

AUTOCORRELATION FUNCTIONS OF TRANSLATIONAL AND ROTATIONAL VELOCITIES AND THEIR SPECTRA OF WATER MOLECULES IN COMPUTER MODELS

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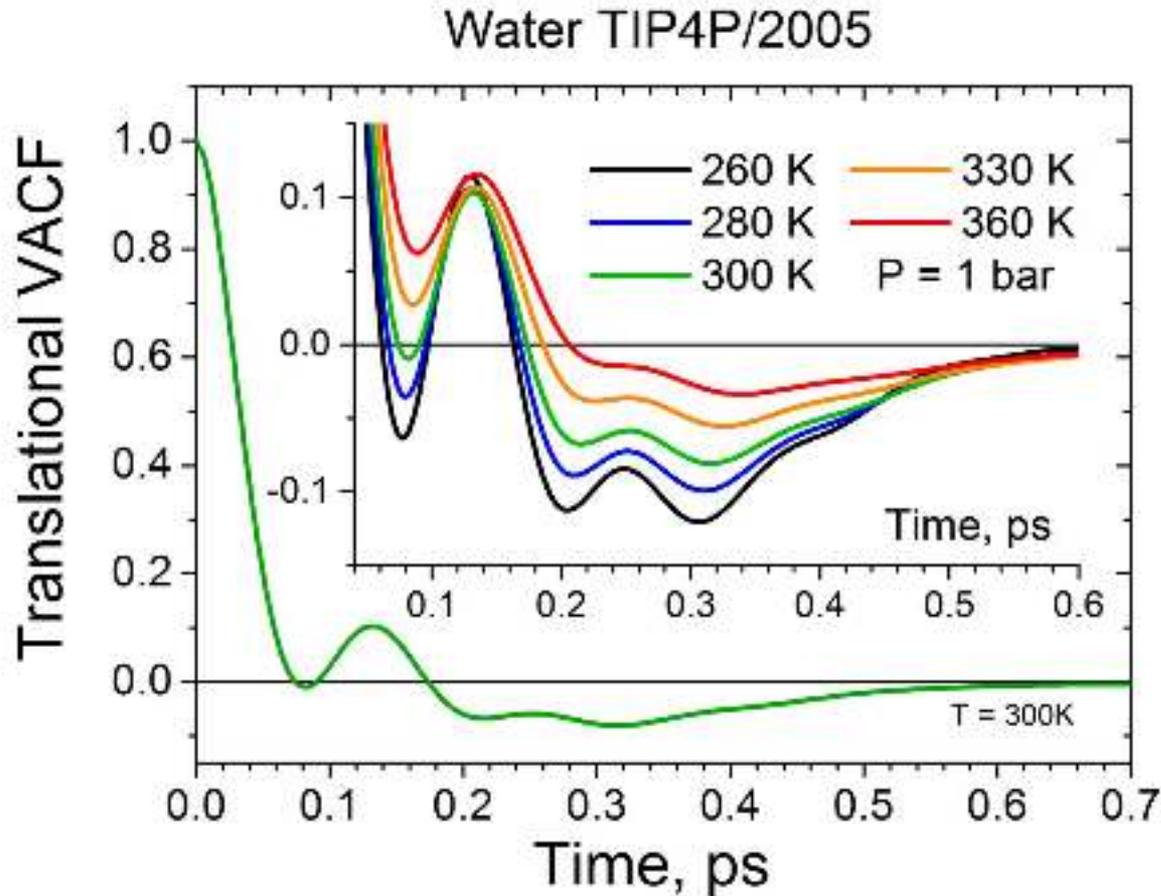
Autocorrelation functions of velocity

Computer simulation makes it possible to obtain information that is not available in a real experiment. For example, calculate the autocorrelation function of the velocities of molecules, showing how quickly the velocity of molecules changes. The function is the average scalar product of the molecular velocities at the initial and subsequent moments of the time interval. Usually normalized to the mean square of the molecular velocities.

$$VACF(t) = \langle \mathbf{v}(0)\mathbf{v}(t) \rangle / \langle \mathbf{v}(0)^2 \rangle$$

The autocorrelation function contains information about the mobility of liquid molecules. Its changes show the characteristic times of the processes occurring in the liquid. Thus, this function describes not only the dynamics, but also the structure of the liquid.

