THF Hydrates as Model Systems for Natural Gas Hydrates: Comparing their Mechanical and Vibrational Properties

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Abstract

Tetrahydrofuran (THF) hydrates are often used as analogues for natural gas hydrates in experimental research because they can form at atmospheric pressure, despite the fundamental differences between THF and hydrocarbon guest molecules. In this work, we provide new and significant insights regarding the accuracy of this substitution, which has been a point of contention for many years, by investigating the elastic properties, the crystal anisotropy, the atomic structure, and the vibrational properties of THF and THF-xenon hydrates using density functional theory. We found that our computed THF hydrate properties fall within the range of literature values for hydrocarbon hydrates, suggesting that THF hydrates are suitable substitutes for research into the mechanical properties of natural gas hydrates. Furthermore, we found that THF hydrates follow the same structure-property relationships as hydrocarbon hydrates: compressibility is governed primarily by hydrogen bond density, compressional wave velocity is a function of the average guest molecular mass, and the Young’s modulus can be approximated from hydrogen bond properties. Taken together, these results have important implications for the development of THF and natural gas hydrate technologies.
1. Introduction

In experimental research on natural gas hydrates, tetrahydrofuran (THF) hydrates are commonly used as model systems. For example, they have been used to investigate gas hydrate thermal properties,\textsuperscript{1-3} mechanical properties,\textsuperscript{4-8} nucleation and growth kinetics,\textsuperscript{9,10} and inhibitor efficacy.\textsuperscript{11-13} One of the main reasons THF hydrates are used as substitutes is because they can form at atmospheric pressure, at temperatures around 4˚C and below.\textsuperscript{14} Conventional hydrocarbon gas hydrates such as methane, ethane, and propane hydrates, which are of interest for most engineering hydrate applications, can form at similar temperatures, but only under high pressures (i.e., 0.5 - 4 MPa).\textsuperscript{14,15} This makes experimental research on hydrocarbon gas hydrates much more difficult and expensive due to the need for specialized high-pressure equipment. Therefore, THF hydrates have often been used as substitutes. However, the accuracy of this substitution has generated significant discussion over the years and is still a point of contention.\textsuperscript{14,16-19} For example, fundamental differences exist between THF and hydrocarbons as guest molecules. THF is a polar molecule, miscible in water, and capable of hydrogen bonding with the host structure, while hydrocarbons are non-polar molecules, immiscible in water, and cannot easily form guest-host hydrogen bonds. It begs the question whether or not THF hydrates can be used as proxies in order to make conclusions for natural gas hydrate systems. In fact, some researchers have been using cyclopentane hydrates as alternative model systems over perceived differences between THF hydrates and natural gas hydrates.\textsuperscript{20-22} Furthermore, the use of THF hydrates is not only limited to obtaining information about natural gas hydrates. They are also being considered for their own engineering applications, including gas separation (e.g., CO\textsubscript{2} recovery from flue gas),\textsuperscript{23-25} methane gas storage,\textsuperscript{26-28} and hydrogen gas storage.\textsuperscript{29-31}

In this work, we compute the mechanical and vibrational properties of THF hydrates from first principles in order to shed light on the differences and similarities between this model hydrate structure and natural gas hydrates. We also compute the material properties of THF-xenon hydrates to elucidate the effect of adding a second guest to the crystal structure. We show that, for the most part, THF hydrates present no significant differences in terms of their acoustic and elastic properties, their crystal anisotropy, their atomic structure, and the vibrational frequencies of their host water molecules when compared to natural gas hydrates. We also show
that adding another guest leads to some material property differences (e.g., lattice constant, compressional wave velocity, Poisson ratio, density, and bond stretching frequencies), most likely due to the fact that the molecular mass of xenon is so large. We hypothesize that if the second guest were hydrogen or methane, which both have much lower molecular masses, the properties would be much more similar to pure THF hydrates. Overall, these results suggest that THF hydrates may be used as model engineering systems for research on the mechanical properties of natural gas hydrate systems.

