

Vibrational cooling dynamics of nitromethane

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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 other excitations).

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

REFERENCES

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

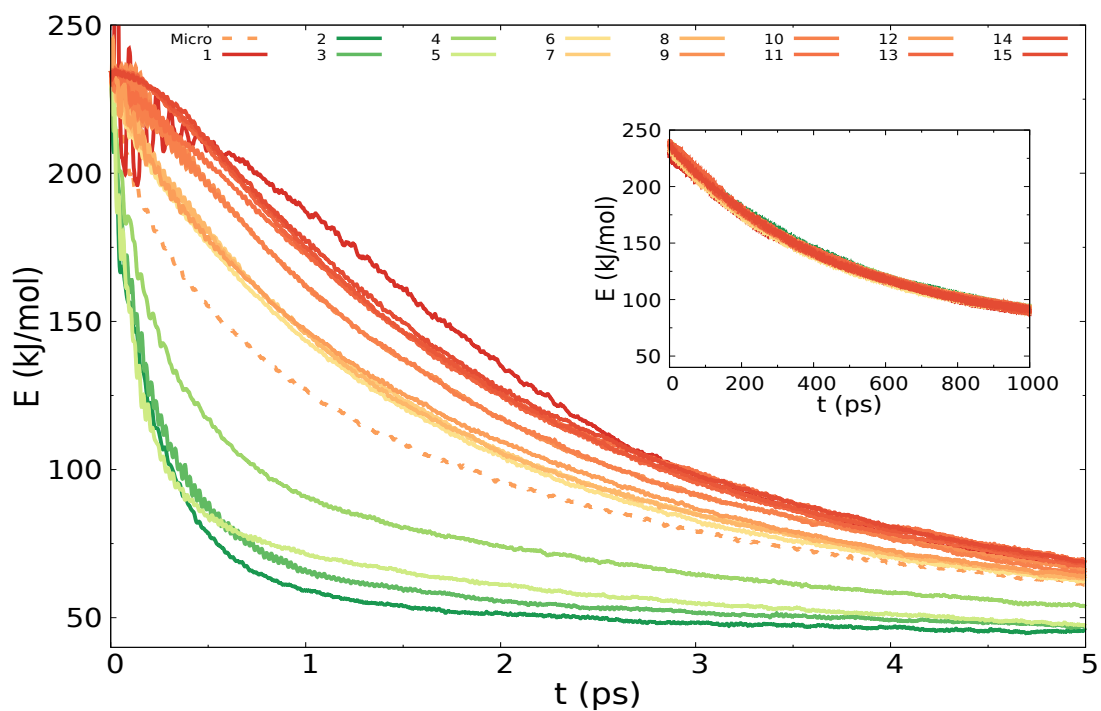


Figure 1: Total vibrational energy of a nitromethane molecule in liquid water after an excitation of 200 kJ/mol in a single normal mode, indicated by the key label. Results for argon are also shown on an inset.