

Infrared and Raman Spectroscopy from *Ab Initio* Molecular Dynamics and Static Normal Mode Analysis: The C-H Region of DMSO as a Case Study

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Abstract

Carbon-hydrogen (C-H) vibration modes serve as key probes in the chemical identification of hydrocarbons and in vibrational sum-frequency generation (SFG) spectroscopy of hydrocarbons at the liquid/gas interface. Their assignments pose a challenge from a theoretical viewpoint. In this work, we present a detailed study of the C-H stretching region of dimethyl sulfoxide (DMSO) using a new *ab initio* molecular dynamics (AIMD) module that we have implemented in NWChem. Through a combination of AIMD simulations and static normal mode analysis, we interpret experimental infrared and Raman spectra and explore the role of anharmonic effects in this system. Comprehensive anharmonic normal mode analysis of the C-H stretching region casts doubt upon previous experimental assignments of the shoulder on the symmetric C-H stretching peak. In addition, our AIMD simulations also show significant broadening of the in-phase symmetric C-H stretching resonance, which suggests that the experimentally observed shoulder is due to thermal broadening of the symmetric stretching resonance.

Introduction

Carbon-hydrogen (C-H) stretching vibrations are sensitive markers of the local chemical environment. Such vibrations are typically strongly infrared and/or Raman-active, and are isolated in the $3000 \pm 200 \text{ cm}^{-1}$ spectral region. These are among the features that render C-H vibrations popular, for instance, in non-linear vibrational spectroscopic and microscopic tools aimed at rapid imaging of biological systems.¹⁻³ C-H vibrations have also been predominantly used as probes in vibrational sum-frequency generation (SFG) spectroscopy to study hydrocarbons at liquid/gas interfaces.⁴⁻⁶ Nonetheless, establishing a direct link between spectroscopic observables and theoretical predictions has proven to be a challenging task. This is a result of the inherent complexity of the high-energy vibrational band profiles, consisting of overlapping fundamental vibrational modes, overtones, combination modes,

and Fermi resonances. Overall, capturing all the aforementioned features is necessary for a faithful reproduction of experimentally recorded vibrational line shapes, and comprises a real challenge from a theoretical viewpoint.

The standard approach of empirically scaling vibrational spectra computed based on the quantum mechanical harmonic oscillator approximation⁷⁻⁹ is often inadequate, particularly when C-H stretching modes are targeted.¹⁰⁻¹³ In this regard, several approaches have been proposed to go beyond the harmonic approximation. These include the vibrational self-consistent field approach,^{10,14-17} methods based on perturbative corrections to the harmonic approximation,^{18,19} and approaches based on *ab initio* molecular dynamics (AIMD) simulations.²⁰⁻²⁹ AIMD simulations are particularly appealing in that they allow conformational sampling in phase space, while treating the electronic structure of the molecular system within the Born-Oppenheimer approximation (i.e. the dynamics are propagated on an adiabatic potential energy surface). This becomes particularly important for molecules with internal rotations that create multiple, thermally-accessible minima on the potential energy surface. The traditional calculation of normal mode-dependent dipole and polarizability derivatives to simulate infrared and Raman spectra in the static approach or frequency domain is replaced by Fourier transforms of the dipole and polarizability correlation functions in the time domain dynamics simulations.²⁶ Since no approximations are invoked to approximate the shape of the potential energy landscape in AIMD simulations, vibrational spectra evaluated from these simulations are inherently more physical than their harmonic analogues that are evaluated at a minimum.³⁰ In principle, with adequate statistical sampling and in the absence of significant mode coupling leading to combination bands and Fermi resonances, the only assumptions stem from the level of the underlying electronic structure approach used to treat the molecular system.^{31,32}

In this work, we present computational results obtained using a new module that we have implemented in the NWChem computational chemistry program³³ to perform Born-Oppenheimer molecular dynamics (BOMD) simulations using Gaussian basis functions to

represent the electronic structure. Using a combination of AIMD simulations and static normal mode analysis, we carefully analyze the C-H stretching region of a prototypical molecular system, namely, dimethyl sulfoxide (DMSO). DMSO was chosen as a test case since it is a relatively simple system that does not show complicated Fermi resonances like those seen in methanol, ethanol, and other hydrocarbons. Additionally, new spectroscopic techniques such as high-resolution broadband sum frequency generation spectroscopy,⁵ have the spectral resolving power to identify overlapping peaks, which offer more stringent tests of computational predictions.^{6,34,35} Our results demonstrate the advantages of combining the two theoretical approaches in order to analyze and interpret experimental IR and Raman spectra. In the remainder of the paper we outline the methodology of computing IR/Raman spectra from AIMD simulations, provide details of the computational parameters and experimental setup, and discuss the insights into the C-H stretching vibrations that were gained.

