Nuclear Quantum Effects in Gas-Phase Ethylene Glycol

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Path integral molecular simulations are used to explore the nuclear quantum effects (NQEs) on the structure, dihedral landscape and infrared spectrum of ethylene glycol. The simulations are carried out on a new reaction surface Hamiltonian-based model potential energy surface, with especial focus on the role of the OCCO and HOCC dihedrals. By contrast with classical simulations, we analyse how the intramolecular interaction between the OH groups changes due to zero-point effects as well as temperature. These are found to be weak. The NQEs on the free energy profile along the OCCO dihedral are analysed, where notable effects are seen at low temperatures and found to be correlated with the radii of gyration of the atoms. Finally, the power spectrum of the molecule from path integral simulations is compared with the experimental infrared spectrum, yielding good agreement of band positions.

I. INTRODUCTION

Ethylene glycol (EG) is the simplest saturated vicinal diol. Its three torsional degrees of freedom, viz. the OCCO and two HOCC dihedrals, provide a rich torsional landscape. The structure and spectroscopy of EG have been extensively investigated from experiments and theory. Of the possible conformers of EG, the tGg− form and its three symmetrically equivalent ones are the lowest energy structures. It has been long debated whether this set of forms are intramolecularly hydrogen bonded. The OHO internal angle is especially bent, and the analysis via the Quantum Theory of Atoms-In-Molecules (QTAIM) did not yield a bond critical point suggesting a possible absence of intramolecular H-bonding. Analysis with the Natural Bond Orbital (NBO) method also showed weak orbital mixing of filled orbital from donor O atom with σOH∗, and it has been suggested that electrostatic effects may guide the conformational preference. Infrared spectroscopic studies indicated a weak red-shift of the fundamental, which is the difference between the two peaks of the OH stretches in the recorded spectrum, in comparison to those in higher analogues 1,3-propanediol and 1,4-butanediol. While the fundamental intensity enhancement in EG is weak in contrast to the latter two molecules, an intensity suppression for the overtone was also seen for all three diols. Non-Covalent Interaction (NCI) analyses also indicates a favourable interaction between the OH groups, leading to the view that the molecule may have a weak intramolecular H-bond.

Most studies on EG have used only electronic structure theory focussed on the key minima. However, a fuller picture of the intramolecular interaction requires treating the nuclei quantum mechanically. A treatment of this nature was carried out by Crittenden et al., who used the diffusion Monte Carlo method and found that the vibrationally averaged O-O distances are, to within uncertainty, close to the minimum equilibrium value. However, these distances are also much like O-O intermolecular H-bond distances in the EG-water heterodimer that they also simulated, indicating a weak intramolecular H-bond in the monomer.

A few other studies have analysed the electronic structure away from the minimum. Varying the geometry along a lowest frequency normal mode, which correlates to the OCCO torsion, Arunan and Mani found in their a bond critical point appears close to the turning point of fundamental excitation where the oxygens are closer than at the minimum. Rosenberg also showed from relaxed scans of the OCCO dihedral that a bond critical point appears en route to the cis geometry along this coordinate. These studies indicate that nuclear quantization would play a role in the structure and spectroscopy of EG. Boussessi et al. have studied the role of the three low frequency OCCO and HOCC torsions in a reduced dimensional variational quantum treatment, successfully modelled the far infrared spectrum of the molecule. They also considered the higher frequency modes within the vibrational second order perturbation theory framework. The latter method was also used by Das et al. in simulating the composition of the infrared spectrum arising from population weighted sum of those from various minima and comparing it with their experimental spectrum at a few temperatures. Howard et al. have previously used a vibrational local mode model to explore the OH stretch vibrational transitions of EG up to high overtone, in terms of both band positions and intensities, and compared their findings with experiments.

In the present work, we explore nuclear quantum effects (NQEs) in EG with special focus on the role of the OCCO and HOCC torsions. Through the use of path integral simulations at various temperatures, we anal-

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TABLE I. Energies of stationary points of EG at the MP2/aVTZ level of theory. The energies (in cm\(^{-1}\)) are relative to the global minimum structure tG\(^{+}\)g\(^{-}\). \(\phi_1 \equiv \phi(O_{\text{CHO}}C_{\text{O}}O_{\text{t}})\), \(\phi_2 \equiv \phi(H_{\text{O}}O_{\text{t}}C_{\text{O}}C_{\text{t}})\), and \(\phi_3 \equiv \phi(H_{\text{t}}O_{\text{t}}C_{\text{O}}C_{\text{t}})\). See Table S-2 for the internal coordinates for each structure and the list of equivalent structures.

<table>
<thead>
<tr>
<th>Struct.</th>
<th>(\phi_1)</th>
<th>(\phi_2)</th>
<th>(\phi_3)</th>
<th>(E)</th>
</tr>
</thead>
<tbody>
<tr>
<td>tG(^{+})g(^{-})</td>
<td>62.15</td>
<td>-168.65</td>
<td>-51.97</td>
<td>0.0</td>
</tr>
<tr>
<td>g(^{-})G(^{+})g(^{-})</td>
<td>57.68</td>
<td>73.91</td>
<td>-44.88</td>
<td>148.9</td>
</tr>
<tr>
<td>g(^{-})G(^{+})g(^{-})</td>
<td>60.53</td>
<td>-80.11</td>
<td>-80.11</td>
<td>330.2</td>
</tr>
<tr>
<td>tTt</td>
<td>180.00</td>
<td>180.00</td>
<td>-180.00</td>
<td>912.1</td>
</tr>
<tr>
<td>g(^{-})T(t)g(^{-})</td>
<td>180.00</td>
<td>70.63</td>
<td>-70.63</td>
<td>979.0</td>
</tr>
<tr>
<td>tTg(^{+})</td>
<td>179.65</td>
<td>-175.90</td>
<td>71.91</td>
<td>971.0</td>
</tr>
<tr>
<td>g(^{-})T(g)(^{+})</td>
<td>176.66</td>
<td>67.26</td>
<td>67.26</td>
<td>1045.9</td>
</tr>
<tr>
<td>tG(^{+})t (\equiv) g(^{-})g(^{+})</td>
<td>73.93</td>
<td>-168.17</td>
<td>-168.17</td>
<td>1084.2</td>
</tr>
<tr>
<td>cCt</td>
<td>65.30</td>
<td>-178.37</td>
<td>59.51</td>
<td>1248.6</td>
</tr>
<tr>
<td>cCt</td>
<td>0.00</td>
<td>0.0</td>
<td>180.00</td>
<td>2298.3</td>
</tr>
</tbody>
</table>

TABLE S-2. Internal coordinates of EG

<table>
<thead>
<tr>
<th>(\phi_1)</th>
<th>(\phi_2)</th>
<th>(\phi_3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\equiv)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\phi(O_{\text{O}}C_{\text{O}}C_{\text{O}}))</td>
<td>(\phi(H_{\text{O}}O_{\text{O}}C_{\text{O}}C_{\text{t}}))</td>
<td>(\phi(H_{\text{t}}O_{\text{O}}C_{\text{O}}C_{\text{t}}))</td>
</tr>
</tbody>
</table>

This paper is organized as follows. Section II discusses the stationary point of EG, followed by the development of the model PES. Details of the path integral simulations are also provided. Sec. IV presents the accuracy of the model PES, followed by analysis of results from path integral and classical simulations using the PES. A brief summary is provided in Sec. V.

