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Lattice dynamics study of low energy guest–host coupling in clathrate hydrate*

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Our lattice dynamics simulation of Xe-hydrate with four-site TIP4P oxygen-shell model can accurately reproduce each peak position in the inelastic incoherent neutron scattering spectrum at the acoustic band (below 15 meV) and yield correct relative intensity. Based on the results, the uncertain profile at ∼6 meV is assigned to anharmonic guest modes coupled strongly to small cages. Blue shift is proposed in phonon dispersion sheet in the case of anticrossing and found to be an evident signal for guest–host coupling that explains the anomalous thermal conductivity of clathrate hydrate.

Keywords: lattice dynamics, clathrate hydrate, guest–host coupling, anticrossing
PACC: 6320D

1. Introduction

In recent years clathrate hydrates have attracted considerable attention because large accumulations of natural gas hydrates have been discovered in ocean floor sediments and in permafrost regions. The well-known glass-like low thermal conductivity[1] of gas hydrate and of semiconductor clathrate compounds with the same structure is now explained by the low energy guest–host phonon couplings, caused by the resonant effect of the anticrossings between the localized rattling modes of the enclathrated gas species and the host lattice acoustic phonon branches of the same symmetry,[2,3] and is exploited in designing thermoelectric materials[4] with clathrate structure I (sI). Recently, the anticrossing has been observed in the dispersion relation experimentally and theoretically in the case of methane and xenon hydrate by Baumert *et al.*[5] In the inelastic incoherent neutron scattering (IINS) studies of this subject, Xe hydrate[6,7] with sI is an ideal system for low frequency dynamics study due to the large differences between xenon atom and water molecule in scattering section and mass. The model and method we use in this paper allow us to determine the uncertain points in previous IINS spectrum and to propose a new measurement for the guest–host coupling in clathrate hydrates.

2. Recent neutron experiment

In Fig.1 the IINS spectrum of Xe hydrate at $T = 100$ K is shown in the energy region of 0–15 meV obtained by Gutt *et al.*[6] Eight peaks can be identified in this spectrum, which is treated as the phonon density of states (PDOS)[8] of host lattice due to the 3 orders of magnitude larger scattering power of H_2O than that of the Xe. Two broad maxima at 7.3 and 10.3 meV are assigned to the transverse acoustic (TA)

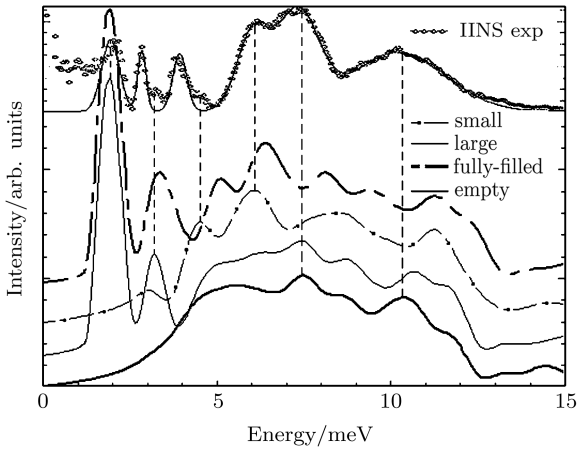


Fig.1. The calculated PDOS of Xe-H_2O hydrate with differently-filled cage compared with IINS result at the acoustic band. Corresponding peaks are connected by dashed lines.

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modes near the boundary of Brillouin zone and their fold-back towards the zone centre, respectively, which are considered as the fingerprints of empty lattice.[9] Three additional distinct profiles at 2.05, 2.87 and 3.94 meV reveal the existence of strong guest–host coupling, while two weak ones at 3.2 and 4.8 meV are then determined to be the couplings directly from the unperturbed flat guest modes at the zone centre with the original vibration frequency of Xe atoms (Fig.5 of Ref.[5]). However, no verdict has been made for the profile at ∼6 meV first proposed in the previous molecular dynamics simulation result.[10]

3. Lattice dynamics simulation details

In our work, the molecular coordinates (the centre of mass positions and the orientation of molecules in the unit cell) are optimized by the conjugate gradient method to obtain the minimized lattice energy. The initial positions of the host oxygen atoms have been obtained from the x-ray analysis of double hydrate by Mak and McMullan,[11] and those for hydrogen atoms are then calculated according to the Bernal–Fowler rules[12] together with the requirements of 2-fold disorder in the hydrogen positions. The water molecules are oriented such that the total dipole moment of the unit cell of the hydrate vanishes for the guest atoms are initially located at the centre of the cavities of host lattice.

