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LETTERS TO THE EDITOR

The Letters to the Editor section is divided into three categories entitled Notes, Comments, and Errata. Letters to the Editor are limited to one and three-fourths journal pages as described in the Announcement in the 1 January 2003 issue.

NOTES

An interpretation of the low-frequency spectrum of liquid water

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The experimental low-frequency (0–400 cm^{-1}) spectrum of liquid water shows two broad bands[1,2] around 60 and 170 cm^{-1}. The interpretation of such features in terms of microscopic mechanical motions has been subject of discussion since the discovering by Segrè[3] of the high frequency band and by Bolla[4] of the low frequency band, both from Raman spectroscopy measurements. More recently, Downing and Williams[5] detected the high frequency band in the experimental infrared spectrum of water and a decade later Hasted *et al.*[6] found the low frequency band, which shows a weaker signature in the infrared data. From the observation of the weakening of both bands for temperature rise,[3,4] the first interpretation of their meaning was due to the breakdown of the intermolecular structure. More specifically, Walrafen and co-workers[1,7] assigned the 60 cm^{-1} band to the bending of water molecules linked by hydrogen bonds and the 170 cm^{-1} band to the hydrogen-bond stretching, although they also indicated that both modes could be generally seen as restricted translations. Such interpretation in terms of frustrated translations is also supported by recent Raman spectroscopy measures.[8] An excellent review by Faurskov-Nielsen[9] addressed the problem and also reported a mechanical interpretation in a similar fashion to Walrafen *et al.*

Theoretical calculations and computer simulations have added relevant information helpful to enlighten the interpretation of both spectral modes. So, normal-mode calculations[2] showed that the low-frequency bands are mostly hindered translational vibrations and they do not contain librational components. A simple analysis of low-energy excitations in water by Nakayama[10] showed that the modes associated with the band near 60 cm^{-1} are strongly localized motions, whereas the band around 170 cm^{-1} can be attributed to modes mesoscopically distributed in the hydrogen-bond network of liquid water. Molecular dynamics calculations of the low-frequency light scattering spectrum of water were first introduced by Madden and Impey.[11,12] These authors reported two spectral bands at 60 and 200 cm^{-1} in the far infrared spectrum region, due to the center of mass contribution (translational spectrum). Ricci *et al.*[13,14] performed molecular dynamics calculations of the Raman spectrum of TIP4P water, observing that such spectrum contains two main bands (around 60 and 180 cm^{-1}) related with hindrance of translational dynamics of molecular pairs. From such calculations, a direct connection between the induction mechanism which activates the scattering and dynamics of the hydrogen-bond network was not observed. Finally, molecular dynamics calculations of spectral densities[15–17] have shown a deep connection between hydrogen bonding and the 170 cm^{-1} band and a direct relationship between the 60 cm^{-1} mode and molecular restricted translations. However, Sutmann and Vallauri[16] indicated that some contribution from librational motions of water triplets (made of three hydrogen-bonded molecules) can be assigned to the lowest frequency band.

The point we would like to emphasize is concerned with the nature of microscopic motions leading to the presence of the 60 cm^{-1} band in the low-frequency spectrum of water. More specifically, we want to analyze the relationship of such frequency band with a bending mode of hydrogen-bonded water molecules. First, we have observed that frequency mode in spectral densities obtained from velocity autocorrelation functions[18] of flexible-SPC[19] water molecules forming less than two hydrogen bonds,[15] as well as in the spectral density of a Lennard-Jones ''water'' model without hydrogen charges[17] (see Fig. 1). Moreover, light and heavy alcohols like liquid methanol or ethanol, both represented by OPLS models[20] produce a similar spectral band located around 60 cm^{-1}, as it is observed in spectral densities obtained from velocity correlation functions of molecules which are nonhydrogen bonded to others[21,22] (Fig. 1). Finally, it should be emphasized that an analogous frequency band is also observed in the spectra of dense nonassociated liquids (noble gases, for instance),[23] which is attributed to

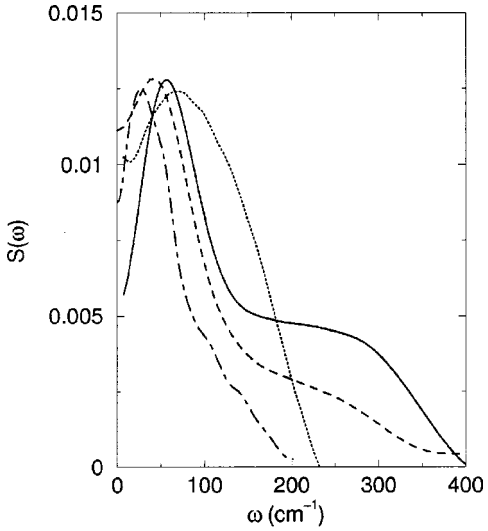

FIG. 1. Low-frequency spectral densities $S(\omega)$ for several systems at room temperature: liquid water (full line), Lennard-Jones "water" (dotted line), subset of water molecules in liquid water forming only one hydrogen-bond (dashed line) and non-hydrogen-bonded molecules in methanol (dotted–dashed line).

the packing effect of neighboring water molecules. According to all these data, such low-frequency band should not be related to a bending mode in clusters of hydrogen-bonded molecules.

All those facts provide a reasonable interpretation for the molecular origin of the 60 cm^{-1} band appearing in the low-frequency Raman and infrared spectra of water and also obtained from computer simulations. It may be attributed to the frustrated translations due to the local structure around a given atom (molecule) that produces the so-called cage effect. Such band would then appear in all sort of atomic or molecular dense liquids (nonassociated, hydrogen bonded) at suitable thermodynamic conditions. In the particular case of liquid water, the existence of hydrogen bonding surely will influence the dynamics of a given molecule producing slight changes in the frequency bands of the spectra but the low frequency band should not be associated with the existence of hydrogen bonding. On the contrary, the frequency band around 170 cm^{-1} is absent in the spectral densities of non-associated liquids (see Fig. 1), which is consistent with the attribution of this band to the stretching of hydrogen-bonded molecules.

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