2. Methodology

2.1. Overall computational details

Our first-principles computations were performed using density functional theory (DFT) as implemented by the Spanish Initiative for Electronic Simulations with Thousands of Atoms (SIESTA) software program. The revised version of the Perdew-Burke-Ernzerhoff (revPBE) exchange-correlation (XC) functional was used, which falls under the Generalized Gradient Approximation (GGA) scheme. In our previous reports, we have shown that this specific XC functional works very well for gas hydrate mechanical and vibrational properties, demonstrating a unique combination of accuracy and low computational cost, when compared to other XC functionals including those that take into account long-range van der Waals interactions (e.g., DRSLL or the DFT-D2 method). Furthermore, the use of revPBE allowed us to perform a direct comparison of material properties between THF hydrates computed in this work and hydrocarbon hydrates computed in our previous work. Other simulation parameters were also kept the same as in our previous work: norm-conserving Troullier-Martins pseudopotentials, a basis set consisting of split-valence double-$\zeta$ plus polarization numerical atomic orbitals, an orbital energy shift of 50 meV, an energy mesh cut-off of 10 Å, and an atomic coordinate optimization force tolerance of 5 meV/Å. One of the advantages of using density functional theory compared to classical molecular dynamics is that empirically-based interatomic potentials are not needed, which is why DFT simulations are often referred to as first-principles calculations. However, one of the main drawbacks associated with DFT is that computations are essentially performed at 0 K from a classical mechanics perspective.
Our simulations were performed on a single unit cell of the THF and THF-xenon sII clathrate hydrate lattices, with periodic boundary conditions, because of the high computational cost associated with first-principles calculations. For sII gas hydrates, the unit cell is cubic and consists of 8 large cages (hexadecahedra) and 16 small cages (pentagonal dodecahedra) for a total of 136 water molecules (or 408 atoms) in the host structure. The initial coordinates for the host structure of THF and THF-xenon sII hydrates were taken from Takeuchi et al.,\textsuperscript{39} which were based on X-ray diffraction data and Bernal-Fowler ice rules. For the THF hydrates, we then placed one THF molecule at the center of each large cage keeping the small cages empty. For the THF-xenon hydrates, we placed one THF molecule at the center of each large cage and one xenon atom at the center of each small cage, resulting in 100% cage occupancy. The small cage, large cage and unit cell lattice of THF-xenon sII hydrates can be seen in Figure 1.

Figure 1. THF-xenon sII hydrate lattice structure: small cage, large cage, and unit cell.

2.2. Equation of state for solids

Structure optimization simulations were performed at different lattice volumes, corresponding to different total system energies. The energy-explicit form of the isothermal Vinet equation of state (EOS),\textsuperscript{40} presented in the Supporting Information, was then fitted to the energy-volume data using the least squares method in order to obtain the parameters for the pressure-explicit Vinet EOS (i.e., the equilibrium volume at zero pressure, the bulk modulus at zero pressure, and the first pressure derivative of the bulk modulus at zero pressure). The two energy-volume data sets for THF and THF-xenon hydrates along with the fitted EOS are shown in Figures S1 and S2. We chose the Vinet EOS based on the results from our previous work.\textsuperscript{34}
2.3. Elastic constants

The single-crystal elastic constants were computed following the same procedure outlined in Vlasic et al.,\textsuperscript{35} using the energy-strain analysis with the same three sets of strain: the volume-conserving tetragonal strain, the [110] strain and the [111] shear strain. The polycrystalline elastic and acoustic properties were calculated from our computed monocry stalline elastic constants using the Voigt-Reuss-Hill approximation\textsuperscript{41} and elastic relations for isotropic solids. These equations are presented in the Supporting Information.

2.4. Infrared spectra

The infrared spectra of THF and THF-xenon hydrates were computed following the same procedure outlined in Vlasic et al.,\textsuperscript{36} based on the method outlined by Fernández-Torre et al.\textsuperscript{42} We used the finite differences approach and chose the same atomic displacement (0.01 Å) and Born charges polarization grid (two points for the line integral and one for the surface integrals) as in our previous study.\textsuperscript{36} The Vibra utility program provided with the SIESTA software package was used to calculate the vibrational frequencies and intensities from the force constants and Born charges matrices. The resulting IR data was convoluted using a Lorentzian function with a half width at half maximum value of 70 cm\textsuperscript{-1} for the OH stretching bands and 30 cm\textsuperscript{-1} for all other bands. The unprocessed IR data for THF and THF-xenon hydrates can be seen in Figure S3.

