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# Infrared Spectra of Gas Hydrates from First Principles

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## Abstract

The infrared spectra of sII gas hydrates have been computed using Density Functional Theory for the first time, at equilibrium, and under pressure. It is also the first account of a full vibrational analysis (both guest and host vibrations) for gas hydrates with hydrocarbon guest molecules. Five hydrate structures were investigated: empty, propane, isobutane, ethane-methane, and propanemethane sII hydrates. The computed IR spectra are in good agreement with available experimental and theoretical results. The OH stretching frequencies were found to increase, while the H-bond stretching, and H<sub>2</sub>O libration frequencies decreased with an increase in guest size and cage occupancy, and with a decrease in pressure. The H<sub>2</sub>O bending vibrations are relatively independent of guest size, cage occupancy, pressure, temperature, and crystal structure. The guest vibrational modes, especially the bending modes, also have minimal pressure dependence. We have also provided more quantitative evidence that gas hydrate material properties are defined by their hydrogen bond properties, by linking H-bond strength to Young's modulus. The results and ensuing vibrational analysis presented in this paper are a valuable contribution to the ongoing efforts into developing more accurate gas hydrate identification and characterization methods in the laboratory, in industry/nature, and even in outer space.

## Introduction

Clathrate hydrates, also known as gas hydrates, are crystalline solids made up almost entirely of water, leading to many similarities with ice.<sup>1</sup> However, unlike in ice, the hydrogenbonded water molecules (i.e. the host) in gas hydrates form cavities which can encapsulate small gas molecules or volatile liquids (i.e. the guests).<sup>2</sup> There are three common structures of gas hydrates: structure I (sI), structure II (sII), and structure H (sH). Methane sI hydrates are located all over the world in ocean floor sediments and in the permafrost where the temperature is low and the pressure is high, and they are considered an enormous potential source of natural gas.<sup>1</sup> This is why methane sI hydrates have received so much attention in the literature, despite the relevance of other structures (e.g. hydrocarbon sII hydrates) in nature and in industry. The significance of gas hydrates lies in their many applications. Depending on the specific application or industry, gas hydrates can be seen as being either beneficial or detrimental. For example, gas hydrate formation is favorable for energy transportation and storage (e.g. natural gas, and hydrogen gas), for carbon dioxide sequestration, for water desalination, and for hydraterelated climate change or geohazard concerns (i.e. avoiding the release of large amounts of methane from natural gas hydrate deposits). On the other hand, gas hydrate inhibition and dissociation are preferred in the oil and gas industry to avoid pipeline blockages, and in energy recovery from natural gas hydrate deposits.

In all the aforementioned applications, whether gas hydrates are seen as a nuisance or as a benefit, having an atomistic-level understanding of their material properties and what affects them is crucial. Being able to identify them (and distinguish them from ice and water) is also vital, whether you are looking at samples synthesized in the laboratory<sup>3-7</sup> (from water/ice and gas), or naturally-occurring gas hydrates in the field<sup>8-12</sup>, and even for evidence of gas hydrates on other planets and natural satellites (e.g. the Moon, where evidence of ice has recently been found using infrared spectroscopic data<sup>13</sup>). One of the most important and fundamental chemical identification tools is vibrational spectroscopy (e.g. infrared or Raman). Rauh and Mizaikoff<sup>14</sup> have outlined the importance of spectroscopy in gas hydrate research, as well as the advantages and disadvantages of using Raman or infrared (IR) techniques. Vibrational spectroscopy has been used to study hydrate formation and dissociation, cage occupancies, composition, structure,

phase transitions, and kinetics.<sup>14</sup> Although Raman spectroscopy has recently become a more prevalent analytical tool in gas hydrate research, IR spectroscopy has very seldomly been used, and analyses of the full range of vibrations in the hydrate structure remain scarce. While both spectroscopic techniques mentioned above calculate vibrational frequencies, they emphasize different vibrational information. For example, guest vibrations in gas hydrates are more prominent in Raman spectroscopy, where guest vibrational signals can be distinguished based on their specific molecular environment (e.g. guest encapsulated in large water cavity versus small water cavity), whereas IR spectroscopy is a bulk measurement technique, where the signal for hydrogen-bonded host water molecules is more prominent. Therefore, IR spectroscopy allows us to obtain a better understanding of the host molecular vibrations; in the current literature on gas hydrates, a lot of analysis has been performed on guest vibrations, but rarely on host vibrations. For gas hydrate systems, due to the high infrared absorptivity of water, it is much more difficult to obtain clear vibrational signals when using IR spectroscopy experimentally as compared to Raman spectroscopy, making theoretical computations of IR spectra that much more valuable. However, with advancements in experimental techniques (e.g. evanescent field techniques), IR spectroscopy may soon become a more accessible and widely used experimental analytical tool for gas hydrates.<sup>14</sup>

Of the relevant experimental studies on gas hydrate vibrational properties, most use Raman spectroscopy as the characterization method;<sup>4, 6, 9, 10, 15-21</sup> very few use IR spectroscopy.<sup>3</sup> In the few theoretical studies (using molecular dynamics or first principles methods) that are available in the literature, gas hydrate vibrational properties are computed either using Raman spectroscopy on individual hydrate cages<sup>22-27</sup> or using Fourier transforms of autocorrelation functions (an indirect calculation method).<sup>28-30</sup> However, when only considering individual cages, important interactions between host and guest molecules in different cages may be overlooked.

Therefore, to the best of our knowledge, this is the first report on the IR spectra of gas hydrates computed from first principles, and also the first report on the complete vibrational spectra of hydrocarbon gas hydrates (both host and guest vibrations). In the following sections, we have shown that Density Functional Theory (DFT) can give results in good agreement with experimental results when computing the vibrational frequencies of the host water molecules of gas hydrates through IR spectroscopy, something that has not been done up to this point. Additionally, we have performed our calculations on complete unit cells of sII gas hydrates, not just on individual cages. Furthermore, we have elucidated the effect of guest size and cage occupancy on the vibrational modes by computing the IR spectra of empty, simple (i.e. propane and isobutane) and mixed (i.e. ethane-methane and propane-methane) sII gas hydrates. We have demonstrated a novel multi-scale property relationship for gas hydrates, relating hydrogen bond stretching frequency to Young's modulus. We have also investigated, for the first time, the effect of pressure on the vibrational modes in sII gas hydrates with hydrocarbon guests. These results fill a significant gap in the current literature on gas hydrate characterization and identification methods.