Autocorrelation Functions of Translational Velocity of Water Molecules

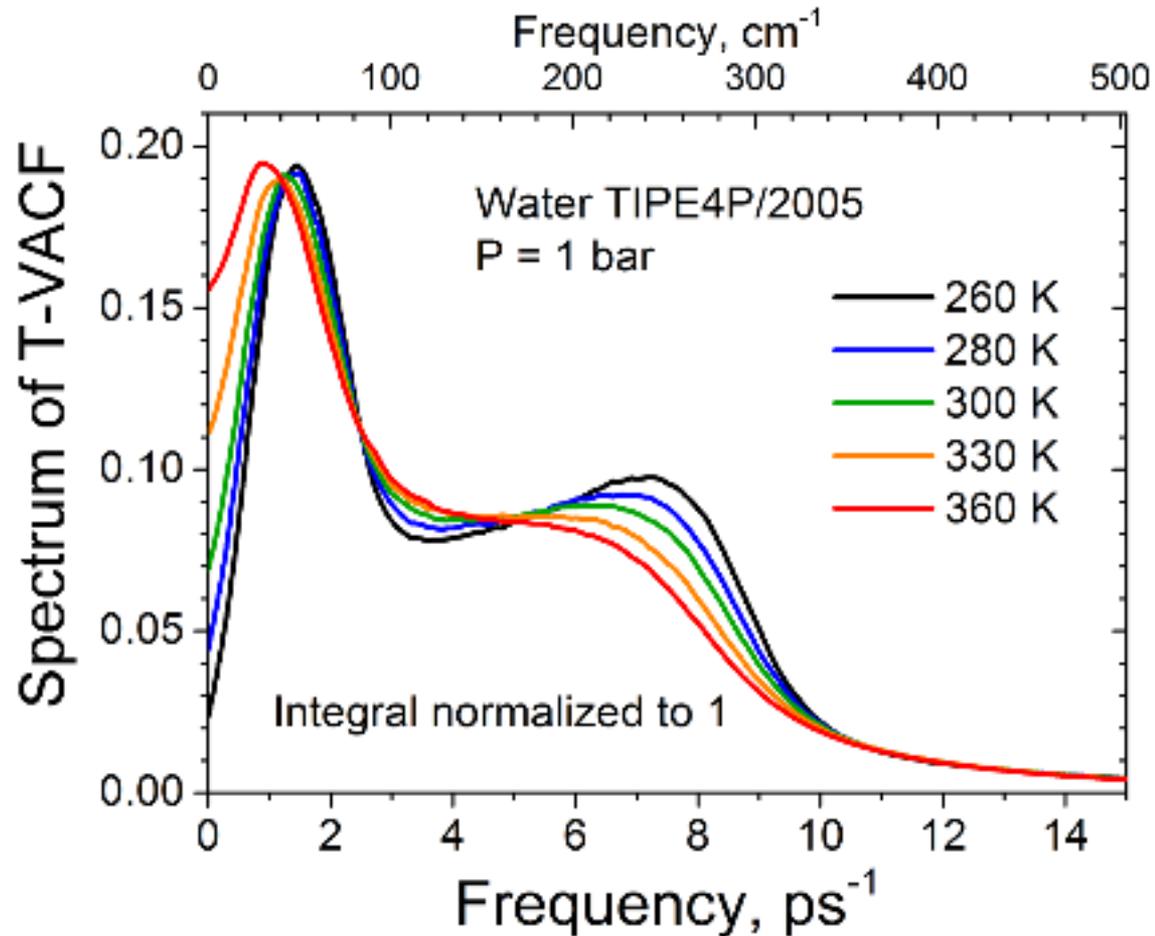
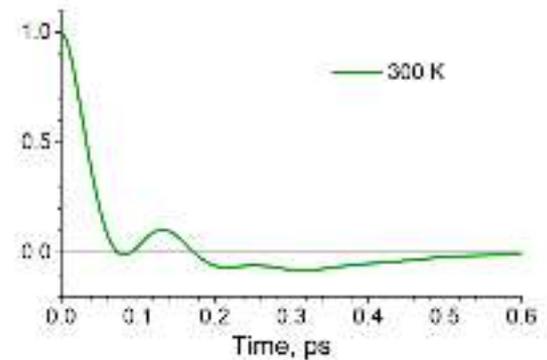


Normalized autocorrelation functions of translational velocities of water molecules at P = 1 bar and different temperatures. Below is the full VACF for 300K, in the inset are the most strongly different areas on an enlarged scale.

Spectra of Autocorrelators of Translational Velocities of Water Molecules

The result of the Fourier transform of T-VACF. At any temperature, the spectrum in liquid water has two maxima. The maximum at 8 ps^{-1} corresponds to the oscillation with the minimum period (see the picture on the right above).

As the temperature increases, the positions of both maxima shift to a low frequency. The high-frequency maximum shifts more, the minimum between the maxima disappears.



Interpretation of the Maxima of the Translational Velocity Spectrum

Each liquid molecule participates simultaneously in many movements of different scales.

