High-pressure Brillouin scattering and elastic properties of liquid and solid methane

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(Received 22 June 1995)

The acoustic velocities in any direction, refractive index, elastic constants, and elastic anisotropy of liquid and solid methane (CH_4) have been determined at pressures up to 5 GPa by applying Brillouin spectroscopy whereby the crystal orientation in a diamond-anvil cell could be found in the same fitting analysis. The elastic constant of C_{12} in a solid phase I shows larger values near C_{11}, which are reflected on the high degree of elastic anisotropy (A) around $A = 5.2$ to 6.3. Anomalously high ratios of longitudinal- to transverse-acoustic velocities indicate the strong rotation-translation coupling in an orientationally disordered phase I, and these ratios increase up to about 5 at 5 GPa with pressure, resulting in a compression, effectively along the $\langle 110 \rangle$ direction for the face-centered-cubic crystalline system of CH_4.

I. INTRODUCTION

Methane (CH_4) is the simplest molecular material, and its condensed phases are of fundamental importance for our solar system. Solid CH_4 has an orientationally disordered (OD) phase, which is closely related to the face-centered-cubic (fcc) crystals of the rare-gas family. However, it is known that solid CH_4 shows some strikingly different physical properties compared to the rare-gas solids.

At atmospheric pressure, methane liquifies at about 112 K and solidifies in OD phase I (fcc) at about 90 K, which is stable down to 20 K. Rand and Stoicheff[1] determined elastic constants C_{11}, C_{12}, and C_{44} at 90.4 K in this phase I by the Brillouin spectroscopy. They found that the velocities of the low-frequency transverse modes are anomalously slow in the $\langle 110 \rangle$ direction, which is indicative of significant rotation-translation (RT) coupling of molecules. This effect of RT coupling was confirmed theoretically by Wonneberger and Hüller.[2]

Hazen *et al.*[3] reported that liquid CH_4 crystallizes in the fcc (space group $Fm3m$) OD phase I at about 1.6 GPa and room temperature, and moreover phase I transforms to another solid phase at about 5.1 GPa. Hebert *et al.*[4] measured Raman and Brillouin scatterings of solid CH_4 under pressures up to 20 and 32 GPa, respectively. By Brillouin study at the backscattering geometry, they estimated pressure dependence of nv (n; refractive index, v; sound velocity) and confirmed the solid-solid phase transition at about 5.1 GPa. Moreover, they determined pressure dependence of the refractive index of the condensed CH_4 up to 12 GPa by the interferometric method.[4] At low temperatures around 20 K and moderate pressures ($P < 1$ GPa), there exist phases II, III, IV, and V in the order of increasing pressure.[5,6]

The purpose of the present work is to determine acoustic velocities for any direction, refractive index, elastic constants, and elastic anisotropy of liquid and solid methane (CH_4) at pressures up to 5 GPa, by using Brillouin measurements with *in situ* identification of the crystal orientation at each pressure by analyzing the observed angular dependence of acoustic velocities. From these results for high-pressure elastic properties, we investigate the compression effect on the rotation-translation coupling in the OD phase of CH_4 in comparison with the rare-gas crystals without molecular rotations.

II. EXPERIMENT

For loading a CH_4 sample in a diamond-anvil cell (DAC), we condensed gaseous CH_4 to liquid CH_4 by spraying its vapor into the gasket hole (diameter 0.3 mm; depth 0.2 mm) of the DAC cooled in liquid nitrogen. The air originally in the vessel containing the DAC had been previously replaced by N_2 gas to prevent contamination.[7] After adequate pressure had been applied, the DAC was warmed to 300 K. A transparent single crystal was grown by increasing the pressure on a seed crystal, which coexists with the liquid CH_4 at about 1.7 GPa. Sometimes, the crystal was twinned,[3] which shows double Brillouin signals. Therefore, we made always measurements for a single crystal without the twin.

