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ABSTRACT

Accurate and efficient simulation of vibrational Raman spectra for systems with strong anharmonicity and nuclear quantum effects remains challenging. Herein, we apply the recently developed constrained nuclear-electronic orbital (CNEO) framework to simulate Raman spectra. We implement analytic static polarizabilities within CNEO density functional theory (CNEO-DFT) and compute Raman spectra using both CNEO harmonic analysis and CNEO molecular dynamics (CNEO-MD). In the harmonic analysis approach, vibrational frequencies are obtained by diagonalizing the mass-weighted CNEO Hessian, and Raman intensities are derived from the projected derivatives of the polarizability with respect to normal-mode coordinates. In CNEO-MD, both frequency and intensity information are extracted from the Fourier transform of the projected polarizability time-derivative autocorrelation function. Applications to formic acid and the mixed water dimer/trimer system show that, compared to conventional DFT, CNEO-DFT achieves substantially improved accuracy, particularly for modes with significant hydrogen motion. Overall, the CNEO framework provides an accurate and efficient approach for simulating vibrational Raman spectra and is especially promising for systems in which hydrogen motion plays a critical role.

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I. INTRODUCTION

Vibrational Raman spectroscopy is a powerful technique for probing the static and dynamic properties of chemical systems, from isolated molecules to condensed-phase environments.^{1–10} It enables nondestructive, real-time measurements and has broad applications in chemistry, materials science, and biology.^{11–13} Computational simulations of Raman spectroscopy complement experiments by predicting spectra, revealing underlying physical mechanisms, and providing atomistic insights.^{5,8,14–29}

The most widely used approach for simulating vibrational Raman spectra is harmonic analysis,^{14,15,17} which assumes a harmonic potential energy surface (PES) around the stationary geometry. In this way, vibrational frequencies are obtained by diagonalizing the mass-weighted Hessian matrix, and Raman intensities are obtained from the first derivatives of the polarizability tensor with respect to mass-weighted normal-mode coordinates.^{14,15,17}

Because of its low computational cost, this approach is widely used in practical applications.^{14,17,30–33} However, harmonic analysis neglects anharmonicity and intermode anharmonic couplings, which can lead to discrepancies between theoretical predictions and experimental results. To mitigate this issue, empirical vibrational scale factors are often applied to harmonic frequencies to improve agreement with experiments.^{34,35} However, the optimal values of such scale factors strongly depend on the underlying electronic structure method and basis set, limiting their transferability and predictive power.

A variety of methods that go beyond the harmonic approximation have been developed to overcome the limitations of harmonic analysis and achieve a more accurate description of vibrational motions. One widely used and computationally efficient method is vibrational second-order perturbation theory (VPT2) and its generalized variant (GVPT2), which introduce anharmonic corrections to harmonic frequencies and polarizability derivatives, thereby

improving agreement with experiment.^{22,36–38} Another family of approaches consists of vibrational wave-function-based methods, which are built upon the vibrational self-consistent field (VSCF)^{39,40} framework. Extensions include vibrational configuration interaction (VCI),^{41,42} vibrational coupled cluster (VCC),^{43,44} and vibrational Møller–Plesset theory (VMP),^{45–47} with the second-order variant (VMP2) also known as correlation-corrected VSCF (cc-VSCF). In these methods, the vibrational Schrödinger equation is solved approximately to obtain vibrational wave functions, after which transition polarizabilities and hence Raman intensities can be evaluated using response theory.⁴⁸ These approaches have been successfully applied to simulate vibrational Raman spectra of a variety of systems and are particularly effective for predicting overtone and combination bands due to their explicit quantum mechanical treatment of nuclear motion.^{24,26,29} However, applications of these methods to large molecular systems remain computationally demanding, primarily because of the high dimensionality of the PESs. To mitigate this challenge, strategies employing semiempirical PESs have been explored to reduce computational cost while maintaining reasonable accuracy.²⁰

In addition to the static approaches above, dynamic approaches offer an alternative way by explicitly simulating nuclear motion in time. In these methods, Raman spectra are derived from the Fourier transform of the polarizability autocorrelation function. Based on this, classical molecular dynamics (MD)—particularly *ab initio* molecular dynamics (AIMD)—propagates nuclear trajectories on a PES, thereby capturing some anharmonicity and intermode coupling through finite-temperature dynamics.^{21,49} However, because access to anharmonic regions occurs primarily via limited thermal motion, classical MD typically underestimates intrinsic anharmonic effects. Path-integral (PI)-based techniques, such as centroid molecular dynamics (CMD),^{50,51} and ring polymer molecular dynamics (RPMD),^{52,53} can incorporate anharmonicity and nuclear quantum effects (NQE) in the simulation of vibrational Raman spectra.^{23,25,28} However, these PI-based approaches also have known limitations for vibrational spectroscopy: RPMD can exhibit spurious resonances arising from the internal ring-polymer modes,^{54–56} while CMD suffers from the curvature problem that distorts high-frequency vibrational modes.^{56,57} Several methodological variants have been developed to mitigate these issues, including thermostatted RPMD (TRPMD),⁵⁸ which damps internal-mode resonances by applying a Langevin thermostat to internal modes of the ring polymer, and (fast)-quasi CMD [(f)-QCMD],^{59,60} which reduces curvature artifacts by replacing Cartesian centroids with curvilinear centroids.

The fact that more accurate methods are computationally expensive, whereas faster approaches either treat nuclei classically or rely on empirical corrections, underscores the need for techniques that can simulate vibrational Raman spectra both accurately and efficiently. Recently, our group developed constrained nuclear-electronic orbital density functional theory (CNEO-DFT),^{61–63} which provides an efficient framework to incorporate NQE, particularly nuclear quantum delocalization, into an effective PES. CNEO-DFT harmonic analysis has shown accuracy comparable to, and in some cases better than, that of DFT-VPT2 in predicting vibrational frequencies.⁶⁴ Moreover, MD simulations on CNEO surfaces (CNEO-MD) have successfully simulated infrared (IR) spectra of highly anharmonic systems involving hydrogen, including a variety of water clusters and shared-proton complexes.^{65,66} However, while

IR spectroscopy, which is governed by dipole-moment-based selection rules, has been explored within the CNEO framework, Raman spectroscopy, which follows polarizability-based selection rules, has not. Herein, we extend the CNEO framework by implementing analytic static polarizabilities within CNEO-DFT and use them for vibrational Raman spectra simulations.

This paper is organized as follows. Section II briefly reviews the CNEO framework and presents the implementation of static polarizability calculations and methods of Raman spectra simulation within this framework. Section III provides computational details. Section IV presents and discusses the results, beginning with CNEO-DFT polarizability calculations, followed by calculation of vibrational Raman spectra for several molecular systems involving hydrogens. Finally, Sec. V offers concluding remarks.

