Describing proton transfer modes in shared proton systems with constrained nuclear-electronic orbital methods

Yuzhe Zhang,† Xi Xu,‡ Nan Yang,† Zehua Chen,† and Yang Yang*,†

†Theoretical Chemistry Institute and Department of Chemistry, University of Wisconsin-Madison, 1101 University Avenue, Madison, WI 53706, U.S.
‡Center for Advanced Materials Research, Beijing Normal University, Zhuhai 519087, China

E-mail: yyang222@wisc.edu

Abstract

Proton transfer is crucial in various chemical and biological processes. Because of significant nuclear quantum effects, the accurate and efficient description of proton transfer remains a great challenge. In this communication, we apply constrained nuclear-electronic orbital density functional theory (CNEO-DFT) and constrained nuclear-electronic orbital molecular dynamics (CNEO-MD) to three prototypical shared proton systems and investigate their proton transfer modes. We find that with a good description of nuclear quantum effects, CNEO-DFT and CNEO-MD can well describe the geometries and vibrational spectra of the shared proton systems. This good performance is in great contrast to DFT and DFT-based ab initio molecular dynamics, which often fail for shared proton systems. As an efficient method based on classical simulations, CNEO-MD is promising for future investigations of large and more complex proton transfer systems.
Introduction

Proton transfer is a fundamental chemical process that involves the movement of a proton from one protonation site to another. It is ubiquitous in nature and plays a vital role in a variety of chemical and biological processes such as photosynthesis\textsuperscript{1,2} and respiration.\textsuperscript{3} Proton transfer is often accompanied by energy transfer. In recent decades, with the ultimate goal of better harnessing energy, many experimental and theoretical efforts\textsuperscript{4–9} have been devoted to understanding the mechanisms of proton transfer and studying proton transfer rates.

In theoretical investigations, a significant challenge for the study of proton transfer is the incorporation of nuclear quantum effects (NQEs),\textsuperscript{10} given that protons are the lightest nuclei with strong NQEs. NQEs often include zero-point effects and tunneling effects, both of which are related to the quantum delocalized nature of nuclei. NQEs are closely related to many anomalous properties of water systems\textsuperscript{11,12} and some other hydrogen-bonded systems.\textsuperscript{8,13} For instance, the quantum delocalization of protons in the active site of the enzyme ketosteroid isomerase (KSI) significantly stabilizes the deprotonated form of an active-site tyrosine residue, resulting in its anomalous acidity.\textsuperscript{14} Additionally, NQEs can be manifested in vibrational spectra, where a good description of NQEs will naturally describe anharmonicity, which is significant in many bonds vibrations involving hydrogen atoms.\textsuperscript{15–18}

There have been many methods developed to incorporate NQEs and anharmonicities in theoretical calculations. Based on high-dimensional potential energy surfaces (PESs), both static calculations using vibrational self-consistent field/vibrational configuration interaction (VSCF/VCI)\textsuperscript{19,20} and dynamic simulations using multi-configuration time-dependent Hartree (MCTDH)\textsuperscript{21,22} can give highly accurate results. More computationally affordable methods are vibrational perturbation theory (VPT2)\textsuperscript{23} and path-integral based simulation methods such as centroid molecular dynamics (CMD)\textsuperscript{24,25} and ring polymer molecular dynamics (RPMD).\textsuperscript{26} Compared to VSCF/VCI, VPT2 only needs local higher order derivative information of the PES to perform calculations. Due to the relatively low computational
cost, it has been widely used to compute anharmonic corrections with high accuracy. However, VPT2 faces challenges in highly anharmonic systems, for example, the shared proton systems in this communication. Path-integral based methods have slightly higher costs than conventional classical molecular simulations. They have been applied to investigate proton transfer in larger systems such as between phenol and trimethylamine in polar solvents and through two-dimensional materials. In general, path-integral methods are excellent for investigating static properties such as structures and free energies but have limitations in predicting dynamic properties, especially in calculating vibrational spectra, although recent developments has made them more reliable for these calculations. Recently, constrained nuclear-electronic orbital density functional theory (CNEO-DFT) has been developed in our group. It simultaneously treats nuclei and electrons quantum mechanically but with a constraint on each quantum nuclear expectation position. The resulting CNEO-DFT energy surface is a function of quantum nuclear expectation positions as well as classical nuclear positions, and it inherently incorporates NQEs. The CNEO-DFT energy surface has many desirable properties. For instance, the harmonic vibrational frequencies obtained directly from Hessian calculations are comparable to the anharmonic frequencies obtained from DFT-VPT2. Additionally, molecular dynamics can be performed on CNEO-DFT energy surfaces (CNEO-MD), which incorporates NQEs in classical simulations with essentially the same computational cost as conventional DFT-based \textit{ab initio} molecular dynamics (AIMD). CNEO-MD has been tested and found to be capable of accurately reproducing the key features in the vibrational spectra of a series of small molecules. Without any empirical scaling, CNEO-DFT and CNEO-MD are especially good at predicting the motion of free X-H bonds, where X is a heavy element.