A Sandercock tandem Fabry-Perot interferometer[8] was used in the triple-pass arrangement for Brillouin-scattering measurements. The 514.5 nm argon-ion laser line (λ_0) providing a single-moded power of about 50 mW was used as the excitation source. The Brillouin frequency shifts ($\Delta\nu$) at 90° and 180° (angles between the incident and the scattered beams) scattering geometries with the DAC are related to the acoustic velocity (v) as follows:[9]
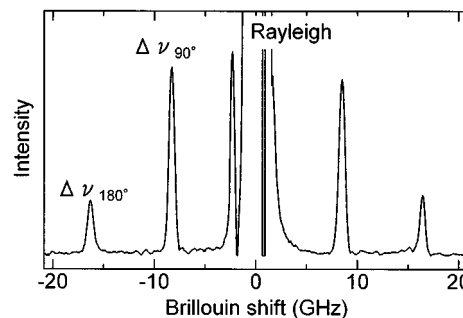
$$\Delta\nu_{90} = \sqrt{2} v_{90} / \lambda_0 \qquad (1)$$

FIG. 1. Brillouin spectrum of liquid CH_4 at $P = 1.15$ GPa. $\Delta\nu_{90°}$ and $\Delta\nu_{180°}$ are Brillouin-shifted signals from 90° and 180° scatterings, respectively.
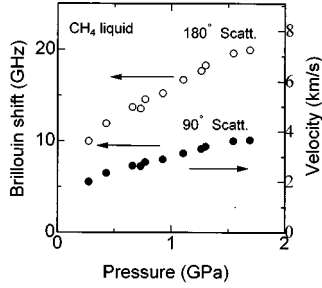
53   111

FIG. 2. Pressure dependence of Brillouin frequency shifts at 90° and 180° scatterings for liquid CH_4. Solid circles (90° scattering) indicate acoustic velocity simultaneously.

and

$$\Delta \nu_{180} = (2n)v_{180}/\lambda_0, \qquad (2)$$

where the wave vector **q** of probed acoustic phonons is parallel (90°) and perpendicular (180°) to interfaces of the input and output diamonds crossed by the laser beam, and v_{90} is independent of the refractive index (n) of the medium in the visible-wavelength region.

III. RESULTS AND DISCUSSION

For the liquid CH_4 at pressures up to about 1.7 GPa and 300 K, we determined the pressure dependence of acoustic velocity and refractive index. A typical Brillouin spectrum of liquid CH_4 ($P=1.15$ GPa) at 90° scattering geometry is shown in Fig. 1. From the Brillouin frequency shift $\Delta \nu_{90}$ and Eq. (1), the acoustic sound velocity can be determined at each pressure (see Fig. 2). There is also a laser beam reflected from the output diamond that serves as incident light, giving the weak 180° scattering signal.[9] Both $\Delta \nu_{90}$ and $\Delta \nu_{180}$ could be detected simultaneously as seen in Fig. 1. Figure 2 shows the pressure dependence of $\Delta \nu_{90}$ (sound velocity) and $\Delta \nu_{180}$ of liquid CH_4 below 1.7 GPa. Because the liquid is acoustically isotropic, the acoustic velocity is the same for any direction. Therefore, we determined the pressure dependence of n by using the ratio of $\Delta \nu_{90}$ to $\Delta \nu_{180}$, $\Delta \nu_{90}/\Delta \nu_{180}=1/(\sqrt{2}n)$ (solid circles in Fig. 3). The n increases sharply with pressure and has a value of about 1.40 near the solidification point ($=1.7$ GPa).
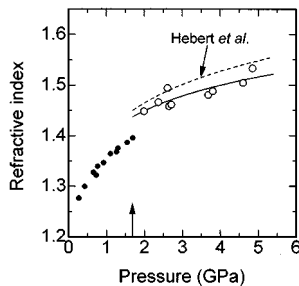

FIG. 3. Pressure dependence of the refractive indices (n) for liquid CH_4 (solid circles) and solid CH_4 (open circles) at 300 K. Vertical arrow indicates the liquid-solid phase transition point at $P=1.7$ GPa. Solid line represents a least-squares fit to the present results, and dashed line shows the result by the interferometric method (Ref. 4).
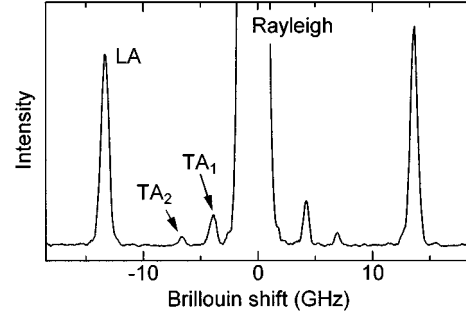

FIG. 4. Brillouin spectrum of solid CH_4 at $P=2.37$ GPa. LA, TA_2, and TA_1 are Brillouin-shifted signals from longitudinal, fast, and slow transverse modes, respectively.