# Methodology

All computations were performed using DFT as implemented by the Spanish Initiative for Electronic Simulations with Thousands of Atoms (SIESTA) software program<sup>31</sup>. We used the revised version of the Perdew-Burke-Ernzerhoff (revPBE) exchange-correlation (XC) functional<sup>32</sup> under the General Gradient Approximation (GGA), in all cases. This particular GGA XC functional has been shown to perform very well for gas hydrate material properties despite its shortcomings.<sup>33-37</sup> GGA XC functionals have also been used in many other recent studies investigating vibrational properties from first-principles.<sup>38-44</sup> We also tested a van der Waals (vdW) XC functional (DRSLL<sup>45</sup>), recently made available for SIESTA, for the empty sII hydrate structure. This resulted in only small differences in the IR spectrum when compared to using the GGA functional, not significant enough to warrant the much larger associated computational cost. The low frequency vibrational modes were virtually unaffected, while the higher frequency vibrational modes (OH stretching) saw small changes, with the largest change affecting the OH symmetric stretching frequency. The basis set in SIESTA consists of numerical atomic orbitals. The double-zeta polarized basis set under the split-valence scheme provided by the SIESTA software and norm-conserving Troullier-Martins pseudopotentials were used. Other notable DFT parameters used include: an orbital energy shift of 50 meV, an energy mesh cut-off of 800 Ry, a

k-grid cut-off of 10 Å, and a force tolerance of 5 meV/Å.

The computation of IR frequencies and intensities was done using the method outlined by Fernández-Torre et al.<sup>43</sup> This method involves an initial geometry optimization, followed by the calculation of the force constants and the Born charges by finite differences, and the diagonalization of the dynamical matrices in order to obtain the vibrational frequencies and the IR intensities. The initial hydrate structure generation and the geometry optimization simulations were performed as described previously in our work.<sup>36, 37</sup> The finite differences method requires the individual displacement of each atom in the unit cell in six directions (i.e. +x, -x, +y, -y, +z, z). The atomic displacement was chosen to be 0.01 Å, similar to other studies.<sup>43, 46</sup> Larger atomic displacements (e.g. 0.03 Å) were tested with no identifiable differences in the vibrational spectra. The Born charges were calculated using a polarization grid with two points for the line integrals and one point for the surface integrals, similar to other studies.<sup>43, 46</sup> We also tested an increase in the number of points in the line integrals to four and the number of points in the surface integrals to two, again with no identifiable difference. Therefore, the lower number of sampling points was chosen in order to reduce the computational time. Once the force constants and Born charges matrices were obtained, the vibrational frequencies along with their corresponding intensities were calculated using the Vibra utility program provided with the SIESTA software package. The raw IR data obtained from Vibra was convoluted using a Lorentzian function in order to obtain a continuous spectrum in the same form as the experimental results. The convolution was done using a half width at half maximum (hwhm) value of 70 cm<sup>-1</sup> for the OH stretching bands and 30 cm<sup>-1</sup> for all other bands. These values were chosen in order to obtain the best representation for the band peaks of our computed spectra, and also based on previous studies.<sup>40,</sup> 43.46

In this work, we focused on sII gas hydrates with hydrocarbon guests (i.e. methane, ethane, propane, and isobutane), which are the main components found in natural gas. Structure II gas hydrates have a cubic lattice structure. All our simulations were performed on only one unit cell (with periodic boundary conditions) due to the high computational cost of DFT calculations. Each unit of the crystal lattice consists of 136 water molecules that are hydrogenbonded to form 16 small cages (i.e. 5<sup>12</sup> cages, or pentagonal dodecahedra) and 8 large cages (i.e. 5<sup>12</sup>6<sup>4</sup> cages, or hexadecahedra), shown in Figure 1, making them by far the largest of the three common hydrate structures. We investigated the vibrational properties of five different sII gas hydrates: empty, propane, isobutane, ethane-methane, and propane-methane hydrates. Therefore, we not only evaluated the vibrational properties of simple and mixed hydrates, but also of the empty sII hydrate structure which contains no guest molecules. The empty hydrate structure is an excellent comparative tool, especially when looking at IR spectra, allowing us to effectively determine the contributions from the guest molecules. For the simple hydrates (i.e. propane and isobutane hydrates), the guest molecules are located only in the large cages, while the small cages remain empty. For the mixed hydrates (i.e. ethane-methane and propane-methane hydrates), the larger guest molecules are located in the large cages, and the smaller guest molecules are located in the small cages. Therefore, the mixed hydrates have 100% overall occupancy, the simple hydrates have 100% large cage occupancy, and the empty hydrates have 0% overall occupancy.



Figure 1. Propane-methane structure II mixed gas hydrates; left: small 5<sup>12</sup> cage containing methane; middle: large 5<sup>12</sup>6<sup>4</sup> cage containing propane; right: hydrate unit cell. Oxygen, hydrogen, and carbon atoms, are colored red, white, and blue, respectively.

# **Results and Discussion**

#### *i)* IR spectra of gas hydrates at equilibrium (i.e. 0 GPa)

In order to get a better representation of each vibrational band, the Lorentzian-convoluted IR spectra were split into two regions: the high frequency region (greater than 2700 cm<sup>-1</sup>) shown

in Figure 2, and the low frequency region (0-1800 cm<sup>-1</sup>) shown in Figure 3. The IR spectra without the convolution can be seen in Figure S1 in the Supporting Information. The first and second peak from the left in Figure 2 are assigned to the symmetric and asymmetric stretching modes of the OH bonds in the water molecules, respectively.<sup>47</sup> In general, symmetric stretches require less energy than their asymmetric counterparts, corresponding to a lower vibrational frequency (in cm<sup>-1</sup>), which can be seen in Figure 2. The intensity of the OH symmetric stretch, in this case, is also much greater than the OH asymmetric stretch intensity, which indicates that the symmetric stretch results in a greater change in the dipole moment.<sup>48</sup> We found that the symmetric and asymmetric OH stretching bands for the five sII gas hydrates are located between 2800-3150 cm<sup>-1</sup> and 3150-3350 cm<sup>-1</sup>, respectively. In Figure 3, the three large vibrational bands associated with the host H<sub>2</sub>O molecules are the translation mode, the libration mode, and the bending mode, from left to right. The H<sub>2</sub>O bending region is very well defined for all five sII hydrates (in the range of 1550-1750 cm<sup>-1</sup>), and we found that a higher number of guest atoms in the structure leads to a narrower band. We also found that the H<sub>2</sub>O libration region is between 625-1100 cm<sup>-1</sup>, and the translation band (i.e. H-bond stretching) is between 0-350 cm<sup>-1</sup> with peaks around 200 cm<sup>-1</sup>.



Figure 2. The OH stretching region (high frequency region) of our computed IR spectra at equilibrium (0 GPa) for empty, propane, isobutane, propane-methane, and ethane-methane sII hydrates.



Figure 3. The low frequency region of our computed IR spectra at equilibrium (0 GPa) for empty, propane, isobutane, propane-methane, and ethane-methane sII hydrates.

