

Supporting Information: Vibrational Relaxation and Energy Migration of N-methylacetamide in Water: The Role of Nonbonded Interactions

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	C	O	C(CO)	N	C(N)	H(CCO)	H(N)	H(CN)
q_i	0.714	-0.567	-0.707	-0.430	-0.032	0.187	0.278	0.061
a_0	1.899	-0.469	-1.468	-1.255	0.437	0.265	0.301	-0.080
a_1	-0.980	-0.079	0.636	0.681	-0.383	-0.067	-0.022	0.116

TABLE I: Electrostatic parameters for NMA in units of e .

This file contains one table and 3 additional figures.

The parameters obtained from the linear fit are reported on Table I.

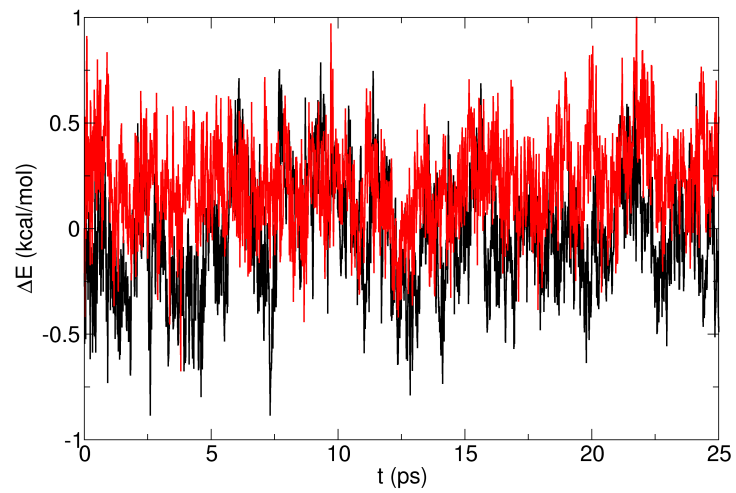


FIG. 1: Averaged water-NMA interaction energy from 250 non-equilibrium runs from FPC/TIP3P (black) and FPC/KKY (red) simulations.

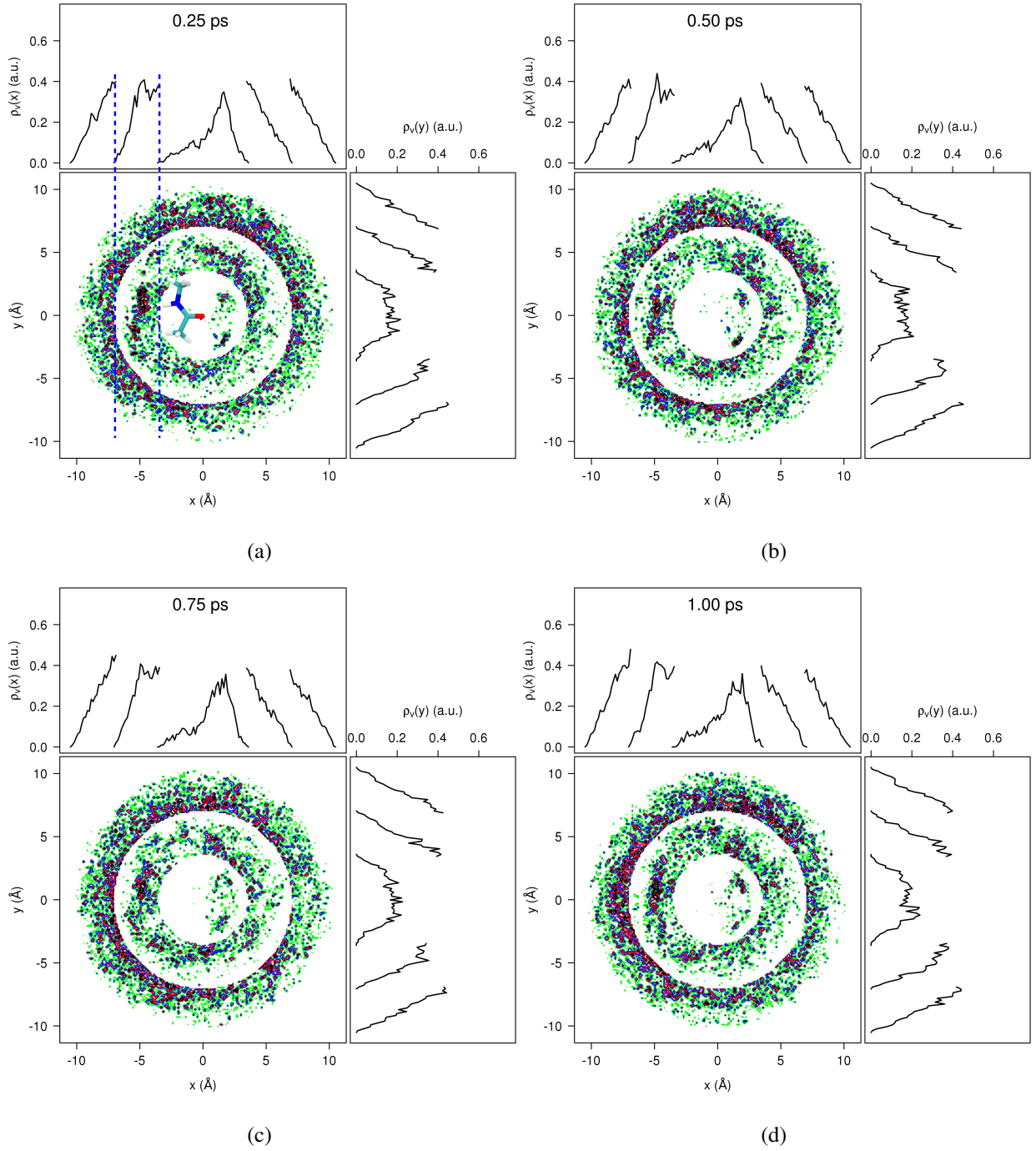


FIG. 2: Isocontours of water velocity distribution amplitude as a function of simulation time from the equilibrium part of the trajectory. The color code is as follows: white (0.0-0.3), green (0.3-0.35), blue (0.4-0.45), red (0.5-0.55), black (0.6-1.0). The black curves are the projection of the velocity density amplitude. The concentric circles are a consequence of analyzing water molecules in their respective solvent shells. Dashed blue lines define the solvent shells. For more detail see text.

