

Water Confinement Effects in Black Soap Films

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Water confined in the ultrathin interstitial core of black soap films has been studied by infrared and Raman spectroscopies. Lowering the water core thickness below 1 nm induces spectral modifications in the multicomponent O–H stretching band which can be associated with environment changes for water molecules. Differences observed between nonionic and ionic surfactants allow us to distinguish the sole effect of confinement from the combined effects of confinement and ionic strength. Both trends correlate with previous experimental observations done on different surfactant solutions and with results from numerical simulations.

1. Introduction

A black film is an ultrathin and self-supported molecular system constituted of two monolayers of amphiphilic molecules with their polar heads facing each other and separated by an aqueous core of variable thickness [1]. As the interstitial water drains, the film becomes much thinner than the wavelength of visible light and consequently becomes black, in reflection, due to the destructive interference between waves reflected at the front and at the back interfaces of the film. From a fundamental point of view, these self-supported films are very well suited to study molecular interactions and molecular organization. Despite their inverted structure relative to that of a cell membrane, they are also of interest in the biological field [2].

Generally, a black film contains a relatively large amount of liquid water and is called a first or common black film (CBF) [1,3]. However, under particular experimental conditions such as the presence of electrolyte, it is possible to obtain second or Newton black films (NBFs) of about 4 nm or even thinner with very little water inside [1,3-6]. Since Newton's observations, considerable attention has been paid to black films and in particular to their stability and equilibrium thickness [3]. By far the most experimental studies have been carried out using optical interferometry [3,7]. This method is very straightforward and convenient, but its accuracy diminishes as the films get thinner. For structure investigation on the thinnest films, grazing incidence X-ray reflectivity has been used successfully [5]. On the other hand, vibrational spectroscopy has recently emerged as a direct pathway to get insights on the molecular organization and conformation in black films. Indeed, some recent studies have pointed out an ordering of the aliphatic chains for the very thin films [8], and some spectral changes of the water bands have been reported [6,9]. However, the relation between these spectral changes and the modifications occurring in water at the molecular level remains an open issue.

Two types of effects can be expected when the film becomes ultrathin: confinement of the water molecules in a very thin layer and interaction with electric charges present at the interfaces when using ionic surfactants. Several studies have revealed changes in the behavior of water when it is spatially confined between planar lamellar phases or in spherical reverse micelles: molecular dynamics simulations indicate that the water dipoles have a preferential orientation and the hydrogen-bonded network is partially broken down in the aqueous core of a reversed ionic micelle [10,11]. Calculations also indicate a nearly 50% decrease of the dielectric constant of water when confined in a cavity of 12 Å in diameter [12]. Using Fourier transform infrared (FTIR) spectroscopy, Roy and co-workers [13,14] have shown that the OH stretching band of water is affected when the water thickness is lower than 4 and 9 nm in the lamellar and reverse micelle configurations, respectively. A similar behavior has been evidenced in IR spectra of sodium dodecyl sulfate (SDS) second black films by Umemura et al. [6] and in multilamellar liposomes by Lafleur et al. [15] using Raman spectroscopy. Recently it was shown that it is possible to use Raman microspectroscopy to characterize black films [16]. In the present paper, emphasis is given to the state of water inside the core of such films and its possible changes with the thickness of these films and with the composition of the surfactant headgroups.

