

Ab initio molecular dynamics simulations of vibrational energy relaxation at the solid/liquid interface

Charge defects at the fluorite/water interface allow very fast intermolecular vibrational energy transfer



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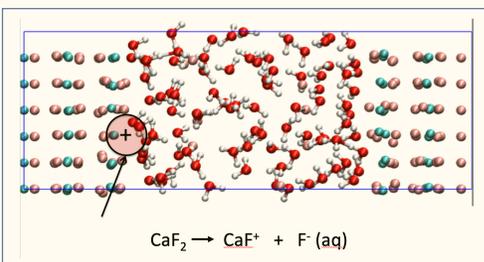


Introduction

The water/fluorite interface is of relevance to diverse industrial, environmental, and medical applications. In this contribution we review some of our recent results on the dynamics of water in contact with the solid calcium fluoride at **low pH**, where **localized charge** can develop upon fluorite dissolution. We use *ab initio* molecular dynamics simulations, including the full electronic structure, to simulate the **vibrational energy relaxation** and to quantify the heterogeneity of the interfacial water molecules.

Methods

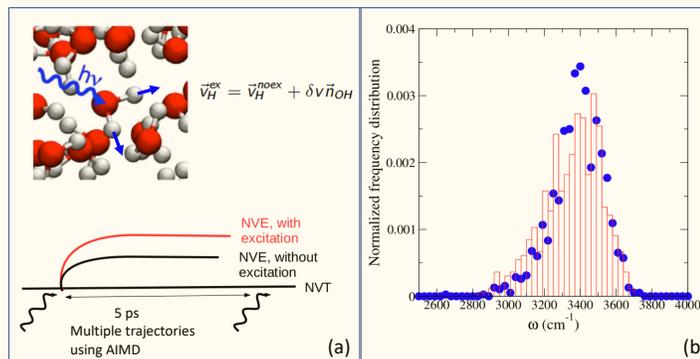
Vibrational energy excitation and relaxation from non-equilibrium trajectories



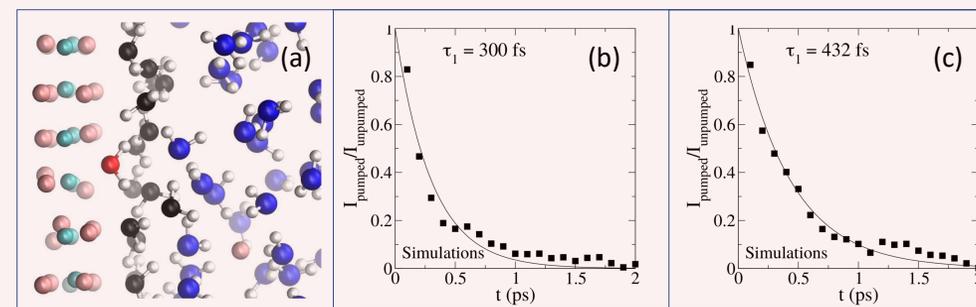
$$P(\omega, t) = \int_t^{t+\Delta t} \left\langle \sum_i \mathbf{v}_i(t) \mathbf{v}_i(t+\tau) \right\rangle e^{-i\omega\tau} d\tau$$

$$I(t) = \int_0^\infty P^{\text{ex}}(\omega, t) d\omega - \int_0^\infty P^{\text{gs}}(\omega, t) d\omega$$

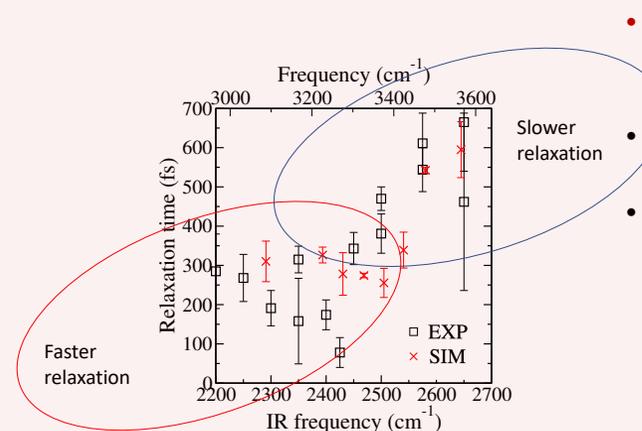
The extra kinetic energy, added to a given molecule, drives, instantaneously, the system out of the equilibrium and the subsequent relaxation process can be followed within NVE trajectories using descriptors, which we introduced in Ref. [1,2], which permit to follow the excess energy redistribution among the given modes.



Results



(a) Snapshot from the simulation: the water molecules highlighted in black are those excited in the non-equilibrium simulations. (b,c) Time evolution of the excess energy of the OH stretch obtained from simulations at low pH (square) for the water ensemble with a pump frequency below 2515 cm^{-1} (b) and above 2515 cm^{-1} (c) normalized by the initial value and its exponential fit (plain line).



- Strongly hydrogen-bonded OH groups display **very rapid** spectral diffusion and vibrational relaxation;
- for **weakly H-bonded** OD groups, the dynamics is instead **much slower**.
- the water molecules in the adsorbed layer, whose orientation is pinned by the **localized charge defects**, can exchange vibrational energy using just half a solvation shell, thanks to the strong dipole-dipole alignment between H-bond donor and acceptor.

[1] Lesnicki, D., Sulpizi, M.: The Journal of Physical Chemistry B 122(25), 6604(6609) (2018).

[2] Lesnicki, D., Zhang, Z., Bonn, M., Sulpizi, M., Backus, E.H.: Angewandte Chemie DOI 10.1002/anie.202004686.