II. METHOD

A. CNEO framework

The CNEO framework originates from multicomponent quantum chemistry,^{67–70} in which both electrons and nuclei are treated quantum mechanically. In conventional multicomponent DFT,^{68,71,72} which is also commonly known as nuclear-electronic orbital DFT (NEO-DFT),⁷³ the total ground-state energy can be obtained by minimizing the multicomponent energy functional, which depends on both the electronic density ρ^e and the set of quantum nuclear densities $\{\rho^n\}$:

$$E = \min_{\rho^e, \{\rho^n\}} E[\rho^e, \{\rho^n\}]. \quad (1)$$

In NEO-DFT, for any fixed set of classical nuclear coordinates, the quantum nuclei are relaxed to their ground-state density distributions. The resulting total energy, which is solely a function of the classical coordinates, defines the NEO PES with reduced dimensionality compared to the conventional all-nuclear PES. This corresponds to an adiabatic picture in which quantum nuclei are assumed to respond instantaneously to the motion of the classical nuclei. As a result, harmonic frequencies obtained directly from NEO-DFT generally do not correspond to experimental vibrational frequencies. In practice, specialized treatments such as NEO-DFT(V)^{74,75} or NEO Ehrenfest dynamics^{76,77} are required.

In contrast, CNEO-DFT offers an alternative formulation in which the conventional concept of molecular geometry is retained. This is achieved by treating quantum nuclei as distinguishable particles, each associated with a classical coordinate defined by the expectation value of its position operator:^{61,62}

$$\langle \mathbf{r} \rangle^u = \langle \phi_1^{n,u} | \hat{\mathbf{r}} | \phi_1^{n,u} \rangle = \mathbf{R}^u. \quad (2)$$

Here, $\hat{\mathbf{r}}$ is the position operator, $\langle \mathbf{r} \rangle^u$, $\phi_1^{n,u}$, and $\mathbf{R}^u$ denote, respectively, the position expectation value, the occupied nuclear orbital, and the classical coordinate of the u th quantum nucleus. Note that because of the distinguishable-particle treatment, each quantum nucleus corresponds to a single occupied nuclear orbital labeled with subscript 1. This treatment is justified by the fact that quantum nuclei remain highly localized and therefore can be assumed distinguishable, each described by its own local nuclear orbital.

The ground state is then determined through a constrained energy minimization procedure, with the following additional terms introduced into the Lagrangian:⁶¹

$$\sum_u \mathbf{f}^u \cdot \langle \phi_1^{n,u} | \hat{\mathbf{r}} - \mathbf{R}^u | \phi_1^{n,u} \rangle, \quad (3)$$

where $\mathbf{f}^u$ is the Lagrange multiplier associated with the position expectation constraint for the u -th quantum nucleus. The stationary condition of the Lagrangian with respect to nuclear and electronic orbitals yields a set of coupled electronic and nuclear Kohn–Sham equations:⁶¹

$$\begin{aligned} \left(-\frac{1}{2} \nabla^2 + V^e \right) \phi_p^e &= \varepsilon_p^e \phi_p^e, \\ \left(-\frac{1}{2M^u} \nabla^2 + V^{n,u} + \mathbf{f}^u \cdot (\mathbf{r} - \mathbf{R}^u) \right) \phi_p^{n,u} &= \varepsilon_p^{n,u} \phi_p^{n,u}. \end{aligned} \quad (4)$$

Here, ε_p^e is the orbital energy of the p -th electronic orbital, and $\varepsilon_p^{n,u}$ is the orbital energy of the P -th nuclear orbital of the u -th quantum nucleus. V^e is the Kohn–Sham effective potential of the electronic orbitals, which includes the Hartree potential, external potential, electron–nuclear correlation potential, and electronic exchange–correlation potential. $V^{n,u}$ is the Kohn–Sham effective potential of the nuclear orbitals of the u -th quantum nucleus, which mainly includes the Hartree potential, external potential, and electron–nuclear correlation potential. M^u is the mass of the u -th quantum nucleus. The additional term in the nuclear Kohn–Sham equation, $\mathbf{f}^u \cdot (\mathbf{r} - \mathbf{R}^u)$, comes from the position expectation constraint for the u -th nucleus. By solving these coupled Kohn–Sham equations self-consistently under the nuclear position expectation constraints, one can obtain the CNEO-DFT ground-state energy as a function of both the classical nuclear positions and the quantum nuclear position expectation values, thereby defining the CNEO effective PES.⁶¹ This full-dimensional effective PES inherently incorporates NQEs, particularly nuclear quantum delocalization, which is critical for accurately describing vibrational spectra and hydrogen-related transfer processes.^{61,63,65,66,78}

In CNEO-MD, the CNEO effective PES serves as the guiding potential for classical nuclear propagation, which is justified by the constrained minimized energy surface molecular dynamics (CMES-MD) formulation.^{63,79} The working equations for quantum nuclei in CNEO-MD are

$$\begin{aligned} m \frac{d\langle \mathbf{R} \rangle}{dt} &= \langle \mathbf{P} \rangle, \\ \frac{d\langle \mathbf{P} \rangle}{dt} &= -\nabla_{\langle \mathbf{R} \rangle} V_{\text{CNEO}}(\langle \mathbf{R} \rangle), \end{aligned} \quad (5)$$

where $\langle \mathbf{R} \rangle$ and $\langle \mathbf{P} \rangle$ are the position and momentum expectation values of the quantum nuclei, respectively. Formally, these equations are identical to those of classical nuclei, except that the classical positions and momenta are replaced by the corresponding position and momentum expectation values of quantum nuclei. CNEO-MD effectively incorporates NQEs into MD while retaining essentially the same computational cost as conventional AIMD.⁶⁵ For vibrational spectra in particular, CNEO-MD has been shown to provide significantly improved descriptions for modes involving hydrogen motions.^{63,65,66}

B. Static polarizability and vibrational Raman spectra within the CNEO framework

Raman spectroscopy is based on the inelastic scattering of light. When an incident photon interacts with a molecule, it can transiently excite the system to a higher energy state. The molecule then relaxes back to a different vibrational level of the ground electronic state, resulting in frequency shifts of the scattered photon that reflect the vibrational energy spacing of the system. For non-resonance vibrational Raman scattering, the scattering cross section has the following dependence:^{15,17}

$$I(\omega) \propto (\omega_L - \omega)^4 \sum_i \rho_i \delta(-\omega + \omega_f - \omega_i) |\mathbf{p}_L^T \alpha_{fi} \mathbf{p}_S|^2, \quad (6)$$

where ω_L is the frequency of the incident photon, typically in the visible range, and ω denotes the frequency shift between the incident and scattered photon. For the more commonly measured Stokes Raman scattering, ω is positive, corresponding to energy transfer from the incident photon to the molecule. $\omega_i = E_i/\hbar$ and $\omega_f = E_f/\hbar$ are the angular frequencies of the initial and final vibrational states, respectively. $\mathbf{p}_L$ and $\mathbf{p}_S$ denote the polarization vectors of the incident and scattered light, respectively. ρ_i represents the population of the initial vibrational state, and α_{fi} is the transition polarizability tensor for the transition from the initial vibrational state $|v^i\rangle$ to the final vibrational state $|v^f\rangle$,

$$\alpha_{fi} = \langle v^f | \hat{\alpha} | v^i \rangle, \quad (7)$$

with $\hat{\alpha}$ the static polarizability operator.

