

ELECTRONIC AND VIBRATIONAL PROPERTIES OF GAS HYDRATES

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INTRODUCTION

The most unique physical property of gas hydrate is the anomalous low and unexpected glassy-like thermal conductivity [1,2]. This interesting behaviour has both significant practical and scientific consequences. Thermal conductivity is a vital parameter required for the computer modelling of the recovery of natural gas from the hydrate [3]. A knowledge on the variation of the thermal conductivity with pressure and temperature is a prerequisite to the exploitation of this important natural resource. Despite the well defined crystalline structures for gas hydrates [4,5], their thermal conductivities are characteristic of amorphous materials. The understanding of the causes responsible for this unusual phenomenon will shed light on the mechanism of thermal transport in the disorder system. In solid, the thermal energy is transported and dissipated by the acoustic lattice vibrations. These vibrations are normally too low in energy to be effectively studied by infrared and Raman spectroscopy. However, they can be conveniently probed by neutron incoherent inelastic spectroscopy. In the following, the results from such measurements will be presented and discussed with the aid of computer simulation of the guest and lattice vibrations with lattice dynamics and molecular dynamics methods.

EXPERIMENTAL AND THEORETICAL DETAILS

Methane hydrate in deuteriated water was prepared by condensation of the gas into a pressure vessel equipped with rolling rods at very low temperature. The vessel was then allowed to warm slowly to -30°C and annealed at this temperature with gentle rotation for 24 hours. The hydrate sample was carefully removed and stored under liquid nitrogen. The neutron incoherent inelastic experiments were performed at the C3 triple axis spectrometer at Chalk River Nuclear Laboratory [6]. Lattice dynamics [7] and molecular dynamics calculations [8] were performed on a single unit cell of 8 methane and 46 water molecules using the SPC [9] and TIP4P [10] water intermolecular potential, respectively.

RESULTS AND DISCUSSION

The experimental vibrational frequencies for the motions of the methane in the cavities of the hydrate can be obtained directly from the neutron scattering experiments. At 5 K, two peaks were observed at $32, 57$ and 72 cm^{-1} in the experimental spectrum which are in excellent agreement with the theoretical predicted values [11,6] at $35, 54$ and 78 cm^{-1} . These results reassured the reliability of the interaction potential models employed in the calculations. The motions of the enclathrated methane in the hydrate cages can be examined from the variation of the intensity of the $J = 0 \rightarrow 1$ rotational excitation peak with the neutron momentum transfer (Q) (fig. 1). If the methane is freely rotating the intensity of the excitation peak will be proportional to the first order Bessel function $J_1(Qr)$, where r is the C-H distance. A fit to the experimental data gives an effective C-H distance of 1.23 \AA

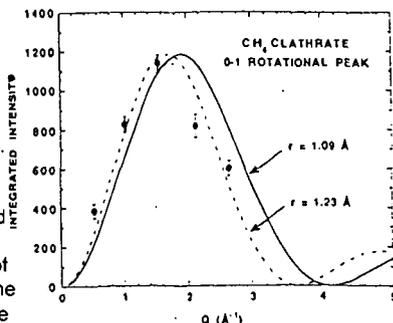


Fig. 1 Variation of the intensity (I) of the rotational peak with neutron momentum transfer (Q)

which is close to the correct value of 1.09 Å. This result indicates that the methane molecules rotate almost freely inside the hydrate cages and are in complete agreement with a previous NMR study [12]. Another important observation is the lack of energy dispersion in the rotational mode as the temperature is raised (fig.2). This effect is the consequence of a strong coupling between the low frequency acoustic lattice vibrations with the localized methane motions [13]. A clear picture of the interactions between the enclathrated methane with the host water lattice is now emerged from the neutron experiment. Although the methane molecule behaves like a free molecules, its motions are directly coupled with the lattice vibrations. This coupling provides a plausible mechanism for the transfer of thermal energy from the lattice to the methane. The heat transport can be dissipated via the thermal excitation of the methane thus reducing the thermal conductivity of the material