Computational Details

The absorption line shape $I(\omega)$ for infrared absorption and the differential Raman scattering cross sections $\lambda_s^4 \left(\frac{d^2\sigma}{d\omega d\Omega} \right)$ can be related to Fourier transforms of autocorrelation functions of molecular properties:³⁶

$$I(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt \exp^{-i\omega t} \langle \boldsymbol{\mu}(0) \cdot \boldsymbol{\mu}(t) \rangle \quad (1)$$

where I is the intensity, ω is the frequency, and $\boldsymbol{\mu}$ is the molecular electric dipole moment,

$$\begin{aligned} \lambda_s^4 \left(\frac{d^2\sigma}{d\omega d\Omega} \right)_{\parallel} &= \frac{1}{2\pi} \int_{-\infty}^{\infty} dt \exp^{-i\omega t} \frac{1}{15} \sum_{i,j} \langle \alpha_{ii}(0) \alpha_{jj}(t) + 2\alpha_{ij}(0) \alpha_{ij}(t) \rangle \\ &= \frac{1}{2\pi} \int_{-\infty}^{\infty} dt \exp^{-i\omega t} \frac{1}{15} \langle 15\bar{\alpha}(0)\bar{\alpha}(t) + 2\text{Tr}\boldsymbol{\beta}(0) \cdot \boldsymbol{\beta}(t) \rangle \end{aligned} \quad (2)$$

$$\begin{aligned}
\lambda_s^4 \left(\frac{d^2\sigma}{d\omega d\Omega} \right)_\perp &= \frac{1}{2\pi} \int_{-\infty}^{\infty} dt \exp^{-i\omega t} \frac{1}{30} \sum_{i,j} \langle 3\alpha_{ij}(0)\alpha_{ij}(t) - \alpha_{ii}(0)\alpha_{jj}(t) \rangle \\
&= \frac{1}{2\pi} \int_{-\infty}^{\infty} dt \exp^{-i\omega t} \frac{1}{10} \langle \text{Tr} \boldsymbol{\beta}(0) \cdot \boldsymbol{\beta}(t) \rangle
\end{aligned} \tag{3}$$

where $2\pi\lambda_s$ is the wavelength of the scattered radiation, σ is the scattering cross section, Ω is a solid angle, $\bar{\alpha} = \frac{1}{3}\text{Tr}\boldsymbol{\alpha}$ is the isotropic part of the molecular polarizability tensor, and $\boldsymbol{\beta} = \boldsymbol{\alpha} - \bar{\alpha}\mathbf{I}$ is the anisotropic part and \mathbf{I} is a unit tensor. The angle brackets refer to an ensemble average. Equation 2 corresponds to radiation scattered parallel to the polarization of the incident light and Eq. 3 corresponds to radiation scattered perpendicular to the polarization of the incident light.

To calculate the relevant correlation functions, we have performed AIMD simulations of an isolated DMSO molecule within the canonical ensemble. We have found for DMSO that performing calculations in the canonical ensemble rather than the micro-canonical ensemble leads to better agreement with experimental spectra (see Supporting Information). Since we are using classical correlation functions instead of their quantum analogues, we apply the harmonic approximation quantum correction, Q_{HA} :

$$Q_{HA} = \frac{\hbar\omega}{k_B T \left(1 - \exp\left[-\frac{\hbar\omega}{k_B T}\right] \right)}. \tag{4}$$

where \hbar is the reduced Planck constant, k_B is the Boltzmann constant, and T is the temperature of the simulation. The quantum line shape and scattering cross sections are obtained by multiplying the classical values by Q_{HA} . Ramírez et al. found that this correction was the only one to obey the fluctuation-dissipation theorem and comprises the best approximation in most cases.³⁷

In order to perform the molecular dynamics simulations, we have implemented a new module into NWChem that is capable of performing BOMD using Gaussian basis functions with various thermostats and at any level of theory in NWChem where gradients of the electronic energy are available, including excited-state molecular dynamics using linear-

response time-dependent density functional theory (LR-TDDFT).³⁸ The velocity-Verlet algorithm was used³⁹ to propagate nuclei. For temperature control, we have implemented the stochastic velocity-rescaling thermostat of Bussi, Donadio, and Parrinello,⁴⁰ which correctly samples the canonical ensemble (under the assumption of ergodicity) and minimally impacts dynamic properties. The electronic structure was calculated with the B3LYP^{41–43} exchange-correlation functional in conjunction with the 6-311++G**^{44,45} basis set. This functional and basis set combination was used in a previous study of the Raman spectrum of DMSO and found to give reliable agreement with experiment.⁴⁶

Following the suggestions of Horníček, et al.,³¹ we performed several short trajectories, which were averaged together to obtain the final result. The geometry of DMSO was initially optimized on the electronic ground state without enforcing symmetry. We then initiated a ~ 5 ps trajectory starting from the minimized structure. The system was propagated at 300 K, and 20 structures were randomly extracted and used as initial structures for our production runs. Initial velocities were assigned from a 300 K Maxwell-Boltzmann distribution with center of mass translation and rotation removed. We integrated each of the 20 trajectories for 430,000 a.u. with a time step of 10 a.u. (~ 0.2419 fs) for a total simulation time of over 200 ps. Note that for the length of trajectory that we utilized, our spectral resolution is approximately 3.5 cm^{-1} . In the Supporting Information we have also calculated an IR spectrum using only the first half of each trajectory in order to verify that our results are converged with respect to trajectory length. Frequency-dependent molecular polarizability tensors for Raman analysis were computed at every step in each of the trajectories in the velocity gauge using the response module of NWChem^{47–52} at an incident wavelength of 800 nm to match with the excitation wavelength used in the experiments outlined below. Prior to analysis, all quantities were rotated to a common frame-of-reference in order to remove any spurious rotations that may have occurred during the AIMD simulations. The first 3000 steps of each trajectory were discarded in the calculation of the correlation functions and spectra. Fast Fourier transforms (FFTs) were used to calculate the correlation functions,

and an exponential or Poisson window function⁵³ was applied to the correlation functions before another FFT was performed to obtain the spectra according to Eqs. 1-3. We chose a parameter for the window function such that the resulting Lorentzian line shapes feature a full-width at half-maximum of 10 cm⁻¹.