3. Results and Discussion

3.1. Equation of state

Our computed solid equation of state parameters, at 0 GPa, for THF and THF-xenon sII hydrates are shown in Table 1, obtained from the energy-explicit form of the Vinet EOS. These properties can then be used in the pressure-explicit form of the Vinet EOS to obtain a pressure-volume relationship, illustrated in Figure 2. When comparing to other hydrate structures, also shown in Figure 2, THF hydrates behave very similarly in terms of compressibility, specifically
when looking at gas hydrates from hydrocarbon guests. In fact, the pressure-volume curve for THF hydrates falls in the middle of all the pressure-volume curves for hydrocarbon gas hydrates; they are virtually indistinguishable.

<table>
<thead>
<tr>
<th></th>
<th>THF</th>
<th>THF-xenon</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volume, $V_0$ ($\text{Å}^3$)</td>
<td>5077.6</td>
<td>5414.0</td>
</tr>
<tr>
<td>Bulk modulus, $B_0$ (GPa)</td>
<td>10.25</td>
<td>8.92</td>
</tr>
<tr>
<td>First pressure derivative of bulk modulus, $B'_0$</td>
<td>6.52</td>
<td>6.32</td>
</tr>
</tbody>
</table>

**Figure 2.** Our computed pressure-volume relationship for THF and THF-xenon sII gas hydrates along with relevant experimental and theoretical data.\textsuperscript{34, 37, 43}

Furthermore, there is good agreement between the compressibility of our theoretically computed THF-xenon hydrates and the experimentally determined relationship from the literature,\textsuperscript{43} especially at pressures less than 2.5 GPa. However, we found that THF-xenon hydrates are the most compressible when compared to the other hydrates in Figure 2. Adding a guest in the small cages of the pure THF hydrate structure increases its compressibility. We might have expected that a larger cage occupancy would lead to higher resistance to compression due to the additional guests. However, as we will discuss in the next section, the compressibility of clathrate hydrates is governed first and foremost by the hydrogen bond density, which is not necessarily related to cage occupancy; a higher number of hydrogen bonds per unit volume leads to a higher resistance to compression, and therefore, a lower compressibility or a higher bulk modulus.

**3.2. Hydrogen bond density**
We previously showed in another study that the bulk modulus for hydrocarbon sII gas hydrates was a function of hydrogen bond density. In Figure 3, we have updated this relationship in order to include our new results for THF and THF-xenon sII hydrates as well as some relevant literature data for THF-xenon sII, methane sI, and CO$_2$ sI hydrates. In this case, we are referring to hydrogen bonds between the host water molecules, not to be confused with guest-host hydrogen bonds, which will be discussed in section 3.4. The bulk moduli presented in Figure 3 were all calculated using the EOS fitting method. In Figure S4, bulk moduli calculated from elastic constants are shown.

![Figure 3. The effect of hydrogen bond density on the isothermal bulk modulus of sI and sII hydrates (calculated using the EOS fitting method).](image)

Figure 3 shows that an increase in hydrogen bond density leads to an increase in bulk modulus, for both hydrocarbon hydrates and THF hydrates alike. A larger number of hydrogen bonds per unit volume translates to a higher resistance to compression. This relationship not only highlights the underlying chemistry behind hydrate compressibility, but it can also be used predictively to determine the bulk modulus of hydrates based on their hydrogen bond density, and therefore their unit cell volume.

3.3. Monocrystalline elastic constants

Our computed elastic constants for THF and THF-xenon hydrates, along with their anisotropy factors for cubic crystals, are shown in Table 2. Relevant literature data for other sI
and sII hydrates\textsuperscript{35, 37, 44, 45} are shown in Table S1 for comparison. First of all, THF hydrates show no significant differences when compared to sI and sII gas hydrates with hydrocarbon guests (i.e., methane, ethane, propane, and isobutane); all three of our computed elastic constants for THF hydrates fall within the range of literature values for the hydrocarbon hydrates. Adding a guest to the small cages of THF hydrates leads to slight changes in elastic constants, as seen in Table 2 for THF-xenon hydrates. However, their values remain within the range of values presented in the literature for hydrocarbon hydrates. Furthermore, our computed anisotropy factors indicate that THF hydrate crystals are nearly isotropic, with \( A_z \approx 1 \) and \( A_e \approx 0 \), similar to the results presented in the literature for hydrocarbon hydrates, seen in Table S1. For a perfectly isotropic cubic crystal \( A_z = 1 \) and \( A_e = 0 \).

We found that THF-xenon hydrate crystals are also nearly isotropic (\( A_z = 1.17 \), \( A_e = -0.18 \)), indicating that adding a second guest to the small cages of the THF hydrate structure has minimal impact on anisotropy.

