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Dynamics of Kr in dense clathrate hydrates

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The dynamics of Kr atoms as guests in dense clathrate hydrate structures are investigated using site specific ⁸³Kr nuclear resonant inelastic x-ray scattering (NRIXS) spectroscopy in combination with molecular dynamics simulations. The dense structure H hydrate and filled-ice structures are studied at high pressures in a diamond anvil high-pressure cell. The dynamics of Kr in the structure H clathrate hydrate quenched recovered at 77 K is also investigated. The Kr phonon density of states obtained from the experimental NRIXS data are compared with molecular dynamics simulations. The temperature and pressure dependence of the phonon spectra provide details of the Kr dynamics in the clathrate hydrate cages. Comparison with the dynamics of Kr atoms in the low-pressure structure II obtained previously was made. The Lamb-Mössbauer factor obtained from NRIXS experiments and molecular dynamics calculations are in excellent agreement and are shown to yield unique information on the strength and temperature dependence of guest-host interactions.

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I. INTRODUCTION

The study of clathrate hydrates has recently interested researchers for many reasons including their basic thermodynamic properties for possible use of gas storage including hydrogen storage, novel dense structures for the study of the hydrophobic interaction potential between guests in clathrate cages, and the glass-like thermal conductivity observed in many clathrate hydrates.¹⁻³ In addition, clathrate hydrates are a possible source of energy in the form of natural gas hydrates which have been identified in large quantities on the ocean floor and in cold underground deposits.

Recently it has been demonstrated that certain dense forms of clathrate hydrates can be recovered at low temperature and ambient pressure.^{4,5} It has been shown that structural details of the guest positions in the cages of dense clathrate structures could be accurately characterized. In addition, a new clathrate structure was revealed that was suggested to develop from the classical structure H clathrate.⁶ At high pressures some clathrates also transform to a filled-ice structure that appears to be stable to very high pressures.⁷

The clathrate hydrates formed at moderate pressures are constructed from cages of hydrogen-bonded water molecules consisting of hydrogen-bonded squares, pentagons, and hexagons and are denoted as structures I, II, and H. Structure II clathrate is a cubic crystal built from cages formed either entirely from pentagons or from 12 pentagons and 2 hexagons formed by hydrogen-bonded water molecules. The cages can hold single inert gas atoms such as Ar or Kr or small molecules in the larger cage. In the case where hydrogen is the guest molecule, there can be as many as four H₂ molecules in the large cage and one to two H₂ molecules in the small cage.⁸ Structure H clathrate [Fig. 1] is a hexagonal crystal consisting of small and medium diameter cages made up of either 12 pentagons or 3 squares, 6 pentagons, and 3 hexagons. The largest cage in this structure is made from 12 pentagons plus 8 hexagons and has a large radius of about 5.7 Å. This large cage can accommodate more than one atom or molecule.⁹

At high pressures a filled-ice structure¹⁰ can be formed which consists of a lattice of water molecules forming channels that surround guest molecules or atoms [Fig. 1].

The dynamics of guest motions in the ambient pressure Kr structure II clathrate have been recently characterized at low temperatures using site-specific ⁸³Kr nuclear resonant inelastic scattering spectroscopy and incoherent inelastic neutron scattering.¹¹ This study showed that the guest motions in clathrate cages were highly anharmonic and provided basic information for understanding the thermal conductivity in this class of materials.

The objective of this study is to help characterize guest-host interactions in a dense clathrate structure H system, the dense filled-ice structure¹⁰ at high pressures, and a quenched recovered structure H clathrate using site-specific ⁸³Kr nuclear resonant inelastic x-ray spectroscopy (NRIXS). In addition, molecular dynamics (MD) simulations are used to characterize the dynamics of structure H clathrate at high pressure and at ambient pressure and low temperatures. We show that the Lamb-Mössbauer factor, obtained from NRIXS and MD simulations, provide unique information for characterization of guest-host interactions in clathrate hydrates.

