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Raman Spectroscopy of Nitrogen Clathrate Hydrates

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Nitrogen hydrate samples were synthesized using liquid nitrogen and powder ice at 16 MPa and 253 K. Confocal laser Raman spectroscopy was used to investigate the characteristics of nitrogen clathrate hydrates. The results show that the Raman peaks of N–N and O–H stretching vibration in nitrogen hydrates are observed at 2322.4 and 3092.1 cm^{-1} , respectively, which are very similar to those in natural air clathrate hydrates. For comparison, we measured the Raman peaks of N–N stretching vibration both in liquid nitrogen and nitrogen molecules saturated water, which appear at 2326.6 and 2325.0 cm^{-1} , respectively. The Raman spectroscopic observations on the dissociation process suggest that nitrogen molecules occupy both the large and small cages in nitrogen clathrate hydrates. However, only one Raman peak is observed for N–N stretching vibration because the difference of the environment of nitrogen molecules between large and small cages is too small to be differentiated by Raman spectroscopy.

Key words: Raman spectroscopy, Nitrogen clathrate hydrates, Nitrogen bond vibration, Raman shift

I. INTRODUCTION

Clathrate hydrates are molecular inclusion compounds that trap small molecules within polyhedral hydrogen-bonded water cages. Three types of structures (*i.e.* sI, sII, and sH) are well known for gas hydrates, and the difference between them depending mostly on the sizes of the guest molecules [1]. The structure of nitrogen hydrates has been a subject of some debate. Historically it was thought that nitrogen forms sI hydrates, based on the general rule that guest molecules with van der Waals diameters smaller than 5.8 Å form sI [2]. However, Davidson *et al.* found that some small molecules like Ar, Kr, N₂, and O₂ form sII hydrates by using X-ray and low-temperature neutron diffraction [3–5]. These findings suggest that very small molecules are preferentially enclathrated in the smaller cages (dodecahedron) of sII hydrates. For instance, pure hydrogen gas forms sII hydrates which may contain up to four hydrogen molecules in the large cages and one hydrogen molecule in the small cages [6,7].

Model study shows that nitrogen can form either sI or sII hydrates in special conditions [8]. Recently, a number of researchers have found that nitrogen hydrates un-

dergo a phase transition under high pressure based on *in situ* Raman spectroscopic investigations [9–11] and X-ray and neutron diffraction study [12]. In addition, pressure-dependent high resolution neutron diffraction studies [13,14] showed that the transient and partial formation of sI nitrogen hydrates began to appear at pressures exceeding several ten million Pa, and provided strong evidence that the large cages are doubly occupied in both sI and sII nitrogen hydrates. These results were theoretically supported by Klaveren *et al.* [15–17], who suggested that nitrogen hydrates may remain stable even for the case of a full double occupation of large cages by using molecular dynamics simulations for sII nitrogen hydrates with varying nitrogen cage occupancies in different conditions. Also, they calculated three N–N stretching vibration Raman peaks for the single occupied small cages (2325.1 cm^{-1}), the double occupied large cages (2323.5 cm^{-1}), and the single occupied large cages (2322.0 cm^{-1}) for sII nitrogen hydrates.

The published data for Raman shifts for N–N stretching vibration are quite different from each other. For example, the air clathrate hydrates recovered from ice cores from Arctic and Antarctic ice sheets were measured by Champagnon *et al.* [18] and Pauer *et al.* [19–21], who gave the Raman peaks of N–N stretching vibration at 2322.1 and 2330 cm^{-1} , respectively. In addition, the Raman shift of N–N stretching vibration increases with pressure based on *in situ* Raman spectroscopic observation at high pressure, and is also larger

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than that from natural air hydrates. As to the Raman spectrum of nitrogen gas, attention has been focused on room air at 10^5 Pa, and the values are also different. For instance, Champagnon *et al.* [18] measured the value of 2335 cm^{-1} , while Lavorel *et al.* [22] gave the value of only 2328.5 cm^{-1} . Pauer *et al.* measured the bubbles from the natural air hydrates samples, and got the Raman shift of 2326.6 cm^{-1} for nitrogen gas [21]. Until now, Raman shifts of N–N stretching vibration in liquid nitrogen and nitrogen gas saturated water are still unavailable. There are limited experimental data and thermodynamic modeling on pure nitrogen hydrates synthesized under ambient conditions [23].