The static polarizability is a tensor that describes the response of the dipole moment of a molecule to an applied external electric field or, equivalently, the second derivative of the total energy with respect to the applied electric field:

$$\alpha \equiv \frac{\partial \mu}{\partial \mathbf{F}} = -\frac{\partial^2 E}{\partial \mathbf{F}^2}. \quad (8)$$

Under the influence of the applied electric field $\mathbf{F}$, the CNEO Kohn–Sham equations become

$$\left(-\frac{1}{2} \nabla^2 + V^e + \mathbf{F} \cdot \mathbf{r} \right) \phi_p^e = \varepsilon_p^e \phi_p^e, \quad (9)$$

$$\left(-\frac{1}{2M^u} \nabla^2 + V^{n,u} + \mathbf{f}^u \cdot (\mathbf{r} - \mathbf{R}^u) - Z^u \mathbf{F} \cdot \mathbf{r} \right) \phi_p^{n,u} = \varepsilon_p^{n,u} \phi_p^{n,u}, \quad (10)$$

where Z^u is the nuclear charge of the u -th quantum nucleus. The electronic equation closely resembles that in conventional DFT in the presence of an external electric field. However, the main difference is that in conventional DFT, only the electronic response to the external electric field is considered, whereas in CNEO-DFT, the quantum nuclei are allowed to respond. Importantly, the positions of the quantum nuclei are still constrained to their designated position expectation values, and therefore the nuclear density does not directly contribute to the induced dipole. Nevertheless, because the electronic and nuclear equations are coupled, the redistribution of the quantum nuclear density has some indirect influence on the electronic response and thus the overall polarizability.

Based on the previously developed CNEO coupled-perturbed Kohn–Sham equations,⁶⁴ we can derive the analytic polarizability as follows (see the [supplementary material](#) for more details):

$$\begin{aligned}\alpha_{kl} &= -\frac{\partial^2 E_{\text{CNEO}}}{\partial F_k \partial F_l} \\ &= -2 \sum_i^{\text{occ}} \sum_p^{\text{all}} U_{pi}^k r_{pi}^l + 2 \sum_u^{\text{nuc}} \sum_p^{\text{all}} U_{p1}^{uk} r_{p1}^{ul} \\ &= 2 \sum_i^{\text{occ}} \sum_p^{\text{all}} U_{pi}^k r_{pi}^l,\end{aligned}\quad (11)$$

where k, l denote the x, y , or z directions, i is the index for the occupied electronic orbitals, and u is the index for the u -th quantum nucleus. The index $p(P)$ goes over all electronic (nuclear) orbitals. U_{pi}^k denotes the element of the transformation matrix that connects the unperturbed electronic orbital coefficients to their first-order perturbed electronic orbital coefficients, which can be obtained from the CNEO coupled-perturbed Kohn–Sham equations with an electric field applied along the k direction, and r_{pi}^l is the electronic dipole matrix element along the l direction. U_{p1}^{uk} and r_{p1}^{ul} are defined analogously for the u -th nucleus. Note that for nuclear orbitals, the occupied orbital index can only be 1 because of the distinguishable particle treatment; thus, each nucleus possesses only a single occupied orbital. In addition, note that because of the imposed position constraint, the second term in the middle line of Eq. (11) vanishes, leaving only the first term (see the [supplementary material](#) for more details).

With the calculated polarizabilities, Raman intensities can be obtained using either CNEO-DFT-based harmonic analysis or CNEO-MD, following procedures analogous to those used in conventional DFT or AIMD.^{21,49}

In harmonic analysis, the polarizability is expressed as a Taylor series with respect to normal mode displacements around the equilibrium geometry, and the total vibrational wave function is approximated by the product of the harmonic oscillator wave functions of the normal modes. Under this treatment, the scattering cross section in Eq. (6) becomes^{15,17,21}

$$I(\omega) \propto \sum_k (\omega_L - \omega)^4 \frac{\beta \hbar}{\omega (1 - e^{-\beta \hbar \omega})} \left| \mathbf{p}_L^T \frac{\partial \alpha}{\partial Q_k} \mathbf{p}_S \right|^2 \delta(\omega_k - \omega). \quad (12)$$

Here, Q_k represents the k -th mass-weighted harmonic normal mode and ω_k its corresponding harmonic frequency, both obtained by diagonalizing the mass-weighted Hessian matrix at the optimized geometry. The polarizability derivatives with respect to normal modes ($\partial \alpha / \partial Q_k$) are evaluated numerically in practice.

For dynamical calculations, by expanding the delta function in Eq. (6) in the time domain, the scattering cross section can be expressed as the Fourier transform of the quantum autocorrelation function of the projected polarizability ($\mathbf{p}_L^T \dot{\alpha} \mathbf{p}_S$),²¹

$$I(\omega) \propto \frac{1}{2\pi} (\omega_L - \omega)^4 \int_{-\infty}^{+\infty} e^{-i\omega t} \langle (\mathbf{p}_L^T \dot{\alpha}(0) \mathbf{p}_S) (\mathbf{p}_S^T \dot{\alpha}(t) \mathbf{p}_L) \rangle dt. \quad (13)$$

Obtaining the exact quantum autocorrelation function is generally challenging. Nevertheless, based on the principle of quantum–classical correspondence, quantum correction factors are commonly used to build the connection between quantum and classical autocorrelation functions, thereby enabling classical MD to

simulate vibrational spectra. Various quantum correction factors have been proposed in the past based on different models,^{80–82} and one of the most widely used is derived from the harmonic oscillator model. Specifically, for a one-dimensional harmonic oscillator in the canonical ensemble, the Fourier transforms of the quantum and classical position autocorrelation functions differ only by a frequency-dependent factor:

$$\frac{\int_{-\infty}^{\infty} dt e^{-i\omega t} \langle \hat{x}(0) \hat{x}(t) \rangle_{\text{qm}}}{\int_{-\infty}^{\infty} dt e^{-i\omega t} \langle \hat{x}(0) \hat{x}(t) \rangle_{\text{cl}}} = \frac{\beta \hbar \omega}{1 - e^{-\beta \hbar \omega}}. \quad (14)$$