Although the low computational cost of CNEO-MD makes it directly applicable to the simulation of proton transfer processes in large-scale systems, the complexity of such systems and the interplay between different factors may make it hard to clearly assess the performance and understand the strengths and weaknesses of CNEO-MD. Fortunately, shared
proton systems, in which a proton is shared between two neutral or charged moieties, have been widely investigated both experimentally and computationally. As prototypical patterns for the presence of protons in hydrogen-bonded networks, the shared proton systems can offer valuable insights into the nature of proton transfer processes in different chemical environment and are ideal systems for benchmarking. In water, there are two well-known structures for proton transfer processes: Eigen (e.g. \( \text{H}_9\text{O}_4^+ \)) and Zundel (e.g. \( \text{H}_5\text{O}_2^+ \)). In the Eigen structure, the proton is possessed by one water only and it can be perceived as the starting and ending structure of the proton transfer process, whereas in the Zundel structure, the proton is shared equally by two adjacent water molecules, which is like a transition state for proton transfer. Out of the two, the Zundel structure is especially challenging for pure electronic structure calculations since the shared proton lies on a highly flat and highly anharmonic PES. As a result, not only the conventional harmonic approximation based on electronic structure calculations but also the popular VPT2 method fails to describe the vibration spectra of the Zundel structure, and more expensive methods are needed, such as diffusion Monte Carlo (DMC), MCTDH, and VSCF/VCI.

In this communication, we will apply the CNEO method to investigate the vibrational spectra of shared proton systems, or more specifically, the challenging Zundel-like structures: \( \text{H}_5\text{O}_2^+ \), \( \text{H}_3\text{O}_2^- \), and \( \text{HCOO}^- \cdot \text{H}^+ \cdot \text{OOC}^- \). We will start with a brief introduction on the theory of CNEO in Section II. Then we will provide our computational details in Section III, followed by results and discussions in Section IV. We give our conclusions in the last section.

Method

The CNEO methods are based on the multicomponent quantum theory, in which both electrons and nuclei are treated quantum mechanically. Based on the physical intuition that in most chemical and biological systems of interest, nuclei are still relatively localized in space, we treat nuclei as distinguishable particles and use the quantum nuclear expectation...
positions to denote geometries in the CNEO framework. Thus, for a particular geometry, the multicomponent quantum ground state is obtained by minimizing the total energy subject to the constraint on the quantum nuclear expectation positions:

\[ \langle \mathbf{r}_I \rangle = \mathbf{R}_I, \quad \forall I, \]

Here \( \mathbf{R}_I \) is the nuclear position for the \( I \)th nucleus, \( \langle \mathbf{r}_I \rangle \) is the quantum expectation position for the \( I \)th nucleus, and this constraint needs to be satisfied for all quantum nuclei. With this constraint, the Lagrangian for the multicomponent quantum system consists an extra term:

\[ \sum_I f_I \cdot (\langle \mathbf{r}_I \rangle - \mathbf{R}_I) \]

where \( f_I \) is the Lagrange multiplier associated with the expectation position constraint for the \( I \)th quantum nucleus. Making the Lagrangian stationary with respect to electronic and quantum nuclear orbital variations will yield a new set of coupled multicomponent Kohn-Sham equations that can be solved self-consistently together with the nuclear expectation constraints. The energy of the final quantum states is a function of both quantum nuclear expectation positions and classical nuclear positions. Thus, it can be evaluated at any molecular geometry, resulting in the CNEO energy surface that naturally incorporates NQEs of the quantum nuclei. It can be proved that the Lagrange multiplier \( f_I \) acts as the classical force on the \( I \)th quantum nucleus in the complete basis limit, although in practical calculations with a finite basis set, the Pulay force for quantum nuclei will be included in gradient calculations.\(^{31,42}\)