The computed IR spectra are all very similar in shape; the major differences between them are the band peak frequencies (i.e. the frequency of each vibrational mode). The peak frequency of each band in Figures 2 and 3 corresponding to the host H<sub>2</sub>O vibrational modes are summarized in Table 1 for the five sII gas hydrates that we investigated.

Table 1. The convoluted IR peak frequencies (in cm<sup>-1</sup>) for the H<sub>2</sub>O vibrations in sII gas hydrates at equilibrium, obtained from our computed IR spectra.

Guest	H-bond	H <sub>2</sub> O libration	H <sub>2</sub> O	OH symmetric	OH asymmetric		
molecule(s)	stretch		bending stretch		bending stretch str		stretch
Empty	221	989	1634	2969	3200		
Propane	201	951	1632	3024	3240		
Isobutane	184	924	1634	3063	3275		

Ethane- methane	195	922	1631	3067	3260
Propane- methane	184	907	1631	3094	3285

Our results are very similar to most values presented in the literature for gas hydrates even though direct comparisons can be made in only rare instances due to the lack of both theoretical and experimental data.<sup>3, 7, 15-17, 22, 23, 28, 42, 49</sup> A summary of available gas hydrate vibrational data is presented in Table 2. The low frequency region is under-represented in the literature, but our H-bond stretching bands agree well with those found for methane hydrates<sup>16,49</sup> between 206-218 cm<sup>-1</sup>, for THF hydrates<sup>18</sup> at 235 cm<sup>-1</sup>, and for empty hydrates<sup>49</sup> at 213 cm<sup>-1</sup>. We have also presented H<sub>2</sub>O libration frequencies for gas hydrates, which remain extremely scarce in the literature. Our H<sub>2</sub>O bending bands are also in very good agreement with gas hydrate literature values between 1620-1647 cm<sup>-1</sup>.<sup>3, 22, 23, 42</sup> A larger difference between our calculated frequencies and literature values can be seen for the OH stretching region. In particular, three DFT studies found that the OH symmetric and asymmetric stretching frequencies are between 3449-3572 cm<sup>-</sup> <sup>1</sup>, and 3604-3843 cm<sup>-1</sup>, respectively.<sup>22, 23, 42</sup> However, these values are much more similar to the OH stretching frequencies in water than in ice or in gas hydrates presented in experimental studies. In fact, experimental hydrate studies show that the OH symmetric and asymmetric stretching frequencies are between 3068-3278 cm<sup>-1</sup>, and 3198-3396 cm<sup>-1</sup>, respectively.<sup>3, 7, 9, 15-17</sup>, <sup>21</sup> Also, one other DFT study found that the OH stretching band in methane sI hydrates is located around 3000 cm<sup>-1</sup>.<sup>28</sup> When compared to literature values for vibrations in ice and water<sup>7, 15, 16, 18,</sup> <sup>38, 50-57</sup> (see Table 3), our computed H<sub>2</sub>O libration frequencies for sII gas hydrates present noticeable differences, suggesting that the libration mode could be used as a feature to distinguish between the three structures of water. Similarly, distinctive differences can also be seen in terms of hydrogen bond stretching frequencies, where our computed values for gas hydrates are higher than literature values for liquid water, but lower than literature values for ice. However, our calculated frequencies are more similar to those in ice than in water, which is expected since the structure of gas hydrates resembles ice much more than it resembles water.

Table 2. Literature vibrational frequencies (in cm<sup>-1</sup>) for H<sub>2</sub>O molecules in gas hydrates.

Hydrate structure	H-bond	H <sub>2</sub> O bending	OH symmetric	OH asymmetric
	stretch		stretch	stretch

50% sl CH <sub>4</sub> + 50% water ATR-IR exp. at 274.2 K, 4.5 MPa <sup>a</sup>		1643	3278	
THF sll Raman exp. at 255 K <sup>b</sup>			3144	
CH <sub>4</sub> sI / sII Raman exp. <sup>c</sup>	206 / 218		3153 / 3398	3369 / 3635
CH <sub>4</sub> -C <sub>2</sub> H <sub>6</sub> -C <sub>3</sub> H <sub>8</sub> sll Raman exp. <sup>c</sup>			3190	3396
H <sub>2</sub> sII Raman exp. at 78 K, 10 kPa / at 227 K, 200 MPa <sup>d</sup>			3068 / 3089	3198 / 3205
THF sll Raman exp. at 90 K <sup>e</sup> / 10 K <sup>f</sup>	222 / 235		3092 / -	3220 / -
Empty sI / CH <sub>4</sub> sI Raman DFT theo.		1626 - 1629 /	3484 - 3643 /	3802 - 3811 /
at 0 K <sup>g</sup>		1625 - 1627	3449 - 3572	3797 - 3808
Empty sll Raman DFT theo. at 0 K <sup>h</sup>		1645 - 1647	3484 - 3486	3604 - 3637
CH <sub>4</sub> sI DFT theo. at 0 K <sup>i</sup>			~3000	
Empty, CH <sub>4</sub> , C <sub>3</sub> H <sub>8</sub> , <i>i</i> -C <sub>4</sub> H <sub>10</sub> sI and sII DFT theo. at 0 K <sup><i>j</i></sup>		1620 - 1624		3838 - 3843
Empty / CH <sub>4</sub> sI hydrate MD theo. at 110 K / 145 K <sup>k</sup>	213 / 217			

<sup>a</sup>Ref. <sup>3</sup>, <sup>b</sup>ref. <sup>15</sup>, <sup>c</sup>ref. <sup>16</sup>, <sup>d</sup>ref. <sup>17</sup>, <sup>e</sup>ref <sup>7</sup>, <sup>f</sup>ref. <sup>18</sup>, <sup>g</sup>ref. <sup>22</sup>, <sup>h</sup>ref. <sup>23</sup>, <sup>i</sup>ref. <sup>28</sup>, <sup>j</sup>ref. <sup>42</sup>, <sup>k</sup>ref <sup>49</sup>