In this work, we synthesized nitrogen hydrates at 16 MPa and 253 K. Raman spectroscopic observations were carried out on the N–N stretching vibration for nitrogen molecules in cages of clathrate hydrates and in other phases (*i.e.* gas and liquid). This work aimed to investigate the characteristics of nitrogen hydrates and provide a series of Raman data for N–N stretching vibration of nitrogen molecules in different phases.

II. EXPERIMENTS

A. Sample preparation

Nitrogen hydrates were prepared by using liquid nitrogen ($-196\text{ }^\circ\text{C}$) and powder ice. The ice was ground to powder ($150\text{ }\mu\text{m}$) with a mortar in liquid nitrogen. Firstly, some powder ice was put in a pressure vessel (500 mL) which was immersed in liquid nitrogen, and then filled with a small amount of liquid nitrogen and sealed quickly. The vessel was put into dry ice ($-78.5\text{ }^\circ\text{C}$), and the pressure kept increasing as the temperature went up. The desired pressure (16 MPa) was attained by releasing the extra nitrogen gas from the vessel. The vessel was put into a refrigerator at $-20\text{ }^\circ\text{C}$ to ensure that the pressure was nearly twice as high as required for nitrogen hydrates stability. After five days at stable pressure, the vessel was opened and the nitrogen hydrate samples were taken out and preserved in liquid nitrogen for Raman spectroscopic measurements.

B. Measurement methods

The experiments were carried out with a confocal microscopic Raman spectrometer (Acton Research Corporation, Model: Spectropro 2500i) equipped with a Witec confocal microscope and Ar^+ laser (Spectro-Physics Laser: Model 177G, 100 mW) operating at 514.5 nm . The groove of the grating used in this work is $1800/\text{mm}$, with a resolution of 2 cm^{-1} .

The test sample was loaded into an aluminum sample holder, which sat in a custom-made box with a 3-cm-diameter window covered with a sapphire glass and

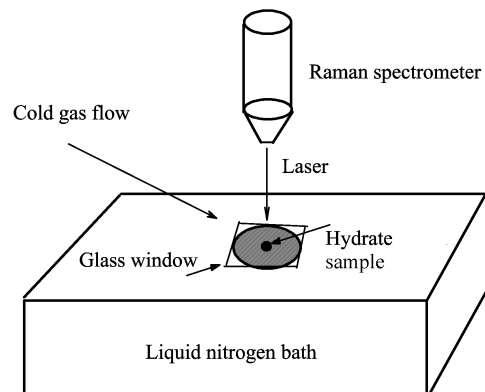


FIG. 1 Schematic diagram of Raman spectroscopic observation on nitrogen hydrates.

was pre-cooled down to the temperature of liquid nitrogen. This box was filled with liquid nitrogen to make sure that the hydrate samples did not decompose during measurements. The laser was delivered to a high efficiency fiber probe. Using a $10\text{ mm}\times 0.25\text{ mm}$ microscope objective, the laser was focused in the hydrate samples through the optical windows and the scattered light was collected with the same lens. Figure 1 shows the schematic diagram of Raman spectroscopic observation on nitrogen hydrates samples. A video camera was used to monitor the position on which the laser focused. Spectra were obtained from different spots within each sample. For determination of Raman spectra of liquid nitrogen, the laser was focused directly on the cryogenic liquid nitrogen in a temperature-proof box through a glass window. The measurements for nitrogen gas and nitrogen gas dissolved in water were carried out at room temperature.

No peaks were observed in a sample-measuring interval when the hydrate samples were outside the focus range of the laser beam, which may exclude the possibility of interference caused by the surrounding atmosphere.

III. RESULTS AND DISCUSSION

A. N–N stretching modes in nitrogen hydrates

Raman scattering is a powerful method to investigate the stage of guest molecules in host water cages of clathrate hydrates by measuring the molecular vibrational mode, which is caused by the interaction between the guest molecules with each other and between the guest molecule and the host cage [24].

Nitrogen hydrates formed under modest pressure are believed to be sII clathrates. It is well established that in sII clathrates, the small cages are pentagonal dodecahedra (5^{12}), almost spherical with a radius of 3.9 \AA . The large cages are 16-hedra containing both pentag-

onal and hexagonal faces ($5^{12}6^4$) resembling an oblate ellipsoid with a mean radius of 4.7 Å. From geometrical considerations and experimental work on artificial clathrates, nitrogen is expected to enter both types of cages [12]. Nakahara *et al.* have predicted that the values for N–N Raman shifts in small and large cages in sII hydrates are 2316 and 2324 cm^{-1} , respectively [25], assuming the cages are spherical with different diameters. However, our results show that N–N stretching vibrations in nitrogen hydrates are described by just a single peak, and so far only one single peak has been observed in Raman experiments for natural air hydrates [19–21], which is in contradiction to this prediction. Hondoh explained this discrepancy by considering that the environments of guest molecules are almost identical for both types of cages [26].