The CNEO energy surface can be employed for classical molecular simulations. The underlying theoretical justification is the constrained minimized energy surface molecular dynamics (CMES-MD),\(^{34}\) a MD framework that our group developed to incorporate nuclear
quantum effects in classical simulations. The equations of motion for CMES-MD are

$$m \frac{d\langle x \rangle}{dt} = \langle p \rangle$$

and

$$\frac{d\langle p \rangle}{dt} \approx -\nabla_{\langle x \rangle} V_{\text{CMES}}(\langle x \rangle)$$

where $\langle x \rangle$ and $\langle p \rangle$ are expectation position and expectation momentum, respectively, and $V_{\text{CMES}}(\langle x \rangle)$ is the CMES, an effective potential energy surface obtained from constrained energy minimization. This set of equations of motion highly resembles the classical Newton’s equation, but instead of the conventional PES, here the $V_{\text{CMES}}(\langle x \rangle)$ is used, which includes NQEs of the quantum nuclei. In practical molecular simulations, the CNEO methods, especially CNEO-DFT, can be used to obtained $V_{\text{CMES}}(\langle x \rangle)$ and the CNEO gradients can be used to obtain the force. As such, CNEO-MD can be performed essentially in the same way as the widely used conventional AIMD simulations by replacing the on-the-fly DFT calculations with CNEO-DFT calculations. This slight change leads to a minor increase in computational cost but makes it possible to incorporate NQEs in AIMD simulations.

### Computational Details

We choose three challenging Zundel and Zundel-like structures for vibrational spectra calculations: $\text{H}_5\text{O}^+_2$, $\text{H}_3\text{O}^-_2$, and $\text{HCOO}^− \cdot \text{H}^+ \cdot \cdot \cdot \text{OOCH}$. They all have the shared proton sitting at the center, and their experimental gas phase infrared (IR) spectra have been available through cold-ion vibrational action spectroscopy.\textsuperscript{23,35,37} For comparison, we calculate their vibrational spectra using both DFT and CNEO-DFT methods. Static energy, gradient, and Hessian calculations are performed using an in-house version\textsuperscript{43} of PySCF,\textsuperscript{44,45} and MD simulations are performed with Atomic Simulation Environment (ASE).\textsuperscript{46} In CNEO calculations, we only treat hydrogens quantum mechanically because heavy atoms generally have smaller
NQEs, although we note that full-quantum calculations are possible.\textsuperscript{32,33} For all the calculations in this communication, if not specified, the aug-cc-pVDZ basis set\textsuperscript{47} is adopted for electrons and the PB4-D basis\textsuperscript{48} is used for protons. Three electronic exchange-correlation functionals, B3LYP,\textsuperscript{49,50} PBE\textsuperscript{51} and ωB97X,\textsuperscript{52} are tested in both DFT and CNEO-DFT calculations. Electron–nuclear correlations and nuclear–nuclear correlations are not included. For additional comparison, DFT-VPT2 calculations are performed using Gaussian 16.\textsuperscript{53} Since DFT-ωB97X has the best agreement with CCSD(T)\textsuperscript{54} in terms of harmonic frequencies for the proton transfer modes in H\textsubscript{5}O\textsuperscript{+}\textsubscript{2} and H\textsubscript{3}O\textsuperscript{−}\textsubscript{2}, we adopt ωB97X for MD simulations with the minimal error from the choice of the electronic functional. In principle, simulating IR spectra requires an ensemble average of a large number of \textit{NVE} trajectories with starting configurations sampled from an equilibrated \textit{NVT} trajectory. To reduce the calculation cost, we follow the practice established by existing literature\textsuperscript{55,56} and use a single 20 ps \textit{NVT} trajectory at 10 K to simulate the IR spectra. We set the initial positions and velocities of each atom following the equipartition law at 10 K with equal amount of energy added to each vibrational mode obtained from Hessian analysis.\textsuperscript{57} In practical simulations, a time step of 0.5 fs is chosen and the Nose–Hoover thermostat\textsuperscript{58,59} with a large characteristic timescale being 1 ps is employed. In the end, the dipole autocorrelation function is calculated from each trajectory and then Fourier transformed to obtain the IR spectrum of each system.\textsuperscript{55,56}