II. METHODOLOGY

A. Stationary points

Following the literature on EG, the possible torsional conformations of the OCCO dihedral (\(\phi_1\)) are denoted G\(^{+}\), G\(^{-}\), and T, while those for the HOCC dihedrals (\(\phi_2\) and \(\phi_3\)) are G\(^{+}\), G\(^{-}\), and t. Put together, 27 conformations are possible, 10 being unique. Various equivalent structures are related by the transformations (\(\phi_1, \phi_2, \phi_3\) → (\(-\phi_1, -\phi_2, -\phi_3\)) and (\(\phi_1, \phi_2, \phi_3\) → (\(\phi_1, \phi_3, \phi_2\)). From optimizations at the MP2 level with the aug-cc-pVTZ (aVTZ) basis using GAUSSIAN 16 \(^{[38-41]}\), we find that the tG\(^{+}\)g\(^{-}\) structure and its equivalent forms have the lowest energy. The next energetic higher set comprises of g\(^{-}\)G\(^{+}\)g\(^{-}\) and its degenerate forms that are only about 150 cm\(^{-1}\) higher in energy. In Fig. 1 are the 9 unique conformations that are found to be minima, the relative energies for which are given in Table I. A comparison of their relative energies at different levels of theory is given in Table S-1 in the Supplementary Material. The geometries and normal mode frequencies at the minima at the MP2/aVTZ level are provided in Tables S-2 and S-3.

It may be noted that all 10 unique structures were found to be minima in some earlier studies.\(^{[22-23,31,33,34]}\) Still, others found 9 and also differed in the conformer that was found to be a saddle point.\(^{[38-39]}\) The differences between these results are likely due to the different combinations of levels of theory and basis sets used for structure optimization. In the present work, we find that the g\(^{-}\)G\(^{+}\)g\(^{-}\) and g\(^{-}\)G\(^{-}\)g\(^{-}\) are saddle points at MP2/aVTZ level, as also found previously by Boussessi et al. at the same level of theory.\(^{[10]}\)

Fig. 1 and Table S-2 also gives the structure of a high energy geometry tCc that separates the enantiomeric pair tG\(^{+}\)g\(^{-}\) and tG\(^{-}\)g\(^{+}\). Unlike 2-fluoroethanol, whose Cc structure is a first order saddle point, tCc is a second order saddle point; see Table S-3. This suggests that lower energy pathways around this geometry would be available between the enantiomeric forms.

B. PES modelling

Towards the study of NQEs in EG, we have developed a full-dimensional PES following the reaction surface Hamiltonian approach.\(^{[35-37]}\) The potential expansion is given as

\[
V(S, \phi_1, \phi_2, \phi_3) = V_{\text{rs}}(\phi_1, \phi_2, \phi_3) + V_0(S|\phi_1, \phi_2, \phi_3),
\]

where \(V_{\text{rs}}(\phi_1, \phi_2, \phi_3)\) is the ‘reaction surface’ potential obtained by relaxing all other internals while the contributions from displacements of other internals are captured in \(V_0\).

In developing the expansions of the terms on the RHS, we make use of the required symmetries \(V(\phi_1, \phi_2, \phi_3) = V(-\phi_1, -\phi_2, -\phi_3) = V(\phi_1, \phi_3, \phi_2)\). Following Boussessi et al.\(^{[10]}\) the expansion of \(V_{\text{rs}}\) in carried out as a Fourier series in (\(\phi_1, \phi_2, \phi_3\)) space. The requirement of the symmetries \(V_{\text{rs}}(\phi_1, \phi_2, \phi_3) = V_{\text{rs}}(-\phi_1, -\phi_2, -\phi_3)\) =
FIG. 1. Stationary points of EG. The geometries are optimized at the MP2/aVTZ level of theory. The $tG^+g^-$ structure and its equivalent forms are the minimum energy conformers. Other conformers are also minima, except cCt, which is a second-order saddle point. The uppercase/lowercase notation refer to the OCCO/HOCC torsions. The relative energies and geometrical parameters of the structures are given in Tables I and S-2.

$$V_{rs}(\phi_1, \phi_3, \phi_2)$$ restricts the expansion as

$$V_{rs}(\phi_1, \phi_2, \phi_3) = \sum_{m \geq 0} \sum_{n \geq 0} A_{mnl}^{(rs,1)} \cos(m\phi_1) \cos(n\phi_2) \cos(n\phi_3)$$

$$+ \sum_{m \geq 0} \sum_{n \geq 0} A_{mnl}^{(rs,2)} \cos(m\phi_1) \left[ \cos(n\phi_2) \cos(l\phi_3) + \cos(l\phi_2) \cos(n\phi_3) \right]$$

$$+ \sum_{m \geq 0} \sum_{n > 0} A_{mnl}^{(rs,3)} \cos(m\phi_1) \sin(n\phi_2) \sin(n\phi_3)$$

$$+ \sum_{m \geq 0} \sum_{n > 0} \sum_{l > 0} A_{mnl}^{(rs,4)} \sin(m\phi_1) \sin(l\phi_3) + \sin(l\phi_2) \sin(n\phi_3)$$

$$+ \sum_{m > 0} \sum_{n \geq 0} \sum_{l > 0} A_{mnl}^{(rs,5)} \sin(m\phi_1) \sin(l\phi_3) + \sin(l\phi_2) \cos(n\phi_3),$$

where $A_{mnl}^{(rs,i)}$ are the Fourier coefficients. Using the energies of a sufficient number of geometries optimized with fixed $(\phi_1, \phi_2, \phi_3)$, $V_{rs}$ can be fit to high accuracy with a suitable choice of the expansion sizes $(M, N)$.

