

Supporting information for:

Infrared and Raman Spectroscopy from *Ab Initio*

Molecular Dynamics and Static Normal Mode

Analysis: The C-H Region of DMSO as a Case

Study

Sean A. Fischer,[†] Tyler W. Ueltschi,[‡] Patrick Z. El-Khoury,^{*,¶} Amanda L. Mifflin,[‡] Wayne P. Hess,[¶] Hong-Fei Wang,[†] Christopher J. Cramer,[§] and Niranjan Govind^{*,†}

William R. Wiley Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory, P.O. Box 999, Richland, WA 99352, USA, Department of Chemistry, University of Puget Sound, Tacoma, WA 98416, USA, Physical Sciences Division, Pacific Northwest National Laboratory, P.O. Box 999, Richland, WA 99352, USA, and Department of Chemistry, Supercomputing Institute and Chemical Theory Center, University of Minnesota, Minneapolis, MN 55455, USA

E-mail: patrick.elkhoury@pnnl.gov; niri.govind@pnnl.gov

^{*}To whom correspondence should be addressed

[†]Environmental Molecular Sciences Laboratory, PNNL

[‡]University of Puget Sound

[¶]Physical Sciences Division, PNNL

[§]University of Minnesota

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More specifically, the stochastic velocity rescaling thermostat of Bussi, Donadio, and Parrinello^{S1} is an extension of the classic velocity rescaling approach to controlling the temperature of a simulation. This thermostat has been constructed to sample the proper distribution for the canonical ensemble, and to minimally impact the dynamical behavior of the system. Bussi et al. showed that their thermostat was able to reproduce the microcanonical ensemble result for the vibrational spectrum of hydrogen in ice. Their test was on a condensed-phase system, while our simulations are of isolated molecules. Though we would not expect to achieve the same result between a thermostated and unthermostated simulation on a single molecule, we do feel that the thermostated simulation gives us physically reasonable results since in the limit of a simulation of an ensemble of molecules, the thermostated results agrees with the unthermostated result. Additionally, the thermostated simulations provide a better sampling of phase space as demonstrated below.