For solid CH_4 at pressures above 1.7 GPa, the acoustic and elastic properties have been studied by using the method of high-pressure Brillouin spectroscopy recently developed for simple molecular solids.[10–12] A typical Brillouin spectrum of solid CH_4 at 2.37 GPa is shown in Fig. 4. Longitudinal (LA) and two transverse (TA_1, TA_2) modes are clearly seen. Brillouin measurements at 90° scattering geometry were made in 10° intervals of rotation angle ϕ about the load axis of DAC in the laboratory frame. The observed Brillouin shifts, that is, acoustic velocities at 2.37 GPa, are plotted as a function of ϕ by open circles in Fig. 5. To analyze the angular dependence of velocities of the LA and the two TA_1 (slow) and TA_2 (fast) modes at each applied pressure, it is necessary to use Every's expressions[13] relating acoustic velocities for an arbitrary direction to the elastic constants (C_{ij}). Because the pressure-induced solid phase I of CH_4 above 1.7 GPa is cubic,[3] the velocities can be expressed as a function of six parameters: $v_j = g_j(C_{11}/\rho, C_{12}/\rho, C_{44}/\rho, \theta, \phi, \chi)$,[10–12] where the subscript j indicates LA, TA_1, and TA_2 modes and ρ is density, and (θ, ϕ, χ) are the Euler angles relating the laboratory frame (DAC) to the crystal reference frame. The computerized least-squares fit was applied to determine elastic constants and Euler angles (orientation of a CH_4 single crystal grown in the DAC). The best-fit calculations are represented by dashed lines in Fig. 5. There is excellent agreement between the measured and the fitted values, which yielded, for example, $C_{11}/\rho = 19.15$,
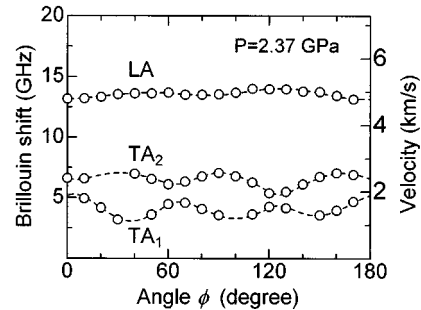

FIG. 5. Brillouin frequency shifts and acoustic velocities of LA, TA_2, and TA_1 modes as a function of angle ϕ at a 90° scattering geometry for solid CH_4 at $P=2.37$ GPa. The ϕ shows the rotation angle about the road axis of DAC. Open circles indicate experimental points, and the dashed lines represent the calculated best-fit velocities.
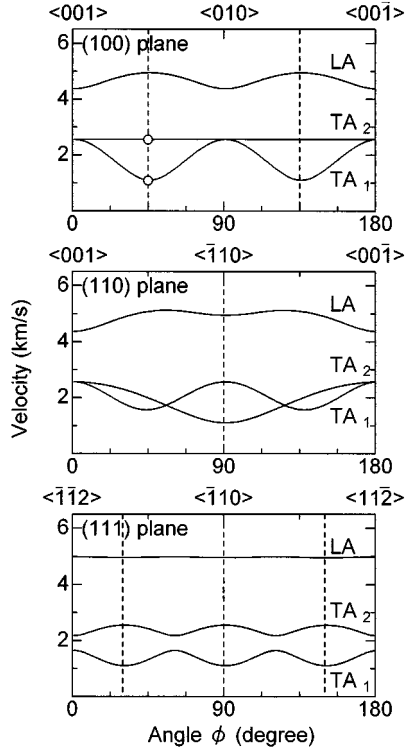
FIG. 6. Angular dependence of acoustic velocities in typical (100), (110), and (111) planes of crystalline CH_4 at $P=2.37$ GPa. LA, TA_2, and TA_1 are longitudinal, fast, and slow transverse modes, respectively. Open circles indicate sound velocities of TA_2 and TA_1 modes propagating along $\langle 011 \rangle$ direction for the determination of elastic anisotropy (A).
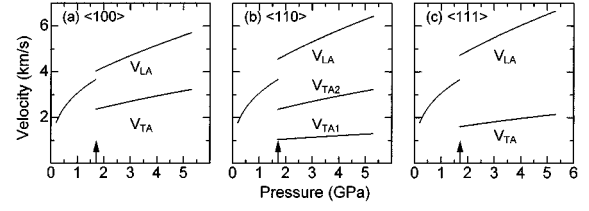

FIG. 7. Pressure dependence of acoustic velocities for liquid and solid CH_4 at 300 K. Vertical arrows indicate the freezing point ($P=1.7$ GPa). In the solid phase I, the velocities for typical directions are shown: (a) $\langle 100 \rangle$, (b) $\langle 110 \rangle$, and (c) $\langle 111 \rangle$ directions. LA, TA_2, and TA_1 are longitudinal, fast, and slow transverse modes, respectively.