Table 2. Our computed single-crystal cubic elastic constants, Zener (\( A_z \)) and Every (\( A_e \)) anisotropy factors for THF and THF-xenon sII hydrates, at 0 GPa.

<table>
<thead>
<tr>
<th>Hydrate structure</th>
<th>( c_{11} ) (GPa)</th>
<th>( c_{12} ) (GPa)</th>
<th>( c_{44} ) (GPa)</th>
<th>( A_z )</th>
<th>( A_e )</th>
</tr>
</thead>
<tbody>
<tr>
<td>THF sII, theo., this work</td>
<td>16.0</td>
<td>6.4</td>
<td>5.8</td>
<td>1.20</td>
<td>-0.19</td>
</tr>
<tr>
<td>THF-Xe sII, theo., this work</td>
<td>17.2</td>
<td>5.8</td>
<td>6.7</td>
<td>1.17</td>
<td>-0.18</td>
</tr>
</tbody>
</table>

3.4. Polycrystalline elastic properties

The polycrystalline elastic and acoustic properties of THF and THF-xenon hydrates that we calculated using the methodology described in section 3.2 are summarized in Table 3. When compared to literature values for THF hydrates,\textsuperscript{46-51} shown in Table S2, our computed THF hydrate properties are in reasonable agreement. However, our theoretical results are systematically higher than the experimental results in the literature, which is expected since our calculations are performed at 0 K, while the experimental results\textsuperscript{46-48} for THF hydrates were obtained at temperatures between 256 K and 274 K. The effect of temperature causes a softening of the crystal lattice and is accompanied by a decrease in elastic moduli and wave velocities.

When compared to the results by Bathe et al.,\textsuperscript{46} our computed shear modulus and Young’s modulus for THF hydrates are both about twice as large. This significant difference could be due to erroneous assumptions that apparently may have been present in their calculation methods in
order to determine the elastic properties of their THF hydrates. Furthermore, Pohl et al. found evidence of residual water in their tested sample at 274 K, and frozen residual water in their sample at 263 K, which could explain the much lower compressional wave velocities that they obtained. Unlike the elastic moduli and wave velocities, the hydrate lattice constant is expected to increase with temperature. Our computed THF hydrate lattice constant of 17.18 Å at 0 K is in very good agreement with the experimental value of 17.14 Å at 20 K found by Tse and the theoretical value of 17.14 Å at 5 K found by Fang et al. Alavi et al. found a lattice constant of 17.14 Å for THF hydrates despite being at a much higher temperature of 250 K. However, they acknowledged that the SPC/E water potential that they used in their molecular dynamics (MD) simulations underestimates the lattice constants.

Table 3. Our computed polycrystalline mechanical properties of THF and THF-xenon sII hydrates, at 0 GPa: lattice constant, $a_0$ (Å), isothermal bulk modulus, $B$ (GPa), shear modulus, $G$ (GPa), Young's modulus, $E$ (GPa), compressional wave velocity, $V_p$ (km/s), shear wave velocity, $V_s$ (km/s), Poisson ratio, $\nu$, and density, $\rho$ (Kg/m$^3$).

<table>
<thead>
<tr>
<th>Hydrate structure</th>
<th>$a_0$</th>
<th>$B$</th>
<th>$G$</th>
<th>$E$</th>
<th>$V_p$</th>
<th>$V_s$</th>
<th>$\nu$</th>
<th>$\rho$</th>
</tr>
</thead>
<tbody>
<tr>
<td>THF sII, 0 K, theo., this work</td>
<td>17.18</td>
<td>9.60</td>
<td>5.36</td>
<td>13.56</td>
<td>4.11</td>
<td>2.326</td>
<td>0.264</td>
<td>990.6</td>
</tr>
<tr>
<td>THF-Xe sII, 0 K, theo., this work</td>
<td>17.55</td>
<td>9.61</td>
<td>6.25</td>
<td>15.42</td>
<td>3.37</td>
<td>1.993</td>
<td>0.233</td>
<td>1574.1</td>
</tr>
</tbody>
</table>

We found that adding a second guest, such as xenon, to the THF hydrate structure leads to a much larger lattice constant and lower wave velocities, but similar elastic moduli, as seen in Table 3. The lower compressional wave velocity for THF-Xe hydrates is consistent with previous reports that hydrate compressional wave velocities and average guest molecular mass are inversely proportional, a relationship that we presented in a recent study and have updated in Figure 4 to include our new data. Other structure-property relationships can be seen in Figures S5, S6, and S7. The significantly larger lattice constant for THF-xenon hydrates was also found experimentally by Manakov et al. However, Alavi et al. found a smaller lattice constant of 17.23 Å for THF-Xe hydrates at 263K, using MD. Therefore, our computed lattice constant of 17.55 Å at 0 K seems to be overestimated as we would expect the lattice constant to increase with temperature, and yet the value obtained experimentally by Manakov et al. at 298 K was 17.46 Å.
Figure 4. The effect of the average guest molecular mass on the compressional wave velocity of sII hydrates.