To complement our AIMD analysis, we have also performed harmonic and anharmonic normal mode analyses and vibrational self-consistent field (VSCF) calculations. A static normal mode analysis (NMA), including IR intensities and Raman activities, was performed using Gaussian 09⁵⁴ with the same basis set and functional. The frequencies predicted by the standard normal mode analysis are often qualitatively correct, yet lack quantitative accuracy due to the anharmonicity of the potential energy surfaces. As mentioned in the introduction, one commonly adopted approach to correct the harmonic frequencies is to apply empirical scaling factors, either individually to different Hessian matrix elements or a single value to all harmonic frequencies, to align the computed spectra with their experimental analogues.⁵⁵ However, merely scaling the frequencies to match experiment offers no deeper insight into the molecular vibrations and can mask deficiencies in the underlying theory. A more rigorous approach is to directly account for anharmonicities through perturbation theory. This also allows for the calculation of overtones, combination bands, and Fermi resonances, quantities that are absent in the harmonic normal mode analysis and the AIMD-based simulations. In the present work we computed anharmonic corrections to the harmonic frequencies and IR intensities, using second-order perturbation (VPT2) with numerical third and fourth derivatives¹⁸ as implemented in Gaussian 09. We applied the same width parameter used to broaden the MD spectra to broaden the computed static spectra.

Experimental Methods

The high-resolution femtosecond stimulated Raman (HR-FSRS) spectrometer used to record simulated Raman loss (SRL) spectra is described in detail elsewhere.⁶ The system is based

on an amplified ~ 90 ps Raman pump synchronized with a ~ 40 fs laser source used to generate white light continuum. The fundamentals of the fs and ps sources are centered at ~ 800 nm, and operated at a repetition rate of 1 KHz. The ps pump source (50 mW) and fs white light continuum are focused into a quartz cell (1 cm path length) containing a spectroscopic-grade liquid DMSO sample. SRL of the pump is recorded using a 500 mm spectrograph and a charge coupled device camera by the consecutive ratio of on/off modes of the long 800 nm pulse. The combination of a 500 mm spectrograph and a 1200 mm^{-1} grating amounts to an effective spectral resolution of $\sim 1.5\text{ cm}^{-1}$. The gas-phase infrared absorption spectrum was taken from the NIST chemistry WebBook.⁵⁶

Results and Discussion

Before examining the Raman spectra, we first validated our AIMD approach against the experimental gas-phase and static normal mode IR spectra of DMSO. Vibrations in DMSO have been previously assigned based on a combination of experimental IR and Raman spectroscopy and normal coordinate analyses.^{57,58} These previous works also considered deuterated DMSO; however, in the present study we only concern ourselves only with non-deuterated isotopologue DMSO. Our normal coordinate analysis is in agreement with the assignment of the lower frequency feature in the C-H-stretching region to the symmetric C-H stretch and the higher frequency feature assignment to the degenerate stretch. Table 1 gives the harmonic and anharmonic frequencies from the normal mode analysis, along with the mode assignments and irreducible representations of the modes. We use the same labeling conventions as Horrocks and Cotton.⁵⁷ From this static analysis we can see that the degenerate stretch feature is composed of four fundamental transitions while the symmetric stretch feature is composed of two fundamentals. Figure 1 shows the IR spectrum computed analytically from the harmonic normal mode analysis at the ground state minimum and that obtained from the MD simulations. These are compared with the experimental

gas-phase IR spectrum taken from the NIST database.⁵⁶ Both simulated spectra overestimate the frequencies of the features as well as the spacing between features which is not unexpected. After the VPT2 correction to the NMA spectrum, there is significantly better agreement with the experimental spectrum. While the AIMD approach inherently captures the anharmonicity of the potential energy surface, the anharmonic shift that is obtained is proportional to the amplitude of the vibration. Due to the use of classical mechanics for the nuclear dynamics in the AIMD simulation, the energy available to the C-H stretching modes at the simulation temperature of 300 K is significantly below the quantum zero point energy of the modes. This is the origin of the small shift from the harmonic values seen in the AIMD IR spectrum. Some recent work has looked at attempting to capture certain nuclear quantum effects while still performing classical dynamics.^{59–61} The limited exploration of the potential means the AIMD results have to be looked upon with caution. However, given that the anharmonic IR intensities calculated with VPT2 are so similar to the harmonic ones, we feel confident that for this system the main effect of the limited exploration of the potential will be overestimated frequencies. The simulated spectra predict very similar envelopes for the degenerate stretching feature, while the AIMD simulation naturally predicts a broader peak for the symmetric stretching feature. Overall, all simulated results are in reasonable agreement with the experimental measurement.

