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A Revisit to High-pressure Transitions of Pyridine: A New Phase Transition at 5 GPa and Formation of a Crystalline Phase over 20 GPa

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A new high-pressure phase transition of pyridine at 5.0 GPa was found using Raman and IR spectroscopy. Application of pressure over 20 GPa induced irreversible polymerization of pyridine, and a yellow-brownish solid material was recovered at ambient condition. The X-ray diffraction pattern revealed that the recovered solid material contained a crystalline phase in contrast to amorphization of other aromatic compounds in a similar pressure region.

Behavior of aromatic compounds under high pressure has been a target of intensive study because of their importance in fundamental and applied sciences. Benzene has been the focus of many reports as a representative compound of the aromatic family. According to the phase diagram, benzene under ambient temperature solidifies at 0.07 GPa,[1] and a solid–solid phase transition occurs at 4 GPa.[2,3] Chemical reaction takes place above 23 GPa at 540 K, and a solid amorphous compound is obtained after releasing pressure.[3] Furan solidifies at 1.2 GPa under room temperature, and a solid–solid phase transition occurs at around 3 GPa.[4] Chemical transformation to amorphous with yellow-brown color takes place above 10–12 GPa at ambient temperature.[4] The lower *P*–*T* conditions in which amorphization occurs compared with that of benzene can be explained by the less aromatic nature of furan.[4] Pyridine is also an aromatic compound with electronic structure a little different from that of benzene. The presence of a nitrogen atom in a conjugated ring lowers the energy level of the LUMO, which makes pyridine more electrophilic.[5] On the other hand, pyridine is nucleophilic at the nitrogen atom because the lone pair of electrons on nitrogen is not delocalized around the ring.[5] This dual nature of pyridine makes it an interesting target to be studied. Recently, Zhuravlev et al. (2010)[6] reported Raman and IR spectra at high pressure under room temperature. They showed reversible phase transitions of pyridine at 1 (solidification), 2, 8, 11, and 16 GPa and an irreversible amorphization at 24 GPa. The transformation at 2 GPa is supported by Raman spectroscopic observation reported by Heyns and Venter (1985).[7] On the other hand, Jia et al. (1985)[8] reported the phase transitions at 1 and 6 GPa in the pressure range of <9 GPa from the Raman spectra. The inconsistency in the behavior of pyridine among those three reports may be caused by the difference in the pressure increments in those experiments (Heyns and Venter: 0.2–0.5 GPa, Jia et al.: 0.5–1 GPa, and Zhuravlev et al.: about 0.5–1.5 GPa). Spectroscopic resolution may also affect observations of slight pressure-induced changes. In this study, we measured Raman spectra of pyridine with small pressure increments (0.1–0.3 GPa), using a real-time calibrating method.[9] IR spectra were measured at high pressure to obtain supplementary information for the phase transitions. We also measured XRD patterns of the material recovered from compression over 20 GPa in order to confirm its amorphous transition.

Pressure was generated using a diamond anvil cells (DAC) equipped with type Ib diamonds (600-µm-diameter culets) or type IIa diamonds (300-µm-diameter culets). Liquid pyridine (purity >99.5%, water <0.005%, purchased from Wako pure chemical industries, Ltd., Osaka, Japan) was loaded into a 120–250-µm hole drilled into SUS301 or Re gasket and compressed directly without pressure medium. The applied pressure was determined by ruby fluorescence.[10]

In situ measurements of Raman spectra were performed using a micro-Raman spectrometer (STR-500; Seki Technotron) equipped with a CCD camera (1024 × 128 pixels, DU-401-BR-DD; Andor Technology) and an Ar^+ ion laser (514.5 nm, 543-AP-A01; Melles Griot). The Raman shift was initially calibrated using naphthalene before the measurements, and the deviations in peak position derived from changes in room temperature during measurement[11] were compensated based on the peak position of a neon emission line[9] at 540.06 nm. For determining peak position, each peak was fitted to a log-normal function ($<400\,\mathrm{cm^{-1}}$) or Lorentzian function ($>400\,\mathrm{cm^{-1}}$). The combination of real-time calibration using the neon emission line and peak-fitting analysis can improve precision of Raman shift down to $0.05\,\mathrm{cm^{-1}}$. Spectra below $130\,\mathrm{cm^{-1}}$ were not observed because of the cutoff by the edge filter.