The interaction between the lattice acoustic vibrations with the localized motions of the guest has been proposed on the basis of molecular dynamics calculations [6] and experimental measurement of the lattice vibrational spectra of the gas hydrates [12]. This proposal can be quantified through the calculation of the cross time correlation function of the lattice and the guest motions by molecular dynamics techniques. The fourier transform of the correlation function gives the vibrational modes of the motions are correlated. If there is no correlation between the motions of the guest and the water lattice, time function will decay exponentially with time. Otherwise, the time decay will be modulated by the appropriate coupling frequencies. The results for such calculation for the structure I xenon hydrate and a hypothetical "light xenon" hydrate where the mass of the xenon has been set to 1 amu but retaining the interaction potentials as in the real xenon hydrate are shown in figs. 3 and 4. Inspection of the time correlation functions and their fourier transforms provide valuable information on the role of the guest-host coupling mechanism. In the case of the real xenon hydrate, it is evident that the correlation time extends to very long time (10 psec). The vibrational frequencies that couple the lattice and the guest vibrations occur at 23, 34 and 52 cm^{-1} . These frequencies are the same as the localized vibrations calculated for xenon [14] and fall within the acoustic region of the lattice vibrations [15]. Since the vibrational frequency of the rattling motion of the guest is inversely proportional to the square root of the reduced-mass [14], a "light xenon" should

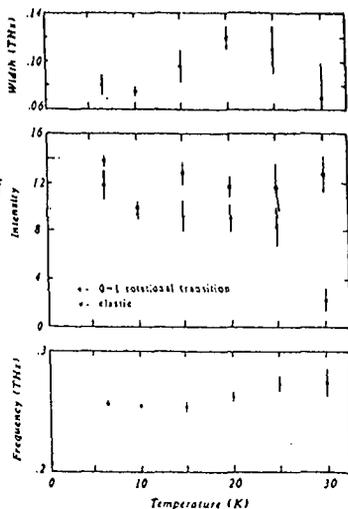


Fig. 2 The variation of the position, lineshape and intensity of the rotational peak with temperature.

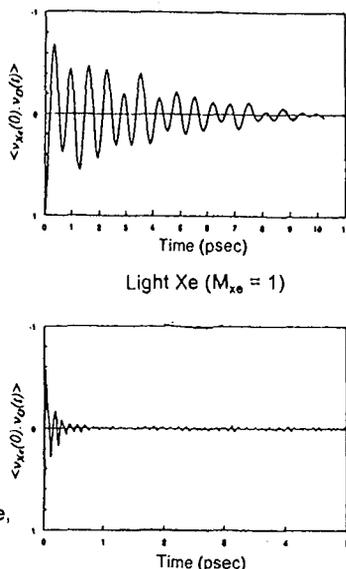


Fig. 3 The cross velocity correlation function for xenon and "light xenon" hydrate.

moves the guest vibrations out of the lattice acoustic region. This fact is shown in the calculations on the hypothetical hydrate. The correlation time between the "light xenon" and the lattice is extremely short and less than 1 psec. The corresponding "coupled" vibrations are located from 250 to 600 cm^{-1} , which are outside the translational region of the lattice vibrations. To summarize, it is shown from the present molecular dynamics calculations, the coupling between the guest and water lattice vibrations only occurs at the low frequency region. In practice, the hydrocarbons enclathrated in the hydrate structure all possess low frequency librational and rattling motions thus permitting the exchange of thermal energy with the host lattice.

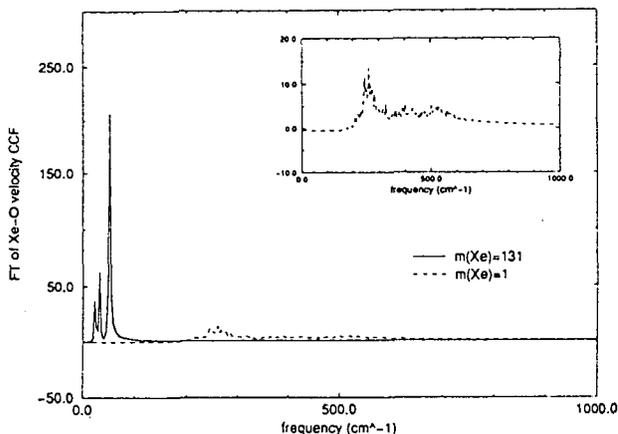


Fig. 4 The fourier transform of the cross velocity correlation function for xenon and "light xenon" hydrate.