II. EXPERIMENTAL AND COMPUTATIONAL DETAILS

Clathrate samples of the type II clathrate were prepared with Kr with natural abundance of isotope composition by exposing continuously a finely ground powder of H₂O ice in a reaction vessel to Kr gas at a pressure of 30 bar for 7 days and temperatures in the range -10 to 0 °C.¹² Samples were recovered at 77 K and stored and shipped in liquid nitrogen to the Advanced Photon Source (APS) at the Argonne National Laboratory. Samples were installed in a diamond anvil pressure cell together with ruby chips which were used to monitor the pressure via ruby fluorescence. Additional samples were prepared at the National Research Council of Canada by pressurizing the Kr structure II in

FIG. 1. (Color online) Structures of structure H clathrate hydrate and Kr filled-ice (Ref. 10). Blue, red, and white spheres represent Kr, O, and H atoms, respectively.

an indium lined piston-cylinder apparatus. Samples were quenched recovered at 77 K in liquid nitrogen and stored for shipment to the APS. The structural characterization of the quenched recovered samples was reported in Ref. 5. Data were obtained at 27, 50, 66, and 100 K. The NRIXS measurements were performed at 3-ID at the APS. A four-silicon-crystal high-resolution monochromator (HRM) based on a weak-link structure¹³ with 1 meV energy bandwidth was used in the experiment. The high resolution and high throughput of this HRM make it possible to measure the low-energy phonon modes of ⁸³Kr in the clathrate at its natural abundance (11.5%) of Kr. Quenched recovered samples were installed on a specially designed beryllium windowed low-temperature sample holder that allowed maximum view of the samples by the avalanche photodiode time resolved detector. Data were obtained at 27, 66, and 100 K. The PHOENIX software¹⁴ was used for analysis of the phonon spectra obtained by NRIXS.

Molecular dynamics simulations were performed on structure II and structure H clathrate hydrates. The extended simple point charge (SPC/E) model¹⁵ was used to describe the water intermolecular interaction. This potential is described by three-point masses with the O-H distance of 1 Å and the H-O-H angle as a tetrahedral angle. In addition, oxygen interactions are described by a Lennard-Jones potential. A Lennard-Jones (12-6) potential is chosen to describe the van der Waals interactions of the rare gas atoms. The standard combination rules $\epsilon_{ij}^0 = (\epsilon_{ii}^0 \epsilon_{jj}^0)^{1/2}$ and $\sigma_{ij} = (\sigma_{ii} + \sigma_{jj})/2$ were used to derive Lennard-Jones potential parameters between water

and Kr. Isotropic NPT molecular dynamics simulations with the Nosé-Hoover barostat algorithm¹⁶ and the Melchionna *et al.*¹⁷ modification with thermostat and barostat relaxation times of 0.5 and 2.0 ps, respectively, were performed on a periodic $3 \times 3 \times 3$ ($36.99 \text{ Å} \times 36.99 \text{ Å} \times 29.76 \text{ Å}$ initial dimensions) sH clathrate hydrate supercell consisting of 918 water using version 2.14 of the DL_POLY program.¹⁸ A time step of 1 fs was used to integrate the equations of motion. Coulombic long-range interactions were calculated using the Ewald summation method with a precision of 1×10^{-6} and all intermolecular interactions in the simulation box were calculated within a cutoff distance of $R_{\text{cutoff}} = 13.0 \text{ Å}$. The simulations were carried out for a total time of 80 ps with 30 ps used for temperature scaled equilibration.

For the structure II clathrate, 8 Kr are in the large cages and 16 Kr are located in the small cages of a unit cell. For the structure H clathrate, each small and medium sized cage contained one Kr atom and the large cage contained three Kr atoms. Three Kr atoms were placed in the large cages since this was previously determined to be the optimum number via free-energy integrations performed on inert gas hydrated. Initial positions of the oxygen atoms of sH clathrate were taken from the experimental x-ray structure. The hydrogen atoms of the water molecules were placed according to the Bernal-Fowler ice rules.¹⁹ The resulting model has an H disordered structure with no net dipole moment. The one phonon part of the vibrational spectrum was calculated from the evaluation of the velocity autocorrelation function $[\sum v_j(0) \cdot v_j(t)]$. Simulations were performed on the ambient pressure clathrate at 27, 66, and 100 K and for the structure H clathrate at 1.6 GPa.

III. RESULTS AND DISCUSSION

The NRIXS data and Kr phonon density of states derived using the PHOENIX software for the structure H and MH-III filled ice obtained at 1.6 and 4.3 GPa, respectively, are shown in Figs. 2 and 3. The Kr vibrational density of states (VDOS) in structure H covers the energy range from 3 to 17 meV. The dominant contribution is at $\sim 6.5 \text{ meV}$ and can be attributed to the Kr atoms in the large cage. There are an optimum number of three Kr atoms in the large cage of the structure H clathrate²⁰ that has an effective mean cavity radius of 5.7 Å. The other two cavities have diameters of nearly equal radii of 4 and

FIG. 2. The experimental NRIXS spectra after removal of the elastic peak for the Kr structure H and Kr filled ice structures at 1.6 and 4.3 GPa, respectively.