The symmetry requirements of $V_b(S|\phi_1, \phi_2, \phi_3)$ necessitates the identification of symmetries of the internal modes $S$. It is useful to define the parity and permutation transformations as

$$(\phi_1, \phi_2, \phi_3) \xrightarrow{\hat{\pi}} (-\phi_1, -\phi_2, -\phi_3),$$

$$(\phi_1, \phi_2, \phi_3) \xrightarrow{\hat{P}_{23}} (\phi_1, \phi_3, \phi_2).$$

On this basis, a categorization of symmetries of various physical quantities of EG can be defined based on whether they retain or change sign upon the action of $\hat{\pi}$ and $\hat{P}_{23}$. This is provided in Table II Fourier expansions of quantities $Y(\phi_1, \phi_2, \phi_3)$ that belong to the four categories, viz. $Y_{es}$, $Y_{ea}$, $Y_{os}$, and $Y_{oa}$, are given in the Eqs. S1a-d in the Supplementary Material. Of course, $V_{rs}$ is of the $Y_{es}$ form.

It is readily appreciated that several simple internals $R_j$ given in Table S-2 do not transform as eigenfunctions of the symmetry operators $\hat{\pi}$ and $\hat{P}_{23}$. However, suit-
TABLE II. Types of symmetries of physical quantities in EG.

<table>
<thead>
<tr>
<th>Type</th>
<th>Abbrev.</th>
<th>( \pi \hat{P}_{23} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>even symmetric</td>
<td>es</td>
<td>1 1</td>
</tr>
<tr>
<td>even asymmetric</td>
<td>ea</td>
<td>-1 -1</td>
</tr>
<tr>
<td>odd symmetric</td>
<td>os</td>
<td>-1 1</td>
</tr>
<tr>
<td>odd asymmetric</td>
<td>oa</td>
<td>-1 -1</td>
</tr>
</tbody>
</table>

able linear combinations \( S_j \) can be straightforwardly constructed that satisfy the symmetry properties. For example, a simple sum-and-difference combination of the CO bond stretches would respectively satisfy \( es \) and \( ea \) symmetries, while four combinations of the four CH stretches would belong to one symmetry type each. The definitions of all symmetrized internals and their symmetry type are collected in Table S-4. The optimal values \( S^\ast \) of these internals on the reaction surface obtained at the MP2/aVTZ level of theory can be fitted using the appropriate expressions from Eqs. S1a-d. It is useful to define displacements \( \delta S_j = S_j - S^\ast_j \) with respect to the reaction to the reaction surface. It is also convenient to define dimensionless (reduced) coordinates \( s_j = S_j/(\hbar^2G_{jj}/F_{jj})^{1/4} \) using the diagonal elements \( G_{jj} \) and \( F_{jj} \) of the Wilson \( F \) and \( G \) matrices obtained at the \( 1G^+ \) global minimum geometry.

We return to the expansion of \( V_b \), which is given as

\[
V_b(S|\phi_1, \phi_2, \phi_3) = \sum_{i,j} f_{ij}^{(2)}(\phi_1, \phi_2, \phi_3) \delta s_i \delta s_j \\
+ \sum_{i,j,k} f_{ijk}^{(3)}(\phi_1, \phi_2, \phi_3) \delta s_i \delta s_j \delta s_k \\
+ \sum_{i,j,k,l} f_{ijkl}^{(4)}(\phi_1, \phi_2, \phi_3) \delta s_i \delta s_j \delta s_k \delta s_l \\
+ \sum_{n=5}^{8} \sum_{\alpha} f_{\alpha}^{(n)}(\phi_1, \phi_2, \phi_3) \delta S_{\alpha}^{(n)}
\]

(4)

Since the \( \delta s_j \) are dimensionless, the force constants \( f_{ij...} \) are in energy \((\text{cm}^{-1})\) units. All quadratic and cubic terms are included. All quartic terms up to three-body terms and a very large, if not complete, set of four-body terms are included. The latter is in part necessitated by the nature of the symmetrized coordinates \( S_1-S_7 \), \( S_{12}-S_{15} \), \( S_{18}-S_{21} \) which are linear combinations of four simple internals involving the CH hydrogen; see Table S-4. Diagonal one-body terms in the simple internals translate to four-body terms in symmetrized internals. The last term of \( V_b \) is obtained from one-body high (5th to 8th) order expansion terms for all bonds and angles only \((R_1-R_{17})\). Upon re-expressing such terms in symmetrized coordinates (see Table S-4), one obtains products of 1, 2, or 4 \( \delta s's \). This is collectively denoted \( \delta S_{\alpha} \). As will be shown later, the inclusion of diagonal quintic up to octic terms resulted in an improvement in the quality of the potential for large displacements. All the force constants in Eq. [4] are functions of the dihedrals and can be expanded with the appropriate symmetry-adapted expressions (Eqs. S1a-d) based on the symmetry of the product of the displacement coordinates that follow them.

It remains to discuss how all the force constants are obtained at a sufficient number of points in \((\phi_1, \phi_2, \phi_3)\) space for fitting them to the symmetrized expansion. The quadratic force constants are obtained at each optimized \((\phi_1, \phi_2, \phi_3)\) reaction surface geometry by transforming the Cartesian Hessian into symmetrized coordinates \( S \). Cubic and quartic (up to three-body) force constants are obtained from five-point numerical differentiation of analytic Hessians obtained at geometries displaced along each \( S_j \) from the reaction surface. For the four-body quartic terms, displacements were carried out in coordinate pairs \((S_2, S_3), (S_4, S_5), (S_8, S_9), (S_{12}, S_{13}), (S_{15}, S_{19})\). In each case, numerical differentiation using analytic Hessians from the four geometries \((\pm \delta S_j, \pm \delta S_j)\) yielded the four-body derivatives. Step sizes of 0.002 Å for bonds and 0.1° for angles and dihedrals were used for both the one- and two-dimensional displacements. As done for 2-fluoroethanol [2], we have computed the quadratic force constants at the MP2/aVTZ level of theory, while the cubic and quartic force constants are evaluated at the MP2/aVTDZ level of theory keeping in mind the very large volume of Hessian calculations necessitated by our approach. The use of a lower basis implicitly requires optimal energies, geometries, and force constants at this level of theory; in effect, an auxiliary PES at the MP2/aVDZ is developed.