Because the polarizability is assumed to depend linearly on the normal coordinates around the equilibrium geometry,¹⁵ the same factor can be applied to the polarizability autocorrelation function. In this way, the Raman intensity can be calculated with

$$I(\omega) \propto \frac{(\omega_L - \omega)^4}{2\pi} \frac{\beta \hbar \omega}{1 - e^{-\beta \hbar \omega}} \int_{-\infty}^{+\infty} e^{-i\omega t} \langle (\mathbf{p}_L^T \dot{\alpha}(0) \mathbf{p}_S) (\mathbf{p}_L^T \dot{\alpha}(t) \mathbf{p}_S) \rangle dt, \quad (15)$$

which requires evaluating the time-dependent polarizability tensor along an ensemble of classical MD trajectories to construct the autocorrelation function. In practice, a formally equivalent expression based on the autocorrelation function of the projected polarizability time derivative [$\mathbf{p}_L^T \dot{\alpha}(t) \mathbf{p}_S$] is commonly employed for better convergence:^{21,27}

$$I(\omega) \propto \frac{(\omega_L - \omega)^4}{2\pi \omega} \frac{\beta \hbar}{1 - e^{-\beta \hbar \omega}} \int_{-\infty}^{+\infty} e^{-i\omega t} \langle (\mathbf{p}_L^T \dot{\alpha}(0) \mathbf{p}_S) (\mathbf{p}_L^T \dot{\alpha}(t) \mathbf{p}_S) \rangle dt, \quad (16)$$

where the projected polarizability time derivative is obtained numerically.

In gas-phase experimental measurements, molecular orientations are isotropically distributed. Then, the orientational averages of both the projected polarizability and the projected polarizability time-derivative autocorrelation function depend only on the polarization geometry of the incident and scattered light.

Specifically, in harmonic analysis, the orientational average of the squared projected derivative of the polarizability with respect to a normal mode can be expressed in terms of two rotational invariants of the polarizability derivative tensor,¹⁵ namely, the isotropic invariant,

$$I_{\text{iso}} \left(\frac{\partial \alpha}{\partial Q_k} \right) = \frac{\partial(\alpha_{xx} + \alpha_{yy} + \alpha_{zz})}{3 \partial Q_k}, \quad (17)$$

and the anisotropic invariant,

$$I_{\text{aniso}}^2 \left(\frac{\partial \alpha}{\partial Q_k} \right) = \sum_{i < j} \frac{1}{2} \left(\frac{\partial \alpha_{ii}}{\partial Q_k} - \frac{\partial \alpha_{jj}}{\partial Q_k} \right)^2 + 3 \frac{\partial \alpha_{ij}}{\partial Q_k}^2. \quad (18)$$

For the commonly used VV polarization geometry, where the incident and scattered light have parallel polarization directions (the same geometry employed for the reference spectra in this work), the orientational average can be simplified to¹⁵

$$\left(\left| \mathbf{p}_L^T \frac{\partial \alpha}{\partial Q_k} \mathbf{p}_S \right|^2 \right)_{\mathbf{p}_L \parallel \mathbf{p}_S} = I_{\text{iso}}^2 \left(\frac{\partial \alpha}{\partial Q_k} \right) + \frac{4}{45} I_{\text{aniso}}^2 \left(\frac{\partial \alpha}{\partial Q_k} \right). \quad (19)$$

Similarly, for dynamic approaches, the orientational average of the projected polarizability time-derivative autocorrelation function can be simplified to

$$\begin{aligned} & \left(\left(p_L^T \dot{\alpha}(0) p_S \right) \left(p_S^T \dot{\alpha}(t) p_L \right) \right)_{p_L \parallel p_S} \\ &= \frac{1}{9} \langle \text{Tr} [\dot{\alpha}(0)] \text{Tr} [\dot{\alpha}(t)] \rangle + \frac{2}{45} \sum_{i < j} \langle (\dot{\alpha}_{ii} - \dot{\alpha}_{jj})(0) (\dot{\alpha}_{ii} - \dot{\alpha}_{jj})(t) \rangle \\ &+ \frac{4}{15} \sum_{i < j} \langle \dot{\alpha}_{ij}(0) \dot{\alpha}_{ij}(t) \rangle. \end{aligned} \quad (20)$$

Applying Eq. (19) to Eq. (12) and Eq. (20) to Eq. (16) yields the working formulas for Raman spectra from harmonic analysis and from MD simulations, respectively.

III. COMPUTATIONAL DETAILS

All DFT and CNEO-DFT calculations were carried out using a locally modified version of PySCF.^{83–85} Molecular dynamics simulations were performed with the Atomic Simulation Environment (ASE) package,⁸⁶ interfaced with PySCF.

The choice of electronic exchange-correlation functional has a great influence on the simulated vibrational spectra. Previously, our group benchmarked⁶⁶ several commonly used functionals against CCSD(T)^{87,88} for the O–H stretch modes in the water dimer and found that the range-separated hybrid meta-GGA functional ω B97M-V^{89,90} gives the closest agreement with CCSD(T), suggesting minimal errors from the electronic part. In this work, we extended this benchmark to both water dimer and trimer complexes, with the results summarized in Table S1. We found that ω B97M-V remains the best-performing functional, with a mean absolute deviation (MAD) of 18 cm^{−1}. Accordingly, we employed ω B97M-V for the following harmonic analysis and MD-based Raman spectra simulations. For electrons, we used the def2-TZVPPD^{91,92} basis set. For protons, we used the PB4-D⁹³ basis set. The proton basis set convergence results using the PB4-D, PB5-F, and PB6-F proton bases are reported in Table S2. The results show that the polarizability is effectively converged at the PB4-D level. Proton–proton correlation was not considered. Electron–proton correlation was also not included, as a recent benchmark study on CNEO vibrational frequencies⁹⁴ showed that the epc17-1⁹⁵ functional yields inaccurate vibrational frequencies similar to conventional DFT, whereas the epc17-2⁹⁶ functional yields results comparable to CNEO-DFT at the no-epc level. In all calculations, only protons were treated quantum mechanically owing to their more pronounced NQEs relative to heavier nuclei, although a fully quantum treatment is feasible within the CNEO framework.⁶²

For CNEO-MD and AIMD, we employed the NVE equipartition protocol,⁶⁶ which initializes the system at its equilibrium geometry and assigns each normal mode a kinetic energy of $k_B T$. The initial velocity along each normal mode coordinate was given a randomly chosen positive or negative direction. This scheme has been shown to be effective for simulating vibrational spectra of moderate-sized molecular systems.⁶⁶ For formic acid studied in this work, we found that 10 independent trajectories of 2 ps each were sufficient to converge the spectra. In contrast, for both water dimer and trimer complexes, whose dynamics are more complex, we found that at least 20 trajectories were required to ensure adequate statistical

averaging (see Figs. S1–S3 for convergence tests with respect to the number of trajectories). Each trajectory was run for 2 ps with a step size of 0.5 fs at an effective temperature of 300 K. We emphasize that this simulation temperature does not correspond to experimental conditions; rather, it serves as a control parameter that modulates the strength of anharmonic intermode coupling, which is absent in harmonic calculations.⁶⁶