H <sub>2</sub> O structure	H-bond	H <sub>2</sub> O	H <sub>2</sub> O	OH symmetric	OH asymmetric
	stretch	libration	bending	stretch	stretch
Ice Ih Raman exp. at 90 K <sup>a</sup> /	233/-			3089 / 31/0	3208 / -
at 255 K <sup>b</sup>	2337-			5009/5140	52007-
Ice Ih Raman exp. <sup>c</sup>	210			3145	3349
Ice XI DFT theo. at 0 K <sup>d</sup>	269	975, 1031	1613	3127 (scaled)	3217 (scaled)
Lee Ib DET thee, at 0 Kd	263	068 1038	1625	2920 (raw)	3001 (raw)
ICE III DE I TIEO. ALO R	203	900, 1030	1025	3130 (scaled)	3216 (scaled)
Ice Ih exp. at 263 K <sup>e</sup>	214	820			
Ice Ih MD theo. at 250 K <sup>f</sup>	309	650	1706	3221	
Ice I <sub>c</sub> at 10 K / 140 K exp. <sup>g</sup>			- / 1615	3206 / 3220	
H <sub>2</sub> O amorphous solid at 10 K			1630 /	2002 / 2027	
/ 130 K exp. <sup>g</sup>			1645	3223/3231	
Ice films ATR-IR exp. at 266			1633	3037	
K <sup>h</sup>			1055	5257	
Ice Ih IR exp. at 4.3 K <sup>i</sup> /	234/228				
Raman exp. at 100 K <sup>j</sup>	234/220				
Ice Ih Raman exp. at 145 K /	229/-			3100 / 3138	
246 K <sup>k</sup>	2237-			310073130	
Water Raman exp. <sup>c</sup>	218			3404	3633
Water at 293 K exp. <sup>e</sup>	180	700			
Water ATR-IR exp. at 266 K <sup>h</sup>			1625	3373	
Water Raman exp. at 313 K	175	780	1645	3450	3630
and IR exp. at 298 K <sup>I</sup>	115	700	1045	00700	0000

<sup>a</sup>Ref<sup>7</sup>, <sup>b</sup>ref. <sup>15</sup>, <sup>c</sup>ref. <sup>16</sup>, <sup>d</sup>ref. <sup>38</sup>, <sup>e</sup>ref. <sup>50</sup>, <sup>f</sup>ref. <sup>51</sup>, <sup>g</sup>ref. <sup>52</sup>, <sup>h</sup>ref. <sup>53</sup>, <sup>i</sup>ref. <sup>55</sup>, <sup>j</sup>ref. <sup>56</sup>, <sup>k</sup>ref. <sup>57</sup>, <sup>l</sup>ref. <sup>54</sup>

Although we have good agreement between our calculated values and literature values for ice and hydrates, computing vibrational frequencies using DFT will inevitably lead to some differences especially when comparing to experiments. DFT vibrational calculations often neglect anharmonicity, and combined with the approximation that using XC functionals entails, it can lead to significant differences in calculated frequencies. In fact, using vdW XC functionals could reduce the error in the computed OH bond stretching band.<sup>39</sup> Scaling factors are commonly used to obtain better agreement between DFT and experiments. However, these scaling factors can vary significantly from one DFT study to the next. In fact, Malik et al.<sup>58</sup> use scaling factors from 0.942 to 0.975 for all frequencies above 800 cm<sup>-1</sup>, while Liu et al.<sup>38</sup> use a scaling factor of 1.072 for the OH stretching frequencies only. Our OH symmetric stretching frequency for empty sII hydrates (2969 cm<sup>-1</sup>) is close to the unscaled OH symmetric stretching frequency for ice Ih from Liu et al.<sup>38</sup> (2920 cm<sup>-1</sup>). On the other hand, their scaled frequency (3130 cm<sup>-1</sup>) is much closer to experimental results.<sup>15, 16, 57</sup> Despite the fact that DFT calculations are essentially done at 0 K, the effect of temperature is often not taken into account, which usually leads to large changes in values. For example, THF sII hydrate OH stretching frequencies were found to increase with temperature.<sup>15, 18</sup> If we extrapolate the THF sII hydrate OH stretching frequency at 255 K (3144 cm<sup>-1</sup>) found by Johari and Chew<sup>15</sup> back to 0 K using their rate of change with temperature (0.58 cm<sup>-1</sup>K<sup>-1</sup>), the experimental OH stretching frequency for THF sII hydrates becomes 2996 cm<sup>-1</sup> at 0 K. Our calculated OH stretching frequencies then become much more similar, without having to use scaling factors. Likewise, Minceva-Sukarova et al.<sup>57</sup> found a similar temperature dependence for the OH stretching frequencies in ice Ih. If we extrapolate their frequency at 145 K (3100 cm<sup>-1</sup>) back to 0 K using their temperature dependence (0.38 cm<sup>-1</sup>)  $^{1}$ K<sup>-1</sup>), the OH stretching frequency for ice Ih becomes 3045 cm<sup>-1</sup> at 0 K, which again is in the range of our calculated values (2969-3094 cm<sup>-1</sup>). Although, Kato et al.<sup>59</sup> found that the temperature dependence on the OH stretching frequency in THF hydrates and ice Ih was not linear, and in fact was around 3076 cm<sup>-1</sup> and 3078 cm<sup>-1</sup> at 4 K, respectively, albeit still within our range of values.

Furthermore, we have found that the type of guest molecules in the hydrate structure does in fact have an effect on the lattice vibrational modes of the host water molecules, unlike the observations made by Giannasi et al.<sup>60</sup> and by Richardson et al.<sup>61</sup> Tse et al.<sup>62</sup> also found evidence that guest type affects the vibrations of the host water molecules, however they were looking at the phonon density of states and only in the translational region, using molecular dynamics. We have elucidated the effect of guest size and cage occupancy on all the host vibrational modes obtained from our computed infrared spectra. We have found that the H-bond stretching frequency and the librational frequency decrease, while the OH stretching frequencies increase with guest size and cage occupancy, as can be seen in Table 1. A larger guest molecule causes larger stresses on the hydrate lattice and repels the water molecules in the surrounding cage causing an increase in volume (by increasing the H-bond lengths). Both of these consequences lead to a weakening of the H-bonds, and therefore a strengthening of the OH bonds. Since a higher stretching frequency is characteristic of a stronger bond, a larger guest is expected to increase the stretching frequency of the OH bonds, but decrease the stretching frequency of the H-bonds, as we see in Table 1. However, we found that guest size has no effect on the H<sub>2</sub>O bending modes; the bending modes seem to be relatively independent of pressure, temperature, guest size, cage occupancy, and crystal structure, as the H<sub>2</sub>O bending frequencies do not change significantly among all the data presented in Tables 1, 2, and 3.

The guest vibrational modes can also be seen in the IR spectra of Figure 3, but especially in Figure 4, a zoomed in view of the guest bending region. As expected, empty sII hydrates show no visible bands other than the five vibrational modes for the  $H_2O$  molecules presented in Table 1. The contributions from the propane and isobutane molecules can be obtained by comparing the propane and isobutane hydrate spectra with the empty hydrate spectrum. Likewise, the contributions from the methane guest molecules can be obtained by comparing the propane hydrate spectrum with the propane-methane hydrate spectrum. The guest vibrational modes and our computed band peak frequencies are summarized in Table 4.



Figure 4. The guest molecules bending region of our computed IR spectra at equilibrium (0 GPa).