Our computed THF sII hydrate properties are almost indistinguishable when compared to literature values for hydrocarbon hydrates,\textsuperscript{35, 37, 44, 51, 52, 54} shown in Table S2, especially when looking at properties calculated using a similar method and appear to be most similar to ethane-methane and propane-methane sII gas hydrates. In Tables S2 and 3, we show that THF hydrates have a similar bulk modulus, shear modulus, Young’s modulus, compressional and shear wave velocity, Poisson ratio, and density when compared to methane sI, propane sII, ethane-methane sII, isobutane sII, and propane-methane sII hydrates. However, Fang et al.\textsuperscript{51} found a significant difference between the bulk moduli of THF hydrates (6.0 GPa) and propane (8.96 GPa) and propane-methane (9.93 GPa) hydrates, at 287.15 K and 14.5 MPa using MD simulations. They also found a significant increase in bulk modulus with the addition of a second guest in the THF hydrate structure. On the other hand, it can be seen from Table 3 that we found virtually no difference when adding a second guest to the THF hydrate structure (9.6 GPa for THF sII vs 9.61 GPa for THF-Xe sII). It should be noted that their additional guests were methane and carbon dioxide, while our guest was xenon.

Fang et al.\textsuperscript{51} suggested that the higher compressibility that they found for pure THF hydrates compared to hydrocarbon gas hydrates was due to guest-host hydrogen bonding which causes crystallographic defects, adding imperfections in the hydrate lattice making it more amenable to compression. It has been shown that THF guest molecules can indeed form hydrogen bonds with the host water molecules, leading to the formation of Bjerrum L-defects.\textsuperscript{50, 53} It has also been shown that temperature plays a large role in mediating these interactions;\textsuperscript{50, 53} as temperature increases, hydrogen bonding is more likely to occur. Conversely, as temperature
decreases, hydrogen bonding is less likely to occur. At temperatures below 180 K, Alavi et al.\textsuperscript{53} observed very little guest-host hydrogen bonding. As expected, we see no guest-host hydrogen bonding in THF hydrates in our first-principles computations at 0 K, and also no corresponding crystal defects. This could explain why we observed a much larger bulk modulus for THF hydrates than Fang et al.,\textsuperscript{51} because our lattice structure had no defects. However, Alavi et al.\textsuperscript{50} obtained a bulk modulus value of 10.62 GPa for THF hydrates at 250 K, using MD, even though they observed guest-host hydrogen bonding, which is higher than our computed value of 9.60 GPa at 0 K (without guest-host hydrogen bonding). Furthermore, Alavi et al.\textsuperscript{53} found that adding CO\textsubscript{2} into the small cages of THF hydrates increases the probability of guest-host hydrogen bonding from 1% to 5% at 263 K. Therefore, we might expect THF-CO\textsubscript{2} hydrates to be more compressible than pure THF hydrates due to an increase in Bjerrum defects associated with guest-host hydrogen bonding. However, Fang et al.\textsuperscript{51} found that adding CO\textsubscript{2} into the small cages increased the bulk modulus from 6.0 GPa to 7.8 GPa (i.e., less compressible). It is evident that the relationship between guest-host hydrogen bonding and hydrate compressibility is not so simple.

Whether or not THF hydrate mechanical properties are similar enough to hydrocarbon hydrate properties to use them as model systems may be a question of temperature, due to the potential of guest-host hydrogen bonding. According to our computations at 0 K, we have shown that THF hydrates can be used as proxies for natural gas hydrates when looking at elastic and acoustic properties. However, similar investigations into hydrate material properties at higher temperatures, where guest-host hydrogen bonding has been shown to occur in THF hydrates, would be very useful, specifically for the shear modulus which could be significantly affected by the presence of lattice defects associated with guest-host hydrogen bonding.