Table 1: Irreducible representations, mode assignments, and unscaled harmonic frequencies based upon the static normal mode analysis (NMA) and anharmonic frequencies from VPT2. All frequencies are given in wave numbers (cm^{-1}). The labeling follows that of Horrocks and Cotton.⁵⁷

Mode	NMA	VPT2
Degenerate stretches		
$A' \nu_1$	3148.2	2999.1
$A'' \nu_{14}$	3147.1	2998.4
$A' \nu_2$	3139.1	2991.1
$A'' \nu_{15}$	3135.2	2987.8
Symmetric stretches		
$A' \nu_3$	3040.2	2924.0
$A'' \nu_{16}$	3037.9	2921.1

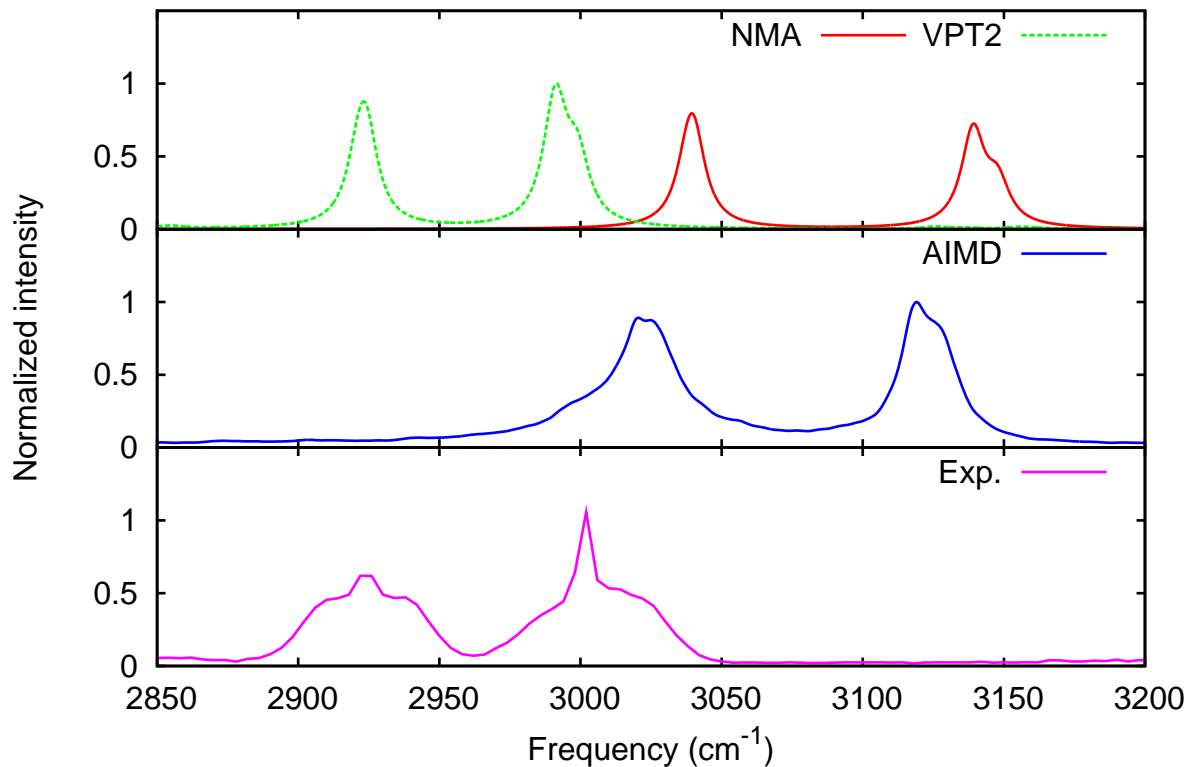


Figure 1: Infrared absorption spectra the standard normal mode analysis (top row) at both the harmonic frequencies (NMA) and anharmonic frequencies (VPT2), MD simulation using Eqs. 1 and 4 (middle row), and experimental gas-phase measurement⁵⁶ (bottom row). The simulated spectra have been artificially broadened by 10 cm⁻¹.

Turning to the Raman spectra shown in Fig. 2, the comparisons between simulated and measured Raman spectra are similar to those observed for the IR spectra. We note that while the experimental Raman spectra were obtained in the liquid phase and the simulations were on an isolated DMSO molecule, previous work on methanol and ethanol found that the experimental gas-phase and liquid-phase Raman spectra were very similar.^{62,63} AIMD and harmonic static frequencies are blue-shifted relative to the experimental spectra, and the spacing between symmetric and degenerate stretching modes is again overestimated. Better agreement is obtained when the intensities of the harmonic spectra are shifted to the anharmonic frequencies, though the intensity of the degenerate stretching peak is overestimated. While Raman intensities are known to be very sensitive to the basis set employed,⁶⁴ previous work⁶⁵ found that the 6-311++G** basis set, the one employed in the current study, had an average percent normalized root mean square deviation of 4.3% when compared to the results obtained with larger basis sets. Both simulation methods give good depolarization ratios for the degenerate stretch, and the AIMD result is in good agreement with the relative intensities of the experimental symmetric stretching and degenerate stretching features.