The lower basis set was also used to compute the higher order force constants along the dihedral surface. Towards this, one-dimensional displacements in \( R_1-R_{17}, \) i.e. all bonds and angles, were carried out from the reaction surface points. Table S-5 provides the ranges of the displacements used. After subtracting the energetic contribution up to quartic order at the displaced points (using the aVDZ-based auxiliary potential up to quartic order), the residual energy was fit to a one-dimensional expansion in the corresponding \( R_i \) from quintic up to octic order. After all derivatives are computed, they are transformed to the \( S_j \) as per the definitions in Table S-4; this step leads to products of symmetrized internals as indicated in the last term of \( V_b \). Fitting the force constants so obtained as a function of \((\phi_1, \phi_2, \phi_3)\) completes the expansion of \( V_b \).

Once the values of the various force constants are computed at a sufficiently large set of well-sampled points of \((\phi_1, \phi_2, \phi_3)\) space, they are fitted to the appropriate symmetrized expansions with well-chosen \((M, N)\) values that determine the sizes of each of the expansions. The final choices of these integer pairs for various orders of force constants and the resulting quality of the fit are discussed in Section III A below.
C. Dynamical simulations

We have performed path integral molecular dynamics (PIMD) simulations\(^{52-54}\) to study the effect of NQEs on EG. These have been carried out at 50 K, 100 K, 200 K and 300 K starting from random initially sampled geometries at the T\(^7\)g\(^-\) minimum. The propagations are carried out for 4 ns with a time step of 0.25 fs. The temperature was controlled using massive Nosé-Hoover chains with a time constant of 10 fs and a chain length of 4. For the propagator, we have used the factorization scheme due to Shiga\(^{55}\). Also, the reference system propagator algorithm (RESPA)\(^{55}\) was employed, wherein a larger time step is used for the evolution of the centroid thermostat and that of the system due to the external forces. In the PIMD simulations, a Trotter factorization into \(n = 5\) steps is used. Additionally, a smaller time step is employed for the MNHC update using the Suzuki-Yoshida factorization\(^{55}\) with parameters \(n_c = 3\) and \(n_{ys} = 5\). For classical simulations at the same temperatures, a Langevin thermostat was used with a time constant of 25 fs.

For various analyses, the trajectories were saved every 250 fs in each case. The first 50 ps was treated as the equilibration time and not analysed. From the saved data, the averages of various integrals are computed from the values of all beads and over the length of the simulation. The distribution of a given internal is similarly obtained by binning its values for all beads.

Towards the calculations of free energy profiles along the OCCO dihedral \(\phi_1\), we have carried out path integral umbrella sampling (PI-US) simulations for EG. Harmonic biases are applied to the centroid value \(\phi_{1c}\) of the dihedral. Detailed information about biases for all simulations, including without and with deuteration are provided in Table S-7. The distributions of the \(\phi_{1c}\) obtained from such simulations were used to obtain the free energy profiles (FEPs) for EG at various temperatures via the weighted histogram averaging method\(^{55}\).

In the computation of free energy profiles, application of the bias to the beads is a more rigorous procedure\(^{55-60}\)

\[
-\beta F_{qmb}(\phi_1) = \ln \left[ \frac{1}{P} \sum_{k=1}^{P} (\delta(\phi_{1c} - \phi_1)) \right], \tag{5}
\]

where \(\beta = 1/k_BT\). Lamaire et al\(^{59}\) and Cendagorta et al\(^{60}\) have shown that one can evaluate \(F_{qmb}\) using the \(F_{qm,c}\) from the expression

\[
e^{-\beta F_{qmb}(\phi_1)} = \frac{\int p(\phi_{1b}|\phi_{1c}) e^{-\beta F_{qm,c}(\phi_{1c})} d\phi_{1c}}{\int e^{-\beta F_{qm,c}(\phi_{1c})} d\phi_{1c}}, \tag{6}
\]

where \(p(\phi_{1b}|\phi_{1c})\) is the conditional probability of a bead having a dihedral of \(\phi_{1b}\) whenever the centroid dihedral is \(\phi_{1c}\). From the centroid-biased PI-US simulation discussed above the distribution \(p(\phi_{1b}|\phi_{1c})\) is evaluated and used to obtained \(F_{qm,b}\). In order to better understand the trends in the quantum free energy profiles as a function of temperature and isotopic variation, we have analysed the radii of gyration \(R_g\) of the atoms, defined as

\[
R_{g,i}^2 = \langle \frac{1}{P} \sum_{k=1}^{P} |\mathbf{r}_{ik} - \mathbf{r}_{ic}|^2 \rangle \text{ for the } i\text{th atom, where } \mathbf{r}_{ic}\text{ is the position of its ring polymer centroid.}
\]

Finally, we have carried out thermostatted ring polymer molecular dynamics (T-RPMD) simulations\(^{52}\) on EG towards the calculation of spectra. In contrast to RPMD\(^{52}\) artifacts due spurious resonances between the molecular frequencies and those of the ring polymer are removed by thermostating the non-centroid degrees of freedom of the ring polymer. We have used the Cayley transform-based modification proposed by Korol et al. for the simulations\(^{61-64}\). In particular, we have used the BCOCB scheme proposed in their work. A total of 52 initial conditions each at 50 K and 300 K were sampled from PIMD trajectories. Each T-RPMD trajectory was 100 ps long with a timestep of 0.5 fs. As recommended in the original work by Rossi et al., \(\lambda = \frac{1}{5}\) is used for the optimal damping.\(^{61}\) Counterpart classical simulations at both temperatures were carried out from 100 initial geometries, each for a total time of 100 ps with 0.25 fs timesteps. In all cases, the trajectory was saved every 1 fs. From the saved trajectories, power spectra are calculated via the computation of the velocity autocorrelation function.

### III. RESULTS AND DISCUSSION

#### A. PES fit and quality

For the development of the PES for EG as per Eq. (1), we begin with the sampling of points in \((\phi_1, \phi_2, \phi_3)\) space.
energies were fit to the even symmetric expansion for the dihedrals, a geometry optimization of other variables obtained a total of 3588 geometries. Fixing the values of with $(\phi_1, \phi_2, \phi_3)$, yielding an RMSE of 1.0 cm$^{-1}$.

As a test of the quality of the potential surface, we have compared the energies and forces obtained from our PES with ab initio values at the MP2/aVTZ level of theory at 15150 geometries. These were sampled from a combination of methods as follows.