FIG. 3. (Color online) The Kr vibrational density of states (VDOS) for (a) the Kr structure H at 16 kbar and (b) Kr filled ice structure at 43 kbar, and (c) from quench recovered structure H at 27, 66, and 100 K obtained from NRIXS.

4.1 Å and this is reflected in the higher energy features. The additional weaker feature at about 12.5 meV is most likely from cages that contain less than the maximum number of Kr atoms. For the quench recovered structure H [Fig. 3(c)], there is only a very small temperature dependence. This contrasts with the fairly strong temperature dependence seen in the structure II clathrate¹¹ for Kr in large diameter cages that are singly occupied. In comparison with the results for the structure II clathrate,¹¹ the harmonic approximation appears to provide a good description of the dynamics in the denser high pressure phases. There is a significant shift to higher energies for the denser MH-III filled ice where Kr atoms are located in the narrow channels of this structure and also in close contact with neighboring Kr atoms.

The calculated VDOS obtained from the Fourier transform of the velocity autocorrelation function and for the Kr structure H at 1.6 GPa and for the quench recovered structure H at 27, 66, and 100 K are shown in Fig. 4. The VDOS obtained from the NRIXS data for the quench recovered structure H Kr clathrate is also compared with that obtained for the filled-ice structure in Fig. 3. There is a shift in the maximum

of the VDOS between the ambient pressure and 1.6 GPa by ~ 0.5 meV reflecting the decrease in cavity size upon compression. The calculated VDOS at 1.6 GPa and 300 K has a very similar energy dependence [Fig. 4(b)] and matches well to the NRIXS result. The calculated energies and temperature dependence of the VDOS for the quench recovered structure H are in very good agreement with the experimental NRIXS result although distributed over a slightly higher frequency range. This lack of distinct temperature dependence in both the NRIXS experimental data and in the MD simulation suggests that there is a minimal anharmonic guest-host interaction potential for Kr in the structure H clathrate at ambient pressure.

The question of the thermal conductivity mechanism in clathrate hydrates has been debated for several decades and it has been shown that a resonant scattering mechanism provides one explanation for the anomalous thermal conductivity in these materials.²¹ It is therefore interesting to compare the phonon spectrum of the Kr in structure II and H clathrate with that of other gas clathrates such as the methane and xenon clathrates. The Xe and methane clathrates have been examined, for example, regarding their anomalous thermal conductivity

FIG. 4. (Color online) The calculated vibrational densities of states from MD simulations for (a) the Kr structure H at 16 kbar and (b) the quench recovered structure H clathrate at 27, 66, and 100 K.

behavior and the relationship to the rattling vibrations of the included guests. Inelastic x-ray and neutron scattering spectra of the methane and xenon hydrates have been reported.²² It was shown that there was symmetry avoided crossings of the guest vibrations and the acoustic lattice vibrations in these clathrates. The methane phonon density of states and thermal conductivity of the methane clathrate for structures I, II, and H have also recently been calculated²³ and related to the thermal conductivities of these structures. It may therefore be expected that the thermal conductivity of structure H with Kr atoms as the guests may be similar. For xenon and methane clathrates the vibrational modes in the energy ranges 2.11, 2.85, and 3.97 meV for Xe and 27.7 and 7.44 meV for CH₄ in a structure I clathrate. This compares with a maximum in the DOS of 4 meV for Kr in a structure II clathrate at low temperatures and 3.9 meV (31.5 cm⁻¹) for the quench recovered structure H in the temperature range 27–100 K. The maximum in the DOS for the quench recovered structure H occurs at nearly the same energy and this reflects the fact that the small cage size in structures H and II are equal and indicates that the three Kr atoms located in the large structure H cage are experiencing nearly the same potential energy sites. The DOS for the quench recovered structure H is independent of temperature in the range 27–100 K for Kr as a guest and calculated to change very little over the range 30–200 K. This weak temperature dependence for the Kr structure H is similar to that calculated for a methane structure H where higher occupancy is used for the largest cages in structure H. Although the temperature dependences for Kr vibrations in structures II and H Kr clathrate structures differ, their vibrations occur in the expected energy range of the acoustic branches for these materials and this most likely results in a significant contribution to the thermal conductivity of the Kr clathrate structures. The significantly larger anharmonicity seen in structure II rattling vibrations compared to that in structure H may indicate somewhat different thermal conductivity behavior. In addition, the somewhat higher vibration frequency seen in the MH-III filled ice indicates that it may be possible to increase the vibration frequency for the Kr guest atoms above that of an acoustic branch for the cage lattice. This would lead to a possible significant change in the thermal conductivity at high pressures.