The C-C-C bending band can be seen in our computed isobutane hydrates IR spectrum around 428 cm<sup>-1</sup>, and in the propane-methane hydrates spectrum, it is located around 369 cm<sup>-1</sup> (see Figure 3). In the propane hydrates spectrum, however, it merges with the translation band. In the ethane-methane hydrates spectrum there are no visible bands in that region as expected. We found that CH<sub>3</sub> rocking in the propane molecule is around 1120-1150 cm<sup>-1</sup> for propane and propane-methane hydrates, however, for isobutane hydrates, the band at that frequency is characteristic of the C-CH<sub>3</sub> bending in isobutane. Other guest vibrations (besides the ones shown in Table 4) that appear in our raw IR data are too weak to appear as clear bands in our convoluted IR spectra (e.g. CH<sub>2</sub> scissor in propane at 1396 cm<sup>-1</sup>, CH<sub>3</sub> rocking in ethane at 1145 cm<sup>-1</sup>, and CH<sub>3</sub> symmetric bending in ethane at 1312-1351 cm<sup>-1</sup>). Methane and ethane molecules have vibrational modes that are IR inactive (but Raman active) such as the CH symmetric stretch in methane or the C-C stretch in ethane.<sup>63</sup> This is the reason why some of their vibrational modes do not show up in our calculated IR spectra, and why ethane-methane sII hydrates have fewer visible guest vibrational bands than the other three hydrocarbon sII hydrates. The CH stretch in ethane, propane and isobutane should appear in the computed spectra, however they cannot be identified in Figure 2.

Guest	C-C-C	CH₃	C-CH <sub>3</sub>	CH <sub>4</sub>	CH <sub>2</sub>	CH₃	CH₃	CH <sub>4</sub>
molecule	bending	rocking	bending	asymmetric	wag/CH	symmetric	asymmetric	rocking
				bending	bending	bending	bending	
Propane		1132			1287	1346	1423	
Isobutane	428		1152		1288	1345	1432	
Ethane-				1245			1/13	1/75
methane				1245			1415	1475
Propane-	360	1128		1244	1287	1345	1/22	1/75
methane	505	1120		1244	1207	1040	1422	1475

Table 4. The band peak frequencies (in cm<sup>-1</sup>) for guest vibrational modes in sII gas hydrates, obtained from our computed IR spectra.

Most of the literature data on hydrate guest vibrations, presented in Table 5, are for methane hydrates. However, when comparisons can be made with our results, they agree very well. For example, we found that CH<sub>4</sub> bending occurs at around 1245 cm<sup>-1</sup> for both propanemethane and ethane-methane hydrates, while literature values are around 1244-1350 cm<sup>-1</sup>.<sup>3, 22, 29,</sup> <sup>30, 42</sup> Furthermore, CH<sub>4</sub> rocking was found to occur at 1475 cm<sup>-1</sup>, while literature values are around 1457-1526 cm<sup>-1</sup>.<sup>22, 29, 30, 42</sup> Qin and Kuhs<sup>20</sup> observed an asymmetric CH<sub>3</sub> bending frequency of 1460 cm<sup>-1</sup> in ethane sI hydrate at 113 K, comparable to our value (1413 cm<sup>-1</sup>). Our CH<sub>3</sub> rocking and CH<sub>3</sub> asymmetric bending frequencies in propane-methane hydrates are very similar to the results presented by Tang et al.<sup>21</sup> for the same hydrate structure. Most of our other computed guest vibrational frequencies have not been presented in gas hydrate literature, however they are in good agreement with the vibrational frequencies of the isolated molecules<sup>63</sup>, <sup>64</sup> (but systematically slightly lower), which enabled us to make accurate band assignments to the guest vibrational modes. From Table 5, it can be seen that CH stretching in gas hydrates has been found to occur between 2869 and 3167 cm<sup>-1</sup>,<sup>6, 11, 16, 19-22, 25, 27-30, 42</sup> which would explain why we do not obtain clear CH stretching bands in our spectra, because our OH stretching bands are in the same frequency region (2800-3300 cm<sup>-1</sup>). This illustrates the main downside to using IR spectroscopy for gas hydrates; the intensity of the host H<sub>2</sub>O molecule vibrations is much stronger than the intensity of the guest vibrations. Despite this drawback, the vibrational frequencies of the host molecules and the guest molecules presented in this work could be used to identify

specific gas hydrate structures as well as the guest molecules trapped within. For example, we found that the CH<sub>3</sub> asymmetric bending frequency in sII gas hydrates increases with guest size (from ethane to isobutane).

Hydrate structure	CH <sub>3</sub> or CH <sub>4</sub> bending	CH <sub>3</sub> or CH <sub>4</sub> rocking	CH <sub>3</sub> or CH <sub>4</sub> symmetric stretch	CH₃ or CH₄ asymmetric stretch
50% sl CH₄ + 50% water ATR-IR exp. at 274.2 K, 4.5 MPa.ª	1350			
CH₄ sI Raman exp. at 273.6 K, 33.6 bar <sup>♭</sup>			2915	
Ethane in C <sub>2</sub> H <sub>6</sub> -CH <sub>4</sub> sII hydrates Raman exp. at 150 K <sup>c</sup> / at 276 K <sup>d</sup>			2884 / 2887	2940 / 2942
Ethane / methane in C <sub>2</sub> H <sub>6</sub> -CH <sub>4</sub> sII Raman exp. at 95 K <sup>e</sup>			2902 / 2913	
CH4 sI / C2H6 sII Raman exp. at 113 K <sup>f</sup>	- / 1460		2901 - 2913 / 2887 - 2943	- / 2953
Propane in C <sub>3</sub> H <sub>8</sub> -CH <sub>4</sub> sII Raman exp. at 183 K <sup>g</sup>	1449	1156	2869 - 2877	2944
CH <sub>4</sub> sl Raman theo. at 0 K <sup>h</sup>	1315	1526	2939	3071
CH <sub>4</sub> sI Raman DFT theo. at 0 K <sup>i</sup>	1316 -1344	1536 -1540	2925 - 2943	3021 - 3059
Methane in 5 <sup>12</sup> cage Raman DFT theo. at 0 K <sup>i</sup>			2957	3078 - 3088
Methane in $5^{12}$ / ethane in $5^{12}6^4$ cages Raman DFT theo. at 0 K <sup>k</sup>			2921 / 2922	3030 / 2971 - 3000
Propane / isobutane in 5 <sup>12</sup> 6 <sup>4</sup> cage			2915 / 2900 -	2941 - 3010 /
Raman DFT theo. at 0 K <sup>k</sup>			2922	2977 - 3005
CH <sub>4</sub> sl DFT theo. at 0 K <sup>/</sup>	~1400		3014	3167
CH <sub>4</sub> sH AIMD theo. at 113 K <sup>m</sup>	1253	1466	2879	2981
CH <sub>4</sub> sI AIMD theo. at 112.4 K <sup>n</sup>	1254	1463	2871	2976
Methane in 5 <sup>12</sup> cage DFT theo. at 0 K°	1244	1457	2875	3008

Table 5. Literature data for hydrocarbon guest molecule vibrations (in cm<sup>-1</sup>) in gas hydrates.

