Autocorrelation functions of translational and rotational velocities of water molecules and their spectra in computer models

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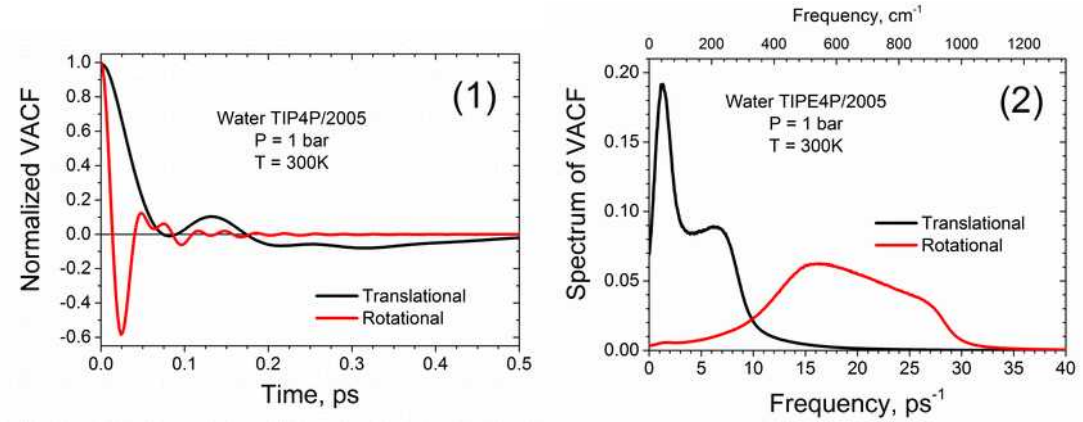
Molecular dynamics simulation provides the researcher with complete structural information - the coordinates and velocities of each atom of the simulated system. This makes it possible to directly calculate the autocorrelation functions of the velocities of atoms and molecules and the spectra of their vibrations [1]. Figure (1) shows the normalized autocorrelation functions of the translational velocities of the centers of mass of TIP4P/2005 water molecules and the rotational velocities of the same molecules. Already from this figure it can be seen that the period of the main rotational oscillations is significantly less than the translational ones. Detailed information about oscillations is presented in Figure (2). The spectra shown are obtained using the Fourier transform of the autocorrelators. These spectra confirm that the frequency of rotational oscillations is significantly higher than that of translational ones. Moreover, the rotational spectrum contains only one maximum, while the translational spectrum has a high low-frequency maximum and a lower high-frequency maximum. In our work, we have shown that the high-frequency maximum describes single-particle oscillations of water molecules relative to their nearest environment, while the low-frequency maximum describes collective oscillations of various scales. The wide maximum of the rotational spectrum combines the oscillations of molecules with different local environments. The high-frequency slope of this maximum is formed by molecules with a large number of strong hydrogen bonds, while the low-frequency slope is formed by molecules with weak bonds or no bonds at all.



1. V.P. Voloshin, Yu.I. Naberukhin, Autocorrelation functions of translational and rotational water velocity, *Russian J. Phys. Chem. A*, **2022**, *96 (7)*, in press.