1. Sampling from the quantum harmonic distribution, as discussed by Brown.[48] This is used at each of the 9 minima as well as the cCt and cCc geometries. For the last two, the magnitudes of the imaginary frequencies were considered for sampling purposes. Using control parameters $A$ values of 0.5, 1, and 2, we have obtained 1000 points per region, i.e. a total of 11000 points. Care was taken that internal variables sampled sufficiently widely but not over-extended and also that no two geometries are too close to each other, as measured by the ‘distance’ in bond-angle-dihedral space. As also used in our earlier study on 2-fluoroethanol,[38] vectors are composed of bond distances, angles and dihedrals for each geometry. Magnitudes of difference vectors between each pair is calculated. Denoting these as $b_1$, $b_2$, and $l_d$ for a pair of geometries, it was ensured for the 11000 points selected that at least two of the following criteria were satisfied: $b_1 > 0.2$ Å, $b_2 > 5^\circ$ and $l_d > 15^\circ$. As this approach yields points near the minima, subsequent sampling was focused on regions away from minima.

2. PIMD trajectories at 300 K with the auxiliary MP2/aVDZ PES including up to octic order terms Data are sampled from selected beads along a 2 ns trajectory every 50 fs. The collected geometries are filtered based on the bond-angle-dihedral proximity criteria. From the geometries that remained, points were sampled based on values in $\phi_1$ and $\phi_2$ (note that $\phi_3$ was not specially considered owing to its formal equivalence to $\phi_2$). (a) 500 points were sampled for $\phi_1$ in the range $[0^\circ, 40^\circ]$ and $[80^\circ, 100^\circ]$ and without restriction on $\phi_2$. (b) For $\phi_1$ outside this range, 500 points were sampled for $\phi_2$ in the ranges $[-130^\circ, -95^\circ]$ and $[-15^\circ, 30^\circ]$. (c) 1000 points in the rest of the $\phi_2$ space with $\phi_1$ again outside the fitted to high suitable expansions as per Table S-4 and Eqs. S1a-d; the RMSE and MAE provided in Table S-6 indicate high accuracy of the fits. Plots of the potential cuts of the fitted $V_{rs}$ are shown in Fig. 2.

The various derivative terms in $V_{rs}$ are also fit to appropriate Fourier expansions, the sizes of which are collected in Table III. The data for the first to second-order terms were obtained with MP2/aVTZ while those for all higher-order derivatives are at MP2/aVDZ (see Sec. II B). As also done for 2-fluoroethanol,[38] a high Fourier expansion order is used for the quadratic terms while those for cubic and higher order terms were chosen out based on the size of their fluctuation range over dihedral space. This approach was adopted to avoid overfitting.

By scanning each of the three angles in steps of 15° and discarding those that are related by symmetry, we obtained a total of 3588 geometries. Fixing the values of the dihedrals, a geometry optimization of other variables was performed at the MP2/aVTZ level of theory. The energies were fit to the even symmetric expansion for $V_{rs}$ with $(M,N) = (9,7)$, yielding an RMSE of 1.0 cm$^{-1}$. The optimal internals were symmetry-adapted ($S^2$) and
FIG. 3. Accuracy of the full dimensional PES for EG against a test set of 15150 points. (a) Distribution of ab initio (MP2/aVTZ) energies at the test points. (b) Distribution of the test points projected onto ($\phi_1$, $\phi_2$) space. (c) Comparison of fitted and ab initio energies. (d) Signed error, $\Delta E = E_{\text{fit}} - E_{\text{ai}}$, as a function of the ab initio energies of the test points.

ranges given in (a). The sample sizes in these regions reflect the density of filtered points. A total of 2000 points were obtained from this approach.

3. Geometries from path integral umbrella sampling simulations along $\phi_1$ using 16 beads at 300 K. Windows of 10° width, except in the ranges 40°-90° and 160°-180° were considered. From most windows and after due proximity filtering, 200 points were taken, except fewer ones from bins closest to the excluded areas. A total of 1850 points were sampled in this manner. In addition, points for $\phi_1 \in [145^\circ, 180^\circ]$ and $\phi_2 \in [-135^\circ, 25^\circ]$ (200 points) and $\phi_1 \in [105^\circ, 140^\circ]$ (100 points) were added to cover regions missed by the above sampling. In this manner, a total of 2150 test points were obtained from PI-US simulations.

Overall, the sampling satisfactorily covers the dihedral space and is also energetically well distributed. Figure 3(a) and (b) provide a graphical view of the choice of sample points used to measure the accuracy of the model PES. Figure 3(c) and (d) compare the ab initio and model PES at these points. Numerical comparisons by way of root mean square errors (RMSE) and mean absolute errors (MAE) are provided in Table IV. The force errors are defined as

$$F_{\text{abs}} = \frac{1}{N} \sum_{i=1}^{N} \sum_{\alpha=x,y,z} |F_{\alpha;\text{fit}} - F_{\alpha;\text{ai}}|$$

$$F_{\text{mag}} = \frac{1}{N} \sum_{i=1}^{N} \sum_{\alpha=x,y,z} |F_{\alpha;\text{fit}}|$$

$$\alpha_{\text{ab,fit}} = \cos^{-1}\left(\frac{F_{\alpha;\text{fit}} \cdot F_{\alpha;\text{ai}}}{|F_{\alpha;\text{fit}}||F_{\alpha;\text{ai}}|}\right),$$

where $F_{\alpha;\text{fit/ai}}$ are the force vectors obtained from the PES and ab initio calculations. As these results show, the PES is quite accurate to high energies. In particular, the force errors are below chemical accuracy ($\sim 1$ kcal/mol/Å/atom or $\sim 350$ cm$^{-1}$/Å/atom), suggesting that the potential is also accurate enough for dynamical studies.

B. PIMD simulations

We begin the analysis of the NQEs in EG with the distributions of the OCCO ($\phi_1$) and the two CCOH ($\phi_2, \phi_3$) dihedrals, shown in Fig. 4, from classical and PIMD simulations at various temperatures. The simulations were initiated in the tG$^+g^-$ well. In Fig. 4(a), the plot for
\(\rho_{cl}(\phi_1)\) exhibits narrow distributions, whose breadth increases with temperatures; more thermal energy allows a larger range of \(\phi_1\) values to be sampled. Fig. 4(b) shows the all-bead quantum distributions \(\rho_{qm}(\phi_1)\) at various temperatures. These are noticeably wider than their classical counterparts, particularly at temperatures below 300K. However, it is interesting to note that the classical distribution at 300K displays a clear transition from the G\(^+\) to the G\(^-\) basin, which is not observed in the quantum distribution in part (b) of the figure. Such transitions are rare at 300 K even for the classical simulations. Moreover, starting the 300 K PIMD simulations with different initial conditions shows similar transitions, leading to distributions similar to the classical one. Therefore, we anticipate that the apparent discrepancy in the 300 K curves in parts (a) and (b) of the figure is only due to the finite length of the simulation.