2. Results and Discussion

The main goal of this work was to study the molecular structure of the aqueous core of very thin soap films. To distinguish between ionic effects and pure confinement effects, anionic (SDS) and nonionic ($C_{12}E_5$) surfactants have been used. For this purpose, we have utilized complementary optical techniques: ellipsometry to obtain accurate information on the total thickness of the films and FTIR spectroscopy which is very sensitive to the structure of the water. To obtain films with different thicknesses, we used horizontal films using the porous glass technique or vertical films the draining of which was monitored. The core thickness of the films could be measured using a combination of Raman spectroscopy and ellipsometry for the horizontal films or infrared spectroscopy for the draining vertical films. Films obtained with SDS (at a concentration of 10 mM, slightly higher than the critical micellar concentration) show a thickness dependent on the salt concentration. Figure 1 shows the combined results of both techniques: Raman and ellipsometry. We distinguish two branches in the resulting thickness: NBFs with a roughly constant water core thickness of 2 nm and the thicker CBFs whose water core thickness varies with salt concentration and seems to reach a constant value of about 4 nm. The upper branch is metastable: during the draining, the film keeps this thickness for some time before it transits to the smaller thickness on the lower branch. The decrease in thickness with the increase in NaCl concentration is caused by an increase in the ionic screening of the electrostatic repulsion of the two monolayers of anionic molecules in favor of van der Waals attraction, as described in Derjaguin-Landau-Verwey-Overbeek (DLVO) theory [17-19]. The constant thickness of the NBF is not so surprising since all the water that is left in this very thin film is expected to be bound hydration water [5], hydrating the hydrophilic headgroups and counterions. Taking a molecular area of 20 \AA^2 for a SDS molecule in the film and a volume of 30 \AA^3 for a H_2O molecule, a core thickness of 2 nm corresponds to about seven H_2O molecules per headgroup. The aqueous core of the NBF is indeed mainly composed of hydration water.

For the $C_{12}E_5$, a concentration of 0.25 mM (slightly higher than the critical micellar concentration as determined from surface tension measurements) was chosen for the measurements on black films. The resulting surfactant films were found to be very stable. A core thickness of 6 nm was measured with ellipsometry. It did not change with an addition of 50 mM NaBr, as expected for a nonionic surfactant. In preliminary Raman measurements, different black films resulted depending on the relative humidity of the atmosphere in the cell where the films were studied. Therefore, we proceeded doing the experiments with controlled humidity using different saturated salt solutions poured at the bottom of the completely closed cell. A saturated (38 g/100 mL) KCl solution resulted in a relative humidity of 85%. With a saturated (37 g/100 mL) NaCl solution, a relative humidity of 75% was obtained [20].

We found that for high relative humidity (85% and almost 100%), the $C_{12}E_5$ films are relatively thick with an equivalent water core thickness of about 14 and 20 nm, respectively. The Raman spectra of the $C_{12}E_5$ black films clearly show the difference in water content, as revealed by the intensity of the broad multicomponent band centered at 3400 cm^{-1} which is characteristic of the O–H stretching (ν_{O-H}) modes (see Figure 2). The equivalent water core thickness for the lower humidity rate was very small and less than 1 nm. Clearly, black films are extremely sensitive to the humidity rate as is well-known. In a sense, controlling the

humidity rate for this system can give access to very thin films to study the effects of confinement on the water core as we will see below.

For $C_{12}E_5$, a mean molecular area of about 40 \AA^2 can be considered [21]. It results that a water thickness of 1 nm corresponds to about six H_2O molecules per $C_{12}E_5$ headgroup. The extremely small amount of water in the NBF is consistent with the absence of electrostatic repulsion of the nonionic surfactant molecules and with the predominance of the van der Waals attraction and hydrogen bonding. However, the large thickness observed for the higher relative humidity is somewhat surprising.

As mentioned above, we have used vertical films for FTIR spectroscopy. These vertical films were obtained on frames 2 cm by 3 cm in dimensions in a closed cell under nearly 100% relative humidity. Such films start out thick and drain slowly in time. The draining time was typically of several minutes. At the end of the draining, the aqueous core reaches a thickness of about 1 nm for both surfactant systems (the SDS solution contained 100 mM NaCl).