The cubic unit cell has a lattice parameter of $a = 11.83$Å, containing 46 water molecules that form two small dodecahedron cages, each with 12 pentagonal faces (5^{12}), and six large tetrakaidecahedron cages, each with 12 pentagonal and two hexagonal faces ($5^{12}6^2$). The rigid molecular TIP4P potential[13] was used to describe intermolecular interactions, and long-range interactions were computed by Ewald summation method[14] between water molecules. The guests were considered to be spherically symmetrical, and the interaction between the guest and host that dominates the low energy band of PDOS spectrum was described by the "12-6" Lennard-Jones (L-J) function. Lorentz–Berthelot mixing rule[15] was applied to the intermolecular potential parameters which are listed in Table 1. The TIP4P O-shell model we use is a four-site potential model with point charge on each of the two hydrogen atoms (0.52|e|) and on the oxygen-shell (–1.04|e|) that initially overlaps with the O-atom of this model. The O–H bond length and H–O–H angle are 0.09572 nm and 104.50°, respectively. The O-shell separates from O-atom 0.015 nm along the molecular bisector after relaxation.

Table 1. Intermolecular potential parameters.

Interaction	ε/eV	σ/nm
Xe–Xe	0.0200	0.3980
Xe–O	0.0115	0.3567
Ar–Ar	0.0103	0.3405
Ar–O	0.0082	0.3272

4. Results and discussion

Figure 1 shows the calculated generalized density of states ($G(\omega)$) of differently-filled xenon hydrate, i.e. empty water lattice, all cages filled by Xe atoms (fully-filled), small cages filled only, and large cages filled only. The PDOS of empty and partly-filled lattice (large cages or small cages filled only) provide us a frame of reference by displaying two broad excitation peaks centred at 7.4 and 10.4 meV and four distinct guest peaks at 1.9, 3.2, 4.6, and 6.1 meV, which have accurately reproduced the fingerprints of clathrate lattice and the original energy positions for guest vibration in Xe hydrate. Four distinct peaks are observed in the fully-filled $G(\omega)$ at 1.9, 3.4, 5.1 and 6.5 meV well below the first TA maximum that has shifted to higher energy (8.2 meV). Comparison with partly-filled $G(\omega)$ directly shows that the two lower peaks result from guest vibrations in large cages (site symmetry $\bar{4}$2m), corresponding to the motions along the long and the short axes, respectively, while the two higher ones result from guest vibrations in small cages (site symmetry m$\bar{3}$). The theoretical intensity (covering area) ratio yielded by the single particle consideration is 2:1:1 between the first, second and the sum of last two peaks with host modes subtracted from the cage-fully-filled $G(\omega)$, because Xe atoms are singly enclathrated in six large and two small cages in the unit cell, and there are two directions for long axes and one for short axes in the large ellipsoidal cage. This ratio is well approved by our lattice dynamics (LD) results. The profile at ∼6 meV shows a remarkable behaviour known from classical soft modes[16] (Fig.3 of Ref.[6]) i.e. the peak decreases in relative intensity and moves to higher energy at higher temperatures. It is thus

attributed to the anharmonicity in guest vibrations inside small cages.

Blue shift can be easily observed by comparing any two lines for differently-filled cages in Fig.1. And it is explained in schematic dispersion relation in the case of strong coupling in Fig.2(a) based on the semi-classical theory of anticrossing.[17] In the case of Xe hydrate, the guest–host coupling as well as the modes anticrossing is so strong in both of large and small cages that once it happens, it will affect both guest and host modes at higher frequency than that of the crossing centre (i.e. initiating their blue shifts), to a visible degree in the PDOS spectrum.