IV. RESULT AND DISCUSSION

A. Polarizability

We begin by examining static polarizabilities, which are key inputs for Raman intensity calculations. Table I summarizes the mean signed error (MSE) and mean absolute deviation (MAD) of the isotropic polarizability, $\alpha_{\text{iso}} = \frac{1}{3} \text{Tr} [\alpha]$ (in Å³), which are computed by comparing DFT and CNEO-DFT calculations with experimental results using five different electronic exchange-correlation functionals (PBE,^{97,98} PBE0,^{99,100} B3LYP,^{101–104} ω B97M-V,^{89,90} and ω B97X¹⁰⁵). The benchmark set, adopted from a previous study,¹⁰⁶ comprises 37 molecules containing main-group elements (C, H, N, O, F, Cl, and P). All polarizabilities are calculated analytically except for ω B97M-V, for which we use finite-difference calculations because the analytic response implementation in PySCF temporarily does not support the VV10 nonlocal correlation.⁸⁹ The raw polarizability data are provided in Section SIII of the [supplementary material](#).

For most functionals, DFT shows a negative MSE, while CNEO-DFT shows a positive one. The DFT MADs lie in the 0.21–0.32 Å³ range, with B3LYP giving the smallest value among the tested functionals. For CNEO-DFT, the largest MAD occurs with PBE and the smallest with ω B97X. Overall, the errors depend strongly on the choice of electronic exchange-correlation functional, which tends to overshadow differences arising from the inclusion of NQEs. Nonetheless, because members of the ω B97 family are known to perform well for vibrational properties,^{107,108} the good performance of CNEO with ω B97M-V and ω B97X functionals likely reflects a more physically consistent description rather than fortuitous error cancellation.

To probe the sources of error more deeply, we note that the polarizability errors in Table I reflect three contributions: (1) electronic-structure error of the functional, (2) NQEs, and (3) differences in optimized geometries between CNEO-DFT and DFT. To separate these effects, we recomputed all polarizabilities at the

TABLE I. MSE and MAD of calculated isotropic polarizabilities (in Å³) relative to experimental values for five electronic exchange-correlation functionals with conventional DFT and CNEO-DFT. For each method, molecular geometries were optimized at the same level of theory prior to polarizability evaluation.

		PBE	PBE0	B3LYP	ω B97M-V	ω B97X
DFT	MSE	0.17	−0.19	−0.09	−0.16	−0.25
	MAD	0.26	0.27	0.21	0.25	0.32
CNEO-DFT	MSE	0.52	0.13	0.24	0.15	0.05
	MAD	0.53	0.20	0.28	0.22	0.17

TABLE II. MSE and MAD of calculated isotropic polarizabilities (in $\text{\AA}^3$) relative to experimental values for CCSD and for CNEO-corrected CCSD obtained with different exchange-correlation functionals. Results are reported at MP2/aug-cc-pVTZ reference geometries (MP2) and at method-specific optimized geometries (OPT).

Geometry		α_{CCSD}	α_{corr}				
			PBE	PBE0	B3LYP	ω B97M-V	ω B97X
MP2	MSE	-0.18	-0.02	-0.03	-0.02	-0.03	-0.04
	MAD	0.30	0.22	0.22	0.22	0.22	0.22
OPT	MSE		0.16	0.14	0.14	0.13	0.12
	MAD		0.26	0.24	0.24	0.24	0.24

MP2¹⁰⁹/aug-cc-pVTZ^{110,111} reference geometries used in the previous benchmark study,¹⁰⁶ which are commonly regarded as reliable equilibrium geometries for small main-group molecules. At these fixed geometries, CCSD polarizabilities from Ref. 106 serve as reference values. In this setup, the deviation of DFT from CCSD approximates the electronic-structure error for each functional, while the difference between CNEO-DFT and DFT indicates the NQEs correction captured by CNEO. We then define a corrected polarizability,

$$\begin{aligned}\alpha_{\text{corr}} &= (\alpha_{\text{CNEO}} - \alpha_{\text{DFT}}) + \alpha_{\text{CCSD}} \\ &= \alpha_{\text{CNEO}} - (\alpha_{\text{DFT}} - \alpha_{\text{CCSD}}),\end{aligned}\quad (21)$$

which can be interpreted as a CCSD polarizability augmented by the CNEO NQEs correction, or equivalently a CNEO-DFT polarizability with electronic-structure error removed. We note that this analysis assumes approximate additivity of electronic-structure and NQEs contributions at the fixed reference geometry.

The raw data for α_{corr} are provided in Tables S3–S7. In Table II, we present the corresponding MSE and MAD relative to experiment and compare them with errors from direct CCSD calculations. Without NQEs corrections, CCSD generally underestimates polarizabilities with a MSE of $-0.18 \text{ \AA}^3$ and a MAD of $0.30 \text{ \AA}^3$. Applying

the CNEO NQEs correction significantly shifts the MSE toward zero (≈ -0.02 to $-0.04 \text{ \AA}^3$) and slightly reduces the MAD to $\approx 0.22 \text{ \AA}^3$ across all functionals tested. This consistently near-zero MSE indicates that the CNEO correction compensates for the systematic error associated with the omission of NQEs in conventional CCSD, while the lower MAD reflects a modest improvement in precision. These results show that CNEO-corrected CCSD recovers the missing NQE contributions in a consistent and reliable manner. Put differently, if electronic-structure error is minimized, CNEO-DFT will yield accurate static polarizabilities.

In practical calculations, however, geometries are typically optimized with the corresponding method rather than fixed at the MP2 level. To assess the impact of geometry, we re-evaluated the CNEO-corrected CCSD values with the geometric effect included. In this protocol, the corrected polarizabilities were still calculated by Eq. (21), but the CNEO-DFT and DFT polarizabilities were computed at their own optimized geometries, thereby incorporating both the CNEO NQEs corrections and the geometric effect. As shown in Table II, including the geometric effect increases the MSE from close to zero to a positive value (≈ 0.12 – $0.16 \text{ \AA}^3$), whereas the MAD changes only slightly. Both metrics remain better than direct CCSD. The positive MSE indicates a modest overestimation introduced when using method-specific optimized geometries. While the origin of this overestimation remains unclear, we hypothesize that electronic-structure errors can enter through geometry. Specifically, optimized structures inherit functional errors, and polarizability is sensitive to geometric changes. Thus, although the electronic-structure error is mitigated via Eq. (21), residual bias may persist in optimized geometries. To test this hypothesis, a natural next step is to evaluate CNEO-MP2 polarizabilities at CNEO-MP2-optimized geometries, which we defer to future work as the methodology has not yet been developed.

