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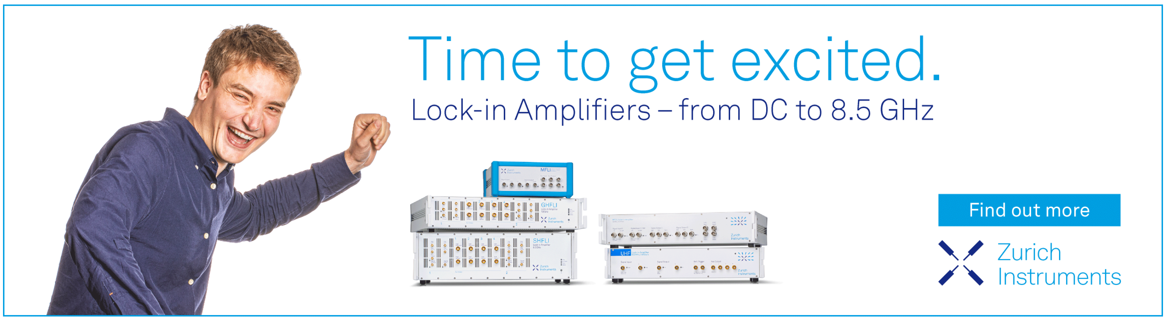

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Response to "Comment on 'An interpretation of the low-frequency spectrum of liquid water' " [J. Chem. Phys. 118, 452 (2003)]

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The comment by De Santis *et al.*[1] to our note[2] adds valuable information to the puzzling interpretation of the low-frequency spectrum of water and other liquids. The controversy arises when the microscopic nature of the two main bands for water, experimentally detected around 60 cm^{-1} (LF) and 180 cm^{-1} (HF) by both Raman[3,4] and infrared spectroscopy,[5,6] is addressed. Both frequency bands have been observed in a wide number of computer simulations studies of liquid water using a big variety of potential models. In particular, spectral densities of flexible SPC water[7] and densities of states of TIP4P water[8] unambiguously indicate the presence of the two spectral features in liquid water. De Santis *et al.*, based on Raman spectra measurements[9] of water and molecular dynamics simulations[1] of water at 70 K and argon at 20 K, suggested that both bands have to be attributed to hindered motions of water molecules due to the existence of hydrogen-bonding and that both LF and HF bands are, respectively, related to transversal and longitudinal motions associated with neighboring molecules for all liquids. This interpretation in terms of frustrated translations is similar to the one reported in other works.[10,11] De Santis *et al.* added that, in the case of simple liquids like argon, both frequency bands contribute to the spectral densities of states in supercooled and melting states.

This response is divided into two parts. First, we address the interpretation of the LF mode. In our note,[2] we indicated from data obtained with spectral density (SD) calculations, that the LF band should have a clear translational nature and for that reason it should be found in all liquid spectra, regardless whether the liquids were associated or not. In particular, it was reported that SD of SPC water and of Lennard-Jones "water," i.e., a waterlike model without point charges and, consequently, hydrogen-bonding, showed the LF signature about 60 cm^{-1}. In addition, SD of SPC water molecules forming less than two hydrogen-bonds[7] clearly contained the LF peak. In summary, the LF band may have a transversal component in hydrogen-bonded liquids, but we think it is a more general effect beyond water. Is in this sense that we state that it is no necessarily related with hydrogen-bonding. We think it is basically the result of restricted translations along all directions in a neighboring molecular cage, and it appears in all sorts of liquids (associated, nonassociated) at nearly ambient conditions. When temperature is well beyond room temperature values, i.e., in high-temperature or in supercritical states, the band tends to vanish since the nearest neighbors cage is broken.[7,12]

Secondly, the high-frequency band appears around 220 cm^{-1} in the SD of water obtained from molecular dynamics[2] and around 240 cm^{-1} in the densities of states reported by De Santis *et al.*[1] The position of the frequency band is very close in both works. De Santis *et al.* also observed that band in liquid low-temperature states of water and argon, but they did not prove that such frequency remains when temperature increases. Only the guess of a masked presence was reported. What it has been recently found[13] is that in liquidized noble gases as neon a double band structure appears in SD computed for supercooled states but, as temperature increases, the HF band tends to vanish. This is in agreement with the data reported in our note,[2] i.e., SD from nonhydrogen-bonded liquids at ambient temperatures, represented by a Lennard-Jones-type fluid, do not show such band at all. It should be also kept in mind that this frequency is detected not only in water but in methanol, ethanol, and other alcohols[14,15] at ambient conditions. In particular, the band is present in the SD of water or methanol molecules involved in one or more hydrogen bonds but it is absent in the SD of water and methanol molecules forming no bonds at ambient conditions.[7,14]

We can conclude that, with the prevention that we have not explored all sorts of liquids, only associated liquids show the 220 cm^{-1} band in their SD at ambientlike conditions. Nevertheless, the band is indeed observed in supercooled liquids or glasses regardless they are associated or not. This suggests that the ordering being destroyed in the change from low-temperature environments to reach the disorder typical of ambientlike conditions is reflected in the fact that the HF vanishes as temperature rises. This would agree with both sets of results: the HF is due to the longitudinal dynamics that, in the case of water, corresponds to hydrogen-bond stretching.

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