3.5. Hydrate atomic structure

Further evidence supporting the observation that THF hydrate properties and molecular structure are similar to hydrocarbon hydrates can be seen in Table S3. Our computed average O-O-O-O angles (109.39°) in THF hydrates are identical to the other hydrates, suggesting that the overall molecular structure of sII hydrates is independent of the nature of the guest molecules.
However, the hexagonal face angles, which are found only in the large cages, have a very small dependence on the size of the large guest molecule. For example, our computed average hexagonal face O-O-O angles of 119.90° for THF hydrates is in between the values previously found for propane and isobutane hydrates, which also corresponds to the trend in their molecular size (i.e., propane < THF < isobutane).

The bond lengths also depend on the size of the guest molecules, as seen in Table S3. We found that the molecular structure of THF hydrates is most similar to ethane-methane sII hydrates based on the OH bond, H-bond and O-O lengths. Alavi et al.\textsuperscript{53} suggested that at temperatures above 250 K, THF hydrates have weaker water-water H-bonds due to guest-host hydrogen bonding, when compared to hydrates with non-hydrogen bonding guests. As a result, weaker H-bonds would lead to longer H-bonds and shorter OH bonds. However, we do not see this in our computations at 0 K, when comparing THF hydrates to hydrocarbon hydrates.

We also found that adding xenon in the small cages of the THF hydrate structure leads to significant changes in bond lengths, but no change in O-O-O angles. The very large change in THF-xenon hydrate bond lengths, compared to the other hydrates, is most likely due to the high molecular mass and the repulsion effect of the xenon atoms. Adding a smaller guest like hydrogen, instead of xenon, to the THF hydrate structure would likely not result in nearly as significant changes. Furthermore, Figure S8 shows that THF hydrates and THF-xenon hydrates follow the same structure relationship of bond lengths to O-O distance as do hydrocarbon hydrates.

3.6. Vibrational properties

The infrared spectra of THF and THF-xenon sII hydrates computed using the methodology described in section 2.4 are shown in Figure 5, where we have split up each spectrum into the low-frequency region, the guest-bending region, and the high-frequency region. The three distinct bands in Figure 5a, associated with the host water molecules, are assigned to the hydrogen bond stretching band, the H$_2$O libration band, and the H$_2$O bending band, from left to right. In Figure 5b, the C-O-C stretching, the CH$_2$ wagging, and the CH$_2$
bending bands, associated with the THF guest molecules, can be seen from left to right (more clearly for THF-xenon hydrates). Finally, the two prominent bands in Figure 5c, associated with the host water molecules, are assigned to the OH symmetric and asymmetric stretching bands, from left to right. In Figure 5c for THF-xenon hydrates, an additional small band is visible before the OH stretching bands and is assigned to the CH₂ stretching band of the THF guest molecules.

The molecular vibrational frequencies in THF and THF-xenon hydrates associated with the band peaks from the IR spectra in Figure 5 are summarized in Tables 4 and 5. Relevant literature data are presented in Tables S6 and S7 for validation and comparison. The host H₂O vibrational frequencies in THF hydrates that we found compare well to literature values.²⁸,⁵⁵-⁵⁹ Furthermore, all five host vibrations that we computed for THF hydrates also fall within the range of values for hydrocarbon hydrates,³⁶,⁶⁰ seen in Table S6, with ethane-methane sII hydrates being the most similar. On the other hand, the host vibrations in THF-xenon hydrates are different than the rest of the hydrate structures; the hydrogen bond stretching and H₂O libration frequencies are significantly smaller, and the OH stretching frequencies are significantly larger. This is most likely due to the presence of the xenon atoms which have a much larger molecular mass than all the other guests in the hydrate structures that we have compared, leading to weaker host-host hydrogen bonds (which is further discussed below and shown in Figure 6). The H₂O bending frequency (1631 cm⁻¹), however, is indistinguishable from the other hydrate structures, evidence that the H₂O bending frequency is independent of guest type, which further supports the observations we made in a previous study.³⁶
Figure 5. Our computed IR spectra for THF (top row) and THF-xenon (bottom row) sll hydrates; a) low frequency region, b) guest bending region, and c) high frequency region.

Table 4. Our computed IR band peak frequencies (in cm$^{-1}$) for the H$_2$O vibrations in THF and THF-xenon sll hydrates.