<sup>a</sup>Ref. <sup>3</sup>, <sup>b</sup>ref. <sup>4</sup>, <sup>c</sup>ref <sup>6</sup>, <sup>d</sup>ref <sup>11</sup>, <sup>e</sup>ref. <sup>19</sup>, <sup>f</sup>ref <sup>20</sup>, <sup>g</sup>ref <sup>21</sup>, <sup>h</sup>ref. <sup>22</sup>, <sup>j</sup>ref. <sup>24</sup>, <sup>j</sup>ref. <sup>25</sup>, <sup>k</sup>ref. <sup>27</sup>, <sup>l</sup>ref. <sup>28</sup>, <sup>m</sup>ref. <sup>29</sup>, <sup>n</sup>ref. <sup>30</sup>, <sup>o</sup>ref.

#### *ii)* Young's modulus approximation for sII gas hydrates

The equation describing the vibrational frequency of a simple harmonic oscillator is:<sup>48, 65</sup>

$$\omega = \frac{1}{2\pi c} \sqrt{\frac{k(m_1 + m_2)}{m_1 m_2}}$$
 Eq. 1

where  $\omega$  is the wavenumber or the bond stretching frequency in cm<sup>-1</sup>, c is the velocity of light in cm·s<sup>-1</sup>, k is the bond force constant (also known as the spring constant) in N·m<sup>-1</sup>,  $m_1$  is the mass of atom 1 in Kg, and  $m_2$  is the mass of atom 2 in Kg. If we approximate the hydrogen bonds and the covalent OH bonds in sII gas hydrates as simple harmonic oscillators, then we can calculate their bond force constants by inputting the vibrational frequencies obtained from the IR spectra into Equation 1. The force constant of a bond is proportional to the strength of the bond.<sup>48</sup> Therefore, from the stretching frequencies in the IR spectra, we can obtain information regarding the strength of the hydrogen bonds and OH bonds. A lower frequency is associated with a lower bond strength, while a higher frequency is associated with a higher bond strength (assuming the atoms forming the bond do not change).<sup>48</sup> The calculated H-bond force constants of the five sII gas hydrates that we investigated are summarized in Table 6. We have found that H-bond strength in sII gas hydrates decreases with increasing guest size and increasing number of guests (or cage occupancy), since the H-bond force constants decrease (the same trend observed in Hbond stretching frequencies seen in Table 1). However, all five sII gas hydrates have H-bond force constants in a very narrow range  $(1.8 - 2.8 \text{ N} \cdot \text{m}^{-1})$ , which agrees very well with the standard value of  $2 \text{ N} \cdot \text{m}^{-1}$ , presented by Ashby and Jones<sup>66</sup> for hydrogen bonds.

Guest	H-bond	H-bond force	Young's modulus	Young's modulus (elastic
molecule(s)	length /Å <sup>a</sup>	constant /N·m⁻¹	(IR) /GPa	constants) /GPa <sup>a</sup>
Empty	1.710	2.726	15.94	14.67
Propane	1.749	2.259	12.92	11.57
Isobutane	1.780	1.886	10.59	11.33
Ethane-	1 772	2 113	11.03	1/ /8
methane	1.772	2.115	11.95	14.40
Propane-	1 703	1 807	10 58	12 58
methane	1.795	1.037	10.50	12.50

Table 6. The Young's modulus approximation for sII gas hydrates at equilibrium using the hydrogen bond properties, obtained from the analysis of our computed IR spectra.

<sup>*a*</sup>Ref. <sup>37</sup>

Logic would indicate that a shorter hydrogen bond would inevitably be a stronger bond. However, if this bond has a lower associated angle (i.e. further from the ideal 180°), then it may be weaker. For example, we found that isobutane sII hydrates have an average equilibrium Hbond length of 1.780 Å, which is lower than the average equilibrium H-bond length of 1.793 Å for propane-methane sII hydrates, and yet their H-bonds are slightly weaker as can be seen by a lower force constant ( $1.886 \text{ N} \cdot \text{m}^{-1}$  versus  $1.897 \text{ N} \cdot \text{m}^{-1}$ ). This is due to the fact that the average H-bond angle in isobutane sII hydrates is  $176.57^{\circ}$  (caused by a greater lattice distortion from the isobutane guest), while propane-methane sII hydrates have an average H-bond angle of  $176.72^{\circ}$ . On the other hand, we found that ethane-methane and propane-methane sII hydrates have the same average H-bond angle ( $176.72^{\circ}$ ), but since ethane-methane hydrates have a smaller average H-bond length, they have stronger H-bonds as can be seen by a larger force constant. The H-bond angles for the five sII gas hydrates are presented in Table S1 along with their associated standard deviation. A schematic of the hydrogen bonding angle is shown in Figure S2 of the Supporting Information for clarity.

The Young's modulus of a material can be estimated from the force constant of the material's bonds and the corresponding equilibrium bond length using:<sup>66</sup>

$$E = \frac{k}{r_0} \qquad \qquad Eq.2$$

where *E* is Young's modulus in GPa, *k* is the bond force constant in N·m<sup>-1</sup>, and  $r_0$  is the equilibrium bond length. Therefore, we can use Equation 1 and 2 to calculate the Young's modulus of sII gas hydrates from the vibrational frequencies of its bonds. Table 6 shows a summary of this Young's modulus approximation for the sII gas hydrates that we investigated. The calculated value of 15.94 GPa for empty sII hydrates is comparable to the Young's modulus value of 14.67 GPa calculated for empty sII hydrates from its elastic constants<sup>37</sup> (only an 8.7% overestimation). The other four hydrates have very good agreement between the two Young's modulus calculation methods as well, with ethane-methane sII hydrates having the largest discrepancy. The fact that this approximation is so close provides even more quantitative evidence that the elasticity of gas hydrates is governed by the properties of their hydrogen bonds (see the bulk modulus relationship in ref. <sup>36</sup>). The same approximation would not be possible if we were to use the OH bond vibrational properties instead. Therefore, we have successfully demonstrated that we can quantitatively relate a microscopic and local atomic bond property (i.e. hydrogen bond stretching frequency and hydrogen bond strength) in gas hydrates to a

macroscopic bulk mechanical property (i.e. Young's modulus), which is an extremely useful tool in obtaining relevant engineering material properties for gas hydrate applications.