Usually, the detector array of a Raman spectrometer shows a resolution of 1.65 cm^{-1} in the N–N region, and the half widths of the respective peaks are 8.2 cm^{-1} [20]. The differences in Raman shifts for N–N stretching vibration between the enclathrated molecules and liquid nitrogen molecules are 4.5 cm^{-1} in this work. Therefore, it can be expected that the difference of Raman shifts for N–N stretching vibration between enclathrated molecules with each other are too small to show splitting using a general Raman spectrometer.

If nitrogen molecules enclathrate both in small and large cages, or double occupancy, do they behave differently when the cages in the clathrate are being destroyed? Can we observe the splitting of peaks in Raman experiment? In order to answer these questions, we have investigated the spectra of N–N stretching vibrations during the process of nitrogen hydrates disso-

ciation (Fig.2).

For hydrate dissociation experiments, the custom-box (Fig.1) was stuffed with dry ice before the nitrogen hydrates sample was loaded into the sample holder. With the sublimation of dry ice, the temperature of the sample holder increased gradually and the nitrogen hydrates started their dissociation. The observations were taken in intervals of 2 min. The experiment was ended when no N–N signal was identified. Through the experiments, the laser was focused on a spot of sample with a 10 fold lens, although focus was adjusted sometimes for a better signal quality. During this process, no splitting peaks were observed although the intensities of the peaks decreased as the hydrate dissociated. It is also important to note that the Raman peak keeps constant at 2322.4 cm^{-1} (Fig.2).

Figure 3 shows the variation of Raman peak intensities for N–N stretching vibration during the hydrate dissociation. It is found that there are several stages in the dissociation process, which is thought to be caused by a layer of ice from dissociated hydrates. This layer coats the hydrates and seals it from further dissociation. This effect is called the “self-preservation” of gas hydrates. Furthermore, this coated ice also decreases the Raman peak intensities of N–N stretching vibration. For example, the Raman peak intensities decrease as the coated ice from hydrates dissociation increases in the first few minutes. However, the temperature of the spot on which the high energy laser focuses can increase, causing the disappearance of the ice layer. Thus, the laser can focus directly on the inner surface of nitrogen hydrate. Therefore, the Raman peak appears to be relatively high, and then it decreases quickly as the nitrogen hydrates decompose. After several circulations, the nitrogen hydrates totally dissociate.

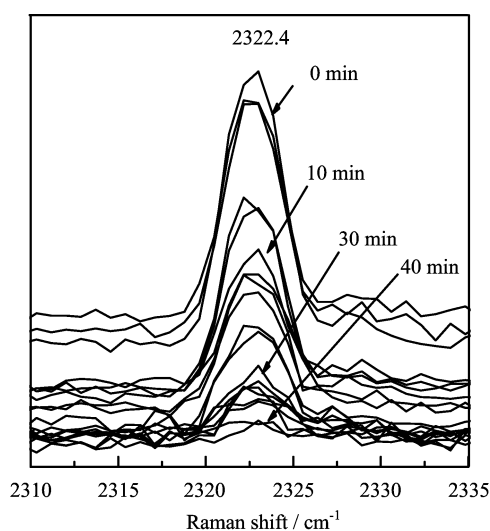


FIG. 2 Raman spectroscopic observations on the dissociation of nitrogen hydrate. Each spectrum was measured at different time with measurement interval about 2 min during the dissociation process, showing the decreasing trend of Raman intensity of nitrogen hydrates.

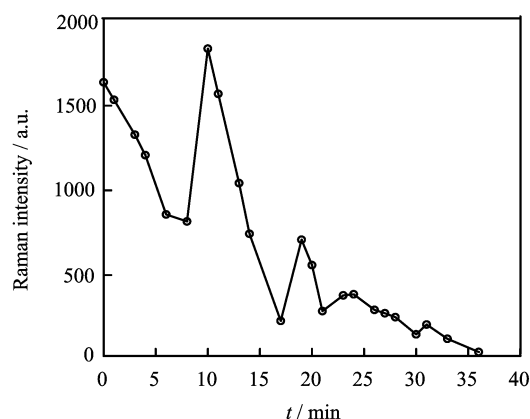


FIG. 3 Raman intensity variations of nitrogen hydrates during dissociation.