B. Formic acid

Having assessed the accuracy of static polarizabilities from CNEO-DFT, we next employ CNEO-MD to simulate vibrational Raman spectra. Formic acid, the simplest carboxylic acid, has been extensively studied for decades and serves as a well-characterized

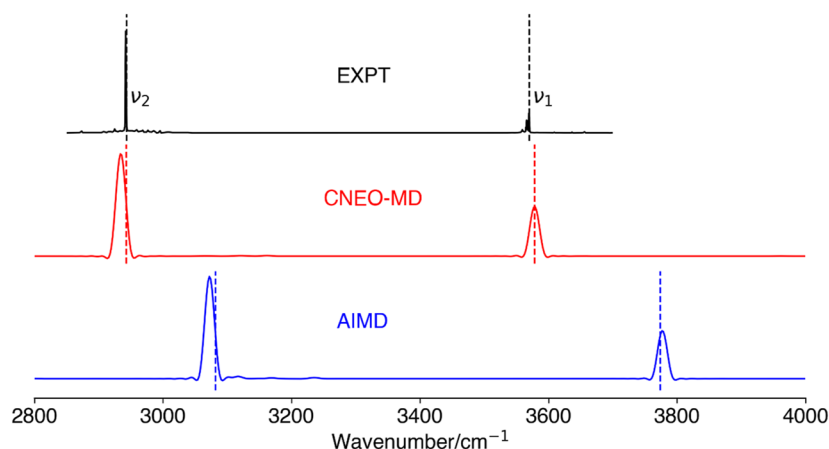


FIG. 1. High-frequency Raman spectra of *trans*-HCOOH from experiment, CNEO-MD, and conventional AIMD. Each spectrum is normalized to have the same maximum intensity. Vertical dashed lines represent experimental peak positions (black) and harmonic frequencies from CNEO-DFT (red) and DFT (blue). Experimental spectra used for comparison were digitized from published Raman jet spectra.¹¹⁵

test system.^{1,4,19,112,113} It exists in two isomeric forms—*trans* and *cis*—arising from rotation around the C–O single bond. In the gas phase, the *trans* isomer is ~ 800 times more abundant than the *cis* isomer.¹¹⁴ Accordingly, we focus on *trans*-formic acid as a prototypical case to evaluate our methods. As a nonlinear five-atom molecule, formic acid has nine vibrational normal modes, including stretching and in-plane and out-of-plane bending motions. For convenience, we label the vibrational modes from ν_1 (highest frequency) to ν_9 (lowest frequency), with their normal-mode displacement vectors shown in Fig. S4. Among the nine modes, O–H and C–H stretches (ν_1 and ν_2) lie in the high-frequency region and are highly anharmonic, whereas the lower-frequency modes are predominantly bending vibrations.

Figure 1 compares the Raman spectrum of *trans*-formic acid in the high-frequency range ($2800\text{--}4000\text{ cm}^{-1}$) from experiment, CNEO-MD, and AIMD. All simulations employed $\omega\text{B97M-V}$ with the def2-TZVPPD electronic basis set and the PB4-D protonic basis set. The vertical dashed lines represent experimental peak positions and harmonic frequencies from CNEO-DFT and DFT. DFT harmonic analysis and AIMD significantly overestimate the O–H (ν_1) and C–H (ν_2) stretching frequencies by ~ 200 and 150 cm^{-1} , respectively, although AIMD partially accounts for anharmonicity via classical finite-temperature propagation on the PES. In contrast, CNEO-DFT harmonic analysis and CNEO-MD reproduce the experimental peak positions within about 10 cm^{-1} . This significant improvement for X–H stretching frequencies is due to the explicit incorporation of NQEs, especially nuclear-quantum delocalization, in CNEO calculations and is consistent with previous CNEO studies.^{63,65,66}

As for intensities, AIMD already shows high-quality agreement with the experimental reference, and CNEO-MD yields similarly accurate results. Although CNEO gives slightly more accurate polarizabilities than conventional DFT, as benchmarked in Subsection IV A, the relative improvement is small, as most molecular polarizabilities are in the range of $1\text{--}10\text{ \AA}^3$ (Tables S3–S7), while the absolute errors for both approaches are on average below $0.3\text{ \AA}^3$. Consequently, any intensity improvement from CNEO is not visually apparent in spectra.

In addition to the high-frequency stretching region, we also investigated the low-frequency portion ($600\text{--}2000\text{ cm}^{-1}$) of the Raman spectrum, as shown in Fig. 2. The modes in this range are comparatively less anharmonic, with smaller deviations between VPT2 and harmonic frequencies,¹¹⁶ and CNEO-MD and AIMD yield similar results in terms of both frequency and intensity. Specifically, modes ν_3 , ν_6 , and ν_9 are dominated by heavy-atom (C, O) motions, and CNEO-MD and AIMD give similar results as heavy nuclei are treated as point charges in both approaches. For modes ν_4 and ν_5 , which correspond to O–H and C–H in-plane bending vibrations, CNEO underestimates the frequencies by $\sim 30\text{ cm}^{-1}$, whereas DFT matches the experimental peaks more closely. This discrepancy does not reflect a limitation of CNEO itself but arises mainly because the $\omega\text{B97M-V}$ functional underestimates these in-plane bending frequencies by $\sim 20\text{ cm}^{-1}$ compared to the CCSD(T) references (see Table S8 of the supplementary material). Consequently, the good agreement between DFT and experiment is due to the error cancellation between the neglect of NQEs and the intrinsic electronic-functional error. If the functional error were eliminated, we anticipate that CNEO would slightly outperform DFT for these modes. Finally, for ν_7 and ν_8 , which involve X–H out-of-plane bending motions and for which $\omega\text{B97M-V}$ frequencies are already close to CCSD(T) references (Table S8), DFT reproduces the experimental results with a deviation of $\sim 30\text{ cm}^{-1}$, while CNEO further improves this agreement, reducing deviations to $\sim 3\text{ cm}^{-1}$ for ν_7 and $\sim 16\text{ cm}^{-1}$ for ν_8 .