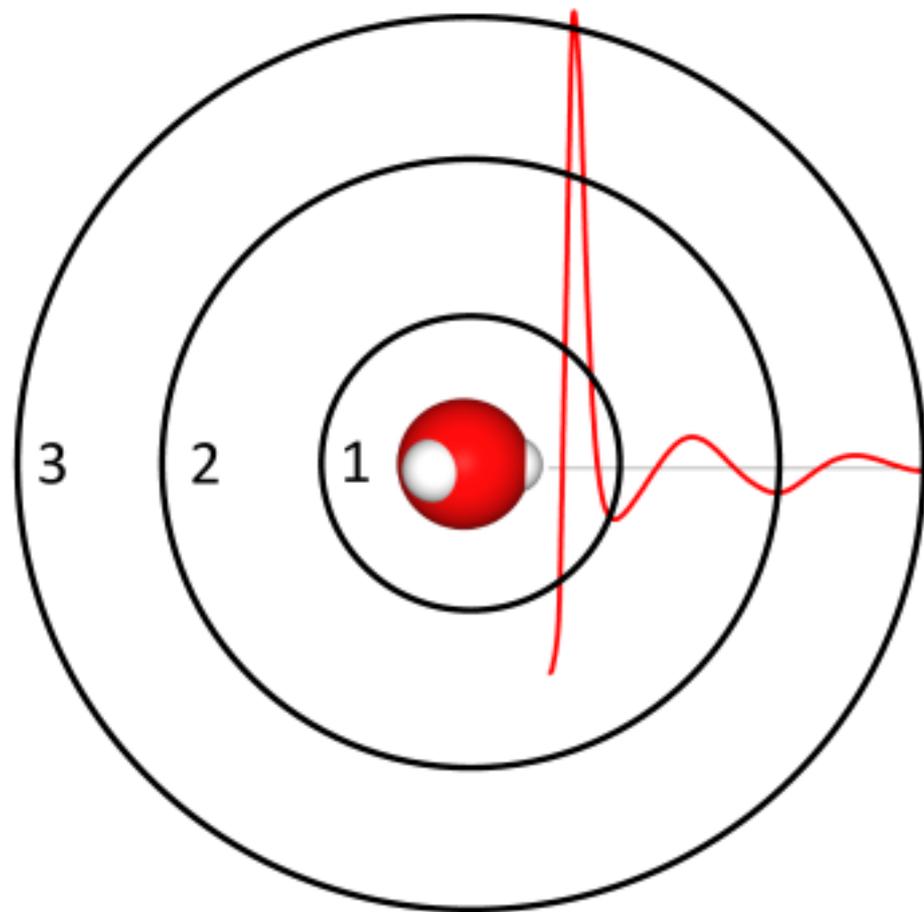
We believe that the **high-frequency maximum** describes the vibrations of a single molecule inside its own potential well formed by its nearest neighbors (Frenkel cell).

In addition, the molecule participates in many collective motions. The greater the number of molecules in the team, the lower their average velocity and the slower it changes. The collective motion spectra form a **low-frequency maximum**.

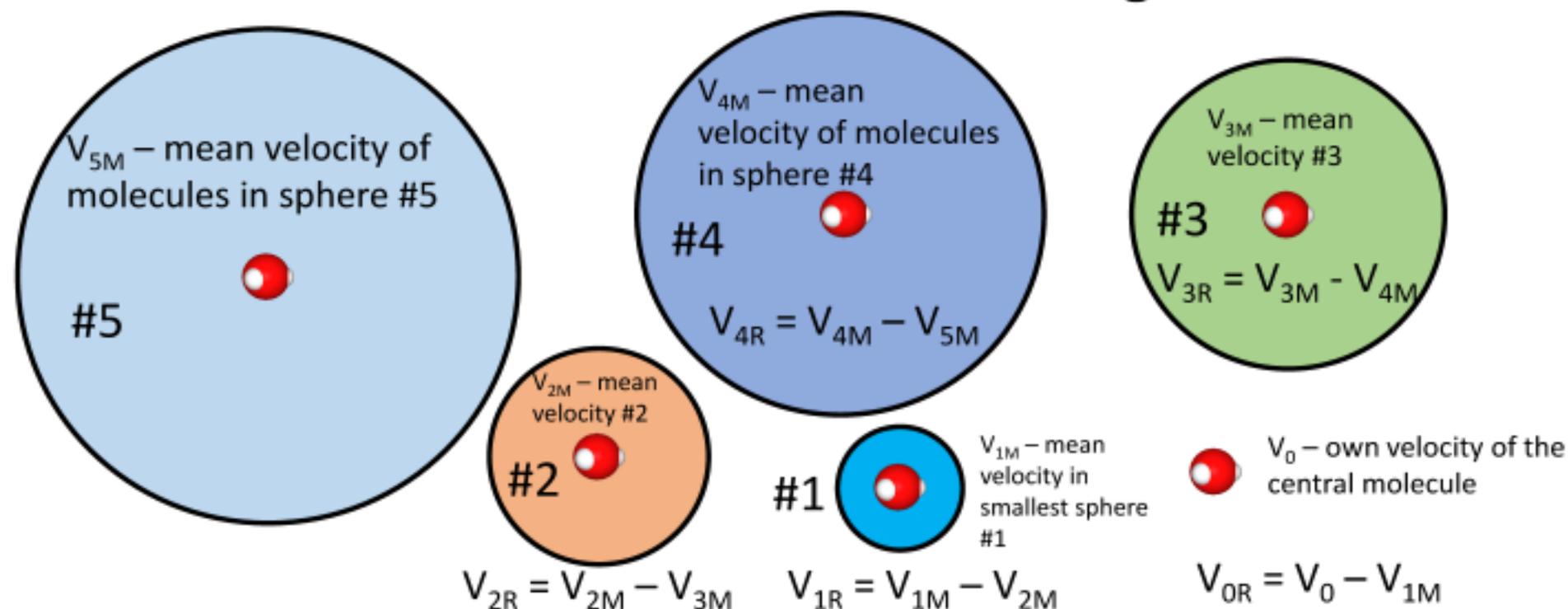
The definition of collective movements is a complex and ambiguous task. For simplicity, instead of defining a collective of molecules moving together, we will define spheres of different sizes around each molecule and study the variability of the average molecular velocities in these neighborhoods.