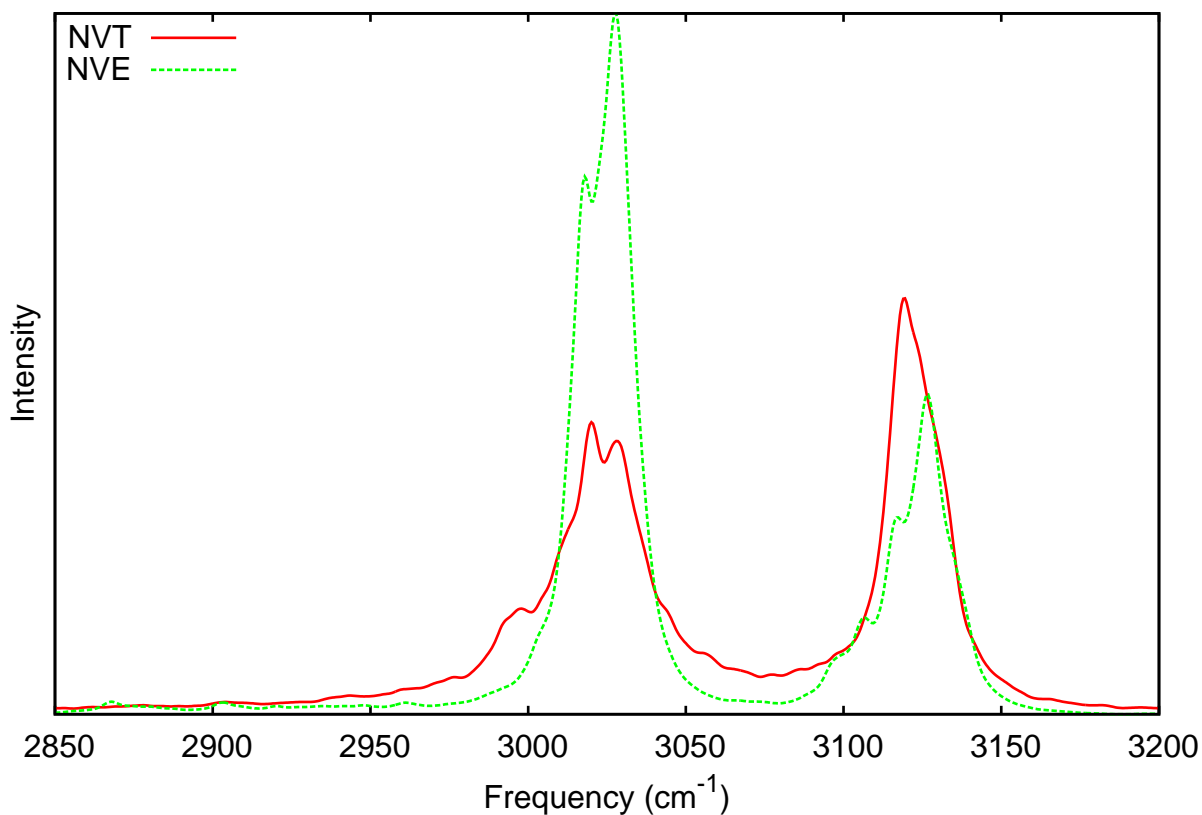


Figure S1: Comparison of the C-H stretching region of DMSO for IR spectra calculated via AIMD in the canonical (NVT, solid line) and microcanonical (NVE, broken line) ensembles. The spectra were generated from 10 trajectories, each approximately 10 ps long. A time step of 10 atomic units was used for each trajectory. While the asymmetric stretching peak is similar in both spectra, the symmetric stretching peak is markedly different. The NVE simulation predicts a more intense and narrow feature, which is at odds with the experimental spectrum. We rationalize the shape of the symmetric stretching feature in the NVE simulation through analysis of the phase space probability distribution shown below.