<table>
<thead>
<tr>
<th>Hydrate structure</th>
<th>H-bond stretch</th>
<th>H$_2$O libration</th>
<th>H$_2$O bending</th>
<th>OH symmetric stretch</th>
<th>OH asymmetric stretch</th>
</tr>
</thead>
<tbody>
<tr>
<td>THF sll, 0 K, theo., this work</td>
<td>194</td>
<td>933</td>
<td>1633</td>
<td>3043</td>
<td>3265</td>
</tr>
<tr>
<td>THF-Xe sll, 0 K, theo., this work</td>
<td>168</td>
<td>872</td>
<td>1631</td>
<td>3125</td>
<td>3328</td>
</tr>
</tbody>
</table>

The THF vibrational frequencies that we computed, shown in Table 5, are in reasonable agreement with literature values, shown in Table S7. 28, 55-57, 61-64 Adding a second guest to the THF hydrate structure makes very little difference to the THF vibrational modes, as can be seen when comparing our results for THF and THF-Xe hydrates as well as the THF and THF-C$_2$H$_6$ hydrate results from Subramanian et al. 64 In our IR spectra for THF hydrates, the C-C-C-C stretch and the CH$_2$ stretch are difficult to pinpoint due to overlap with the H$_2$O libration region and the OH stretching region, respectively, illustrating the main drawback of using infrared spectroscopy for water-based systems. It is worth noting that there are some inconsistencies in the literature as to the correct assignment of the C-C-C-C stretch and the C-O-C stretch, 28, 56, 57, 61-64 but we have found a shoulder and a peak around 980 cm$^{-1}$ and 1065 cm$^{-1}$, which correspond to the two aforementioned vibrations.
Table 5. Our computed band peak frequencies (in cm\(^{-1}\)) for the guest vibrational modes in THF and THF-xenon sII hydrates.

<table>
<thead>
<tr>
<th>Hydrate structure</th>
<th>C-C-C-C stretch</th>
<th>C-O-C stretch</th>
<th>CH(_2) wag</th>
<th>CH(_2) bend</th>
<th>CH(_2) stretch</th>
</tr>
</thead>
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<tr>
<td>THF sII, 0 K, Theo. this work</td>
<td>~984</td>
<td>1067</td>
<td>1326</td>
<td>1421</td>
<td></td>
</tr>
<tr>
<td>THF-Xe sII, 0 K, Theo. this work</td>
<td>~976</td>
<td>1067</td>
<td>1325</td>
<td>1423</td>
<td>2943</td>
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</tbody>
</table>

In a recent study, we showed that the Young’s modulus of gas hydrates can be approximated using the stretching frequency and the equilibrium length of their hydrogen bonds.\(^{36}\) In Table 6, we show that this approximation works for THF hydrates as well. The approximation for THF-xenon hydrates, however, is half the value calculated using the traditional elastic constants approach. The reason for the larger discrepancy between the two approaches for THF-xenon hydrates is most likely due to the large molecular mass of the xenon atoms. The IR method relies on the average H-bond force constant and the average H-bond length which are local bond properties, while the elastic constants method relies on the shear modulus and Poisson ratio which are macroscale crystalline properties.

Table 6. Young’s modulus approximation for THF and THF-xenon sII hydrates compared to sII hydrocarbon hydrates.

<table>
<thead>
<tr>
<th>Guest molecule(s)</th>
<th>H-bond length (Å)</th>
<th>H-bond force constant (N·m(^{-1}))</th>
<th>Young’s modulus (IR) (GPa)</th>
<th>Young’s modulus (elastic constants) (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>THF, this work</td>
<td>1.764</td>
<td>2.110</td>
<td>11.96</td>
<td>13.56</td>
</tr>
<tr>
<td>THF-Xe, this work</td>
<td>1.830</td>
<td>1.584</td>
<td>8.66</td>
<td>15.42</td>
</tr>
<tr>
<td>C(_3)H(_8)(^{a,b})</td>
<td>1.749</td>
<td>2.259</td>
<td>12.92</td>
<td>11.57</td>
</tr>
<tr>
<td>(l)-C(_4)H(__{10})(^{a,b})</td>
<td>1.780</td>
<td>1.866</td>
<td>10.59</td>
<td>11.33</td>
</tr>
<tr>
<td>C(_2)H(_6)-CH(_4)(^{a,b})</td>
<td>1.772</td>
<td>2.113</td>
<td>11.93</td>
<td>14.48</td>
</tr>
<tr>
<td>C(_3)H(_6)-CH(_4)(^{a,b})</td>
<td>1.793</td>
<td>1.897</td>
<td>10.58</td>
<td>12.58</td>
</tr>
</tbody>
</table>