**Results and discussions**

H\textsubscript{5}O\textsuperscript{+}\textsubscript{2} and H\textsubscript{3}O\textsuperscript{−}\textsubscript{2}

H\textsubscript{5}O\textsuperscript{+}\textsubscript{2} and H\textsubscript{3}O\textsuperscript{−}\textsubscript{2} are the simplest water clusters with shared protons. They have been widely studied experimentally and theoretically,\textsuperscript{21,23,35,36,38,61–63} and their proton transfer modes are of particularly high research interest. In H\textsubscript{5}O\textsuperscript{+}\textsubscript{2}, the proton is shared by two water molecules, giving a symmetric structure. Through geometry optimization, this symmetric structure can
Table 1: Vibrational frequencies of the proton transfer mode in \( \text{H}_5\text{O}_2^+ \) and \( \text{H}_3\text{O}_2^- \) (in cm\(^{-1}\))

<table>
<thead>
<tr>
<th></th>
<th>experiment</th>
<th>CCSD(T)</th>
<th>DFT harmonic</th>
<th>DFT-VPT2</th>
<th>CNEO-DFT harmonic</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>B3LYP</td>
<td>B3LYP</td>
<td>B3LYP</td>
</tr>
<tr>
<td>( \text{H}_5\text{O}_2^+ )</td>
<td>1047(^a)</td>
<td>819(^c)</td>
<td>907.3</td>
<td>1014.3</td>
<td>812.3</td>
</tr>
<tr>
<td>( \text{H}_3\text{O}_2^- )</td>
<td>697(^b)</td>
<td>1588.4(^d)</td>
<td>1307.3(^d)</td>
<td>741.7(^d)</td>
<td>1830.5(^d)</td>
</tr>
</tbody>
</table>

\(^a\)From Ref. 23.
\(^b\)From Ref. 35.
\(^c\)From Ref. 60, with basis set aug-cc-pVQZ.
\(^d\)These are bound OH stretch mode frequencies instead of proton transfer mode frequencies as a result of asymmetric proton placement predicted by the underlying theory.
\(^e\)Calculated using Gaussian 16 with the aug-cc-pVTZ basis set.

be predicted by both pure electronic structure calculations and multicomponent CNEO-DFT calculations (Supporting Information, Figure S1). In \( \text{H}_5\text{O}_2^+ \), the proton is shared by two \( \text{OH}^- \) anions, which still leads to a symmetric structure.\(^{35}\) However, the geometry optimization result for \( \text{H}_3\text{O}_2^- \) strongly depends on whether the shared proton is treated classically or quantum mechanically. Pure electronic structure calculations give a double-well ground state PES, and if the proton is considered to be a classical particle, it will locate closer to one of the \( \text{OH}^- \), essentially forming \( \text{H}_2\text{O} \cdot \text{OH}^- \) (Supporting Information, Figure S2). In contrast, if path-integral simulations are performed based on the double-well potential, the quantum treatment of the proton brings the zero-point energy to the system, which is higher than the proton transfer barrier,\(^{64}\) resulting in a proton density centered in the middle.\(^{36}\) With CNEO-DFT, no matter which electronic functional is used, because the proton is treated quantum mechanically together with electrons, the proton is consistently predicted to be at the center and equally shared by the two \( \text{OH}^- \) anions (Supporting Information, Figure S2).

Based on the individually optimized geometries, we obtain the vibrational frequencies of \( \text{H}_5\text{O}_2^+ \) and \( \text{H}_3\text{O}_2^- \) by CCSD(T), DFT, DFT-VPT2, and CNEO-DFT. The results are presented in Table 1. Note that the CCSD(T), DFT, and CNEO-DFT results are harmonic frequencies that are obtained from diagonalizing the mass-weighted Hessian matrices, whereas DFT-VPT2 performs VPT2 calculations at the DFT-optimized geometries, which includes anharmonicity.