Fig. 4(c,d) and (e,f) contrast the classical and quantum distributions for \(\phi_2\) and \(\phi_3\), respectively. Due to the smaller barrier in the \(\phi_2-\phi_3\) space (see Fig. 2), both dihedrals hop to other basins even at 100 K in the classical simulations. However, at 50 K, both \(\phi_2\) and \(\phi_3\) are localized in their initial basin; see Fig. 4(c,e). In contrast, we noted a finite probability for both \(\phi_2\) and \(\phi_3\) to be in g\(^-\) and t basins even at 50 K in PIMD simu-
FIG. 6. Distributions of $H_9-O_3$ and $H_{10}-O_4$ distances from (a, b) classical and (c, d) PIMD simulations of EG-h6 at various temperatures.

...lations; see Fig. 4(d,f). We attribute this to the effects of ZPEs in $\phi_2$ and $\phi_3$. To understand the mechanism of transitions between basins leading to the distributions, we have plotted the variation of $\phi_2$ and $\phi_3$ with time from PIMD and classical simulation at 50 K as shown in Fig. 5. Fig. 5(a) shows the $\phi_2$ and $\phi_3$ with time from the classical simulation at 50 K. Here, both $\phi_2$ and $\phi_3$ are localized in their initial state for the entire 4 ns simulation length. Fig. 5(b) displays the variations for EG-h6 from the PIMD simulation at 50 K, which shows two transitions. A closer look at the trajectory near the occurrence of the first transition (Fig. 5(c)) reveals that $\phi_2$ and $\phi_3$ synchronously switch their role. Fig. S-2 shows the trajectories where the deuterium of either of the hydroxy groups $H_9$ or $H_{10}$ appears to not show such transitions at least on the timescales of the simulations. These results suggest that, at 50 K, the exchange of roles of the two CCOH dihedral may be a function of the ZPE. However, it is known that PIMD simulations do not yield dynamical information. Nonetheless, we anticipate that an exchange of roles of the two OH groups does take place at low temperatures.

Fig. 6 shows the distribution of both $r_{OH}$ distances as a function of temperature from classical and quantum simulations. Expectedly, the distributions for $r_{OH_6}$ and $r_{OH_{10}}$ are very similar. As also expected for high frequency modes, the classical distributions are susceptible to temperature. In contrast, the quantum ones are essentially unaffected by it, since the zero point energy in the oscillators are much higher than the thermal energy. The classical and quantum averages $\bar{r}_{OH_6}$ and $\bar{r}_{OH_{10}}$ are depicted in Fig. 7(a). Any differences for EG-h6 in the averages are essentially due to finite simulation lengths. We expect the physically anticipated equal averages for both bond lengths to be achieved with sufficiently longer simulations and more role exchanges of the two OH groups. Considering the average of the two $r$ values, we see a small increase in the classical value due to temperature, while it is essentially constant in the quantum simulations. The OD average bond length is slightly smaller than the OH as its zero point energy is lower and a smaller span of the anharmonic PES is sampled.

Fig. 7(b) and (c) show the average O-O distance and O-H-O angle as a function of temperature. (For the latter, the ‘inner’ OH was identified as the one with a CCOH dihedral in gauche region, while the other CCOH is in the trans region.) Both the classical and quantum average O-O distances increase with temperature. This may be attributed to the increase in the average OOCO dihedral value, $\phi_1(T)$, plotted in part (d) of the figure. Note also that quantum averages are slightly larger than the classical values. From DMC simulations, Crittenden et al. also found the average O-O distance to be larger than the ab initio minimum value. The average OHO angle also decreases slightly with temperature as seen in Fig. 7(c). Also, the PIMD averages are lower (more bent) than the classical values. In contrast, our earlier study of NQEs in 2-fluoroethanol showed that where a slight reduction in...
FIG. 7. Various temperature trends from PIMD and classical simulations. (a) Average OH and OD distances for EG-h6 and EG-d6. (b) Average O-O distances. (c) Average ‘inner’ O-H-O angle. (d) Average OCCO (ϕ₁) dihedral.

the average O-F distance was found in quantum simulations compared to classical ones at all simulated temperatures. The average O-H-F angle was also slightly larger in PIMD than classical simulations. This was interpreted as a slight favouring of the OH and F interaction due to quantum effects. The current trends for EG suggest a small weakening due to NQEs. We note that this result is not inconsistent with prior NCI analyses that suggest a small attractive interaction between the OH groups in the tG⁺g⁻ geometry. The geometrical changes due to NQEs are small and we expected that attractive interaction of similar magnitude would be found from NCI analyses with NQE-averaged geometries.

C. PI-US simulations

Through umbrella sampling simulations, we have explored the effective free energy barriers for EG along its heavier OCCO torsion. The free energy profiles (FEPs) obtained from centroid-biased simulations are given in Fig. S8. Plotted are ∆F_qm,c(ϕ₁) = F_qm,c(ϕ₁) − F_qm,c(min) along with their classical counterparts, where the subscript c indicated the centroid-biasing used. Fig. S8(a) compares the FEPs for PIMD and classical simulations at 50 K and 300 K, where we see that the plots are essentially the same except for a deviation for the ∆F_qm,c at 50 K for ϕ₁ ≥ 120°. Overall, this suggests weak temperature effects for EG. It is also of note that the 0° barrier that separates enantiomeric forms tG⁺g⁻ and tG⁻g⁺ is commensurate with that for the G → T conformation isomerization. This is different from 2-fluoroethanol where the barrier was somewhat higher. We also anticipate that the slightly higher FEP values at 50 K for angles close to the T conformer have origins similar to that given for such a feature in 2-fluoroethanol since their potential landscapes bear similarities. Access to the regions of torsional space in this range of φ₁ varies with temperature, resulting in the observed FEP differences; distributions of (ϕ₁, ϕ₂) and (ϕ₁, ϕ₃) obtained from the umbrella sampling trajectories at both 50 K and 300 K are given in Fig. S-3.

Fig. S8(b) and (c) show the variation of the FEPs with isotope substitution at both 300 K and 50 K, respectively. The plots clearly show that there is a weak effect if any. At 50 K, we find only minor variation depending upon the extent of deuteration. The observed trends are similar to that previously seen for 2-fluoroethanol.