Strong interactions between the guest and water lattice are also expected from a factor group analysis of the symmetry of the translational vibrational modes [13]. It can be easily shown that at the Brillouin zone center, both the guest and lattice translational vibrations possess the T_{1u} representation. However, the lattice acoustic lattice vibrations are strongly dispersive but the guest vibrations are largely localized and non-dispersive. A symmetry avoided crossing between the two vibrational branches must then occur along certain phonon wavevector between the zone center and the zone boundary. The resonance of two vibrational modes of the same symmetry can be a mechanism for energy transfer. A schematic representation of this interaction is shown in fig. 5. A lattice dynamics calculations on xenon hydrate indeed shows a considerable mixing of the positional displacements of the xenon and the water in the eigenvectors associated with the acoustic vibrations after the intersection of the phonon branches.

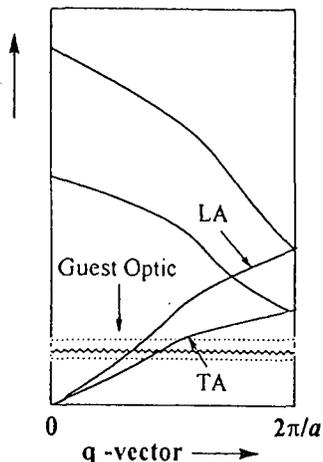


Fig. 5 Schematic diagram for the symmetry avoided crossing of the acoustic branch with the guest localized vibrations.

Realizing the basic mechanism for the coupling between the guest and host lattice, a simple model based on a modified Einstein model can be used to predict the thermal conductivity of gas hydrate [16, 17]. One important feature of this thermal conductivity

model is that only the molecular properties are needed as input parameters for the calculation of the thermal conductivity. In this model, the localized vibrations are assumed to be heavily damped with lifetimes of half a period of the oscillation and the distribution of the localized modes in a solid can be approximate by the Debye model. Using the equivalent of the gas kinetic equation, an expression for the minimum thermal conductivity Λ_{\min} can be derived.

$$\frac{\Lambda_{\min}}{\Lambda_{\infty}} = 2 \left(\frac{T}{\Theta_D} \right)^{2\Theta_D/T} \int_0^{\Theta_D/T} \frac{x^3 e^{-x}}{(e^x - 1)^2} dx$$

At high temperature when $T \gg \Theta_D$, the transport integral approaches unity and the limiting thermal conductivity Λ_{∞} is given by

$$\Lambda_{\infty} = \frac{1}{2} \left(\frac{\pi}{6} \right)^3 k_B n^3 (2v_t + v_l)$$

Where k_B is the Boltzman constant, n is the number density and v_t and v_l are the longitudinal and transverse sound velocity of the hydrate. Therefore, once the experimental density and acoustic sound velocities are known, the thermal conductivity at any temperature can be estimated. Previous calculations show that the calculated thermal conductivities for several gas hydrates employing these are in good accord with experiment [17].

The electrostatic field created by the water forming the cavities in a hydrate has important effects on the vibrations of the guest molecules. In view of the potential use of vibrational - infrared and Raman spectroscopies as an alternative means of the determination of the hydration number, it is imperative to understand these electrostatic effects. An electrostatic potential map (MEP) for the hydrate cavity can be computed from quantum mechanical method. We have computed the MEP for the small and large cage of a structure I hydrate. The MEP can be used to derive appropriate point charge model for the water molecules for the future simulation of the interactions between the guest and the cavities. Details of the computational results will be published elsewhere.

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