IV. THE LAMB-MÖSSBAUER FACTOR

The Lamb-Mössbauer factor or recoil free fraction is obtained from the following integral over the VDOS obtained in the NRIXS analysis:

$$f_{\text{LM}} = \exp \left[-E_R \int \frac{g(E)}{E} \coth \frac{\beta E}{2} dE \right], \quad (1)$$

where $g(E)$ is the density of phonon states at energy E and $\beta = (k_B T)^{-1}$, k_B is the Boltzmann constant, T is the temperature, $E_R = \hbar^2 k^2 / 2M$ is the recoil energy of a free nucleus. M is the mass of the free nucleus and k is the magnitude of the wave vector of the x-ray photon. In this study the Lamb-Mössbauer factor was obtained from the analysis of the NRIXS and calculated DOS obtained from analysis of the MD trajectories. Its physical importance is that it is a measure of the strength of the coupling of the Kr guest atom or

FIG. 5. (Color online) Temperature dependence of the Lamb-Mössbauer factor obtained from the NRIXS measurements and MD simulations for the structure II Kr clathrate and the quench recovered structure H clathrate. The data used for the structure II clathrate analysis is from Ref. 11.

atoms with the clathrate cage. The temperature dependence of the Lamb-Mössbauer factor reflects the changing strength of the interaction of the Kr guest atom with the cage of water molecules. It can be compared with the results for other materials to give a comparison of the interaction strengths and their temperature dependences. In Fig. 5 the temperature dependence of the Lamb-Mössbauer factors for data obtained from NRIXS the quench recovered Kr structure H clathrate and from the MD trajectories on structure H and for structure II clathrate.

The Lamb-Mössbauer factor is a quantity that strongly depends on the interaction strength of the Kr Mössbauer nucleus with the surrounding environment, in this case with the cages of the clathrate formed by water molecules. It has a role that is similar to, but differs in detail, from the Debye-Waller factor in a diffraction experiment.²⁴ The difference between the Debye-Waller and the Lamb-Mössbauer factor can be seen from their precise definitions of these two quantities. The Debye-Waller factor is defined as

$$e^{-2M} = \langle e^{i\mathbf{q} \cdot \mathbf{r}} \rangle^2 \approx e^{-\langle (\mathbf{q} \cdot \mathbf{r})^2 \rangle}, \quad (2)$$

where $\mathbf{r}$ is the instantaneous displacement vector of the atom from its mean position, $\mathbf{q} = \mathbf{k}_f - \mathbf{k}_i$ is the momentum transfer, and the brackets $\langle \rangle$ indicate a time average.

The Lamb-Mössbauer factor describes scattering from Mössbauer nuclei and is defined as

$$f = \langle e^{i\mathbf{k}_f \cdot \mathbf{r}} \rangle \langle e^{-i\mathbf{k}_i \cdot \mathbf{r}} \rangle \approx e^{-\frac{1}{2}[\langle (\mathbf{k}_f \cdot \mathbf{r})^2 \rangle + \langle (\mathbf{k}_i \cdot \mathbf{r})^2 \rangle]}, \quad (3)$$

where averages are taken separately for $\mathbf{k}_f$ and $\mathbf{k}_i$. There is a significant difference between the Debye-Waller and the Lamb-Mössbauer factors in that, even in the case of forward scattering ($\mathbf{k}_f = \mathbf{k}_i$), the Lamb-Mössbauer factor is temperature dependent. For Bragg scattering, for example, there is no temperature dependence for forward scattering ($\mathbf{q} = 0$). A detailed examination of the use of and advantages of the NRIXS method as employed at synchrotron sources for obtaining Lamb-Mössbauer factors has been given by Sturhahn and Chumakov.²⁵

The Lamb-Mössbauer factors and their temperature dependences for the quench recovered structure H are shown in Fig. 5. There is excellent agreement between the experimentally derived factors and that obtained from a MD trajectory. The only difference is that there appears to be a 15 K difference in the calculated and experimental factors but this could be attributed to combined errors in the use of detailed balance and errors associated with the MD simulation itself. Figure 5 shows the temperature dependence of the Lamb-Mössbauer factor as calculated from the structure II VDOS reported in Ref. 11 as obtained from MD trajectories. Since there is a very low-energy peak at 0.94 meV in the calculated VDOS, this could not be obtained from the NRIXS data due to overlap with the zero-energy elastic peak, therefore no comparison can be made with experiment.