For \( \text{H}_5\text{O}_2^+ \), the experimental proton transfer mode frequency is 1047 cm\(^{-1}\), while DFT
harmonic calculations underestimate the frequency with all three functionals tested and the degree of underestimation greatly varies with the underlying functional. It seems that PBE0 is the best functional here, which only underestimates the frequency by \( \sim 30 \text{ cm}^{-1} \). Nevertheless, we note that this seemingly great performance of PBE0 is fortuitous and primarily due to error cancellation: Based on the harmonic approximation, the CCSD(T) with the large aug-cc-pVQZ basis set predicts a frequency of 819 cm\(^{-1}\),\(^{60}\) which is more than 200 cm\(^{-1}\) lower than the experimental reference. Since we can consider CCSD(T) to be mostly free from electronic correlation error, this huge mismatch of the gold standard method mainly comes from the classical nuclear treatment. Then the difference between DFT-PBE0 and CCSD(T) mainly comes from the electronic error. Therefore, the good performance of DFT-PBE0 is accidentally caused by the error cancellation from the electronic part and the classical nuclear part. In this sense, the \( \omega B97X \) functional is the best electronic functional for this system with similar performance to CCSD(T). For DFT-VPT2, although it is generally a reliable method for calculating anharmonicity, it fails badly for this system with the proton transfer mode frequency significantly overestimated by more than 300 cm\(^{-1}\). In fact, it is known that the proton transfer modes in shared proton systems are especially challenging for VPT2 because the local higher order derivative information is not sufficient to capture the behavior of the whole surface. In contrast, even with a harmonic approximation, CNEO-DFT is able to give reasonably good descriptions for the proton transfer modes with slightly overestimated frequencies. The frequencies by CNEO-DFT are also sensitive on the choice of the electronic functional, but we find that \( \omega B97X \) is the best-performing functional here, which overestimates the proton transfer mode frequency by \( \sim 80 \text{ cm}^{-1} \). Considering DFT-\( \omega B97X \) gives the closest results to CCSD(T) with the least error from the electronic part, this result is inspiring because it indicates that CNEO-DFT performs well when the underlying electronic functional is reliable, which suggests the accurate description of the quantum proton by CNEO-DFT.

As to H\(_3\)O\(_2^−\), since both CCSD(T) and DFT optimized geometries are asymmetric, there
is only the bound OH stretch mode instead of the proton transfer mode. Because of the incorrect physical picture, all their vibrational frequencies are significantly higher than the experimental reference values. It is also noteworthy that these DFT harmonic frequencies are extremely sensitive to the choice of the electronic functional, although it seems that $\omega_{\text{B97X}}$ is still the best functional that matches the CCSD(T) result most. Based on the wrong physical picture, DFT-VPT2 gives even more unphysical results with all three functionals giving imaginary frequencies, indicating the failure of the perturbative treatment in such a double-well system. In contrast, CNEO-DFT gives much more reliable results with a quantum mechanical treatment on nuclei. Even though the result is still sensitive to the choice of the electronic functional, we found that $\omega_{\text{B97X}}$ as the best functional that matches CCSD(T) most, manages to give the most accurate CNEO-DFT frequency compared to the experimental reference. All these results demonstrate that the quantum treatment on transferring proton is key to the qualitatively correct description of the proton transfer modes.

![Calculated IR spectra of H$_5$O$_2$+](image)

(a) H$_5$O$_2$+ low frequency  
(b) H$_5$O$_2$+ high frequency

**Figure 1:** Calculated IR spectra of H$_5$O$_2$+ by conventional AIMD and CNEO-MD at 10 K. Experimental IR spectrum is from Ref. 23.