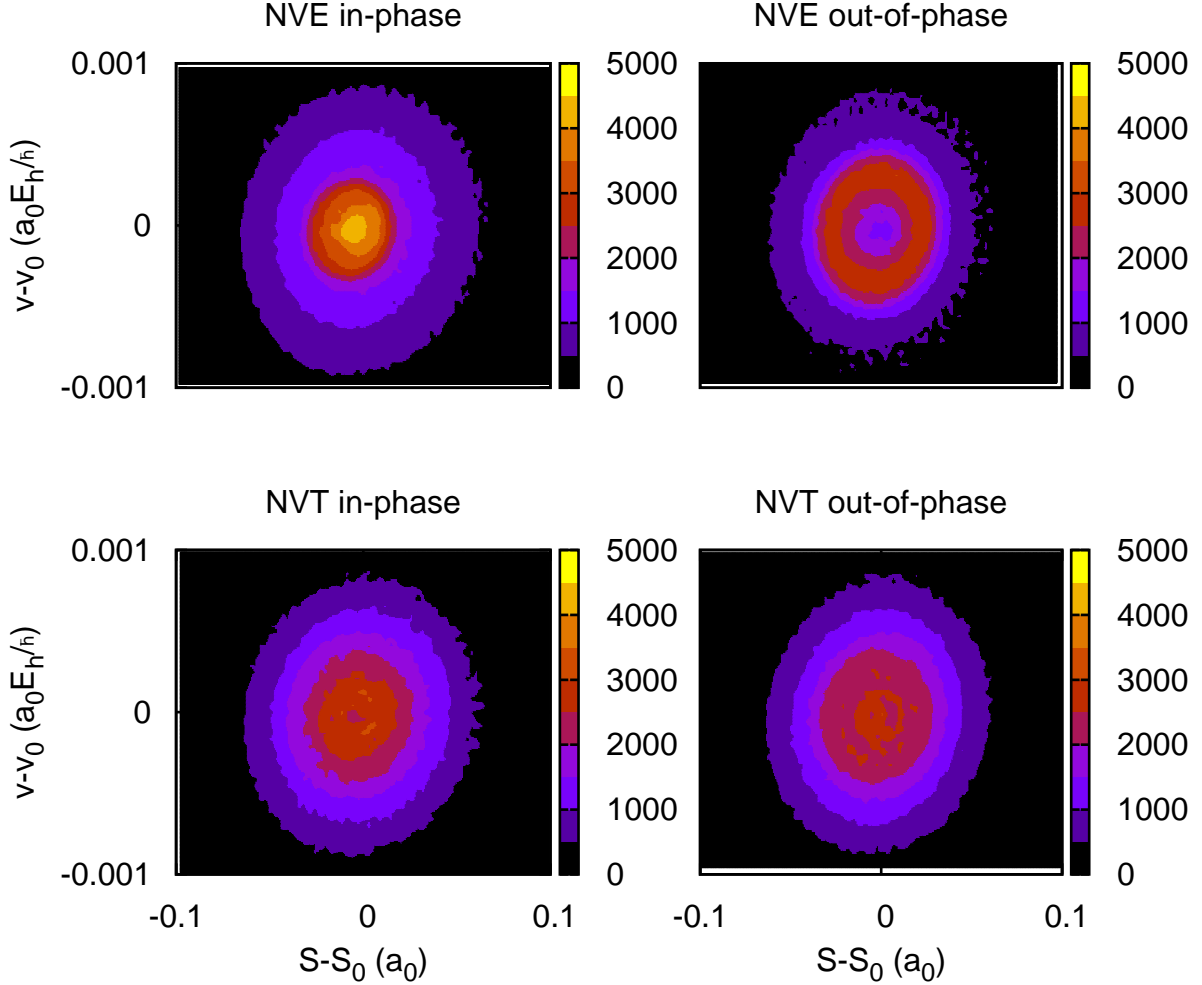


Figure S2: Phase space probability distributions for the in-phase (left) and out-of-phase (right) symmetric C-H stretch of DMSO calculated in the microcanonical (top) and canonical (bottom) ensembles. Plotted are the symmetry coordinates (see main text for definition of the symmetry coordinates) of the modes versus their corresponding velocities. The coordinates and velocities have been referenced to their average values. The distributions are normalized such that the volume under the surface is one. The distributions from the canonical ensemble have the same shape and qualitatively agree with the expectation of the quantum result for a harmonic oscillator.^{S2} The distributions from the microcanonical ensemble on the other hand do not match each other nor the expected quantum result. The in-phase symmetric stretch distribution is too peaked compared to the expected Gaussian shape, while the out-of-phase symmetric stretch shows a dip at the average values of position and momentum. The sharper distribution for the in-phase symmetric stretch in the microcanonical ensemble is the reason for the more narrow feature seen in the IR spectrum.