Construction around a water molecule of local environments of different scales

Let us construct spherical local environments around each water molecule with boundaries near the minima of $g(r)$.



Representation of the velocity of a molecule as the sum of the relative velocities of its neighborhoods

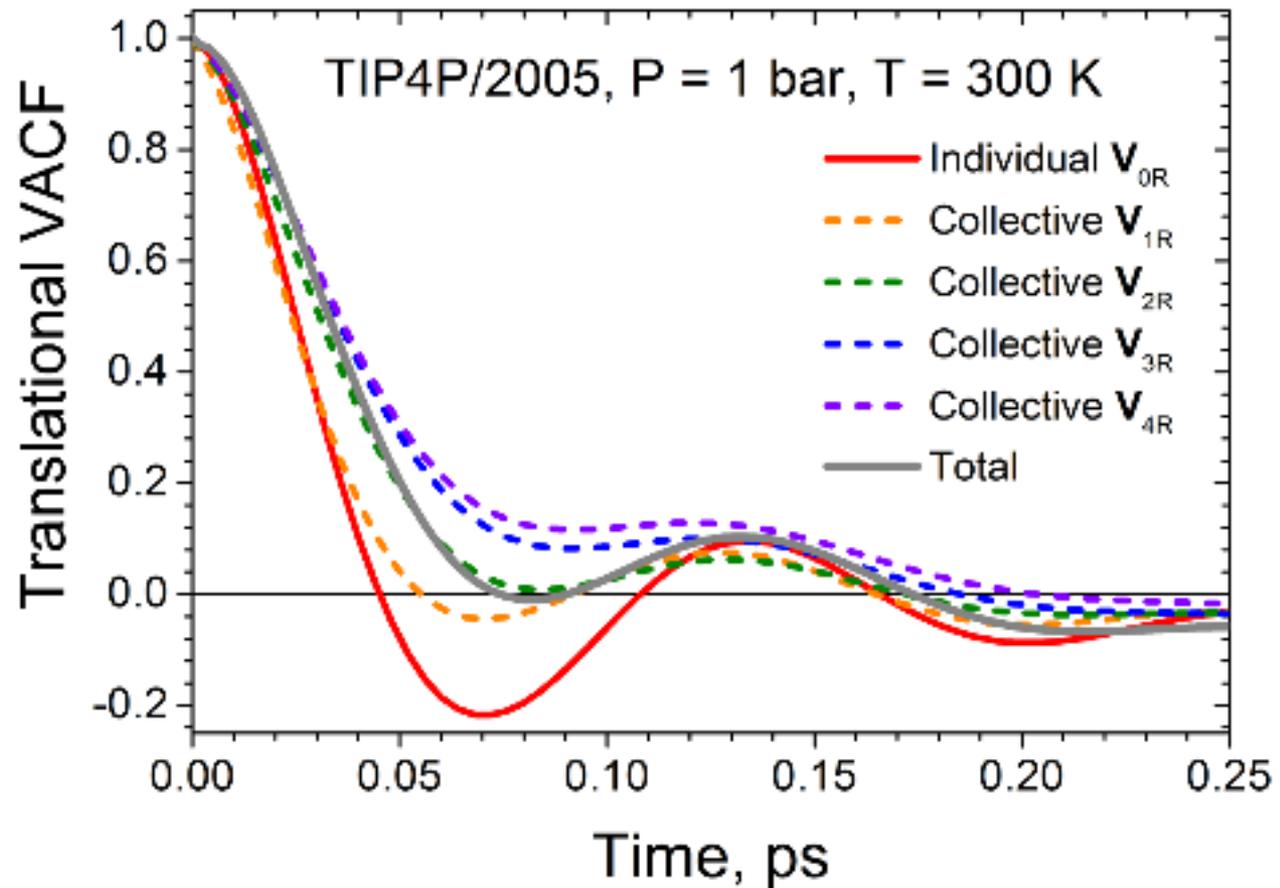


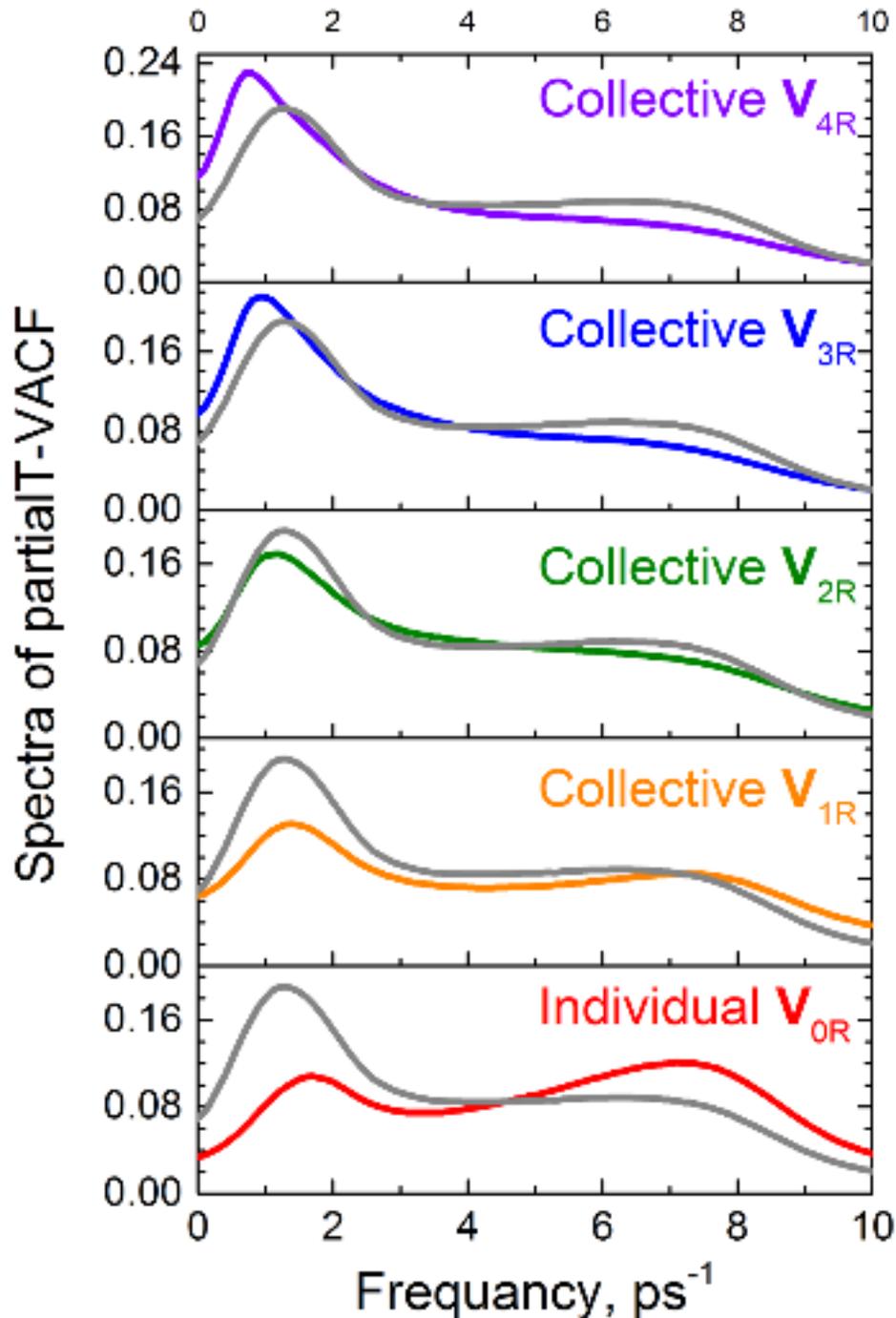
For each sphere #i we calculate the average velocity of molecules V_{iM} . For the inner spheres, we also calculate the relative velocities $V_{iR} = V_{iM} - V_{(i+1)M}$. As a result, we represent the velocity of the central water molecule as the sum of the relative velocities

$$V_0 = V_{0R} + V_{1R} + V_{2R} + V_{3R} + \dots + V_{LAST M}$$

Autocorrelation functions of relative velocities of central water molecules and their environments

Autocorrelation functions of relative velocities: V_{0R} – individual, V_{1R} – V_{4R} – collective velocities of environments of different sizes.