Infrared absorption spectra were obtained using synchrotron radiation at BL43IR at SPring-8, Japan. The high spatial resolution achieved by this beamline (smaller than 10 µm in diameter[12]) minimizes the effect of pressure gradient in a DAC sample room at high pressure. An FTIR spectrometer (Bruker IFS 120HR/X) was used for measurements of infrared absorption spectra.[13] The wavenumber resolution was set to $4\,\mathrm{cm^{-1}}$. Each spectrum was measured for about 20 min.

An X-ray oscillation photograph of solid sample was obtained using an X-ray generator (MicroMax-007; Rigaku) with Mo Kα radiation ($\lambda = 0.7107$ Å, 50 kV, 24 mA) and confocal optics (Varimax-Mo), which produces micro focused X-ray beam with a diameter of ca. 100 µm. The sample was oscillated from −2.5 to +2.5° during exposure. X-ray diffraction patterns were collected on an imaging plate (R-axisIV^{++}; Rigaku).

Figure 1 presents the Raman spectra of pyridine with increasing pressure. Each peak shifted to higher frequency as pressure was increased. Figures 2 and 3 display the plots of Raman shift and pressure in the spectral ranges of <400 and $>970\,\mathrm{cm^{-1}}$, respectively. Appearance of a new peak or disappearance of an existing peak corresponds to a phase transition. Pyridine solidified at 1.3 GPa, and the solidification pressure was consistent with previous studies.[6–8] In the lattice

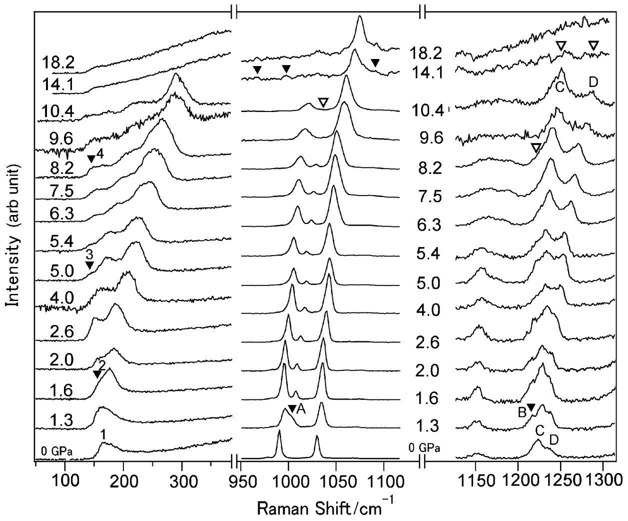

Figure 1. Selected Raman spectra of pyridine with increasing pressure. Solid triangles indicate the appearance of a new peak, and hollow triangles denote the disappearance of a peak. Peaks in the lattice mode are labeled as 1–4, and some of the other remarkable peaks are denoted as A, B, C and D.

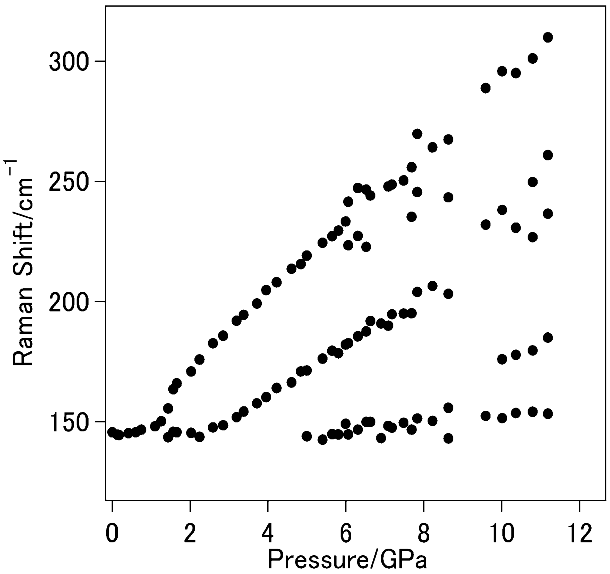

Figure 2. Pressure dependence of Raman peak positions of pyridine in the spectral range <400 cm^{-1}. New peaks appeared at 1.6, 5.0, and 8.2 GPa. Peaks in this region became invisible above 12 GPa.