### *iii)* Vibrational frequencies of sII gas hydrates under pressure

We also computed the IR spectra for three representative sII gas hydrates (empty, propane, and propane-methane) under pressure, both in tension (i.e. negative pressures) and in compression (i.e. positive pressures), shown in the Supporting Information in Figures S3, S4, and S5. Our pressure analysis was limited to only three different structures due to the high computational cost of IR calculations from first principles with our system size. We have determined the effect of pressure (from -1 GPa to 2 GPa) on all of the host water molecule vibrations in gas hydrates (i.e. the H-bond stretching, H<sub>2</sub>O libration, H<sub>2</sub>O bending, OH symmetric stretching, and OH asymmetric stretching frequencies), which is shown in Figure 5, and can be found in tabular form in Table S2. Until now, for gas hydrate systems, the pressure dependence on only the symmetric OH stretching frequency in sII THF hydrates had been reported in a pressure range from 0 to 0.13 GPa.<sup>15</sup> We have found that the H-bond stretching frequency in gas hydrates increases with pressure while the symmetric and asymmetric OH stretching frequencies decrease with pressure. This makes sense, as we already know that with an increase in pressure comes a decrease in H-bond length and an increase in OH bond length.<sup>37</sup> and therefore a stronger H-bond (i.e. higher frequency), but weaker OH bond (i.e. lower frequency). The increase in H-bond strength (i.e. bond force constant) with pressure for empty, propane, and propane-methane hydrates can be seen in Table S3. We also found that the H<sub>2</sub>O libration frequency increases with pressure, while the H<sub>2</sub>O bending frequency decreases slightly with pressure. Furthermore, the gap between the H<sub>2</sub>O libration band and the H<sub>2</sub>O bending band (where we see the guest molecule bending bands; see Figures S4 and S5) decreases with an increase in pressure, making it harder to clearly pinpoint the guest bending modes at higher pressures.



Figure 5. The pressure dependence of the H-bond stretching, libration, bending, OH symmetric and OH asymmetric vibrational modes in empty, propane and propane-methane sII hydrates, obtained from our computed IR spectra.

For the most part, the three sets of data for each vibrational mode in Figure 5 have almost identical shapes, and appear to simply be shifted upward or downward. For example, for the H-bond stretching frequencies, the two lower datasets can indeed be shifted upward to overlap with the empty hydrate frequencies, shown in Figure S7. Vertical shifting, in this case, could be used as a predictive tool, to extrapolate vibrational frequency data for isobutane and ethane-methane hydrates (which were only computed at equilibrium) at other pressures, and can be seen in Figure S9 of the Supporting Information.

We found that the rate of change with pressure for the OH stretching frequency (i.e.  $(\partial v/\partial P)_T$ ; the slope of the OH symmetric stretch frequency data in Figure 5) is -141 cm<sup>-1</sup>GPa<sup>-1</sup>, -122 cm<sup>-1</sup>GPa<sup>-1</sup>, and -124 cm<sup>-1</sup>GPa<sup>-1</sup> for empty, propane, and propane-methane hydrates, respectively. Similarly, the rate of change with pressure for the OH stretching frequency in THF sII hydrates at 255 K has been found to be -156 cm<sup>-1</sup>GPa<sup>-1</sup>.<sup>15</sup> In contrast, in ice Ih the dependence of the OH stretching frequency on pressure has been found to be -78.0 cm<sup>-1</sup>GPa<sup>-1</sup> at 246 K.<sup>57</sup> This would indicate that pressure has a greater effect on the strength of the hydrogen bonds in gas hydrates than in ice.

Furthermore, we observed that the OH stretching bands not only get shifted to a lower frequency with increased pressure (see Figure S3), but the OH symmetric stretching band also increases in intensity while the OH asymmetric stretching band decreases in intensity. At lower pressures, the two OH stretching bands merge together, while at higher pressures, the gap between the two OH stretching bands increases, and the OH asymmetric stretching band broadens. As the OH stretching bands shift right at lower pressures, other weak bands begin to appear. In propane-methane hydrates at -0.5 GPa, a peak can be seen at around 2974 cm<sup>-1</sup>. At -1 GPa, the OH stretching band has shifted so far right that 3 peaks can be seen at 2964 cm<sup>-1</sup>, at 3053 cm<sup>-1</sup>, and at 3118 cm<sup>-1</sup>, possibly corresponding to CH symmetric stretching in propane CH<sub>2</sub> and CH<sub>3</sub>, CH asymmetric stretching in propane CH<sub>3</sub>, and CH asymmetric stretching in methane CH<sub>4</sub>, respectively. However, Tang et al.<sup>21</sup> assigned the three guest bands in propane-methane hydrates in that region to propane CH<sub>3</sub> symmetric stretching (2869-2877 cm<sup>-1</sup>), propane CH<sub>3</sub>

asymmetrical stretching (2944 cm<sup>-1</sup>), and propane CH<sub>2</sub> stretching (2985 cm<sup>-1</sup>). Furthermore, Chazallon et al. assigned a band located at 3053 cm<sup>-1</sup> from Raman spectroscopic investigations of synthetic methane hydrate and natural gas hydrate samples to the asymmetric bending overtone of methane,<sup>9</sup> while the methane CH stretching bands were found to be between 2902-2915 cm<sup>-1</sup>. The three guest bands we see in propane-methane hydrates at -1 GPa merge with the OH stretching band at higher (positive) pressures, which is why we could not see any CH stretching bands in Section I at 0 GPa, not just for propane-methane hydrates, but for isobutane, propane, and ethane-methane hydrates as well. For propane hydrates, at -1 GPa, the OH stretching bands shift right just enough to reveal one band at 2973 cm<sup>-1</sup>, similar to propanemethane hydrates at -0.5 GPa, possibly corresponding to CH symmetric stretching in propane. Our calculated CH stretching frequencies (which were previously not detectable at 0 GPa) are in the same range as available literature data (shown in Table 5).

From our results, the C-C-C bending band for propane-methane hydrates can be seen at 364 cm<sup>-1</sup> at -1 GPa, and at 366 cm<sup>-1</sup> at -0.5 GPa, compared to the value of 369 cm<sup>-1</sup> at 0 GPa (see Figure S4). At higher pressures, however, (i.e. 1 GPa and 2 GPa), the band disappears due to the translation band shifting right. On the other hand, the C-C-C bending band becomes visible for propane hydrates at -1 GPa (365 cm<sup>-1</sup>), and at -0.5 GPa (368 cm<sup>-1</sup>), while it was not visible at 0 GPa. Although this bending mode does not change significantly, it does appear to increase very slightly with pressure. In the guest bending region under pressure, shown in Figure S5, empty hydrates show no signals as expected, since there are no guests. For propane hydrates, unlike at 0 GPa (where we saw 3 bands, and a band shoulder), at -1 GPa, we can see 4 clear bands at 1125 cm<sup>-1</sup>, 1286 cm<sup>-1</sup>, 1343 cm<sup>-1</sup>, and 1420 cm<sup>-1</sup> (CH<sub>3</sub> rocking, CH<sub>2</sub> wag, CH<sub>3</sub> symmetric bending, and CH<sub>3</sub> asymmetric bending, respectively). These peaks occur almost exactly at the same frequency as at equilibrium, and therefore these vibrations have very little pressure dependence. Our computed band peak frequencies for the guest molecule vibrations in the bending region for propane and propane-methane hydrates are summarized in Table 7. In propane-methane hydrates, we see the same six signals as previously discussed at equilibrium, again with very minimal dependence on pressure. However, at higher pressures, we start seeing fewer guest bending signals due to overlap with the H<sub>2</sub>O libration band.

