode of the water molecules. The detailed balance of the permanent and induced dipole moments and specially their interference gives a good quantitative agreement with the experimentally observed spectra, reproducing the absolute absorption strength, the libration peak at 650 cm^{-1} , and to some extent, the stretching mode at 200 cm^{-1} . A similar viewpoint is taken by Gaiduk et al. in Ref. [4]. They propose a two-component analytical model based on a confined rotator (CR) and an extended diffusion (ED) model. The CR component corresponds to the libration mode of the hydrogen bond network, and the ED component corresponds to motion of more mobile water molecules giving rise to the 200 cm^{-1} peak. The two-component picture is also a central theme in Ref. [1].

In spite of its importance only few experimental FIR spectra of liquid water have been published [5–14]. Below 100 cm^{-1} good broadband spectral sources are not available, and the very large absorption coefficient of liquid water ($\alpha \approx 500\text{ cm}^{-1}$) also poses difficulties for traditional transmission spectroscopy. Consequently, the reported FIR spectra for liquid water differ substantially (up to 50%) in the low-frequency region, and weak resonance features are reported by some but not all authors. Only two systematic measurements of the temperature dependence has been reported [8,11] and they disagree substantially.

In order to test the different water models, we have undertaken a systematic study of the FIR spectrum of liquid water as function of temperature. To do this we have employed a new experimental tech-

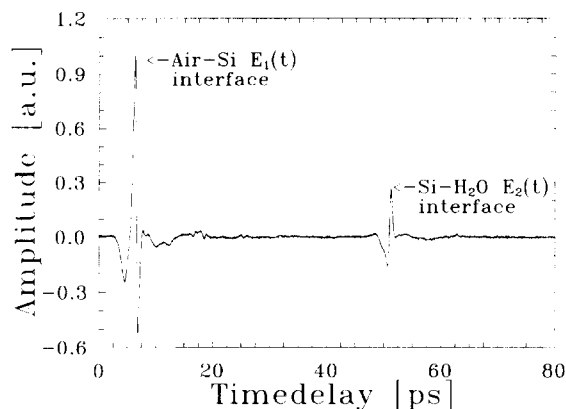


Fig. 1. Time domain spectrum of the THz pulse reflected from the first and second surfaces of the sample cell. The first pulse is reflected from the air–silicon interface and serves as the reference pulse. The second pulse originates from the water–silicon interface. By comparing the amplitude and phase of the two pulses and taking into account the known refractive index of silicon, the optical constants of the water sample can be obtained.

nique based on ultrashort electromagnetic pulses (THz pulses) radiated from small semiconductor antennas driven by femtosecond laser pulses. The details of the experimental technique will be presented in a later publication. An introduction to THz pulses, and their application in FIR-spectroscopy, can be found in Refs. [15–19]. In brief ultrashort electromagnetic pulses consisting only of one cycle of the field are generated and detected by small photoconductive antennas. The bandwidth of the THz pulses is very broad, extending from 50 GHz to several THz ($1\text{ THz} = 33.356\text{ cm}^{-1}$). By reflecting of a silicon–water interface and measuring the frequency-dependent change in phase and amplitude of the pulse, the optical constants, index of refraction and absorption coefficient of liquid water are obtained, assuming knowledge of the optical constants of silicon. By using the air–silicon reflection at the sample window as reference, the optical constants of water are directly obtained from a single room-temperature scan lasting only a few minutes. The pulse sequence obtained from the THz time domain reflection spectrometer is shown in Fig. 1. If the THz pulses reflected from the air–silicon and silicon–water interfaces are denoted $E_1(t)$ and $E_2(t)$, respectively, then the ratio of their Fourier transforms can be

given by the optical constants of air, silicon and water

$$\frac{\hat{E}_2(\nu)}{\hat{E}_1(\nu)} = \frac{t_{AS}t_{SA}}{r_{AS}} \exp\left(i \frac{4\pi n_S d_S \nu}{c}\right) \frac{\hat{n}_W - n_S}{\hat{n}_W + n_S} \Leftrightarrow$$

$$\frac{\hat{E}_2(\nu)}{\hat{E}_1(\nu)} \frac{r_{AS}}{t_{AS}t_{SA}} \exp\left(-i \frac{4\pi n_S d_S \nu}{c}\right)$$

$$\equiv R \exp(i\theta) = \frac{\hat{n}_W - n_S}{\hat{n}_W + n_S}. \quad (1)$$

The t_{AS} , t_{SA} and r_{AS} are the real Fresnel coefficients for amplitude reflection and transmission at the air–silicon (AS) and silicon–air (SA) interfaces. The exponential factor represents the phaseshift (delay) due to propagation in the window material, and the last term is the complex reflection coefficient for the silicon–water interface. Assuming accurate knowledge of the index of silicon (n_S) and the thickness of the silicon window (d_S), we can isolate the silicon–water reflection on the right side, as indicated in Eq. (1). If the left side of Eq. (1) is represented as $R \exp(i\theta)$, then the expression is easily solved for the unknown index of refraction and absorption coefficient of liquid water,

$$n_W = \frac{n_S(1 - R^2)}{1 + R^2 + 2R \cos(\theta)}, \quad (2)$$

$$\alpha_W = \frac{4\pi\nu n_S}{c} \frac{-2R \sin(\theta)}{1 + R^2 + 2R \cos(\theta)}. \quad (3)$$

A different form of time domain reflection spectroscopy with ultrashort electromagnetic pulses has been described earlier in Ref. [19].