A well-known Fermi resonance in *trans*-formic acid occurs between an O–H in-plane bending mode (ν_5) and the overtone of an O–H out-of-plane bending mode ($2\nu_8$). It results in a small peak (ν_{FR}) at around 1220 cm^{-1} in the experimental spectrum.^{117–119} Both CNEO-MD and AIMD simulations capture this feature and produce a resonance peak around 1300 cm^{-1} in the simulated spectra. Notably, Fermi resonance has also been observed with CNEO-MD in a previous study on the HDO molecule.⁶³ However, we acknowledge that methods based on classical MD simulations are generally not expected to rigorously describe inherently quantum-mechanical phenomena such as overtones, combination bands, and Fermi resonances.²¹

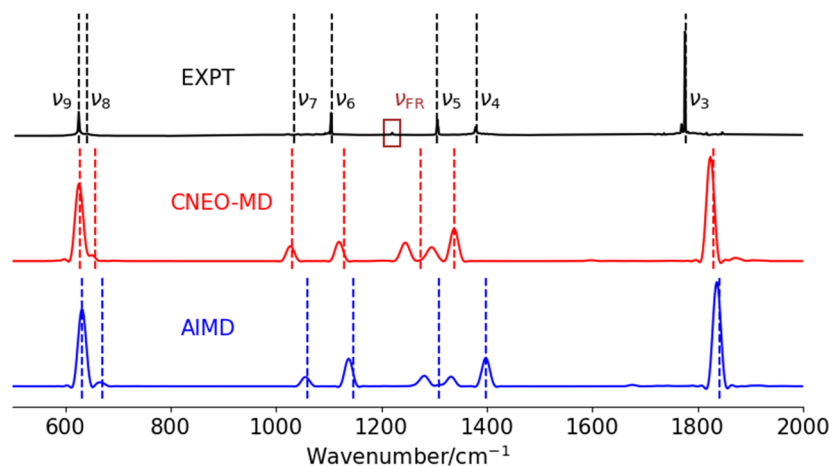


FIG. 2. Low-frequency Raman spectra of *trans*-formic acid obtained from experiment, CNEO-MD, and conventional AIMD. Each spectrum is normalized to the same maximum intensity. Vertical dashed lines denote experimental peak positions (black) and harmonic frequencies from CNEO-DFT (red) and DFT (blue). The brown box highlights the Fermi-resonance peak (ν_{FR} , FR stands for Fermi resonance) between ν_5 and $2\nu_8$. Experimental spectra used for comparison were digitized from published Raman jet spectra.¹¹⁵

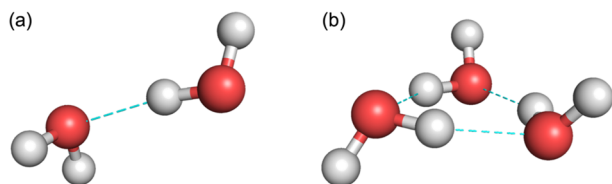


FIG. 3. Schematic representation of (a) the water dimer and (b) the water trimer.

C. Water dimer and trimer

Water clusters are important models for understanding the properties and dynamics of hydrogen-bond networks. They bridge the gap between isolated molecules and bulk water.¹²⁰ The vibrational spectra of the water dimer and trimer have been studied experimentally and theoretically for decades.^{6,121–125} Here, we focus specifically on the O–H stretching modes of these complexes.

In the water dimer [Fig. 3(a)], two water molecules are connected by a single hydrogen bond. The four O–H stretching normal modes comprise the donor free O–H stretch (2f), the donor hydrogen-bonded O–H stretch (2b), and the acceptor symmetric (2as) and asymmetric (2aa) O–H stretches. The water trimer [Fig. 3(b)] forms a cyclic ring in which three water molecules are interconnected by three hydrogen bonds. Notably, this cyclic configuration is asymmetric: one of the three free O–H bonds points to one side of the plane defined by the three oxygen atoms, whereas the other two point to the opposite side. Consequently, the trimer lacks C_3 symmetry, and all three hydrogen-bonded O–H stretches (3b) as well as the three free O–H stretches (3f) are inequivalent.

Before investigating the water dimer and trimer, we first briefly examine the Raman spectrum of the water monomer. The simulated results between 3500 and 4000 cm^{-1} are shown in Fig. S5. Both CNEO-DFT harmonic analysis and CNEO-MD reproduce experimental frequencies with an error below 30 cm^{-1} , in contrast to the $\sim 200 \text{ cm}^{-1}$ errors from DFT harmonic analysis and AIMD. In terms of intensities, the AIMD and CNEO-MD results are comparable, which is similar to the formic-acid case. These results demonstrate the good performance of CNEO in predicting the vibrational features of free O–H stretches, consistent with previous infrared-spectral simulations of gas-phase water molecules.⁶³

Figure 4 compares the experimental Raman jet spectrum of water clusters with the calculated Raman spectra of a 1:1 mixture of water dimer and trimer, with a focus on the O–H stretching region. There are three features in the experimental spectra corresponding to free O–H stretches. The green peak at 3640 cm^{-1} corresponds to the acceptor's symmetric O–H stretch in the dimer (2as), while the yellow peak around 3720 cm^{-1} arises from the acceptor's anti-symmetric O–H stretch (2aa) and the donor's free O–H stretch (2f). The pink feature near 3700 cm^{-1} is attributed to the three free O–H stretches in the trimer (3f), whose close frequencies coalesce into a single peak.

CNEO-DFT harmonic analysis reproduces the frequencies of these modes with less than 40 cm^{-1} deviation from the experimental results, whereas DFT harmonic analysis overestimates them by $\sim 200 \text{ cm}^{-1}$. CNEO-MD predicts similar peak positions to CNEO-DFT, with additional finite-temperature broadening. By contrast, AIMD follows the DFT harmonic-analysis behavior with significantly overestimated peak positions.

Turning to the much more challenging hydrogen-bonded O–H stretch modes, the brown peak near 3600 cm^{-1} in the experimental

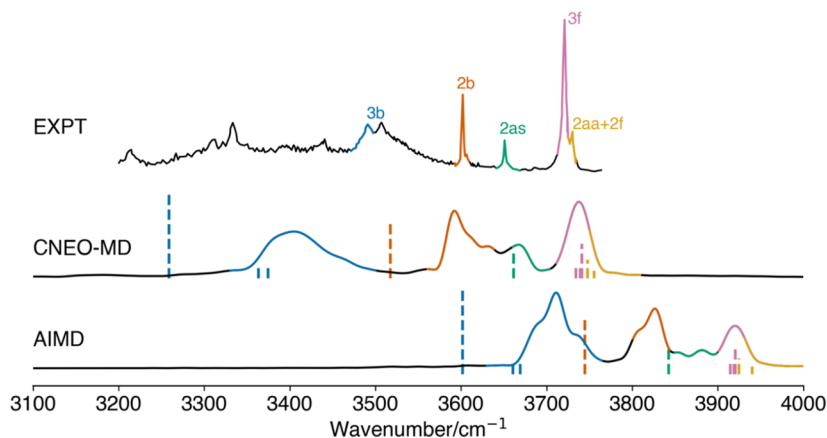


FIG. 4. Experimental and calculated Raman spectra for a mixed water dimer/trimer system from CNEO-MD and AIMD simulations. Dashed lines indicate harmonic frequencies, with heights proportional to the predicted Raman intensities. Peak labels use the numeral to denote the cluster (2 = dimer, 3 = trimer) and letters to denote the mode type: b = hydrogen-bonded O–H stretch, f = free O–H stretch, and as/aa = acceptor symmetric/antisymmetric stretches (in the dimer). The experimental reference is Raman jet spectroscopy of water clusters dominated by monomers, dimers, and trimers, digitized from Ref. 6. Peaks below 3400 cm^{-1} and the peak to the right of 3b arise primarily from larger water clusters (tetramer/pentamer). The monomer fundamental and rovibrational features, as well as the features of larger water clusters above 3600 cm^{-1} , were manually removed to facilitate a clearer comparison with the simulated spectra, because the monomer features are overly saturated and the larger-cluster features make visual comparison difficult. Because the relative dimer/trimer abundance in the experiment is unknown and sensitive to the experimental conditions, a simple 1:1 linear combination of the simulated dimer and trimer spectra for comparison with the experiment was used.

