Modification of water dynamics under vibrational strong coupling from molecular dynamics simulations

BOWLES Jessica;[A] **LAAGE Damien**;[B] **RICHARDI Johannes**;[A] **VUILLEUMIER Rodolphe**;[B] **SPEZIA Riccardo**.[A]

A) Laboratoire de Chimie Théorique, Sorbonne Université, Paris, France; B) PASTEUR, Département de Chimie, École Normale Supérieure, PSL University, Sorbonne Université, CNRS, Paris, France.

jessica.bowles@sorbonne-universite.fr

In the present contribution, we studied how liquid water properties are modified when the system is coupled with a (virtual) Fabry-Perot cavity. At this end, we have employed the Cavity-Molecular Dynamics formalism[1] and a fully atomistic representation of liquid water, which are able to mimic key features of light-matter hybridization under vibrational strong coupling (VSC). The cavity frequency (ω_c) was set to different frequencies corresponding to different modes in the IR spectrum of liquid water : low frequencies (librational modes), medium frequencies (bending mode) and high frequencies (O-H stretching modes).
From simulations, we had access to both equilibrium and dynamical properties. Statistical properties (like water structure or hydrogen bond exchange barriers) should not change throughout the entire frequency range. On the other hand, dynamical properties, and notably the diffusion coefficient and the hydrogen bond jump rate constant[2], could be affected by the coupling with the cavity, showing different behaviors (and intensities) depending on the resonant conditions. An effect on the diffusion coefficient is obtained when the cavity is in resonance with the O-H stretching or with the librational motions, while the effect on the hydrogen bond dynamics occurs only when it is resonant with the librational motions.
In conclusion, we have observed that by using a simple molecular dynamics approach, it is possible to observe an effect of vibrational strong coupling, in particular if the cavity frequency is resonant with pertinent matter modes, in the present case the librational modes of liquid water. More developed models could then be used to understand the effect of VSC on different kinetic properties directly on condensed matter simulations.

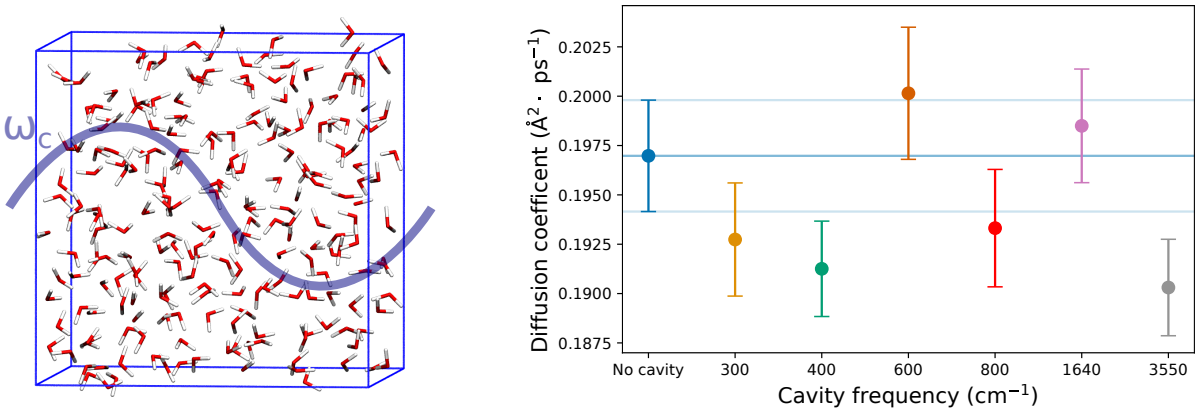

Figure 1: Box of liquid water in a virtual cavity represented by its frequency (ω_c) and the diffusion coefficient calculated without and within this cavity for various values of ω_c.

Keywords: Molecular dynamics, vibrational strong coupling, water properties

[1] T.E. Li, J.E. Subotnik, A. Nitzan, Proc. Nat. Acad. Sci. USA 117 (2020) 18324–18331.
[2] D. Laage, J.T. Hynes, 311 Science (2006) 832–835; D. Laage, J.T Hynes, J. Phys. Chem. B 112 (2008) 14230–14242.