Let us now discuss the water band shape of these ultrathin films. The assignment of the OH stretching band of water (centered around 3400 cm^{-1}) is still controversial. Usually it is divided into three main components. Some authors [22,23] assigned these components to the symmetric OH stretching in Fermi resonance interaction with the overtone of the $\delta(OH_2)$ bending mode (low-frequency component), the antisymmetric OH stretching (medium-frequency component), and the OH stretching of free OH bonds (high-frequency component). Conversely, an assignment in terms of “network water”, “intermediate water”, and “multimer water” molecules has been proposed [14] for the low-, medium-, and high-frequency components, respectively. However, the intensity profile of this band varies with the kinds and degrees of organization that water molecules can exhibit and with the vibrational coupling between neighboring OH groups in interaction by hydrogen bonding. Therefore, we used the position of the barycenter (intensity-weighted center) of the whole band to monitor modifications of the water organization in the films, induced by confinement, with respect to the bulk isotropic water.

Previous FTIR spectroscopy works [6,14] indicated that the spectral properties of confined water were like those of bulk water, until the dimensions of the confinement reached values of some nanometers only. Boissière et al. [13] showed with FTIR spectroscopy that water confined between lamellar bilayers of AOT is spectrally different from bulk water only when the water thickness is below 4 nm. When the water band was decomposed in three Gaussian components, the lower energy component was seen to decrease as the water thickness decreased, accompanied by an increase of the medium energy component, while the higher energy component stayed constant. The spectral position of the components did not shift with changes in the water content. Umemura et al. Showed [6] that the water confined in a SDS CBF (water core thickness of 10 nm) was spectrally not different from bulk water. For the SDS NBF (water core thickness of 1 nm), however, the peak position of the water band was shifted to higher wavenumbers by about 60 cm^{-1} . This spectral shift was attributed to the highly ionic atmosphere resulting from the confinement of the electric double layers to a very thin core.

Using Raman spectroscopy, Lafleur et al. [15] observed a relative decrease of the lower energy side of the O–H stretching region, in measurements on multilamellar

dipalmitoylphosphatidylcholine liposomes (water interlayer thickness of about 2 nm). Since no spectral effects were observed for micellar and unilamellar vesicle solutions, the authors concluded that the changed band shape depended mostly on the confinement of the water and very little on the electrostatic or dipolar water–headgroup interactions. Lhert et al. [9] supported these conclusions, obtaining similar results with confocal micro Raman spectroscopy on dimyristoylphosphatidylcholine black films (water core thickness of 2 nm).

Figure 3a shows our FTIR spectroscopy results for SDS films with various water core thicknesses obtained using draining vertical films. The water thickness is determined from the FTIR spectrum by simulating the water absorbance (full lines in Figure 3a) using an algorithm based on Berreman's matrix formalism [24,25] and known optical constants [26]. However, for the sake of clarity, all experimental and calculated spectra have been normalized with respect to the maximum intensity of the water absorption band. For amounts of water down to 30 nm, the observed changes in the band shape follow those in the simulations and can therefore be attributed to a purely optical effect encountered for films much thinner than the infrared wavelengths [27]. Clear deviations from these simulations, however, are observed for SDS films with a water core thickness of only 1 or 2 nm. As the degree of confinement approaches molecular sizes, the lower energy contribution to the water band shape is seen to decrease. Correlatively, the barycenter of the OH band increases from 3360 cm^{-1} for the bulk to 3395 and 3430 cm^{-1} for the films with a water core thickness of 2 and 1 nm, respectively. In agreement with the observations by Umemura et al., [6] we also see a spectral shift to higher wavenumbers for this ionic system. Figure 3b shows a comparison between the Raman spectrum of a SDS Newton black film of 1.8 nm in water core thickness, obtained using 400 mM NaCl in a horizontal porous glass, and bulk water. Despite the noise on the spectrum, one can discern a slight decrease of the intensity at low wavenumbers (the barycenter of the OH band increases from 3360 cm^{-1} in the bulk to 3390 cm^{-1} in the NBF) but no shift of the peak position is distinguishable, contrary to what happened in the infrared spectrum of a similar thin film. This “discrepancy” is certainly inherent to the spectroscopic methods. Indeed, infrared spectroscopy probes a vibration through the variation of the dipolar moment, while Raman spectroscopy probes a vibration through the variation of the polarizability tensor. This hypothesis is in agreement with previous works demonstrating that the infrared transition moment of an OH bond is much more sensitive to modifications of the polar and electrostatic environment than its Raman scattering cross section [28,29].