$C_{12}/\rho=16.73$, and $C_{44}/\rho=6.55$ km^2 s^{-2} at 2.37 GPa. An independent procedure for different crystal orientations showed excellent consistency for these values within an accuracy of $\pm 2\%$. It has been determined from the identification of the crystal orientation (θ,ϕ,χ) and its pressure dependence that (1) the CH_4 single crystal grows every time with a different orientation relative to the cell axis, and (2) the crystal orientation changes gradually in the DAC with pressure. This change of the crystal orientation can be attributed to an annealing process of the crystal.

Once the six parameters were determined, the acoustic velocities could be calculated for all directions. Figure 6 shows the angular dependence of acoustic velocities in typical (100), (110), and (111) planes of crystalline CH_4 at $P=2.37$ GPa. The characteristic patterns are seen on LA, TA_2, and TA_1 modes, and the direction-sensitive feature can be confirmed. The elastic anisotropy A is defined by the square of the ratio for acoustic velocities of TA_2 to TA_1 propagating along $\langle 011 \rangle$ or $\langle 110 \rangle$ direction with three elastic constants of C_{11}, C_{12}, and C_{44} for a cubic crystalline system ($C_{ij}=\rho v^2$);

$$A=2C_{44}/(C_{11}-C_{12}). \qquad (3)$$

As seen from velocity points marked by open circles in Fig. 6, the factor A could be estimated to be about 5.41 ± 0.11 (see Table I) which is extremely large in comparison with the ordinary value of about 2.[14] This feature will be investigated in a later part. Figure 7 shows the CH_4 sound velocities for typical directions as a function of pressure up to 5 GPa at 300 K. At the freezing point ($=1.7$ GPa), the sound velocity shows discontinuous changes to LA, TA_2, and TA_1 in the solid phase I of CH_4, and they increase with pressure. It is

TABLE I. Ratios of LA to TA velocities in high-symmetry directions of CH_4 and some other cubic crystals under high pressure or atmospheric pressure, and elastic anisotropy $A=2C_{44}/(C_{11}-C_{12})$ for each crystal.

Crystal	$\langle 100 \rangle$ $v_{LA}/v_{TA1,TA2}$	$\langle 111 \rangle$ $v_{LA}/v_{TA1,TA2}$	$\langle 110 \rangle$ v_{LA}/v_{TA2}	$\langle 110 \rangle$ v_{LA}/v_{TA1}	A
CH_4 (300 K, 2.37 GPa)	1.71	2.96	1.93	4.50	5.41
CH_4 (90 K, 0.1 MPa)[a]	1.47	2.46	1.70	3.23	3.60
H_2S (300 K, 1.0 GPa)[b]	1.51	2.48	1.73	3.22	3.45
CCl_4 (244 K, 0.1 MPa)[c]	1.79	3.07	2.01	4.70	5.47
CBr_4 (333 K, 0.1 MPa)[d]	1.62	2.65	1.83	3.54	3.73
Ne[e]	1.40	2.20	1.61	2.65	2.71
Ar[e]	1.46	2.27	1.66	2.75	2.74

[a]Reference 1.

[b]References 10 and 16.

[c]Reference 17.
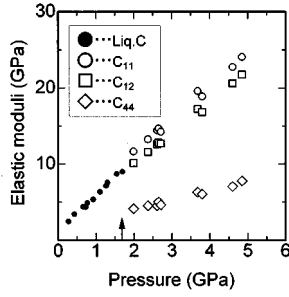
[d]Reference 18.

[e]Reference 1.