The experimental Raman spectra present two features that merit further scrutiny. The shoulder and tail on the low frequency side of the parallel orientation symmetric stretch feature (which begins to rise at $\sim 2880\text{ cm}^{-1}$) has been previously assigned to either an overtone of the CH_3 deformation modes that occur in the $1400\text{-}1450\text{ cm}^{-1}$ region,^{66,67} or as a Fermi resonance between the deformation mode overtone and the C-H symmetric stretch.⁵ There is also a small feature in the perpendicular spectrum that occurs at the same frequency as the symmetric stretch; however, as a symmetric mode, this vibrational resonance should be strongly polarized. The same feature is also observed, albeit without comment, in the work of Forel and Tranquille.⁵⁸ Since neither theoretical prediction includes this small depolarized feature, we are hindered in our ability to comment on it. However, its absence does suggest that the feature possibly arises as a result of intermolecular interactions, which are not accounted for in our present simulations. Further work is warranted to address that issue.

In the ensuing analysis, we will focus our discussion on the origin of the shoulder in the symmetric stretching feature.

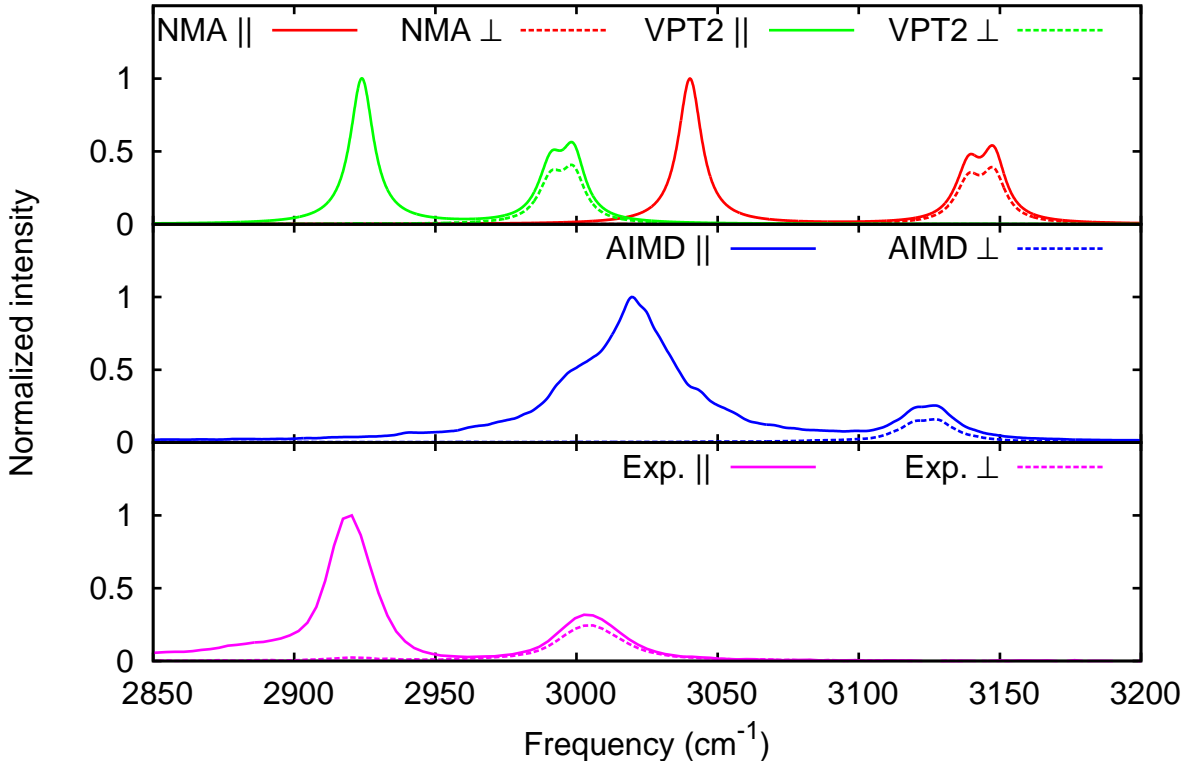


Figure 2: Raman scattering spectra from the normal mode analysis (top) at both the harmonic frequencies (NMA) and anharmonic frequencies (VPT2); from AIMD simulation using Eqs. 2, 3, and 4 (middle); and from the HR-FSRS experiment described above (bottom). The simulated spectra have been artificially broadened by 10 cm^{-1} .