For the nonionic C_{12}E_5 film, we can see a similar relative decrease in the lower energy side of the water band, as measured by FTIR on draining vertical films, when the water core thickness is lower than 2 nm (see Figure 4a). For the thicker film (water core of 83 nm), the barycenter of the band is similar to the one measured in the bulk (3360 cm^{-1}). For the thinner film (water core of 1.7 nm), it increases to 3405 cm^{-1} . However, in this case we do not see the clear spectral shift that was seen for the ionic system, in accordance with the results of Brubach et al [14]. Figure 4b shows results obtained using Raman spectroscopy on horizontal black films of C_{12}E_5 . This figure shows a comparison of the $\nu\text{O-H}$ bands obtained from bulk water, a common black film (water core of 14 nm), and a Newton black film (water core of 0.3 nm corresponding to only two H_2O molecules per C_{12}E_5 molecule). The water band shape changes markedly relative to the bulk sample, the largest effect being obtained with the

thinnest film. We do not observe any shift of the maximum of the band, but a large reduction of the intensity of the low-wavenumber component is observed. The barycenter of the OH band increases from 3360 cm^{-1} for the bulk to 3420 cm^{-1} for the NBF. For this system, a slight decrease of the lower energy region is also observed for a “relatively thick” water core thickness of 14 nm (the barycenter of the OH band is found at 3373 cm^{-1}).

The resulting water bands for the Raman measurements on our two surfactant film systems show the same relative decrease of the lower energy region. Not surprisingly, the effect is most pronounced for the nonionic surfactant which leads to the thinnest films.

The relative decrease of the low-wavenumber component of the O–H band observed in both Raman and infrared spectra could also be due to some molecular anisotropy of confined water. Indeed, it has been shown that water molecules have a preferential orientation at an electrode surface [30] and at a charged interface [31], with their dipoles pointing toward the surface. According to the assignment of the O–H stretching multicomponent band given by Rull and de Saja [22] and Sokolowska and Kecki [23], the low wavenumbers component is associated mainly with the symmetrical mode, whose transition moment is along the water dipole. Thus, a preferential orientation of water molecules with dipoles pointing toward the interface (z direction) in ultrathin black films would result in a decrease of this band component in normal IR transmission. Similarly the Raman intensity will also decrease since the laser is mainly polarized in the (x, y) plane and the elements of the polarizability tensor which contribute to the signal will be much weaker than the elements implying the z direction. This partially explains some of our findings even though the shift of the maximum for the ionic system and the decrease of the low-wavenumber band for the nonionic system (even though anisotropy of the water molecules may also occur at uncharged interfaces) remain unexplained.

3. Conclusion

Infrared and Raman spectra of ultrathin black films reveal clear changes in the shape of the water bands indicating the effects of confinement and high ionic strength in the aqueous core. While confinement of the water molecules induces a reduction of the low-energy side of the OH stretching band, the ionic effects give a noticeable shift of the peak position of this band in the infrared spectra. It remains a challenge to associate these spectral changes to modifications of molecular interaction. Several studies have pointed out different effects related to modifications in degrees of freedom of the water molecules, to perturbations of the hydrogen bonding network [10,12], or to the vicinity of charged interfaces [11,30]. This could give some clues as to what happens at the molecular level when water is confined to very small dimensions.