FIG. 8. Pressure dependence of elastic constants, C_{11}, C_{12}, and C_{44} for the solid CH_4 at 300 K (open symbols). For the liquid phase (solid circles), elastic modulus is $C = \rho v^2$. Vertical arrow indicates the liquid-solid phase transition point at $P = 1.7$ GPa.

noted that the pressure dependence of v_{TA1} for $\langle 110 \rangle$ direction is small, which results in large values of A. Furthermore, we can calculate the sound velocity (v_{180}) along the direction perpendicular to the diamond interfaces, which is available to determine the refractive index (n) by using Eq. (2). From the $\Delta\nu_{180}$ measured at 180° scattering geometry, we can obtain the pressure dependence of n for solid CH_4 as shown by the open circles in Fig. 3. The uncertainties in the measured frequency shifts and in the determined refractive index are about $\Delta(\Delta\nu)/\Delta\nu = \pm 1\%$ and $\Delta n/n = \pm 2\%$, respectively. At the solidification point, n shows a discontinuous increase of about 4% and, moreover, increases gradually with pressure up to $n = 1.52 \pm 0.03$ at 5 GPa. The present results show fairly good agreement with that shown by the dashed line which was determined by the interferometric method ($\Delta n/n = \pm 1\%$).[4] From our present results and the pressure dependence of ρ by the x-ray studies,[3] the Lorentz-Lorenz relation $(n^2 - 1)/(n^2 + 2) = (4\pi N\rho\alpha)/(3M)$ yields the polarizability α, where N is Avogadro's number, and M is the molecular weight. The α shows its value of 2.53×10^{-24} cm^3 at 2 GPa and decreases little with pressure to 2.48×10^{-24} cm^3 at 5 GPa.

Figure 8 shows the pressure dependence of elastic constants which were determined from the best-fitted results of C_{ij}/ρ with the pressure dependence of ρ from x-ray studies.[3] C_{12} of the solid phase I shows a large value close to C_{11} at all pressures, which is reflected on the high degree of elastic anisotropy $A = 2C_{44}/(C_{11} - C_{12})$ as shown in Fig. 9; a best-fitted solid curve shows the increase from $A = 5.2 \pm 0.10$ to 6.3 ± 0.13 with pressure in the solid phase I, and the interpolated value to $P = 0.1$ MPa shows $A = 4.1 \pm 0.1$. This value is near close to $A = 3.6$ and 4.3 for solid CH_4 at 0.1 MPa, $T = 90.4$ K from Brillouin measurements,[1] and $T = 91$ K from molecular-dynamics calculation,[15] respectively. This anomalous feature of increasing A with pressure is due to the increasing coupling between molecular rotations and TA phonon. In Table I we list the typical values of A for OD molecular crystals [CH_4, H_2S,[10,16] CCl_4,[17] CBr_4 (Ref. 18)] and rare-gas solids (Ne, Ar) (Ref. 1) under high pressures or atmospheric pressure. Rare-gas solids can be treated as a standard because they are independent of molecular rotations. The OD crystals show larger A values than rare-gas solids. In order to investigate the RT coupling in the OD phase,[2,19] we list the ratios of LA to TA velocities in high-symmetry directions in Table I, which were determined by
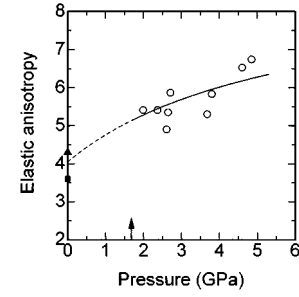
the Brillouin spectroscopy. The ratios v_{LA}/v_{TA1} for OD crystals are anomalously large especially in the $\langle 110 \rangle$ direction, which is due to a strong damping of TA$_1$ phonon, i.e., the $(C_{11} - C_{12})/2$ mode. Furthermore, these ratios are 20–75 % higher than for the rare-gas solids. These results, as predicted theoretically by calculations,[2,19] indicate the importance of the coupling of molecular orientations with the TA phonon and therefore reflect evidence for strong RT effect in the Brillouin scattering. Since the compression can be expected to make a significant effect on the RT coupling, we show the pressure dependence of the ratios v_{LA}/v_{TA} of crystalline CH_4 in the OD phase. It is clearly seen from Fig. 10 that only v_{LA}/v_{TA1} in the $\langle 110 \rangle$ direction depends sensitively on pressure and increases up to about 5 at 5 GPa. This pressure dependence and anomalously high ratios of acoustic velocities indicate that the RT coupling becomes strong with pressure, resulting in a compression, effectively along $\langle 110 \rangle$ direction of the face-centered-cubic crystalline system for solid