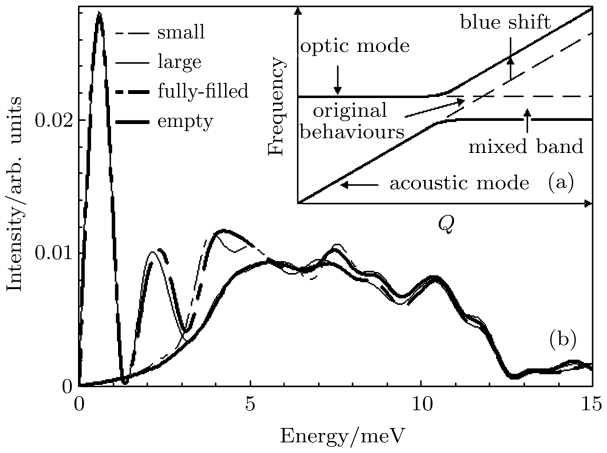


Fig.2. (a): The band for the mixing of eigenvectors due to the resonant interaction between guest and host modes in the case of strong anticrossing, which results in an extended corresponding blue shift. (b): The calculated PDOS of Ar–H_2O with sI, for differently-filled cages.

To compare the different coupling effects, argon atoms are filled, to different degrees, into the sI in Fig.2(b). Three characteristic peaks for guest vibrations are observed at 0.5, 2.3, and 4.1 meV, with line intensity ratio close to 2:1:1. It is particularly interesting, that the spectra for fully- and partly-filled cages give no marked deviation from each other at lower energy or from the spectrum for the empty cage at higher energy region, indicating the absence of strong guest–host coupling. This is verified by Fig.3, where empty modes show a pure Debye character[18] as $\omega \to 0$. In contrast to the Ar modes, the coupling effect leads to obvious depletion in the Debye region between the Xe peaks. It confirms the strong guest–host coupling in the case of Xe hydrate. Both of the third and fourth peaks that fall deeply below Debye level rise in the PDOS of host lattice with high relative intensity (shown in the IINS spectrum), pointing towards stronger coupling in small cages than the previous estimation (paragraph 12 of Ref.[6]) where contribution from the profile at ∼6 meV has been neglected.

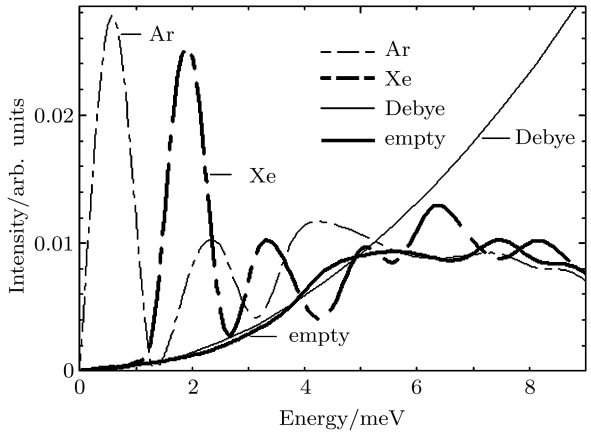


Fig.3. Comparison of the calculated spectra for Ar and Xe in sI with Debye ω^2-line of empty lattice. The PDOS of Xe falls below the Debye level, while no depletion is observed for Ar.

5. Conclusions

The TIP4P oxygen-shell model and L-J potential used in our classical LD simulation have been proved to be efficient in describing the low-frequency dynamics of clathrate hydrate. The accuracy of both reproduced peak positions and relative intensities supports our assignment of the profile at ∼6 meV in IINS spectrum. This is attributed to the anharmonic guest mode strongly coupling to small cages. The proposed blue shift is found to be a perspicuous signal for guest–host coupling by comparing the corresponding peak positions in the spectra for differently-filled cages in sI including Xe and Ar atoms. This blue shift can be confirmed by observing different positions of the fingerprint in the previous IINS spectra of the different gas hydrates under the same experimental condition, indicating the varying strength of the coupling. This should be further investigated quantitatively by future experimental and theoretical work.

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