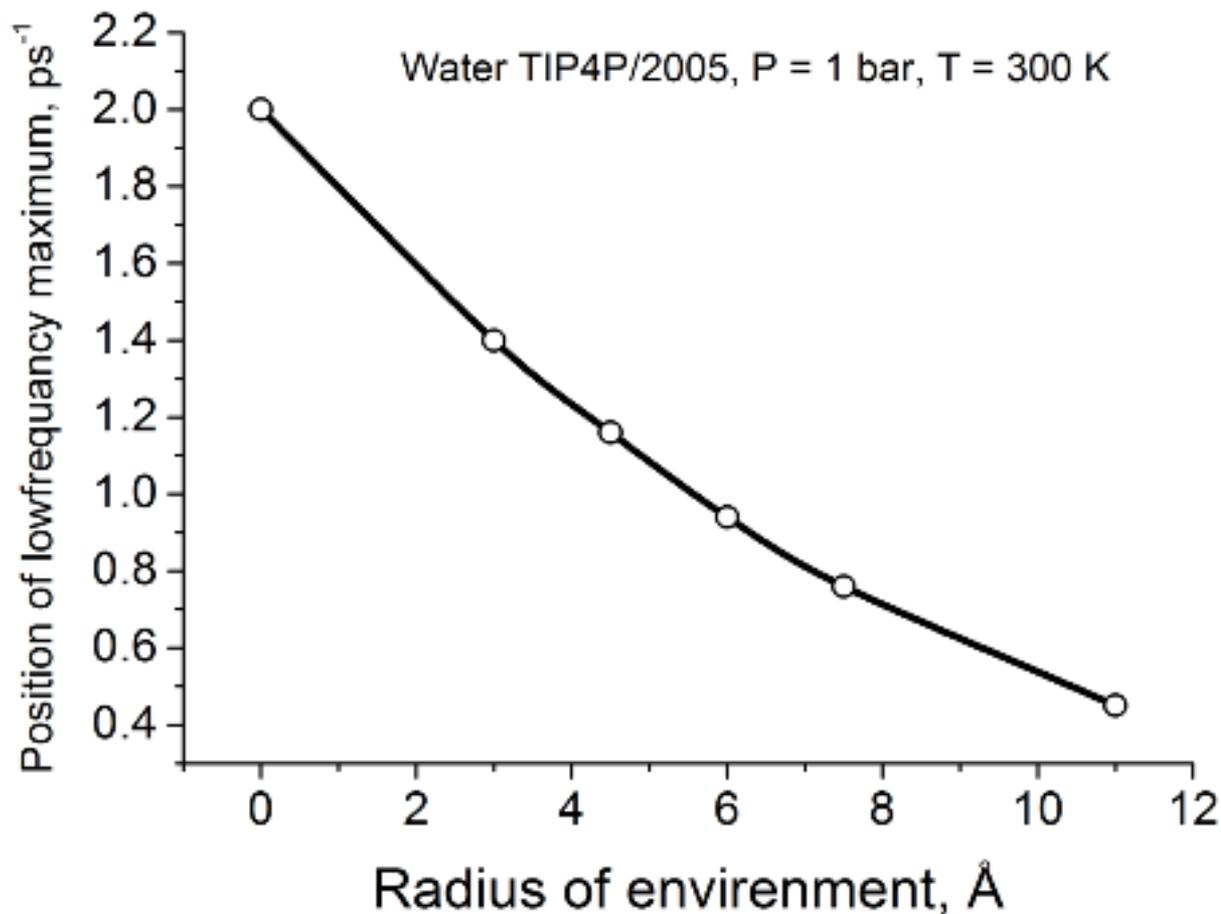


Spectra of partial autocorrelation functions

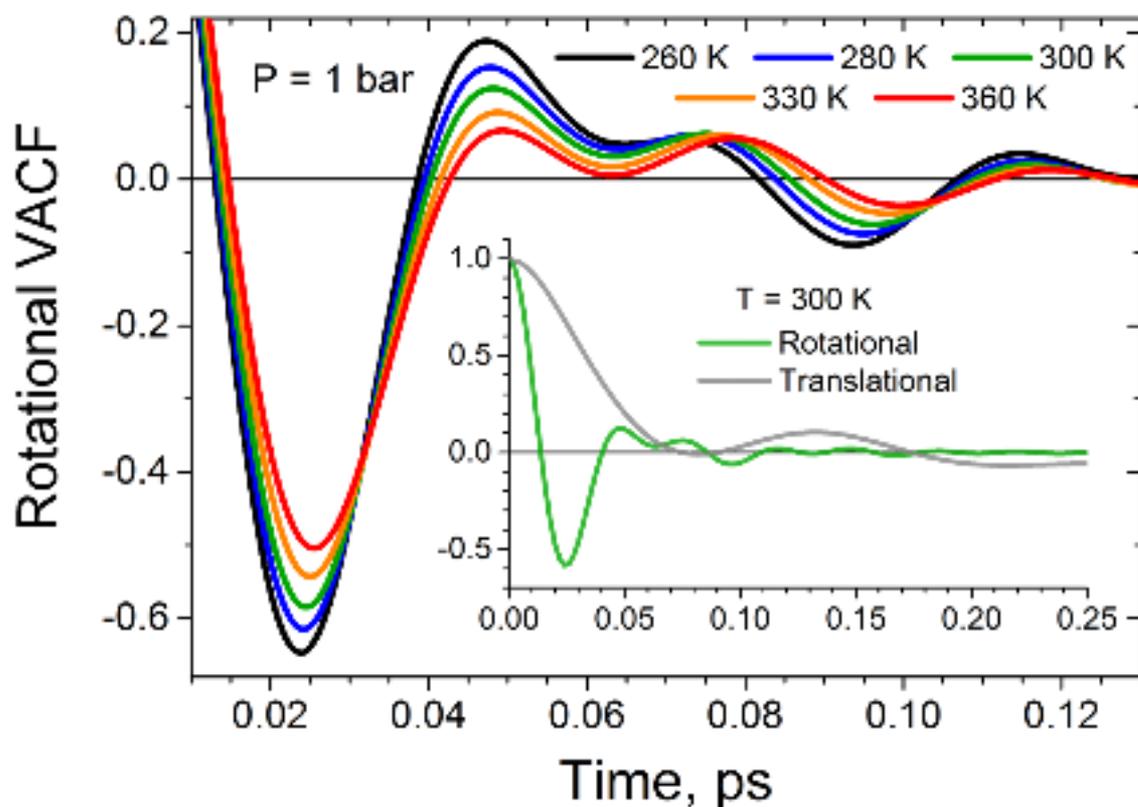
Comparison of the spectrum of full velocities of water molecules (gray line) and spectra of partial velocities. From bottom to top: for individual particle velocities relative to the smallest environment. The above shows the results for increasingly larger environments relative to the next size environments.