Among the three functionals tested, since $\omega_{\text{B97X}}$ is the best one that has the least error from the electronic part, we use it for AIMD simulations. To differentiate conventional
AIMD using DFT PESs from our AIMD using CNEO-DFT energy surfaces, throughout the paper, we call them conventional AIMD and CNEO-MD, respectively. Figure 1 shows the IR predissociation spectra of the $H_5O_2^+ \cdot Ne$ complex$^{23}$ and the simulated spectra for $H_5O_2^+$ using conventional AIMD and CNEO-MD. According to the experimental spectra, the proton transfer mode has strong absorption at 1047 cm$^{-1}$. However, there is an additional strong absorption at 928 cm$^{-1}$. The capture and assignment of the 928 cm$^{-1}$ peak with theoretical simulations have been particularly challenging.$^{15,23}$ MCTDH is the most reliable method that has successfully reproduced the Fermi resonance and characterized it as the resonance between the proton transfer mode and the combination band of the water wagging motion and O-O stretch motion.$^{21}$ Conventional AIMD underestimates the proton transfer mode frequency, whereas CNEO-MD overestimates the mode frequency, which are consistent with the DFT harmonic results and CNEO-DFT harmonic results, respectively. Interestingly, for CNEO-MD, in addition to the main proton transfer mode absorption at about 1138 cm$^{-1}$, we additionally see a satellite peak at 1104 cm$^{-1}$. Through normal coordinate analysis on the CNEO-MD trajectory using Trajectory Analyzer and Visualizer,$^{65-67}$ we find that both the main peak and the satellite peak have significant contributions from proton transfer motion and the wagging motion of water molecules (Supporting Information, Figure S4). Therefore, CNEO-MD seems to have captured some of the mode coupling features, although the quantitative correspondence is not great and it remains challenging for classical MD methods to accurately describe overtones, combination bands, and Fermi resonances. Apart from the proton transfer mode, there are two peaks around 1400 cm$^{-1}$ corresponding to the perpendicular motions of the shared proton. Although the intensities of the two modes are low, CNEO-MD can capture them with vibrational frequencies in good agreement with prior MCTDH calculations.$^{21}$ At around 1600 cm$^{-1}$ and 1750 cm$^{-1}$, there are two water bending modes according to MCTDH calculations.$^{21}$ The one at around 1600 cm$^{-1}$ is a dark state while the intensity of the other mode around 1750 cm$^{-1}$ could vary significantly in experiments depending on the type of noble gas tag.$^{23}$ CNEO methods can accurately
describe the frequencies and intensities of both modes. However, we also see a peak splitting for the bright higher energy mode, which is not expected. Using normal coordinate analysis based on the MD trajectory, we find that although the mode is dominated by water bending, it still has substantial contribution from the proton transfer motion, which can also be coupled with the water wagging motion (Supporting Information, Figure S5). This may be the reason for the peak splitting. Because this splitting is not observed either in experimental or MCTDH spectra, it could be an artifact of our method. In the even higher frequency range (3400-4000 cm\(^{-1}\)), we can see the symmetric and asymmetric free OH stretches. CNEO-MD describes these modes excellently, which is not surprising considering we have observed the great performance of CNEO-MD in gas phase water molecules.\(^{18}\)

For the \(\text{H}_3\text{O}^2^-\) system, Figure 2 presents the IR predissociation spectra of the \(\text{H}_3\text{O}^-\) \cdot \text{Ar} complex\(^{35}\) and the simulated spectra for \(\text{H}_3\text{O}^-\) using conventional AIMD and CNEO-MD. The IR spectrum of \(\text{H}_3\text{O}^-\) is simple with most intensities on the proton transfer mode. Because DFT predicts an asymmetric placement of the shared proton, conventional AIMD gives a bound OH stretch slightly above 1800 cm\(^{-1}\) and thus completely fails to reproduce the experimental proton transfer mode at around 700 cm\(^{-1}\). In contrast, CNEO-MD describes the proton transfer mode well with the peak position matches almost perfectly to the experimental frequency.

\[
\text{HCOO}^- \cdot \text{H}^+ \cdot \text{OOCH}
\]

The good performance of CNEO-MD in \(\text{H}_3\text{O}^2^+\) and \(\text{H}_3\text{O}^-\) demonstrates its great potential as an accurate and efficient method for proton transfer studies, especially in large systems where MCTDH and VSCF/VCI calculations are too expensive to perform. Here we extend our method to another important category of shared proton systems, proton-bound organic molecules/ions, and use the proton-bound formate dimer (AHA\(^-\)) as an example to study.