We now turn our attention to the quantum FEPs 𝐹_qm,c obtained when the beads are biased rather than the
We have analysed the trends of the mean radii of gyration \(R_g\) of the atoms of EG as a means to understand the

![FIG. 8. Centroid-biased free energy profiles, \(\Delta F_{qm,c}(\phi_1) = F_{qm,c}(\phi_1) - F_{qm,c}^{min}\), at various temperatures obtained by path integral umbrella sampling simulations along \(\phi_1\). Classical simulation results are shown alongside. (a) A comparison of profiles at 50 K and 300 K for EG-h. (b) Variation of \(F_{qm,c}(\phi_1)\) with isotopic substitutions, EG-\(D_9\) and EG-\(D_{10}\), at 300 K. (c) Same as (b) but at 50 K. Notation: CHOH \(\equiv\) EG-h6, CHOD9 \(\equiv\) EG-\(D_9\), CHOD10 \(\equiv\) EG-\(D_{10}\), CDOD \(\equiv\) EG-d6.

![FIG. 9. Bead-biased free energy profiles \(\Delta F_{qm,b}(\phi_1) = F_{qm,b}(\phi_1) - F_{qm,b}^{min}\), obtained using Eq. \(\text{(6)}\). (a) Comparison with centroid-based \(F_{qm,c}\) profiles at 50 K and 300 K for EG-h6. (b) Bead-biased FEPs for various H/D isotopic substitutions at 50 K and 300 K. Notation: CHOH \(\equiv\) EG-h6, CHOD9 \(\equiv\) EG-\(D_9\), CHOD10 \(\equiv\) EG-\(D_{10}\), CDOD \(\equiv\) EG-d6.](https://doi.org/10.26434/chemrxiv-2024-l17bl)
(O - O Å) (deg) 3 4 10 2.6 2.8 3.1 105 110 115 120 95 100 105 110 115 120

FIG. 10. Trends of the (a) average O-O distance and (b) average ‘inner’ OHO angle as a function of ϕ.

We clearly see that the radii of gyration do not change much at 300 K with or without deuteration. However, at 50 K, we see a clear increase in the values close to the ϕ = 0°. For example, Rg(C) increases by about 10% and Rg(H) for the CH hydrogen increase by about 20% for EG-h6. The ‘inner’ OH shows a similar trend as the OH in the case of 2-fluoroethanol while the Rg of the ‘outer’ OH changes less. Similar trends are observed upon deuteration as well, as seen in Fig. S-4. Therefore, the effects seen in the FES at 50 K are attributable to the quantum nature of all the atoms in the molecule and not just the OH hydrogens.

We parenthetically note that, for the perdeuterated cases shown Fig. S-4(g,h), the Rg of the carbon atoms decrease compared to the other cases where only the OH hydrogens are deuterated. A similar observation was made for 2-fluoroethanol as well. As also explained in that work, the reduction can be explained based on the observations of Ceriotti and Manolopoulos of an increase in the quantum kinetic energy of oxygen in D2O compared to H2O owing is reduced mass effect. A higher kinetic energy would imply more confinement and hence a smaller radius of gyration. We anticipate such an effect is also applicable to deuterated EG.

We briefly return to the trends in the average O-O distance and ‘inner’ O-H-O angle as a function of ϕ, shown in Fig. 10. The average values of these internal variables are obtained from each umbrella window. (Note: For 30° ≤ ϕ ≤ 90°, one of ϕ2 or ϕ3 are in the range and in the range −90° ≤ φ ≤ −15°, which defines the inner OH. When 0° ≤ ϕ ≤ 30°, the OCOH dihedral that has values in the range −60° ≤ φ ≤ 30° is taken as the inner OH. Corresponding conditions apply for ϕ < 0°.) In both plots of the figure, we see that there are significant trends along with ϕ from classical and quantum simulations, while the effects NQEs and temperature are much smaller. As the OCCO dihedral goes closer to zero, the O-O distance steadily decreases, but this effect is not due to NQEs and ultimately follows the ab initio trend (2.76 Å for tG and 2.55 Å for cCt). The OH bond lengths also show slight increases for lower ϕ values, but the trend is unclear. Fig. 10(b) shows the average ‘inner’ O-H-O angle, which steadily increases as ϕ is lowered to about 20° again and then decreases. The initial increase may be interpreted as slightly favouring the interaction between OH groups. We note that the prior study by Rosenberg indicates from a relaxed ab initio scan along the OCCO dihedral ϕ that the inner O-H-O angle reaches about 120° as ϕ → 0°. In the present simulations, the cause for the drop in the average values when ϕ is below 20° is not clear. However, at these ϕ values, we find that both the HOCC dihedrals, ϕ2 and ϕ3, are very active. We loosely attribute to observed effect of the drop in the average O-H-O angle to this. Overall, Fig. 10 emphasizes that the NQEs on interaction of the OH groups in EG are weak regardless of temperature.

D. T-RPMD simulations: Power spectra

Fig. 12 shows the power spectra of EG obtained from T-RPMD simulations at 50 K and 300 K. Shown also is the gas phase experimental spectrum due to Das et al measured at 303 K. The blue sticks indicate the band positions as measured by Buckley and Giguère at 318 K. The band centers from the present quantum simulations and experiments are compared in Table V. The assignments are based on the closest harmonic frequencies at the tG geometry and the visualized mode motions, which largely agree with the assignments of Buckley and Giguère.

We note that the simulations are carried out without any adjustments to the PES, in particular to the harmonic frequencies. Several low frequency bands are well-captured by the T-RPMD simulations, while a few fall short in the 1000-1600 cm⁻¹ range. Nonetheless, the
FIG. 11. Mean radii of gyration $R_g$ of atoms in EG-h6 at (a, b) 300 K and (c, d) 50 K as a function of $\phi_1$.

computed bands appear within the experimental band width. The CH and OH stretches are computed to be blue-shifted relative to experiments, again mainly due to the unadjusted harmonic frequencies in our PES. Overall, a good match is found, pointing to the quality of the PES. An assessment of the NQEs is provided in Fig. S-5, where the 300 K spectra from classical and quantum simulations on the same PES are compared. Qualitatively, various modes are red-shifted in the latter, but the patterns are otherwise the same.