Sensitivity to the Force Field Parametrization

The details of the force field parametrization have been found to affect the vibrational relaxation times of small molecules in solution, such as for CN^- in water.^{1,2} In this particular case, the importance of electrostatic interactions has been established for some time¹ and confirmed in more recent work using multipolar force fields.² In addition to the electrostatic interactions it was also found that the van der Waals parameters sensitively affect vibrational relaxation times and the solvation free energy.³ This contrasts with other properties, such as the 1d- or 2d-infrared spectra which are mostly sensitive to the electrostatics and less affected by van der Waals interactions.⁴

Hence, the sensitivity of the present results with respect to modifications of the van der Waals radii was also studied. As in previous work, the vdW radii of the C- and O-atom of the carbonyl group were increased by 5 and 7.5%, respectively, in order to probe the dependence of the physical observables on van der Waals ranges. Again, 250 non-equilibrium trajectories were run and analyzed for each case, with KKY as the force field for water.

Figure S3 reports the energy difference relative to the last frame of the equilibrium simulation for the total energy of NMAD and for all water molecules from which relaxation times are determined as was done before. Analysis of the decay times suggests that changes in the van der Waals ranges indeed influence the relaxation times which first decrease to 5.6 ps (for a 5 % increase in the radii) and then increase to 7.6 ps (for a 7.5% increase). These changes should be contrasted with a factor of about 5 in lengthening the vibrational relaxation time when scaling the van der Waals radii by 7.5 % on CN^- .² Hence, for NMA the dependence of the vibrational relaxation time on the van der Waals radii appears to be small. The variations of relaxation times may also be affected by the fact that they quite sensitively depend on the number of water molecules n_W bound to the CO at the time of excitation. Contrary to CN^- in solution, NMAD can vibrationally relax even if the water solvent is described by a rigid TIP3P water model. However, the energy can relax into low-frequency solvent degrees of freedom and into internal NMAD degrees of freedom. The latter is not possible for CN^- where coupling to the low-frequency solvent modes is weak and hence relaxation is very slow for simulations with rigid water.

¹ Rey, R.; Hynes, J. T. *J. Chem. Phys.* **1998**, *108*, 142–153.

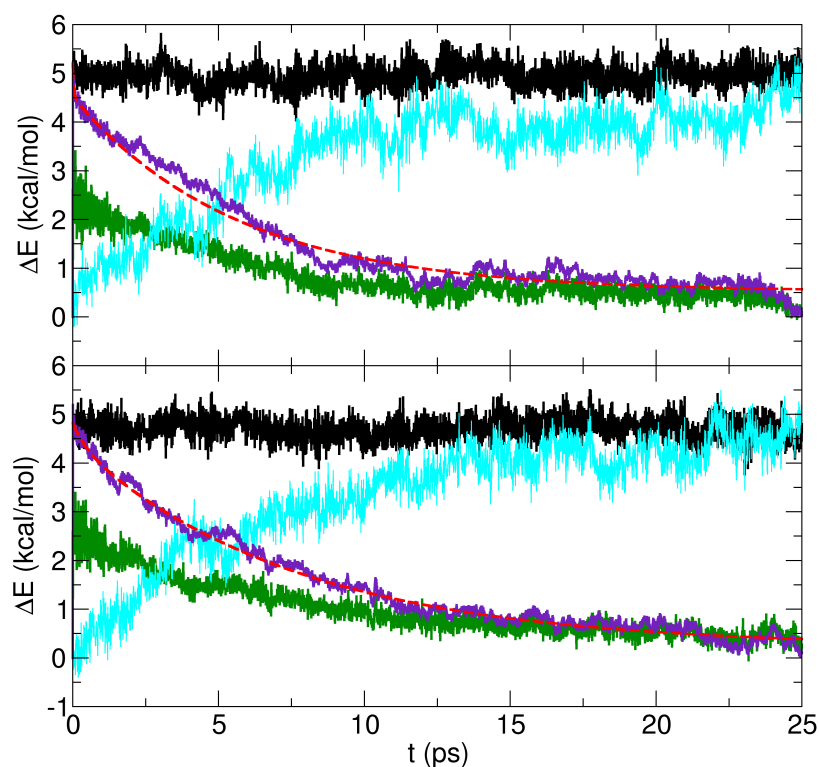


FIG. 3: Total energy difference for NMA (indigo) and water (cyan) for different modified force field parametrizations. All results are averaged over 250 individual nonequilibrium trajectories. Simulations with FPC/KKY and vdW radii on the C- and O-atom of the CO-moiety increased by 5% (top) and 7.5% (bottom).

² Lee, M. W.; Meuwly, M. *J. Phys. Chem. A* **2011**, *115*, 5053–5061.

³ Lee, M. W.; Meuwly, M. *Phys. Chem. Chem. Phys.* **2013**, *15*, 20303–20312.

⁴ Lee, M. W.; Carr, J. K.; Göllner, M.; Hamm, P.; Meuwly, M. *J. Chem. Phys.* **2013**, *139*, 054506.