From the pulses shown in Fig. 1 we have extracted the optical constants at 292 K for liquid water shown in Fig. 2. The solid line through the absorption data is a $\nu^{1/2}$ curve drawn to guide the eye. The measured data are in good agreement with the most recent literature values obtained from microwave [14], dispersive Fourier transform [7], and FIR-laser spectroscopy [9,13] covering different parts of the frequency range from 0 to 1 THz. Presently our bandwidth is limited to 1 THz, but work is in progress to extend this range to 2 THz thereby entering the more controversial spectral range where a shoulder on the absorption curve has been observed by some authors.

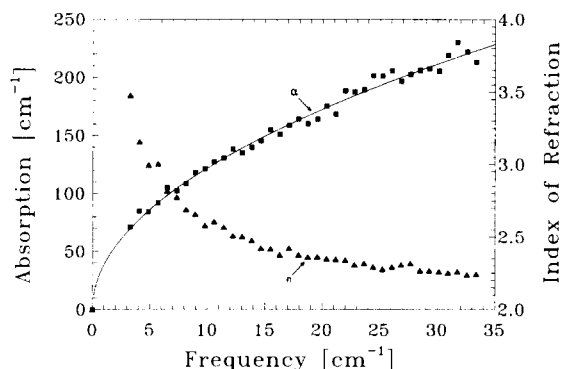


Fig. 2. Absorption coefficient (■) and index of refraction (▲) for liquid water. The solid line is proportional to $\nu^{1/2}$. The water sample was three times distilled and kept at a temperature of 292 K.

In order to measure the properties of liquid water as function of temperature, a closed water cell equipped with silicon windows was placed on a small 70W Peltier-element. This allowed us to change the temperature from the supercooled region (270 K) up to 314 K. Great care was taken to avoid water in the setup. Droplets condensing on the cold sample cell and absorption by water vapor could seriously affect our results. It was also necessary to take into account the small temperature-dependent changes in the refractive index of the silicon window. Index and absorption were measured for ten different temperatures. A detailed presentation of the data will be given in a later publication. All absorption data resemble the data at 292 K, a smooth absorption curve increasing with frequency and temperature. The smooth increase in absorption is in agreement with the observation by Hasted and Birch, but disagrees with the erratic changes in temperature observed by Afsar and Hasted. To represent the temperature-dependent absorption, we have chosen to plot the logarithm of the integrated absorption from 0.06 to 1 THz as function of T^{-1} , an Arrhenius plot, as shown in Fig. 3. The integrated absorption at 314 K was used to normalize the plot. The rationale for this plot comes from the simplest description of a polar liquid, the Debye model. In this model, it can be shown that the integrated absorption is proportional to τ^{-1} , where τ is the orientational relaxation time of the molecular dipoles. Furthermore, τ is expected to follow an exponential temperature de-

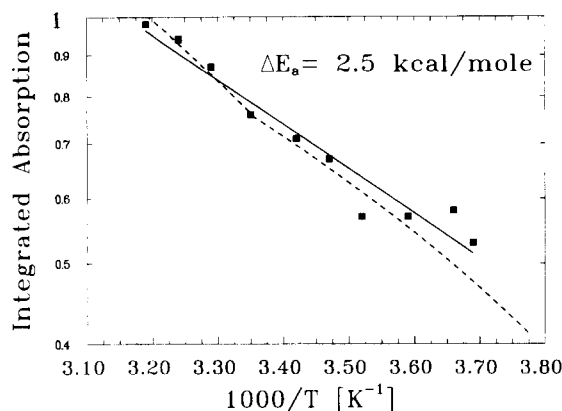


Fig. 3. The integrated absorption normalized at 314 K, plotted against $1/T$. The straight line corresponds to an activation energy of 2.5 kcal/mol. The dashed line is the temperature dependence of the relaxation time as observed in a recent Raman experiment by Mizoguchi et al. [20].

pendence, scaled by the activation enthalpy of the relaxation process,

$$\tau = \tau_0 \exp\left(\frac{\Delta E_a}{RT}\right). \quad (4)$$

With these assumptions, we obtain an activation enthalpy of 2.5 kcal/mol, as given by the full line in Fig. 3. The fitted curve represents the data well, except for the measurements below 283 K, where the integrated absorption is almost constant. We note that the observed temperature dependence is similar to the temperature dependence observed in a recent Raman scattering experiment by Mizoguchi et al. [20]. The energy of the hydrogen bond in liquid water is of the order of 5 kcal/mol [1], in agreement with the activation enthalpy observed in microwave (9 GHz) dielectric studies of water. Our observation of an activation enthalpy less than the energy required to break a hydrogen bond, thus points toward a two component model of liquid water with dynamics governed by 'normal' hydrogen bonds and weakened hydrogen bonds as suggested in Ref. [4].

In summary, we have demonstrated a new simple method for obtaining far-infrared spectra of highly

polar liquids. THz time domain spectroscopy was applied to liquid water and good agreement with previous measurements was obtained. By measuring the temperature-dependent absorption, we inferred an activation enthalpy of 2.5 kcal/mol. This unequivocally shows that reorientation of water dipoles can take place without breaking of hydrogen bonds, in agreement with recent Raman experiments and theoretical models.

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