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Figures

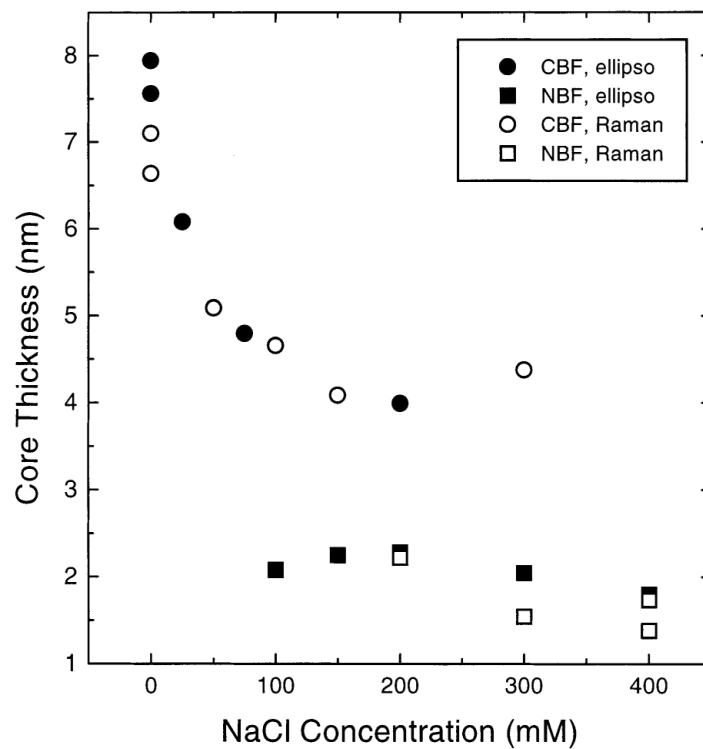


Figure 1 Aqueous core thickness of SDS common black films (CBF) and Newton black films (NBF) versus NaCl concentration, obtained from ellipsometric and Raman measurements.

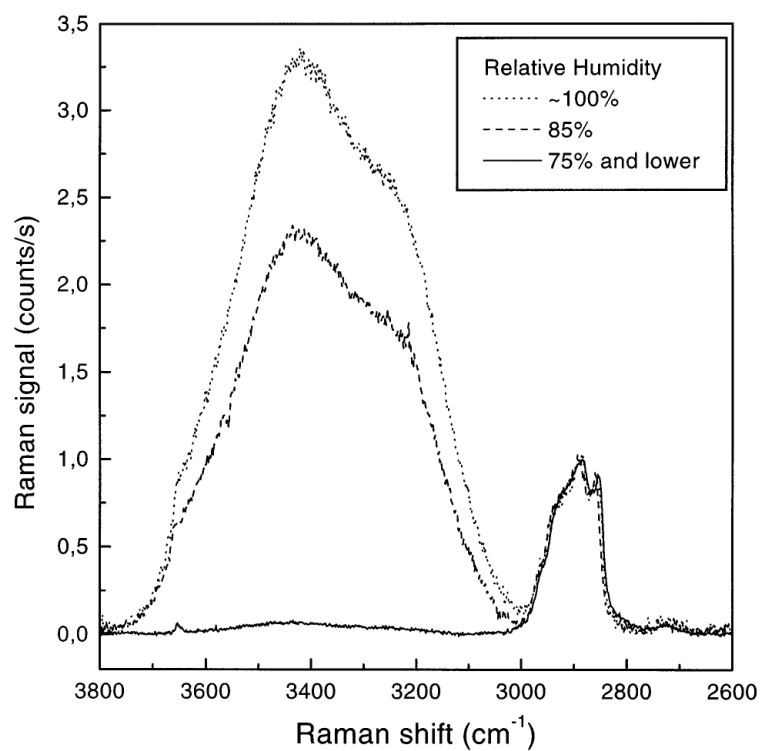


Figure 2 Raman spectra of $C_{12}E_5$ black films obtained under 75%, 85%, and close to 100% relative humidity. The multicomponent band centered at 3400 cm^{-1} is associated with the O–H stretching mode of interstitial water. The multicomponent band centered at 2900 cm^{-1} corresponds to the stretching modes of the $C_{12}E_5$ methylene. The sharp band located at 3655 cm^{-1} in the thinnest film spectrum corresponds to the O–H stretching of the water vapor.