The AHA\(^-\) system was previously studied by cold-ion IR action spectroscopy and discrete variable representation (DVR) analysis, both of which revealed that the bridging proton
is shared equally between two formate anions. It was also found that the fundamental of the proton transfer mode $\nu_{\parallel}$ is strongly coupled to the out-of-phase carboxylate deformation mode, $\delta$(OCO)$_{OOP}$. Similar to the $\text{H}_5\text{O}_2^+$ and $\text{H}_3\text{O}_2^-$ cases, we perform both static calculations and molecular dynamics simulations to the AHA$^-$ system.

With pure electronic DFT, the equilibrium structure of AHA$^-$ is highly sensitive to the functional choice. Specifically, B3LYP and $\omega$B97X give a shallow double-well PES and predict the proton to be on either side of the the complex, whereas PBE0 gives a single-well picture and predicts the proton to be equally shared (Supporting Information, Figure S3). In contrast, the CNEO-DFT geometry is much less sensitive to functional choice with all three functionals predicting the bridging proton to be in the middle of two formate anions (Supporting Information, Figure S3). These results again demonstrate the necessity of the quantum treatment on the shared proton.

Based on the individually optimized geometries, we calculate the harmonic vibrational frequencies with DFT and CNEO-DFT. The results are shown in Table 2. For comparison, we additionally include DFT-VPT2 results and a prior literature results using the DVR analysis in two-dimensional (2D) and four-dimensional (4D) PESs. Note that because
pure electronic DFT-B3LYP and DFT-ωB97X calculations break the $C_2$ symmetry of AHA$^-$, leading to completely different normal modes that cannot correspond well to the experimental results, here we do not present their poor results. In AHA$^-$, there are two modes that have significant contributions from the proton transfer mode. The reason is that the proton transfer mode $\nu_\parallel$ and a hybridized carboxylate deformation mode $\delta(\text{OCO})_{OOP}$ have the same $B$ symmetry within the $C_2$ point group and thus can linear combine to form two new modes, both of which involve a large displacement of the shared proton along the O-O direction.$^{37}$ These two coupled modes are denoted as mode 1 and mode 2 in Table 2 and Figure 3.

Pure electronic DFT with the PBE0 functional can predict the symmetrically shared proton picture, but it greatly underestimates the two proton transfer modes by about 200 cm$^{-1}$. On top of the PBE0 reference, performing vibrational perturbative calculations with VPT2 makes the mode descriptions even worse, which, conversely, dramatically overestimates the vibrational frequencies (1300 cm$^{-1}$ overestimation for mode 1 and 400 cm$^{-1}$ overestimation for mode 2). This poor performance of VPT2 is not surprising since we have observed similar performance of it in $\text{H}_2\text{O}_2^+$. In both cases, because of the high anharmonicity and high complexity of the underlying PES, local higher order derivative information is not sufficient for an accurate description of the whole PES, leading to the failure of the popular VPT2 method. In contrast, CNEO-DFT with harmonic approximations can much more accurately predict the vibrational frequencies of the two modes and give similar results across different functionals. Specifically, the errors are all within 60 cm$^{-1}$ for mode 1 and within 100 cm$^{-1}$ for mode 2 when compared to experimental results. In fact, as a highly efficient method, CNEO-DFT also outperforms the DVR results based on a 2D PES and has a similar or slightly better performance than DVR results based on a 4D PES when two additional modes are included in calculations, all of which demonstrate the high promise of CNEO-DFT in describing the proton transfer modes in larger and more complex systems.

To directly compare with experimental spectra, we also simulated the vibrational spectra of AHA$^-$ using both conventional AIMD and CNEO-MD. Without harmonic CCSD(T)
Table 2: Vibrational Frequencies of Proton Transfer in AHA\(^-\) (in \(\text{cm}^{-1}\))

<table>
<thead>
<tr>
<th>modes</th>
<th>Ar predissociation/He nanodroplet (^a)</th>
<th>2D PES (^a)</th>
<th>4D PES (^a)</th>
<th>DVR</th>
<th>DFT</th>
<th>DFT-VPT2</th>
<th>CNEO-DFT</th>
</tr>
</thead>
<tbody>
<tr>
<td>AHA(^-) mode 1</td>
<td>619/605</td>
<td>656.8</td>
<td>618.3</td>
<td>399.2</td>
<td>1987.8</td>
<td>619.7</td>
<td>661.0</td>
</tr>
<tr>
<td>mode 2</td>
<td>1034/1037</td>
<td>1213.5</td>
<td>943.5</td>
<td>850.8</td>
<td>1415.8</td>
<td>975.9</td>
<td>1073.1</td>
</tr>
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</table>