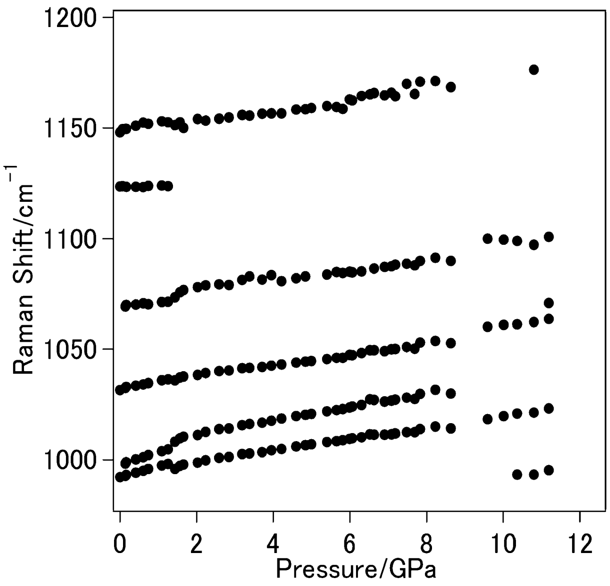

Figure 3. Pressure dependence of Raman peak positions of pyridine for the peaks in the internal vibration mode.

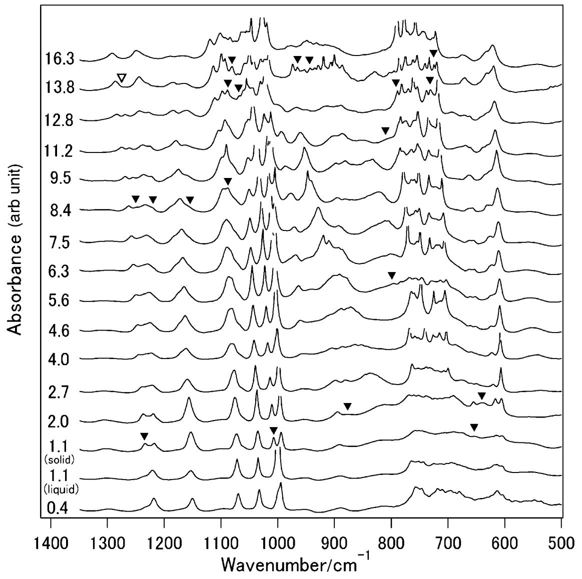

Figure 4. Infrared absorption spectra of pyridine under high pressure. Solid triangles indicate the appearance of a new peak, and hollow triangles denote the disappearance of a peak.

mode region[6] <400 cm^{-1}, four peaks were observed during compression. Each peak was denoted as 1, 2, 3, and 4. Peaks 2, 3, and 4 appeared at 1.6, 5.0, and 8.2 GPa, respectively. Among these three pressure points, 1.6 and 8.2 GPa correspond to phase transition pressures reported by Zhuravlev et al. (2010).[6]

In the internal mode region, three new peaks (A and B in Figure 1) appeared when solidification of pyridine occurred at 1.3 GPa. Peak A shifted to higher frequency with compression and disappeared at 10.4 GPa. Peak A was assigned to the ring breathing mode of pyridine molecules adsorbed on the surface of a ruby particle.[8] Peak B was buried in the neighboring intense peak at 7.5–8.2 GPa. In the pressure range of 10.4–14.1 GPa, peaks C and D became depleted, and three new peaks appeared around 960, 980, and 1080 cm^{-1}.

By analyzing our Raman spectra measured with the small pressure increments, we discovered a phase transition at 5.0 GPa. We also confirmed other transitions at 1.6, 8.2, and 10.4–14.1 GPa, which were reported by previous studies.[6,7] The transition at 6 GPa reported by Jia et al.[8] was not observed.

Figure 4 shows the infrared absorption spectra of pyridine under compression. Appearance of a new absorption or disappearance of an existing peak corresponds to a phase transition. A new broad peak around 800 cm^{-1} appeared

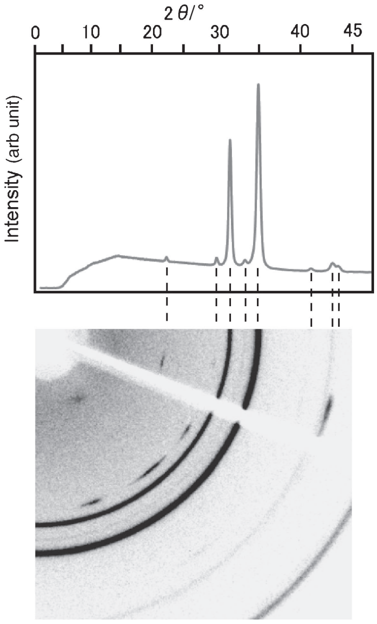

Figure 5. XRD profile and XRD pattern of the solid sample recovered from compression above 20 GPa. Some Bragg spots were observed. Circle patterns are ascribed to diffraction from rhenium gasket.

between 4.6–5.6 GPa, which is consistent with the Raman spectroscopic measurement. The pressure dependence of Raman spectra and infrared absorption spectra supports the discovery of the phase transition at 5.0 GPa.