Dependence of the position of the low-frequency maximum on the radius of the environment

Dependence of the position of the low-frequency maximum on the radius of the environment. On the scale under study, the frequency decreased by almost 5 times.



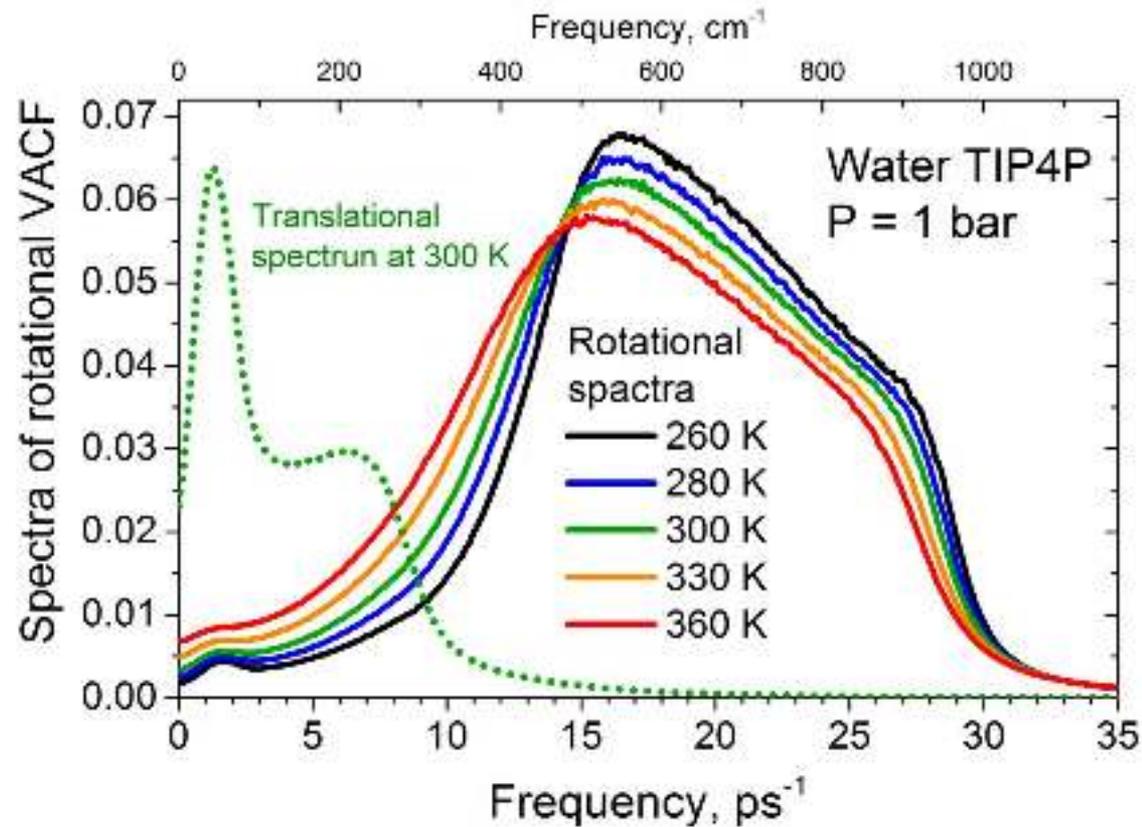
Autocorrelation functions of rotational velocities of water molecules