\(^a\)from Ref. 37.

results, we do not know which functional is the best for the electronic part description. Therefore, to be consistent with the H\(_5\)O\(_2^+\) and H\(_3\)O\(_2^-\) cases, we continue using the \(\omega\)B97X functional for MD simulations. The simulated spectra for AHA\(^-\) along with the experimental Ar predissociation IR spectrum\(^{37}\) are presented in Figure 3. The experimental spectra is highly complex, and many of the peaks may be contributed by combination bands or overtones, which are challenging for classical MD methods. The key features of the spectra are the two proton transfer modes with high intensities, and CNEO-MD can capture them both. Note that although the match is not perfect with about 20 \(\text{cm}^{-1}\) underestimation for mode 1 and 90 \(\text{cm}^{-1}\) underestimation for mode 2, CNEO-MD still gives the best match to the experimental peaks among the methods that have been applied to this system. For conventional AIMD, although there is a mode at 678 \(\text{cm}^{-1}\), which seems to match reasonably with the mode 1, it is actually a HCOOH deformation mode rather than the proton transfer modes (Supporting Information, Figure S7). Therefore, the physical picture of the conventional AIMD is completely wrong. In CNEO-MD, we observe a small satellite peak that is slightly higher in frequency than the main peak of mode 2. Through normal coordinate analysis based on the MD trajectory, we find that this analysis cannot distinguish this peak from the main peak of mode 2 obtained from Hessian (Supporting Information, Figure S8). This small satellite peak could possibly correspond to the experimental peak at around 1200 \(\text{cm}^{-1}\). Another important feature of AHA\(^-\) is the fundamentals of CO\(_2^-\) deformations with peaks showing up as a doublet (1685 and 1700 \(\text{cm}^{-1}\)) separated by 15 \(\text{cm}^{-1}\). These frequencies are between the frequency of the carboxylate antisymmetric stretch (1622 \(\text{cm}^{-1}\))\(^{68}\) and the frequency of the carboxylic acid CO stretch (1818 \(\text{cm}^{-1}\))\(^{69}\), which, together with the small doublet peak splitting, is an experimental evidence for the proton being equally
shared by the two formate anions. CNEO-DFT harmonic analysis predicts the doublet to be at 1771 and 1784 cm\(^{-1}\). Although the frequencies are overestimated, the splitting of 13 cm\(^{-1}\) is consistent with the experimental results. In CNEO-MD spectrum, the two peaks merge into one because of the small splitting between them.

![Calculated IR spectra of AHA\(^{-}\) by conventional AIMD and CNEO-MD at 10 K. Experimental IR spectrum is from Ref.\(^{37}\).](image)

**Conclusions**

In summary, with three prototypical shared proton systems, \(\text{H}_5\text{O}_2^+\), \(\text{H}_3\text{O}_2^-\) and AHA\(^-\), we demonstrated that our CNEO methods can accurately and efficiently describe the proton transfer modes in shared proton systems. In all three systems, CNEO-DFT accurately predicted the proton to be shared equally by the two ending groups whereas pure electronic DFT with classical treatment on nuclei often cannot. Based on the physically correct geometries, both CNEO harmonic analysis and CNEO-MD can well describe the key features related to fundamental transitions in the IR spectra, which is greatly superior to the conventional DFT harmonic analysis, DFT-VPT2, and conventional DFT-based AIMD. Although the descriptions of overtones, combination bands, and Fermi resonances are still challenging and high-level quantum methods such as MCTDH and VSCF/VCI are still needed for the
accurate description of these subtle features, our CNEO methods excel in their abilities to accurately and efficiently capture the key fundamental transition natures in relatively large systems. Therefore, CNEO methods are promising for future applications to larger and more complex systems like biological systems and materials systems in which proton transfer plays a crucial role.

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