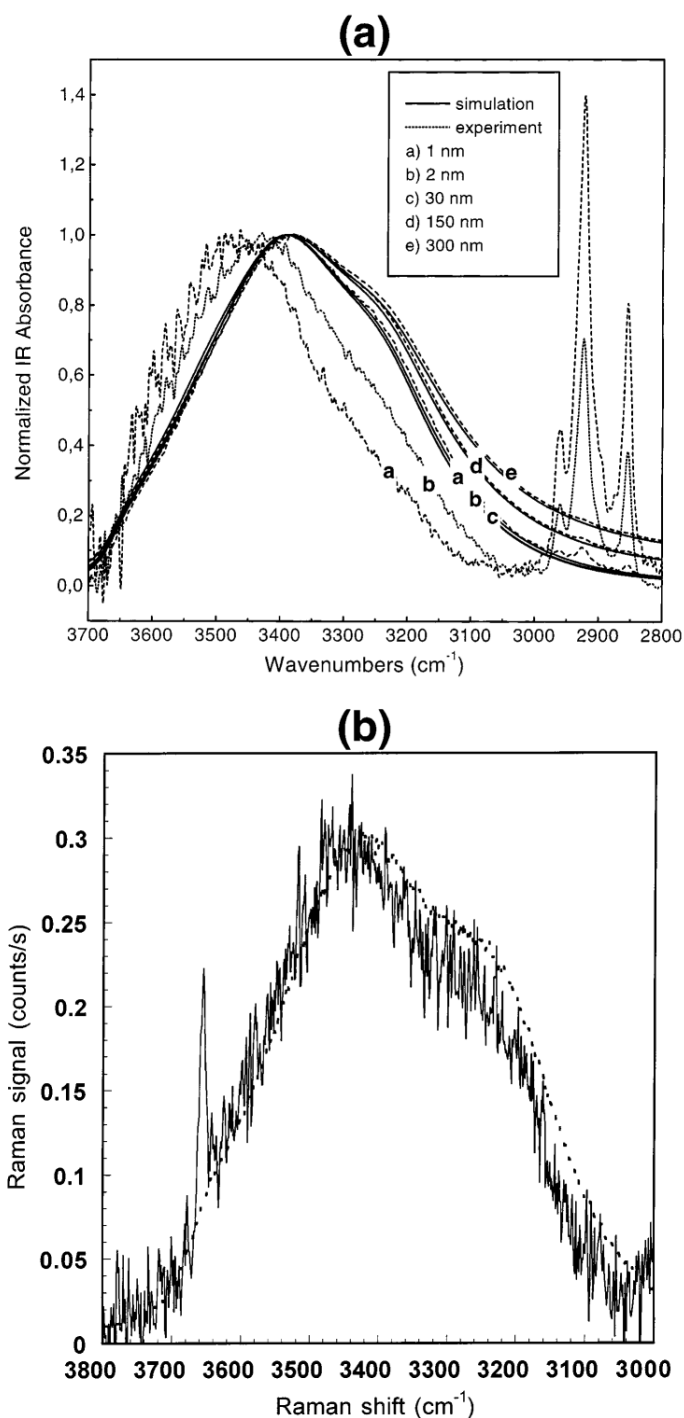


Figure 3 (a) Normalized experimental (dotted lines) and calculated (solid lines) FTIR spectra of SDS films with various water core thicknesses ranging from 300 to 1 nm. The sharp and well-defined peaks located between 2800 and 3000 cm^{-1} correspond to the methyl and methylene stretching modes of SDS. (b) Raman spectrum in the O–H stretching region of bulk water (dashed line) and of a SDS Newton black film with a 1.8 nm water core thickness (solid line). The sharp band located at 3655 cm^{-1} in the Newton black film spectrum corresponds to the O–H stretching of the water vapor.

