

Asymmetric relaxation of vibrational excitations for nitromethane in water

Arnau Jurado Romero¹, Rossend Rey Oriol¹, and Carles Calero Borrallo²

¹Universitat Politècnica de Catalunya, Jordi Girona, 1-3. B5, 08034 Barcelona

²Universitat de Barcelona, Martí i Franquès, 1, 11, 08028 Barcelona

Energy dissipation is of interest for the accurate generation and control of movement in micro and nano-particles. Thus, studying the relaxation of molecules after a vibrational excitation has potential applications in multiple fields.

We consider the nitromethane molecule, whose energy relaxation after vibrational excitation has already been studied in argon gas and for micro-canonical excitations [1, 2]. We first test these previous works by performing individual mode excitations within the normal mode approximation. The obtained results suggests that the relaxation behaviour (shape, characteristic time, etc.) does not depend on the particular excitation in an Argon gas.

Prompted by the polar nature of the nitromethane molecule we study its relaxation in liquid water, based on the assumption that a polar solvent will present different behaviour than for a noble gas. We perform high energy excitations (200 kJ/mol) of individual modes and study their energy relaxation via all-atom molecular dynamics simulations.

Our results show that, as expected, some normal modes relax considerably faster than others. These faster modes have associated motions related to the nitro group of the nitromethane molecule, which is to be expected due to the hydrophilic nature of the functional group.

To get more insight into the relaxation mechanisms we also studied the work performed by the nitromethane molecule on the surrounding water molecules [3]. We divide surrounding molecules in two groups: the one on the nitro group side and the ones on the methyl group side.

Our main finding is that energy relaxation is remarkably asymmetric, favoring the nitro side (30% more work the work is performed to the nitro side than to the methyl side). Excitations to low frequency normal modes associated with the nitro group are significantly more asymmetric, again favoring the nitro side (between 10 and 20% more than for

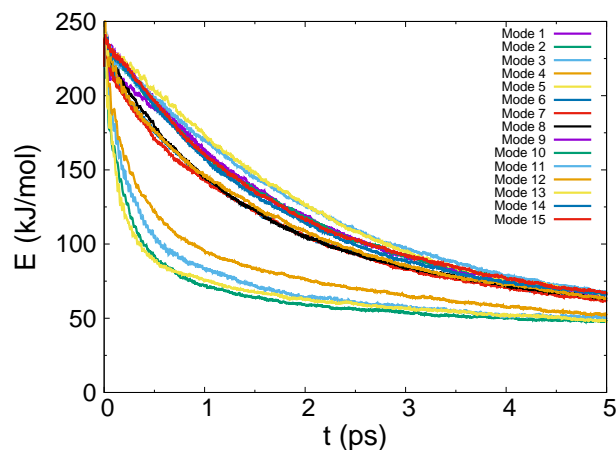


Fig. 1. Total vibrational energy (vibrational kinetic + potential energy) of a single nitromethane molecule after excitations of 200 kJ/mol in the labeled modes. Each curve represents the average of 200 realizations of the excitations in a 300 K SPC/E water system.

other excitations).

To our knowledge this is the smallest molecule for which a marked asymmetry has been found, irrespective of the excited mode.

[1] Rivera-Rivera, L. A., Wagner, A. F., Sewell, T. D., and Thompson, D., *J. Chem. Phys.* **142**, 014303 (2015).

[2] Rivera-Rivera, Luis A. and Wagner, Albert F. and Perry, Jamin W., *J. Chem. Phys.* **151**, 034303 (2019).

[3] Rossend Rey and James T. Hynes, *PCCP* **14**, 6332 (2012).