Guest	Pressure	C-C-C	CH₃	CH <sub>4</sub>	CH <sub>2</sub> wag/	CH₃	CH₃
molecule	(GPa)	bending	rocking	asymmetric	СН	symmetric	asymmetric
				bending	bending	bending	bending
	-1.0	365	1125	-	1286	1343	1421
	-0.5	368	1128	-	1287	1345	1422
Propane	0.0	-	1132	-	1287	1346	1423
	1.0	-	-	-	1285	1349	1424
	2.0	-	-	-	-	1350	1426
	-1.0	364	1124	1241	-	1341	1419
Bronono	-0.5	366	1126	1243	-	1344	1422
methane	0.0	369	1128	1244	1287	1345	1422
	1.0	-	-	1246	-	1347	1424
	2.0	-	-	1248	-	1349	1425

Table 7. The band peak frequencies (in cm<sup>-1</sup>) for guest vibrational modes in sII gas hydrates under pressure, obtained from our computed IR spectra.

Figure 6 illustrates the effect of pressure on the Young's modulus of empty, propane and propane-methane hydrates approximated using the method described in Section II. We found that the Young's modulus increases with pressure for the three sII hydrates, and is systematically the largest for empty hydrates, and the smallest for propane-methane hydrates. This means that as pressure increases, the sII gas hydrates become stiffer (less elastic). Vertical shifting as described earlier is illustrated for the Young's moduli of the sII hydrates in Figures S8 and S10.



Figure 6. Young's modulus as a function of pressure for empty, propane, and propane-methane sII gas hydrates, obtained from our computed hydrogen bond properties.

*iv)* Correlations of vibrational frequencies and bond lengths

In materials with hydrogen bonds, it is well known that a correlation exists between the OH stretching frequencies and the corresponding O-O distances.<sup>18, 67-71</sup> Figure 7 shows some empirical and theoretical correlations for hydrogen-bonding materials presented in the literature along with our sII hydrate data. Our computed OH stretching frequencies agree very well with literature values for smaller O-O distances. At higher O-O distances, however, our values diverge from the literature correlations. In fact, our computed OH stretching frequencies seem to follow the same curve shape as the quantum mechanics approach presented by Goryainov et al.,<sup>68</sup> but simply shifted downward by about 225 cm<sup>-1</sup>. This systematic underestimation could be caused by using approximations (e.g. XC functionals and pseudopotentials) in DFT, or even neglecting anharmonicity.<sup>43</sup> However, neglecting anharmonicity while computing OH vibrations has been shown to upshift calculated frequencies.<sup>72</sup> Using vdW XC functionals could also reduce the error in the computed OH covalent bond stretching band, as mentioned previously.



Figure 7. Hydrogen bond and OH bond stretching frequencies in hydrogen-bonding materials as a function of O-O distance, including our computed results for sII gas hydrates, shown by the red crosses (+, \*).

Figure 7 also shows the relationship between our calculated H-bond stretching frequencies and O-O distances, a correlation much less investigated in the literature, if at all. A nearly linear trend can be seen, for the range of O-O distances available from our sII gas hydrate DFT computations. However, a larger dataset is required in order to determine the correlation at O-O distances greater than 3.0 Å and lower than 2.6 Å. As the O-O distance decreases, the OH stretching frequency decreases, while the H-bond stretching frequency increases (see Figure 7). This is consistent with the concept of length symmetrisation (or hydrogen bond symmetrisation),<sup>73</sup> where the OH length and H-bond length become equal at a specific O-O distance (or pressure). This has been experimentally confirmed for ice<sup>74</sup> at about 60 GPa, and hypothesized to occur at an O-O distance of about 2.4 Å.<sup>68</sup> It has been shown for ice that as pressure increases the stretching frequency of the OH bond decreases and the stretching frequency of the H-bond increases until a transition point (~60 GPa), after which only one vibrational signature is detectable.<sup>74</sup> The concept of length symmetrisation can be seen in Figure 7 with our sII gas hydrate vibrational data along with the data from other hydrogen-bonding materials,<sup>67-69</sup> where the OH stretching and H-bond stretching vibrations could potentially merge to form one band around 700-800 cm<sup>-1</sup>, and 2.40-2.45 Å. Similar to our previous discussion on the subject,<sup>37</sup> the guest molecules trapped in the hydrate structure would most likely act as a barrier to reach the transition point (i.e. length symmetrisation), and the hydrate lattice would rearrange or collapse at higher pressures, and would no longer be characteristic of sII gas hydrates.

# Conclusion

In summary, DFT has successfully been used in order to compute the IR spectra of five sII gas hydrates with hydrocarbon guests at equilibrium, and three representative sII gas hydrates under pressure. We have shown that using DFT to calculate the vibrational frequencies of the host water molecules of gas hydrates can give comparable results to previously reported experimental data, something that had not been done until now. We were able to analyze all of the host vibrational modes, and several of the guest vibrational modes, which is an important contribution to the current literature on gas hydrates, especially when taking into account the effect of pressure (both tensile and compressional). The significance of our results is twofold. Firstly, the gas hydrate IR spectra and vibrational signatures presented within can be used as material fingerprints in order to detect the presence of gas hydrates (e.g. in the laboratory, in the field, and in outer space), and also to distinguish them from ice and liquid water, when using IR spectroscopy as an analytical tool. For example, our computed H-bond stretching frequencies for gas hydrates are slightly higher than literature values for liquid water, but slightly lower than literature values for ice Ih. Similarly, our computed H<sub>2</sub>O libration frequencies for gas hydrates

show significant differences when compared to ice and liquid water. Secondly, we were able to develop multi-scale property relationships, combining gas hydrate structure and composition. For example, we found that with an increase in guest size and cage occupancy comes a change in host vibrational modes (e.g. decrease in H-bond stretching and H<sub>2</sub>O libration frequencies, and increase in OH stretching frequencies). We also quantitatively linked hydrogen bond stretching frequency and hydrogen bond strength, which are local microscopic properties, to the Young's modulus of gas hydrates, which is a macroscopic mechanical property essential to many gas hydrate industrial applications. By doing so, we have provided evidence that the elasticity of gas hydrates is primarily determined by the properties of their hydrogen bonds.

### Associated Content

*Supporting Information.* Raw IR spectra at equilibrium, sII gas hydrate hydrogen bond angles and schematic, convoluted IR spectra under pressure, vibrational mode peak frequency data, hydrogen bond force constants under pressure, and vertical shifting examples.

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