Using a sum of spectra derived from VPT2 calculations at various minima, Das et al. were able to estimate that the spectrum is largely (over 90% intensity) composed of $tG^+g^-$, $g^+G^+g^-$ and $g^+G^-g^-$ conformers. Their contributions were about 56%, 23% and 13%, respectively, from their Boltzmann populations. (See Table I for their ab initio relative energies). Note that these conformers are different only in the OH dihedral orientation. Particularly at 300 K, the path integral dynamics of EG accesses all three conformers in a single simulation, and therefore permits a direct computation of an anharmonic spectrum with contributions from the basins.

IV. SUMMARY AND CONCLUDING REMARKS

In this work, we have analysed the role of nuclear quantum effects (NQEs) on ethylene glycol (EG). By means of path integral simulations, zero-point energy and thermal effects are analysed on the structure, dihedral energy landscape and infrared spectrum. To facilitate the simulations, an accurate full dimensional potential energy surface in the reaction surface Hamiltonian framework has been constructed.

At ambient (300 K) temperature, both quantum and classical simulations show that the three key dihedrals, viz. the OCCO ($\phi_1$) and HOCC ($\phi_2$, $\phi_3$) torsions, are active; the molecule samples multiple minima. However, at lower temperatures, while the motion of $\phi_1$ is restricted, $\phi_2$ and $\phi_3$ are able to sample the gauche and trans conformations. The simulations also suggest role exchange between inner and outer OH groups. Examining the NQEs on the interaction between the two OH groups in the global minimum region, the O-O distance slightly increases when compared to classical simulations, suggesting a slight weakening of the interaction. This trend is consistent with prior work but opposite to our recent finding on 2-fluoroethanol, where the O-O distance slightly decreases. However, from umbrella sam-
FIG. 12. Power spectra at 50 K (green curve) and 300 K (red curve) computed with T-RPMD simulations compared with experimental spectra from Das et al. (black curve) and Buckley and Giguère (blue lines). The spectrum is split into (a) low, (b) mid and (c) high frequency ranges for clarity. See also Fig. S-5.

Sampling simulations as a function of the OCCO dihedral, it is seen that the difference between classical and quantum averages are minor compared to the magnitudes of changes between the limiting dihedral values. Overall, the NQEs on structural parameters that define the intramolecular interaction between the OH groups are small.

More prominent effects are found in the dihedral landscape, where we find that the barrier in the cis region of the OCCO dihedral is strongly decreased at low temperatures (50 K) compared to the ab initio or classical simulation value. Analysing the radii of gyration of the atoms along the dihedral, those of the backbone C and H atoms increase significantly in this region and their cumulative effect results in the observed NQEs. At ambient temperatures, the NQEs are weak and there are no significant changes in the radii of gyration at various dihedral values. The result at low temperatures is similar to our recent finding for 2-fluoroethanol, where a reduction of barrier height was found for the FCCO dihedral close to 0°. It is of note that ab initio calculations also suggest that this dihedral region shows an intramolecular H-bond, albeit weak. Despite weak intramolecular interactions, similar systems with large amplitude motions may also show notable NQEs in specific regions of their potential landscape.

Lastly, we have analysed the NQEs on the spectrum of the EG. A comparison of the quantum and classical simulations primarily indicate a red-shift between them. It is encouraging that the quantum results agree well with experimental spectra. A key advantage of path integral simulations is that for molecules like EG with large amplitude degrees of freedom, multiple minima can be accessed in the course of such simulations, and the analysis of correlation functions derived from the trajectories gives direct access to a a fully anharmonic computed spectrum. Contributions of various minima are embedded in the spectrum automatically to the extent of the residence of the simulations in those regions. The use of path integral techniques should be therefore quite fruitful for molecules with more large amplitude degrees of freedom.
TABLE V. Comparison of computed power spectra from T-RPMD simulations at 50 K and 300 K with experimental spectral band centers. All values are in cm$^{-1}$. The band assignments are based on an approximate correspondence between the harmonic frequencies at the tG$^+g^-$ minimum and the simulated band centers.

<table>
<thead>
<tr>
<th>Description</th>
<th>T-RPMD</th>
<th>Expt$^a$</th>
<th>Expt$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>50 K</td>
<td>300 K</td>
<td>318 K</td>
</tr>
<tr>
<td>OCCO torsion</td>
<td>165</td>
<td>159</td>
<td></td>
</tr>
<tr>
<td>OH torsion (inner)</td>
<td>204</td>
<td>204</td>
<td>210</td>
</tr>
<tr>
<td>CH$_2$OH twist</td>
<td>322</td>
<td>316</td>
<td>325</td>
</tr>
<tr>
<td>OH torsion (outer)</td>
<td>383</td>
<td>385</td>
<td>375</td>
</tr>
<tr>
<td>CCO bend</td>
<td>519</td>
<td>519</td>
<td>522</td>
</tr>
<tr>
<td>CH$_2$ rock</td>
<td>872 871</td>
<td>861 875</td>
<td></td>
</tr>
<tr>
<td>CH$_2$ rock &amp; OH bend</td>
<td>1046 1049</td>
<td>1036 1000</td>
<td>1055</td>
</tr>
<tr>
<td>CC str &amp; CO asym str</td>
<td>1110 1106</td>
<td>1085</td>
<td></td>
</tr>
<tr>
<td>OH bends &amp; CH$_2$ rock</td>
<td>1158 1161</td>
<td>1146 1141</td>
<td>1160</td>
</tr>
<tr>
<td>CH$_2$ twist &amp; OH bends</td>
<td>1246 1246</td>
<td>1254 1279</td>
<td>1265</td>
</tr>
<tr>
<td>OH bends &amp; CH$_2$ wags</td>
<td>1354 1343</td>
<td>1386 1385</td>
<td>1310</td>
</tr>
<tr>
<td>CH scissor</td>
<td>1486 1482</td>
<td>1456</td>
<td>1440</td>
</tr>
<tr>
<td>CH str</td>
<td>2950 2935</td>
<td>2878 2883</td>
<td></td>
</tr>
<tr>
<td>OH str</td>
<td>3758 3715</td>
<td>3644 3590</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ From Buckley and Giguère.

$^b$ From Das et al. Band centres are estimated from the experimental spectrum. Where bands are broad or when more than one computed band falls under an experimental band, ranges are given instead.

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

Mrinal Arandhara: Conceptualization (equal); Data Curation (lead); Methodology (lead); Software (lead); Writing - original draft (lead); Writing - review and editing (equal). Sai G. Ramesh: Conceptualization (equal); Supervision (lead); Resources (lead); Writing - review and editing (equal).

DATA AVAILABILITY

The data that support the findings in this study are available from the corresponding author upon reasonable request.

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