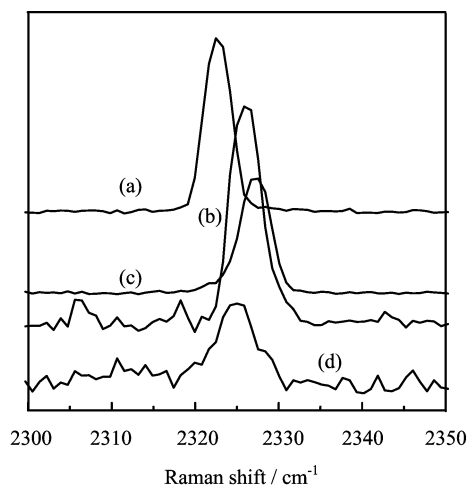


FIG. 4 Raman shifts showing the N–N stretching vibrations in the nitrogen hydrates (a), liquid nitrogen (b), nitrogen gas (c), and nitrogen saturated water (d), respectively.

B. Raman spectra of nitrogen in different phases

In this research, Raman spectroscopic observations on N–N stretching vibration were carried out for the nitrogen molecules in different phases, including solid, gas, and liquid states. Figure 4 shows the Raman spectra of the N–N stretching vibration for nitrogen molecules both in cages of hydrates and in other states (*i.e.* gas and liquid). We can see from Fig.4 that only one Raman peak is observed for nitrogen hydrates at 2322.4 cm^{-1} . We measured the hydrates samples at different times using naphthalene for calibration of the results, and found that the errors for the values were less than 0.5 cm^{-1} . The Raman spectra of nitrogen gas at pressures from 1 MPa to 12 MPa were measured using a small high-pressure cell with a quartz glass covered window. We have also measured the N–N stretching vibration in air, and found that the Raman peak is at 2327.5 cm^{-1} , which is always the same as those from nitrogen gas at pressures below 15 MPa. This indicates that pressure has no impact on Raman shift of N–N stretching vibration at modest pressure. As for the measurement of dissolved nitrogen in water, a small amount of water was put into the cell, and nitrogen gas was charged into it up to 10 MPa. After several hours, Raman spectra of dissolved nitrogen were determined while the laser was focused in the water. In this work, we present the Raman data for liquid nitrogen and dissolved nitrogen in water for the first time, the Raman shifts of which can be seen at 2326.1 and 2325.0 cm^{-1} , respectively, which are 1.4 and 2.5 cm^{-1} lower than that of free nitrogen molecules, respectively.

For comparison, some Raman data for N–N stretching frequencies from the literature are also listed in Table I, covering both natural and synthesized nitrogen hydrates, and the different states of nitrogen (*i.e.* gas

TABLE I Raman peaks of N–N stretching vibration in both natural and synthesized hydrates and different phases.

| Description | Raman peak/ cm^{-1} | | | | |
|--------------------------|------------------------------|--------|--------|--------|--------|
| | Hydrates | Gas | Liquid | Water | Fluid |
| This work ^a | 2322.4 | 2327.5 | 2326.1 | 2325.0 | |
| Ref.[18] ^b | 2330 | 2335 | | | |
| Ref.[19–21] ^c | 2322.1 | 2326.6 | | | |
| Ref.[27] ^d | 2323 | | | | |
| Ref.[22] ^e | | 2328.5 | | | |
| Ref.[10] ^f | 2324.7 | | | | 2327.8 |
| Ref.[12] ^g | 2324.5 | | | | |

^a Hydrates synthesized at 15 MPa and 243 K, N₂ gas measured under 1–12 MPa, liquid nitrogen from cryogen at 77 K, N₂ saturated water under 10 MPa.

^b Natural air hydrates recovered from the Vostok ice core, gas from air.

^c Natural air hydrates recovered from the GRIP ice core, gas corresponding to bubbles from the hydrates sample.

^d Natural single crystal air hydrates recovered from the Dye-3 ice core.

^e Nitrogen molecule at room temperature and 10^5 Pa .

^f Synthesized hydrates and fluid nitrogen at 450 MPa and 295 K.