The anharmonic frequency calculation does not predict a Fermi resonance between the symmetric C-H stretching and an overtone of the CH_3 deformation modes. Additionally, the overtones of the deformation modes are predicted to occur between 2583 cm^{-1} and 2855 cm^{-1} . While we cannot readily rule out the shoulder as an overtone, the 66 cm^{-1} gap between the highest frequency deformation mode overtone and the lowest frequency symmetric stretching mode, makes the assignment of this spectral signature to an overtone somewhat questionable. Additionally, an overtone is generally expected to have a much smaller intensity than the fundamental transition. Using the anharmonic IR intensities calculated by VPT2 as a guide

since we do not have access to anharmonic Raman intensities, the difference in intensity of an overtone is at least an order of magnitude smaller than the fundamental. If this holds for the Raman intensities, the intensity of a deformation overtone relative to the symmetric stretching fundamental would be approximately 2 orders of magnitude smaller. Experimentally, the intensity of the shoulder is 10% that of the symmetric stretch. We have verified the results of our static calculations by performing the same calculations with MP2/6-311++G** (NMA and VPT2) and CCSD/6-311++G** (NMA). Those results can be found in the Supporting Information. In the parallel Raman spectrum calculated from the AIMD simulations, there is a clear asymmetry in the symmetric stretch features. It should be noted that while the AIMD simulation is inherently anharmonic since no assumptions are made about the shape of the potential, certain anharmonic effects, such as combination bands and Fermi resonances, are not captured since the nuclear motion is treated classically.³⁰⁻³² In order to address the origin of the shoulder observed in the parallel spectrum, we calculated the vibrational density of states from the Fourier transform of the autocorrelation function of the mass-weighted atomic velocities.³⁰ For additional detail, we separated the contributions by element. As expected, carbon and hydrogen are the only elements that contribute to the C-H stretching region (Fig. 3).

Based upon the normal mode analysis, only the in-phase, symmetric C-H stretch contributes to the symmetric stretch feature in the Raman spectra. To ascertain the contribution of the two symmetric stretching modes to the AIMD spectra, we have computed the Fourier transforms of the autocorrelation functions of the symmetry coordinates for the in-phase and out-of-phase symmetric C-H stretching modes (ν_3 and ν_{16} , respectively). These are given in terms of the C-H bond lengths (r) as

$$S_3 = 6^{-1/2} (r_1 + r_2 + r_3 + r_4 + r_5 + r_6) \quad (5)$$

$$S_{16} = 6^{-1/2} (r_1 + r_2 + r_3 - r_4 - r_5 - r_6) \quad (6)$$

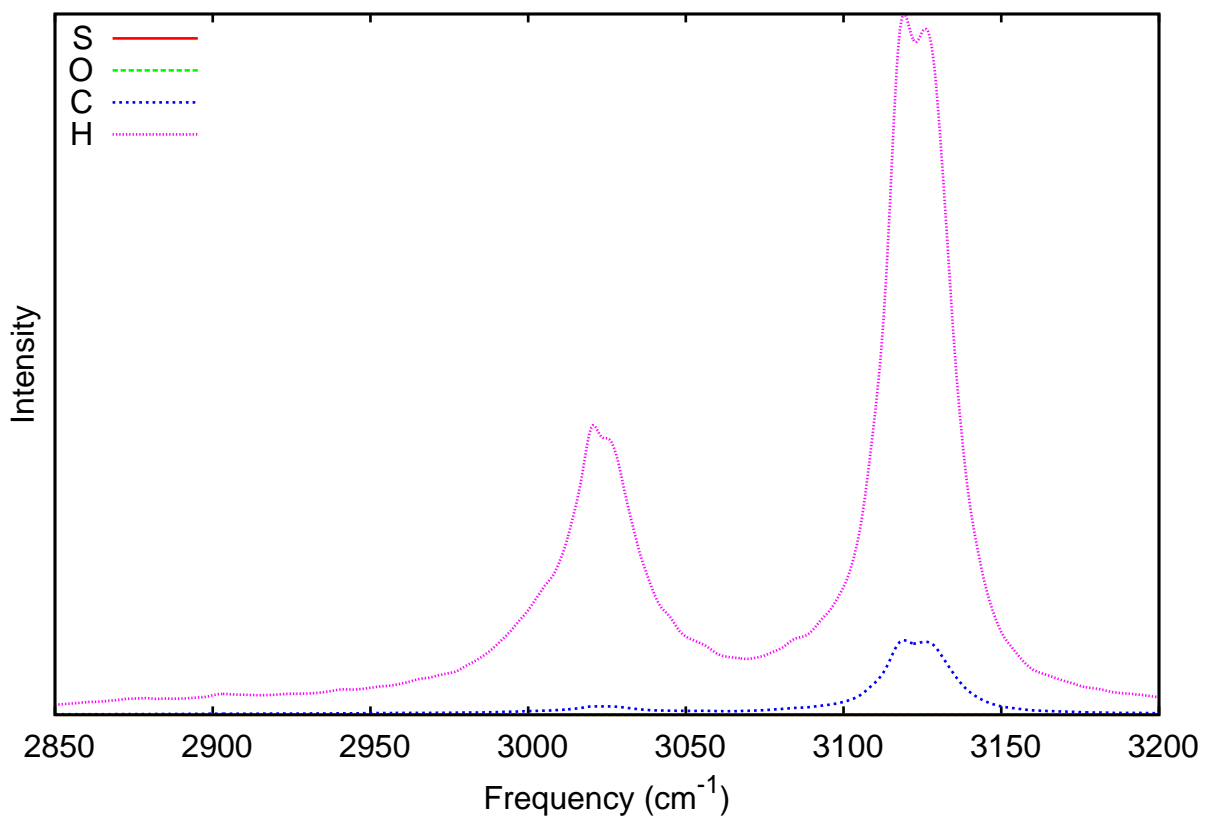


Figure 3: Element-wise decomposition of the vibrational density of states calculated from the Fourier transform of the momentum autocorrelation function.