spectrum is attributed to the dimer, while the blue broad peak near 3490 cm^{-1} arises from the trimer and includes contributions from all three of its hydrogen-bonded O–H stretches. The additional feature to the right of the bonded O–H stretch (3b) at around 3510 cm^{-1} has been assigned to tetramers or pentamers.⁶ The hydrogen-bonded O–H stretch modes have strong anharmonic intermode couplings. In particular, the trimer's cooperative hydrogen bonding leads to shorter O···O distances relative to the dimer, further enhancing anharmonicity.^{120,126}

Although CNEO-DFT harmonic analysis includes nuclear-quantum delocalization, its neglect of anharmonic intermode coupling leads to significant underestimation of peak positions—by about 100 cm^{-1} for the dimer and 200 cm^{-1} for the trimer. By contrast, DFT harmonic analysis, which neglects both nuclear-quantum delocalization and anharmonic intermode coupling, overestimates these frequencies by about 140 and 100 cm^{-1} , respectively. This seemingly better performance of DFT harmonic analysis is due to the significant error cancellation between the two missing physical effects.

By incorporating both nuclear-quantum delocalization and intermode anharmonic coupling through finite-temperature simulation, CNEO-MD demonstrates substantially improved accuracy, with errors reduced to about 10 cm^{-1} for the dimer and 90 cm^{-1} for the trimer. In contrast, conventional AIMD, which includes only anharmonic intermode coupling but not nuclear-quantum delocalization, loses the partial error cancellation seen in DFT harmonic analysis and exhibits a much larger error of $200\text{--}300\text{ cm}^{-1}$ for these complexes.

Beyond peak positions, harmonic analysis reveals that, for the water trimer, most Raman intensity within the hydrogen-bonded O–H band arises from the lowest-frequency mode of the three, with only moderate contributions from the two higher-frequency ones. With finite-temperature peak broadening introduced by CNEO-MD and AIMD, these peaks merge into a single asymmetric band with intensity skewed toward the low-frequency side and a tail on the high-frequency side.

We note that, in principle, the intensity information could be used to deconvolute the Raman spectrum and determine the dimer/trimer ratio by comparison with experiment. However, in practice, this is challenging due to the complexity of the experimental spectra. In the original experimental data,⁶ the O–H stretching region is heavily congested by strong monomer rovibrational features and by contributions from larger clusters. Although we manually removed these features when digitizing the experimental spectra to enable a clearer comparison with the simulation results, this procedure introduces uncertainty in the peak intensities and makes a reliable quantitative deconvolution difficult. Consequently, we did not pursue a quantitative determination of the dimer/trimer ratio. Instead, we employed a simple 1:1 combination and limited our analysis to peak positions and shapes, rather than the more delicate relative intensities.

Overall, among the methods tested, CNEO-MD provides the most accurate description of the mixed dimer/trimer spectrum, which essentially reproduces all major features with accurate peak positions and shapes. Although it exhibits a notable underestimation for the hydrogen-bonded O–H stretches in the trimer, it nonetheless captures the correct intensity distribution and mode ordering. This strong overall performance highlights the reliability of

CNEO-MD for simulating Raman spectra in complex hydrogen-bonded systems.

V. CONCLUSIONS

In summary, we implemented analytic static polarizabilities within CNEO-DFT using the coupled-perturbed CNEO Kohn–Sham equations. Building on this capability, we computed Raman spectra using both CNEO-DFT harmonic analysis and CNEO-MD. In harmonic analysis, vibrational frequencies were obtained by diagonalizing the mass-weighted CNEO Hessian, and Raman intensities were obtained from the derivatives of the polarizability with respect to normal-mode coordinates. In CNEO-MD, both frequencies and intensities were extracted from the Fourier transform of the projected polarizability autocorrelation function.

Benchmark tests on a set of gas-phase molecules show that CNEO-DFT yields static polarizabilities comparable to, or slightly more accurate than, conventional DFT. In addition, using a CNEO-corrected CCSD scheme, we demonstrated that the NQEs captured by CNEO can improve agreement with experimental polarizabilities. For vibrational Raman spectroscopy, we evaluated the performance of CNEO-DFT harmonic analysis and CNEO-MD using formic acid and a mixed water dimer/trimer system and compared them with DFT harmonic analysis and conventional AIMD. Among all methods tested, CNEO-MD performed the best, with both NQEs and anharmonic intermode coupling effects incorporated. Notably, the computed Raman spectrum by CNEO-MD for the mixed water dimer/trimer system is in excellent agreement with experiment.

Taken together, this study establishes the CNEO framework as a robust and computationally efficient tool for calculating static polarizabilities and simulating vibrational Raman spectra. With recent developments in periodic CNEO-DFT^{127,128} and CNEO QM/MM,¹²⁹ the CNEO framework holds strong promise for accurate and efficient simulations of Raman spectra in condensed-phase systems with significant hydrogen motions.

SUPPLEMENTARY MATERIAL

The [supplementary material](#) includes a detailed derivation of the analytic static polarizability within CNEO-DFT, O–H stretching benchmarks for water dimer and trimer with various exchange–correlation functionals, convergence tests of CNEO-MD and AIMD power spectra, polarizability protonic basis-set convergence tests, raw polarizability benchmark tables, vibrational frequencies of *trans*-formic acid from CNEO-DFT/DFT and experimental references, and additional Raman spectra of the water monomer from CNEO-MD, AIMD, and experiment.

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

Haoran Chen: Data curation (lead); Formal analysis (lead); Investigation (lead); Methodology (equal); Visualization (lead); Writing – original draft (lead); Writing – review & editing (supporting). **Yuzhe Zhang:** Formal analysis (supporting); Investigation (supporting); Methodology (equal); Writing – review & editing (supporting). **Yiwen Wang:** Formal analysis (supporting); Investigation (supporting); Writing – review & editing (supporting). **Kecai Xuan:** Formal analysis (supporting); Investigation (supporting). **Zehua Chen:** Formal analysis (supporting); Supervision (supporting); Writing – review & editing (supporting). **Yang Yang:** Conceptualization (lead); Formal analysis (supporting); Funding acquisition (lead); Investigation (supporting); Project administration (lead); Supervision (lead); Writing – review & editing (lead).

DATA AVAILABILITY

The data that support the findings of this study are available within the article and its [supplementary material](#).

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