^g Synthesized hydrates at 240 MPa and 296 K.

and fluid). The Raman shift of N–N stretching vibration for nitrogen hydrates we measured is very similar to those of the natural air hydrates [19–21,27], but 7.6 cm^{-1} lower than that of Champagnon *et al.* [18], who observed the Raman peak at 2330 cm^{-1} using polarized Raman spectrometer. This stretching vibration frequency also shifts by about 2 cm^{-1} lower than those hydrates synthesized at high pressure [9,11], suggesting that N–N stretching frequencies are pressure-dependent. In contrast, the frequency does not shift too much as long as the pressure is still kept in the stable range for sII nitrogen hydrate. However, when the pressure exceeds 0.85 GPa, the clathrate undergoes a phase transition, and Raman peak for N–N vibration shifts largely. For example, the frequency may reach up to 2342 cm^{-1} at 6 GPa for nitrogen clathrate at room temperature [11]. Compared to the free nitrogen molecules, the frequency of N–N stretching vibration for nitrogen hydrates shifts 5.1 cm^{-1} lower in this study. This can be attributed to nitrogen molecules in the clathrate structure. The Raman frequencies for dissolved nitrogen in water and liquid nitrogen also shift to lower wavenumbers. From the tendency of stretching frequency shift, one can conclude that there is a considerable interaction between the guest molecules and the cages. The attractive interaction loosens the intermolecular bond and shifts the frequency to a lower value [18]. This can also explain why Raman shifts for nitrogen molecules in clathrate and different states are pressure-dependent and/or temperature-dependent. At

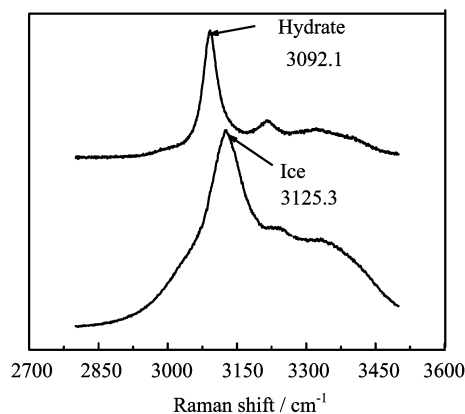


FIG. 5 Raman shifts showing the O–H stretching vibration of sII hydrates and ice.

higher pressure, the attractive interaction is decreasing, but even at the highest experimental pressure at which the clathrate structure does not change, the frequencies of nitrogen within the cage are lower than that of a free molecule [11]. The attraction among nitrogen molecules decreases due to the interaction from O–H of water molecules when nitrogen is dissolved in water. As for liquid nitrogen, the very low temperature (77 K) can also decrease the attractive interaction between nitrogen molecules, and therefore, result in a lower shift of vibrational frequency.

C. O–H stretching vibration modes

Figure 5 shows O–H stretching vibration in nitrogen hydrates and in ice. The Raman peak at 3092.1 cm^{-1} is the O–H stretching vibration mode of water molecules in hydrates, while that at 3125.3 cm^{-1} is for ice. In this work, the ice we used was from a refrigerator and was ground to powder in liquid nitrogen. The frequency is quite similar to that of hexagonal ice, whose Raman peak of O–H stretching vibration is at 3130 cm^{-1} , due to the symmetric stretching mode [28]. However, the frequency of the O–H stretching vibration observed for nitrogen hydrates in this work is quite different from those for natural air hydrates [27] and tetrahydrofuran structure sII hydrate [29], with the wavenumbers about 43 cm^{-1} lower than those of the two later sII hydrates. The reason for this difference of O–H stretching vibration between nitrogen hydrates and other sII hydrates still remains unknown and requires further investigation.

IV. CONCLUSION

In this work, the N–N stretching vibration of nitrogen molecules in clathrate and in some different states (*i.e.* gas and liquid) was investigated systematically.

Raman frequencies of N–N stretching vibration increase in the order of nitrogen hydrates < dissolved nitrogen in water < liquid nitrogen < nitrogen gas. Only one Raman peak is observed for nitrogen hydrates at 2322.4 cm^{-1} , while a peak at 2327.7 cm^{-1} is found for nitrogen gas. We also present the Raman spectra for liquid nitrogen and dissolved nitrogen in water for the first time, which show peaks at 2326.6 and 2325.0 cm^{-1} , respectively.

The Raman spectra of nitrogen hydrates synthesized at modest pressure is very similar to that of natural air hydrates, and about 2 cm^{-1} lower than that of nitrogen hydrates synthesized at high pressure. Raman spectroscopy can only observe one peak for N–N stretching vibration in nitrogen hydrates, which is not able to tell the details of cages occupancy of sII nitrogen hydrates.

V. ACKNOWLEDGMENTS

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