

Energy relaxation pathways in liquid water

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The mechanisms of vibrational (bend) and rotational relaxation in liquid water are examined via a detailed analysis of energy fluxes between molecular modes [1,2,3].

Classical nonequilibrium MD runs are conducted for neat liquid water (SPC/E model) at different temperatures. Results are averaged for sets of trajectories in which at the initial time either: (a) the bend mode of a single flexible water molecule is excited or, (b) a purely rotational excitation is created for a single rigid molecule.

Analysis of energy fluxes is possible through the computation of the various contributions to the power and the work. In this way one can determine, for instance, which percentage of vibrational energy flows into self-rotation through centrifugal coupling, and to which particular axis this flow is maximal [1,2]. Moreover the spatial extent of energy flow into other water molecules can be ascertained as well, together with the specific molecular modes (translational, rotational) to which excess energy is transferred.

Bend relaxation is found to be dominated by energy flow to the hindered rotation (libration) of the bend excited water molecule, due to a 2:1 Fermi resonance for the centrifugal coupling between the water bend and rotation. The remaining energy flow from the excited water bend is dominated by transfer to the first hydration shell. A slowdown of vibrational relaxation with increasing temperature is observed [3], compatible with recent experimental findings [4].

The energy flow from (the ensuing) rotational excitation of the central water molecule is less local in character, with slightly more than half of the energy being directly transferred to molecules in the first hydration shell of the initially excited water, and almost half of it being transferred to molecules beyond that shell.

Finally, it is observed that, following an initial increase in interaction energy, transfer to hindered rotational (librational) modes of neighbours is substantially more important than that to translational motions [3].

[1] F. Ingrosso, R. Rey, T. Elsaesser, J.T. Hynes, *J. Phys. Chem A* **113**, 6657 (2009).

[2] R. Rey, F. Ingrosso, T. Elsaesser, J.T. Hynes, *J. Phys. Chem A* **113**, 8949 (2009).

[3] R. Rey, J.T. Hynes., in preparation.

[4] S. Ashihara, S. Fujioka, K. Shibuya, *Chem. Phys. Lett.* **502**, 57 (2011).