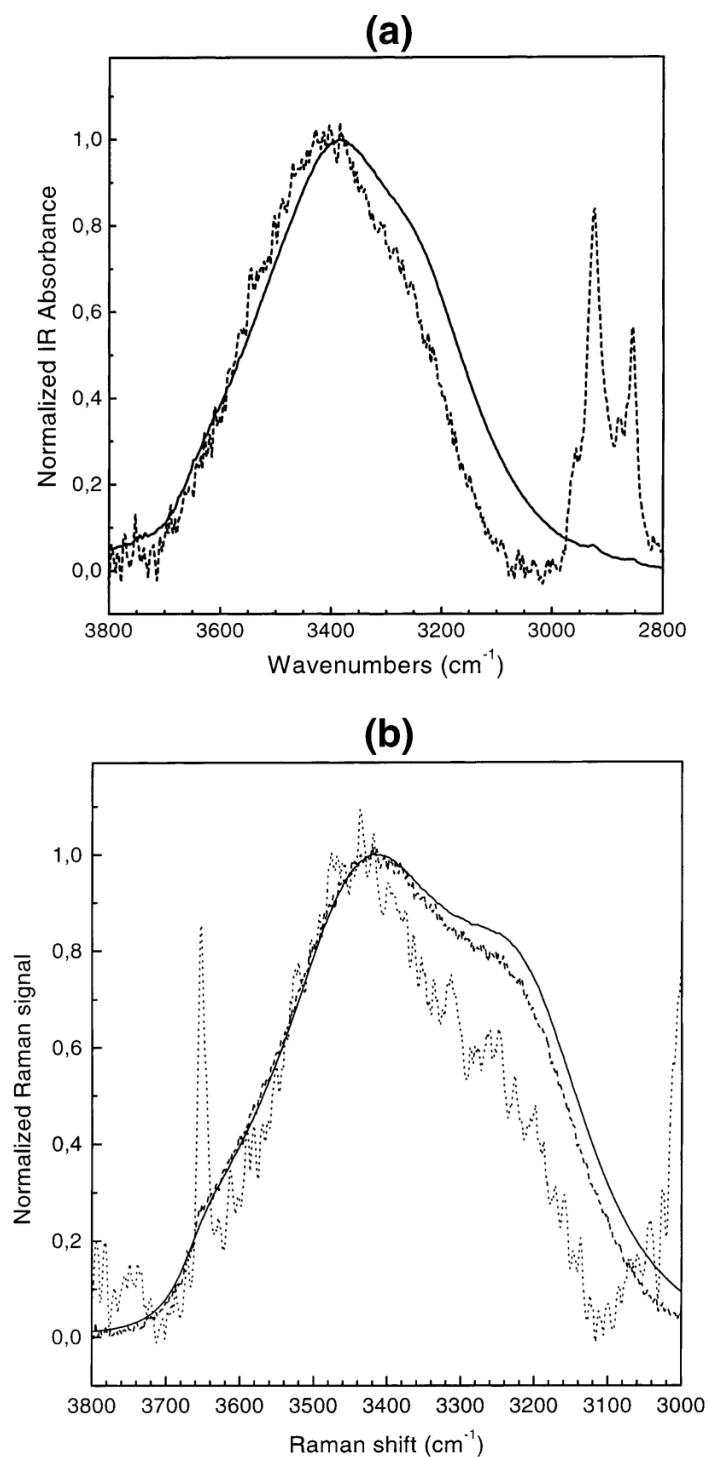


Figure 4 (a) Normalized FTIR spectra of nonionic C₁₂E₅ black films with a relatively thick 83 nm water core (solid line) and an ultrathin 1.7 nm water core (dashed line). (b) Raman spectrum in the O–H stretching region of bulk water (solid line) and of C₁₂E₅ black films of 14 nm core thickness (dashed line) and 0.3 nm core thickness (dotted line). The sharp band located at 3655 cm⁻¹ in the spectrum of the thinnest film corresponds to the O–H stretching of the water vapor.