where r_1 through r_3 cover one methyl group and r_4 through r_6 cover the other methyl group. A full list of symmetry coordinates for DMSO can be found in the work of Horrocks and Cotton.⁵⁷

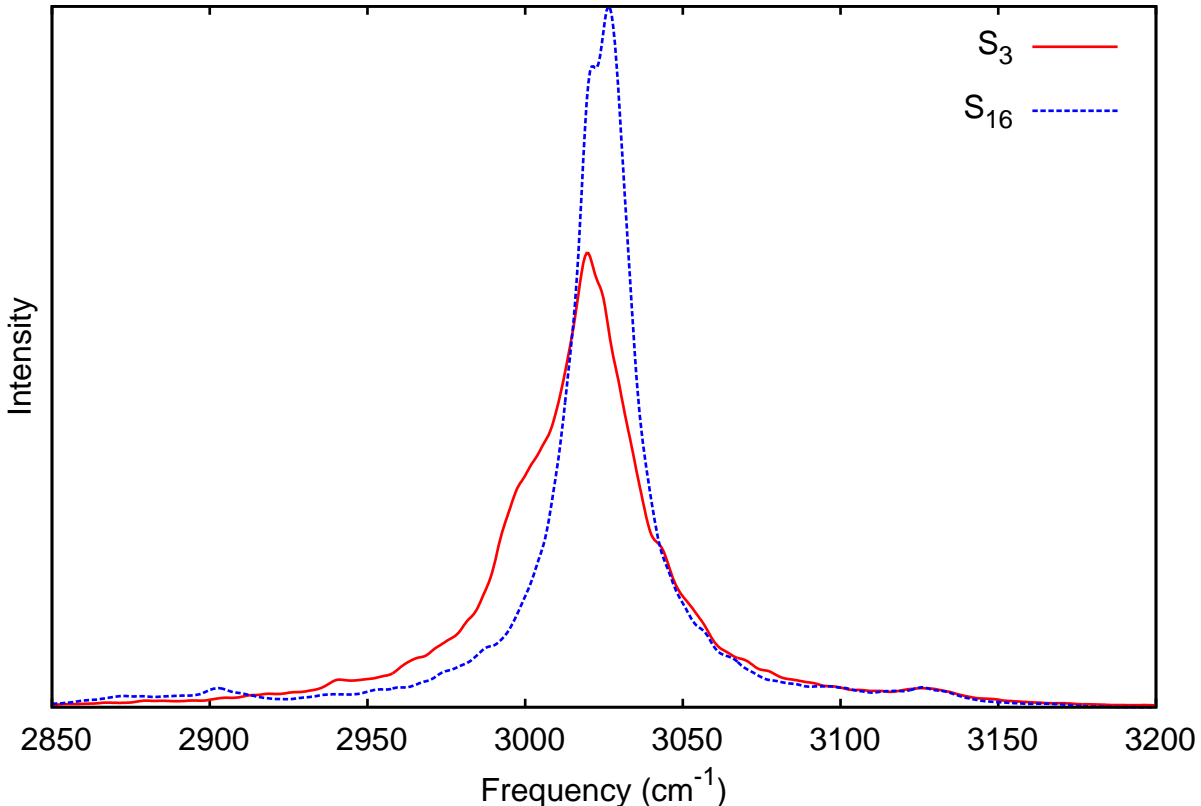


Figure 4: Fourier transform of the autocorrelation functions of the symmetry coordinates for the symmetric C-H stretching modes, Eqs. 5 and 6.

We can see from Fig. 4 that the in-phase mode, S_3 , features the same envelope as the calculated Raman parallel spectrum, in agreement with the selection rules derived from the static calculations. This suggests that the shoulder on the Raman spectrum could be a finite temperature effect rather than an overtone or a Fermi resonance. Recall that for an anharmonic potential the frequency is dependent upon the amplitude of vibration. Except for an isolated diatomic molecule, there is no reason to assume that the amplitude of a vibration will remain constant over the course of a molecular trajectory. If there is any anharmonicity in the potential, then variations in the amplitude of a vibration would lead

to a distribution of frequencies, and thus, to vibrational line broadening. We note that it is implicitly assumed that each vibration has a fixed amplitude in the static calculations, which is why only a single frequency is calculated for each mode, even for the perturbative anharmonic correction. To further explore this effect, we calculated the energy of DMSO as the atoms were displaced along the in-phase and out-of-phase stretching modes.