We performed several sets of compression–decompression experiments with different maximum pressures. For experiments with maximum pressure below 18 GPa, liquid pyridine was recovered when pressure was released. When pyridine was compressed above 20 GPa, the color of sample became dark yellow. After releasing pressure, a yellow-brownish solid was recovered. Irradiation of laser light (514.5 nm) to the recovered solid produced strong fluorescent emission, suggesting pressure-induced polymerization in the sample. In addition, some Bragg spots were obtained by XRD measurement (Figure 5), indicating a coarse-grained crystalline solid in the spatial range of X-ray beam diameter (about 100 µm). Other chemical analyses such as NMR, MS, and elemental analysis will provide direct information about the structure of the recovered sample. Larger-scale experiments using a multianvil press will be required for detailed chemical analyses because the amount of the product obtained in a DAC was insufficient for such analyses.

In conclusion, we systematically searched for pressure-induced phase transitions of pyridine using Raman and IR spectroscopies and discovered a new solid–solid phase transition at 5.0 GPa. We also confirmed previously reported transitions at about 1.2 (solidification),[6,7] about 1.6,[6,7] about 8.2,[6] and about 10 GPa.[6]

Application of pressure over 20 GPa induced irreversible polymerization of pyridine which was recovered as a yellow-brownish solid material at ambient conditions. The XRD patterns revealed the recovered sample to be nonamorphous and nonpowdery, contrast to previous study[6] and other aromatic compounds.[3,4]

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References

1 G. J. Piermarini, A. D. Mighell, C. E. Weir, S. Block, *Science* **1969**, *165*, 1250.
2 L. Ciabini, F. A. Gorelli, M. Santoro, R. Bini, V. Schettino, M. Mezouar, *Phys. Rev. B* **2005**, *72*, 094108.
3 L. Ciabini, M. Santoro, F. A. Gorelli, R. Bini, V. Schettino, S. Raugei, *Nat. Mater.* **2007**, *6*, 39.
4 M. Ceppatelli, M. Santoro, R. Bini, V. Schettino, *J. Chem. Phys.* **2003**, *118*, 1499.
5 J. Clayden, N. Greeves, S. Warren, P. Wothers, *Organic Chemistry*, Oxford University Press, **2001**, pp. 1149–1150.
6 K. K. Zhuravlev, K. Traikov, Z. Dong, S. Xie, Y. Song, *Phys. Rev. B* **2010**, *82*, 064116.
7 A. M. Heyns, M. W. Venter, *J. Phys. Chem.* **1985**, *89*, 4546.
8 W. Jia, Y. Shang, R. Tang, Z. Yao, Y. Wang, J. Liu, S. He, *Acta Phys. Sin.* **1985**, *34*, 1215.
9 S. Odake, S. Fukura, H. Kagi, *Appl. Spectrosc.* **2008**, *62*, 1084.
10 G. J. Piermarini, S. Block, J. D. Barnett, R. A. Forman, *J. Appl. Phys.* **1975**, *46*, 2774.
11 S. Fukura, T. Mizukami, S. Odake, H. Kagi, *Appl. Spectrosc.* **2006**, *60*, 946.
12 Y. Ikemoto, T. Moriwaki, T. Hirono, S. Kimura, K. Shinoda, M. Matsunami, N. Nagai, T. Nanba, K. Kobayashi, H. Kimura, *Infrared Phys. Technol.* **2004**, *45*, 369.
13 H. Kimura, T. Moriwaki, S. Takahashi, H. Aoyagi, T. Matsushita, Y. Ishizawa, M. Masaki, S. Oishi, H. Ohkuma, T. Namba, M. Sakurai, S. Kimura, H. Okamura, H. Nakagawa, T. Takahashi, K. Fukui, K. Shinoda, Y. Kondoh, T. Sata, M. Okuno, M. Matsunami, R. Koyanagi, Y. Yoshimatsu, T. Ishikawa, *Nucl. Instrum. Methods Phys. Res., Sect. A* **2001**, *467–468*, 441.