\(^{a}\)Vlasic et al.\(^{35}\), \(^{b}\)Vlasic et al.\(^{38}\)

Therefore, we would expect the IR approximation of the Young’s modulus to be more significantly affected by the local atomic environment (i.e., large changes in guest molecular mass). In fact, we have found that the average hydrogen bond force constant, which is a measure of bond strength, in hydrates depends on the molecular mass of the guests, shown in Figure 6. On the other hand, the elastic constants method takes into account host-host and guest-host
interactions as a whole, and how they affect the energy of the crystal lattice, not just of individual bonds.

![Figure 6. Average hydrogen bond force constant as a function of the average guest molecular mass per cage in sII hydrates.](image)

Furthermore, the much smaller average H-bond force constant for THF-xenon hydrates compared to the other hydrates in Table 6 cannot be due to the deviation of the average H-bond angle from its ideal configuration (i.e., 180°) since THF hydrates have a similar average H-bond angle (see Table S4), and yet a much larger average H-bond force constant. This is why we suspect that the significantly weaker hydrogen bonds in THF-xenon hydrates are caused by the presence of the xenon atoms which have a very large molecular mass leading to significant large and small cage stretching, shown in Table S5.

4. Conclusion

In summary, we computed the material properties of THF hydrates from first-principles using DFT and compared them to the properties of gas hydrates with hydrocarbon guests in order to determine the suitability of their use as model hydrate systems. More specifically, we investigated the PV relationship using an EOS, the elastic and acoustic properties, the crystal anisotropy, the molecular structure, and the vibrational properties of THF and THF-xenon sII hydrates. Our computed properties were in good agreement with available literature data for THF and THF-xenon hydrates. Our computed THF hydrate properties were nearly indistinguishable from hydrocarbon hydrate properties; the properties of THF hydrates fell within the range of
values for hydrocarbon hydrates in the literature (i.e., methane sI, propane sII, isobutane sII, ethane-methane sII, propane-methane sII hydrates) and were most similar to ethane-methane sII hydrates.

Therefore, according to our computations, we have determined that THF hydrates are appropriate substitutes for natural gas hydrates when investigating their mechanical and structural properties. However, it is important to note that other material properties and hydrate behaviour not computed in this work may still be significantly different for THF hydrates and hydrocarbon hydrates, such as their water dielectric relaxation, their thermal properties, their formation mechanisms, and their interactions with anti-agglomerants or kinetic inhibitors. In this paper, we simply set the foundation for future experiments on the structural, mechanical or vibrational properties of gas hydrates by providing evidence that THF hydrates could potentially be used instead in order to obtain relevant data much more readily.

We also found that THF hydrates follow the same structure-property relationships as hydrocarbon hydrates, such as the effect of hydrogen bond density on compressibility, the effect of guest molecular mass on compressional wave velocity and the Young’s modulus approximation from hydrogen bond properties. We found that the addition of xenon, a very large molecular mass guest, into the THF hydrate structure led to some significant changes in hydrate properties including a larger lattice volume, a lower compressional wave velocity, a lower Poisson ratio, a larger density, a larger hydrogen bond length, a lower hydrogen bond stretching frequency (lower H-bond force constant), and a larger OH stretching frequency. We suspect that adding a guest with a much smaller molecular weight, such as hydrogen or methane, instead of xenon into the THF hydrate crystal structure would not have nearly the same impact on the material properties.

It is worth noting that in our simulations we found no evidence of guest-host hydrogen bonding in THF hydrates, and no crystal defects, which may have had an impact on our results. Further investigations into hydrocarbon gas hydrate and THF hydrate mechanical and structural properties at higher temperatures, where guest-host hydrogen bonding plays a much more significant role, would be very useful to complement the results presented in this work,
specifically for the shear modulus which could be significantly affected by the presence of lattice defects.

Associated Content

Supporting Information. Vinet equation of state fitting to energy-volume data, unprocessed infrared data, monocrystalline elastic constants, polycrystalline elastic properties and equations, hydrate structure-property relationships, hydrate atomic structure, and hydrate vibrational frequencies.

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References


TOC Graphic

THF hydrates  \equiv  Hydrocarbon hydrates