FIG. 9. Pressure dependence of elastic anisotropy $[A = 2C_{44}/(C_{11} - C_{12})]$ in the solid phase I of CH_4 at 300 K. Open circles show experimental values, and solid line represents a least-squares fit to the present results, and dashed line indicates its interpolated curve to $P = 0.1$ MPa. Solid square and triangle at 0.1 MPa show $A = 3.6$ and 4.3 for solid CH_4 at 90.4 K from Brillouin measurements (Ref. 1) and at 91 K from molecular-dynamics calculation (Ref. 15), respectively.
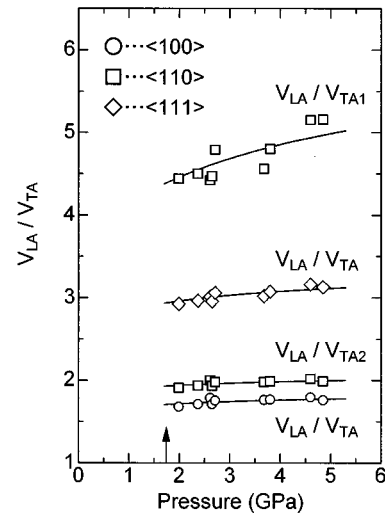

FIG. 10. Pressure dependence of ratios of LA to TA velocities in typical $\langle 100 \rangle$, $\langle 110 \rangle$, and $\langle 111 \rangle$ directions for solid CH_4 at 300 K. Vertical arrow indicates the freezing point ($P = 1.7$ GPa). v_{LA}/v_{TA1} along the $\langle 110 \rangle$ direction shows the highest values and the pressure-sensitive feature.

CH_4. This feature characterizes the microscopic nature of the orientational disorder in solid phase I of CH_4.

In conclusion, we have determined acoustic velocities for any direction, refractive index, elastic constants, and elastic anisotropy of liquid and solid methane at pressures up to 5 GPa by using single-crystal Brillouin spectroscopy. From these results for high-pressure elastic properties, we investigated the pressure effect on rotation-translation coupling in

the orientationally disordered solid phase I of CH_4 in comparison with the rare-gas crystals without molecular rotations. The ratio of v_{LA}/v_{TA1} in the $\langle 110 \rangle$ direction depends sensitively on pressure and increases up to about 5 at 5 GPa. This pressure dependence and anomalously high ratios of acoustic velocities indicate that the coupling of molecular rotations with TA phonon is strong, and becomes stronger with increasing pressure, effectively along $\langle 110 \rangle$ direction of the fcc crystalline CH_4.

[1] S. C. Rand and B. P. Stoicheff, Can. J. Phys. **60**, 287 (1982).

[2] S. Wonneberger and A. Hüller, Z. Phys. B **66**, 191 (1987).

[3] R. M. Hazen, H. K. Mao, L. W. Finger, and P. M. Bell, Appl. Phys. Lett. **37**, 288 (1980).

[4] P. Hebert, A. Polian, P. Loubeyre, and R. Le Toullec, Phys. Rev. B **36**, 9196 (1987).

[5] F. D. Medina and W. B. Daniels, J. Chem. Phys. **70**, 2688 (1979).

[6] M. M. Thiery, D. Fabre, and K. Kobashi, J. Chem. Phys. **83**, 6165 (1985).

[7] H. Shimizu, Y. Nakamichi, and S. Sasaki, J. Chem. Phys. **95**, 2036 (1991).

[8] R. Mock, B. Hillebrands, and R. Sandercock, J. Phys. E **20**, 656 (1987).

[9] H. Shimizu, E. M. Brody, H. K. Mao, and P. M. Bell, Phys. Rev. Lett. **47**, 128 (1981).

[10] H. Shimizu and S. Sasaki, Science **257**, 514 (1992).

[11] H. Shimizu, T. Kitagawa, and S. Sasaki, Phys. Rev. B **47**, 11 567 (1993).

[12] H. Shimizu, M. Ohnishi, S. Sasaki, and Y. Ishibashi, Phys. Rev. Lett. **74**, 2820 (1995).

[13] A. G. Every, Phys. Rev. Lett. **42**, 1065 (1979).

[14] H. Shimizu, H. Sakoh, and S. Sasaki, J. Phys. Chem. **98**, 670 (1994).

[15] D. G. Bounds, M. L. Klein, and G. N. Patey, J. Chem. Phys. **72**, 5348 (1980).

[16] S. Sasaki and H. Shimizu, J. Phys. Soc. Jpn. **64**, 3309 (1995).

[17] J. Zuk, H. Kiefte, and M. J. Clouter, J. Chem. Phys. **92**, 917 (1990).

[18] J. Zuk, D. M. Brake, H. Kiefte, and M. J. Clouter, J. Chem. Phys. **91**, 5285 (1989).

[19] I. R. McDonald, D. G. Bounds, and M. L. Klein, Mol. Phys. **45**, 521 (1982).