The Lamb-Mössbauer factors and their temperature dependence obtained from the Kr clathrates can be compared with the results from other materials as measured using NRIXS.²⁵ For example the Lamb-Mössbauer factor for bcc iron metal drops only slightly from 0.92 to 0.9 over the temperature range below 100 K. Very similar results are found for hematite (Fe_2O_3) over the same temperature range. This is a result of course of these materials being much harder or stronger bonded materials than the clathrate hydrates. The lower values and stronger temperature dependences for the clathrate hydrates are similar to that reported for some glasses where there are reported to be low-energy floppy vibrational modes.²⁶

The Kr phonon density of states in the filled-ice MH-III structure at 1.9 and 4.0 GPa can be compared with that of bulk Kr.¹³ The peak in density of states for Kr in the MH-III is significantly sharper than for bulk Kr at similar pressures and this is a direct result of the more localized nature of the Kr vibrations in the MH-III lattice. The phonon DOS for solid Kr at 2.9 GPa for example covers the range 0 to ~ 15 meV, whereas in both the structure H and MH-III structures the Kr DOS has a sharper peak structure with a half width of about 5 meV with a weaker high-energy contribution extending to ~ 15 meV in the structure H clathrate. The experimentally determined L-M factors for structure H can also be compared with that of bulk Kr. The measured L-M factors²⁷ for bulk Kr have a much stronger temperature dependence than for Kr in the structure H clathrate with the L-M factor for Kr in bulk Kr dropping from about 0.75 at 7 K to 0.15 at 85 K. This difference is most likely due to the approach to the melting point of Kr (115.79 K) that leads to a rapid softening of the bulk Kr.

Unique information can be obtained from this analysis of the Lamb-Mössbauer factor in structure H and II clathrates. First the magnitude of the Lamb-Mössbauer factor at low temperatures allows characterization of the strength of the interactions of the guest Kr atoms with their cages. The magnitude of the Lamb-Mössbauer factor for the structure II clathrate hydrate at low temperature reflects directly the existence of very low Kr frequency motions and a weaker interaction than in the structure H structure. Even though the

Kr structure H clathrate has a much larger cage with a mean cavity radius of about 5.7 Å, it is occupied by three Kr atoms and results in stronger Kr-Kr and Kr- H_2O interactions with a mean vibration frequency near 3.7 meV (Fig. 3). The almost factor of 2 difference between the low-temperature limiting values of the Lamb-Mössbauer factors for the structure H and II clathrate indicates that the Kr-host lattice interactions are much stronger in the hexagonal Kr clathrate. There is also a strong temperature dependence over the low-temperature range 20–150 K and this is much greater than seen in rigid solids such as Fe or Fe_2O_3 for example. The temperature dependence is however similar to that found in softer materials and network glasses.²⁶ As seen from Eq. (3) the temperature dependence is determined by the energy of the photon absorbed $\mathbf{k}_i$ or scattered $\mathbf{k}_f$ and the effective rigidity of the lattice as reflected in the dynamical displacements $\mathbf{r}$. This rigidity is determined by the strength of the Kr- H_2O interactions in structure II and by both the Kr- H_2O and Kr-Kr interaction strengths in structure H. The stronger coupling of the Kr atoms to the host lattice or clathrate cages in structure H results in a higher value of the Lamb-Mössbauer factor as compared to that of the structure II clathrate. There is a stronger temperature dependence of the Lamb-Mössbauer factor in structure H than in structure II. This is a result of the small temperature dependence of the Kr vibrations in structure H together with the higher frequencies for Kr vibrations in structure H.

V. SUMMARY

The NRIXS technique has been employed to characterize the dynamics of Kr guest atoms in structure H clathrates and the filled-ice structure at high pressure and for structure H at low pressure for quench recovered samples. Analysis of the temperature-dependent data for quench recovered structure H demonstrates that the VDOS and Lamb-Mössbauer factors which are used to characterize the strength of the guest-host interactions in this material can be accurately characterized. Analysis of molecular dynamics simulations on structure H clathrate yields the VDOS and Lamb-Mössbauer factors that are in excellent agreement with experiment. The VDOS obtained for Kr structure H is much less anharmonic and contains higher energy contributions than that obtained for the Kr structure II. This is reflected in the Lamb-Mössbauer factors which are significantly higher and have greater temperature dependence for structure H than for structure II as a result of the stronger interaction of the Kr guest atoms with the host cages.

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