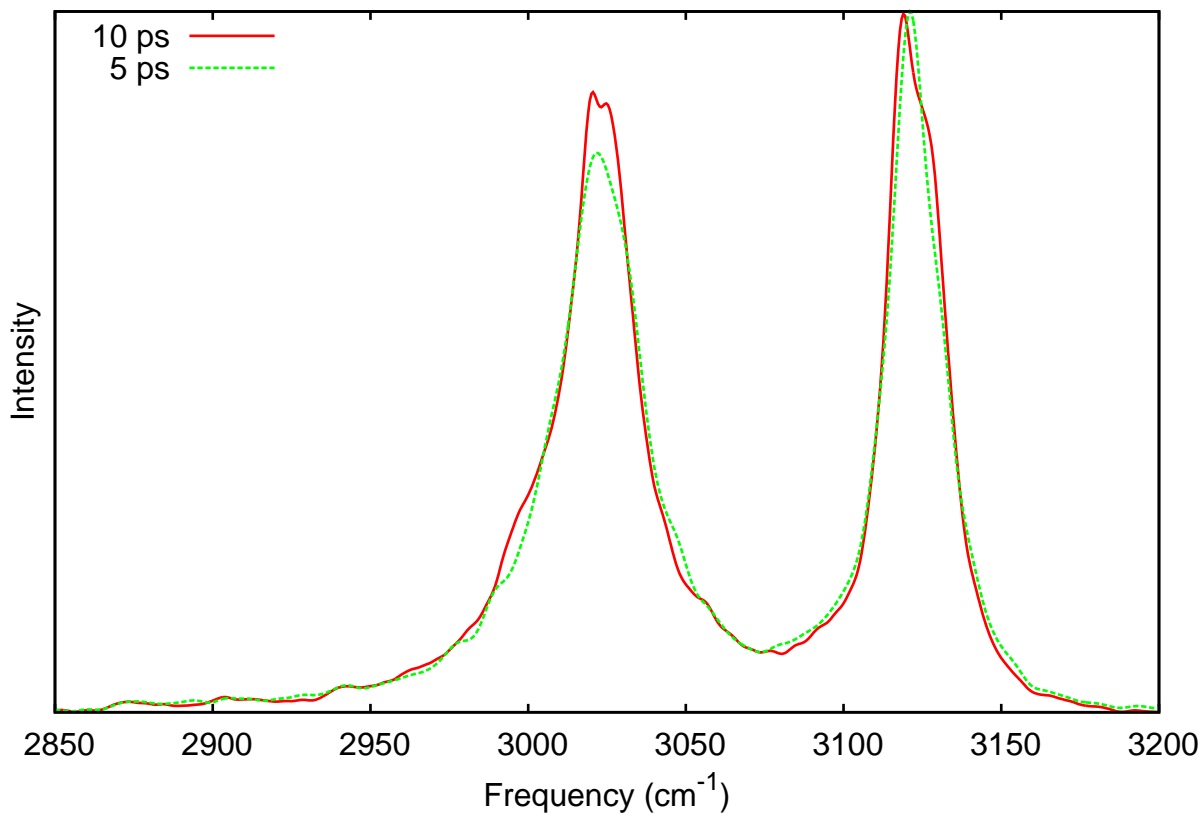


Figure S3: Comparison of IR spectra calculated from 20 AIMD trajectories of approximately 10 ps each (solid line) and 20 AIMD trajectories of approximately 5 ps each (broken line). These results demonstrate that the broadening that we obtain is not an artifact of simulation length.

Table S1: Irreducible representations, mode assignments, and frequencies of the C-H stretching and deformation modes calculated with B3LYP/6-311++G**, MP2/6-311++G**, and CCSD/6-311++G**. All frequencies are given in wave numbers (cm^{-1}). The labeling follows that of Horrocks and Cotton.^{S3} The frequencies of the deformation overtones are given in parenthesis after the fundamentals. As with the B3LYP-VPT2 calculation, the MP2-VPT2 calculation does not predict a Fermi resonance between a symmetric stretching mode and an overtone of a deformation mode. The gap between the deformation modes and symmetric stretching modes is the same for the B3LYP-NMA and CCSD-NMA calculations, suggesting that a Fermi resonance would not be predicted with CCSD if the VPT2 calculation were feasible. Given the agreement between the higher level calculations and the B3LYP calculations, we have added confidence in our assertion that the shoulder seen in the experimental Raman spectrum is not due to a Fermi resonance or overtone.

Mode	B3LYP-NMA	B3LYP-VPT2	MP2-NMA	MP2-VPT2	CCSD-NMA
Degenerate stretches					
A' ν_1	3148.2	2999.2	3202.0	3061.9	3177.8
A'' ν_{14}	3147.1	2998.4	3201.3	3061.3	3176.8
A' ν_2	3139.1	2991.2	3193.4	3052.3	3169.8
A'' ν_{15}	3135.2	2987.9	3189.9	3049.6	3165.7
Symmetric stretches					
A' ν_3	3040.2	2924.0	3078.1	2967.1	3067.2
A'' ν_{16}	3037.9	2921.1	3076.9	2966.5	3064.6
Degenerate deformation					
A' ν_5	1470.7	1431.4 (2855.1)	1481.5	1445.2 (2882.9)	1486.1
A'' ν_{18}	1455.3	1417.4 (2828.0)	1466.1	1424.6 (2842.9)	1471.5
A' ν_4	1453.6	1412.5 (2818.3)	1465.6	1428.5 (2850.3)	1471.3
A'' ν_{17}	1440.2	1398.8 (2791.1)	1451.9	1411.4 (2816.0)	1458.9
Symmetric deformation					
A' ν_6	1342.5	1315.9 (2623.6)	1377.9	1332.6 (2671.3)	1389.7
A'' ν_{19}	1319.7	1295.3 (2583.5)	1353.4	1316.9 (2625.3)	1365.4

References

- (S1) Bussi, G.; Donadio, D.; Parrinello, M. Canonical Sampling through Velocity Rescaling. *J. Chem. Phys.* **2007**, *126*, 014101.
- (S2) Robinett, R. W. Quantum and Classical Probability Distributions for Position and Momentum. *Am. J. Phys.* **1995**, *63*, 823–832.
- (S3) Horrocks Jr., W. D.; Cotton, F. A. Infrared and Raman Spectra and Normal Coordinate Analysis of Dimethyl Sulfoxide and Dimethyl Sulfoxide-D6. *Spectrochim. Acta* **1961**, *17*, 134–147.