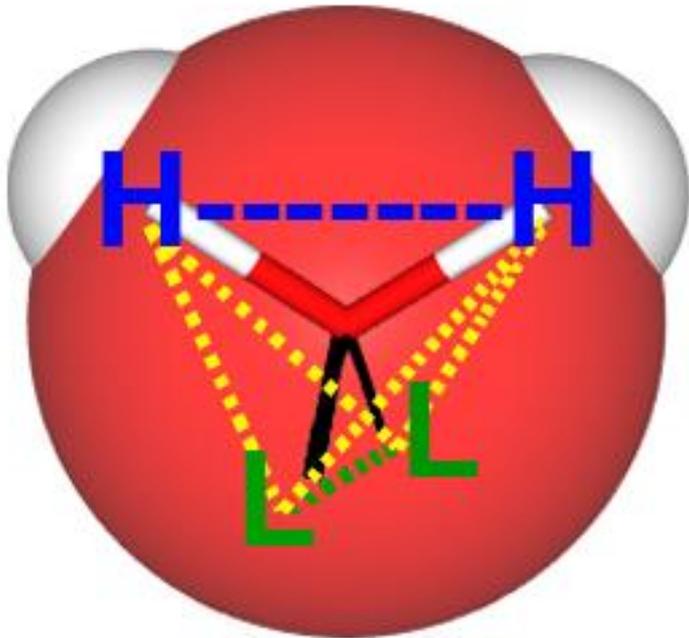
Autocorrelation functions of rotational velocities of water molecules. On the main field for different temperatures on an enlarged scale. The inset contains a comparison of the autocorrelators of rotational (green line) and translational (gray line) motions. Rotational frequencies are much higher than translational ones.

Spectra of rotational velocities of water molecules

Spectra of angular velocities of water molecules. At all temperatures, the spectra contain only one main asymmetric maximum and a small prepeak at low frequencies corresponding to the position of the left maximum of the translational velocity spectrum.

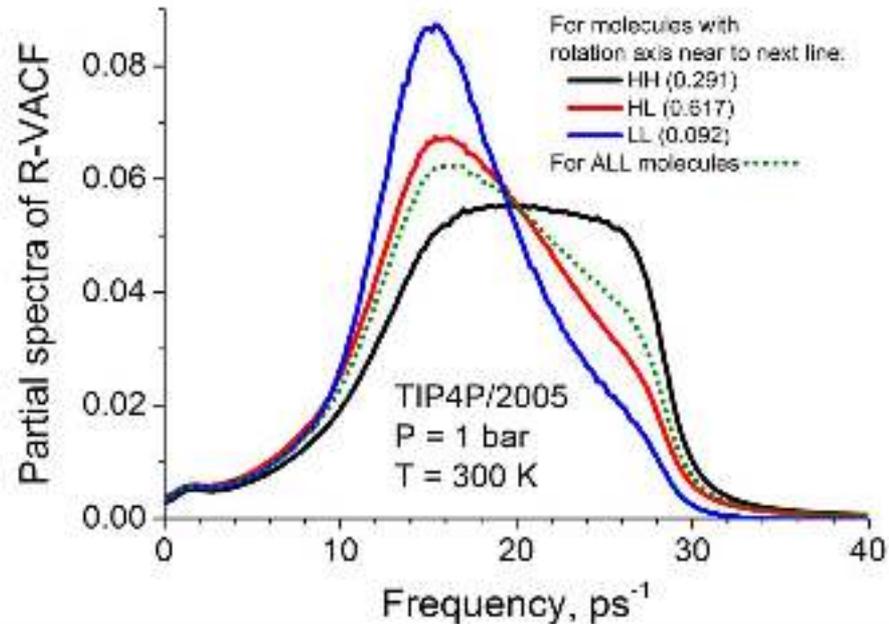
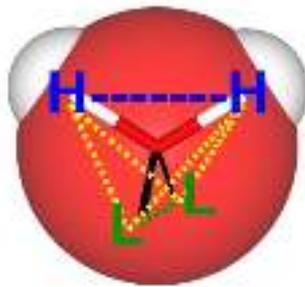


Analysis of the asymmetric maximum of the angular velocity spectrum



Let us describe a water molecule in the form of a tetrahedron, in two vertices of which the centers of hydrogen atoms (H) are located, and in the other two - the centers of lone pairs of electrons (L). Let's find the direction of the axis of rotation of the molecule relative to its own coordinate system and determine with which vector from the set HH, LL and HL it forms the smallest angle.

Analysis of the asymmetric maximum of the angular velocity spectrum



The highest oscillation frequency is observed if the water molecule rotates around the HH line. This happens when the molecule rocks on two strong donor H-bonds. The lowest frequency is observed when rocking is performed on two acceptor bonds. Rocking on one donor and one acceptor bond corresponds to the average frequency. This is because the donor bond is more rigid than the acceptor bond. Therefore, its bending occurs with greater frequency.

Conclusions

- The autocorrelation functions of the translational and rotational velocities of liquid molecules contain information about the motion of these molecules and the structure of the liquid as a whole.
- Velocity spectra make it possible to present this information in a clearer form.
- The fastest motions of a molecule are its oscillations in a local potential well formed by its nearest neighbors (Frenkel cell). These movements form a high-frequency maximum.
- At the same time, the molecule participates in many collective movements of different sizes. The larger the size of the collective, the lower the frequency of this movement. Collective motions jointly form the low-frequency maximum of the spectrum.
- The frequency of rotational movements of a water molecule is much greater than the frequency of its translational movements. This frequency, as well as the orientation of the axis of rotation, depends on the number and strength of the hydrogen bonds of a given molecule. The more donor H-bonds and the stronger they are, the higher the frequency of rotational oscillations.