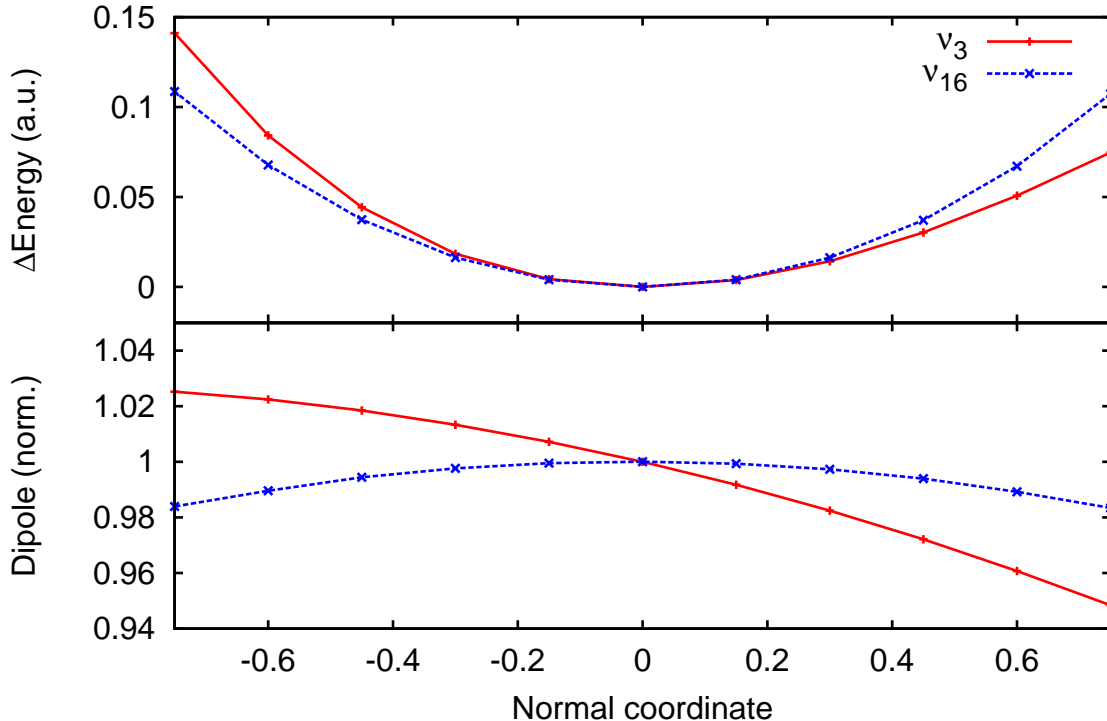


Figure 5: Energy in atomic units as a function of normal mode coordinates for the symmetric C-H stretching modes (top). The energy is referenced to that of the ground state minimum. The in-phase mode (ν_3) potential shows a clear, significant cubic component, while the out-of-phase mode potential is far more symmetric. The bottom panel shows the corresponding dipole moment magnitudes. The dipoles have been normalized to the equilibrium value.

Figure 5 clearly demonstrates that the in-phase mode, ν_3 , has significant anharmonicity; in particular, there is a clear cubic component to the potential. Due to the cubic nature of the potential, the dipole moment of DMSO is not symmetric about displacements along the in-phase normal mode (bottom panel Fig. 5). This cubic contribution is important as

it will give rise to an asymmetric line shape as different parts of the potential are explored. The standard practice of dressing the results of a static calculation with a Lorentzian or Gaussian function to mimic broadening completely misses this asymmetry in the line shape. These characteristics of the potential could explain the appearance of a shoulder on the low frequency side of the symmetric stretching feature in the Raman spectrum. Based on the evidence from the anharmonic static calculations and the AIMD simulations, we propose that the observed shoulder on the symmetric stretching feature is due to thermal broadening of the in-phase symmetric stretching mode.

Conclusions

We have described and demonstrated a powerful new functionality of NWChem: Gaussian basis set based Born-Oppenheimer molecular dynamics. The molecular dynamics module leverages the scalability of NWChem to allow for large-scale molecular dynamics simulations. As a prototypical application, we have used this new module in concert with a more conventional static normal mode analysis, to perform a somewhat detailed analysis of the C-H stretching region of the Raman spectra of DMSO. Our anharmonic normal mode analysis calls into question the previous experimental assignment of the shoulder on the symmetric C-H stretching peak as an overtone or Fermi resonance. No Fermi resonance between the C-H stretching modes and the CH₃ deformation modes is predicted, and the overtones of the deformation modes are at least 60 cm⁻¹ away from the C-H stretching modes and expected to have an intensity far below what is seen in experiment. The AIMD simulations also shows significant broadening of the in-phase symmetric C-H stretching resonance. This result is rationalized in terms of the strong cubic component of the in-phase symmetric stretching mode and the asymmetric dipole moment with displacements along this mode. Our findings therefore lead us to suggest that the shoulder is due to thermal broadening of the symmetric stretching resonance.

Our results highlight the advantage of combining traditional normal mode analyses with AIMD-based vibrational spectra. The normal modes from the static calculations allow for more detailed interpretation of the AIMD results, while AIMD offers a detailed analysis of the role of anharmonicities predicted with the static calculations. In future work we will expand our simulations of vibrational spectroscopies to include sum frequency generation (SFG) spectroscopy. The high-resolution and low signal-to-noise ratio of new SFG techniques^{5,6,34,35} present the opportunity to test computational predictions and would benefit greatly from the interpretive power of simulations.

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Supporting Information Available

Comparison of microcanonical and canonical ensemble results for the AIMD IR spectrum, and MP2 and CCSD normal mode analyses, with VPT2 corrections for the MP2 results. This material is available free of charge via the Internet at <http://pubs.acs.org/>.

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