

## X-ray absorption of bromonaphthalene dissolved in supercritical fluid xenon

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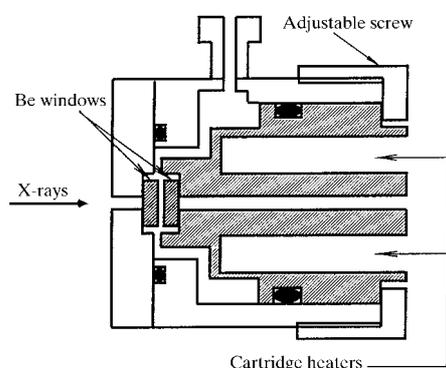
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The results of Br *K*-edge X-ray absorption measurements of 1-bromonaphthalene dissolved in supercritical fluid Xe are reported. As the pressure of Xe confined in a high-pressure cell is increased, the absorption spectrum of bromonaphthalene gradually appears, showing that Xe in the supercritical fluid state solvates the bromonaphthalene molecule. The spectrum of the dissolved sample shows a remarkable difference from that of the pure liquid sample in the near-edge region of the X-ray absorption spectrum, reflecting the interaction of the solute material with solvent Xe. *Ab initio* full multiple-scattering calculations can reproduce the spectral features qualitatively. A large value of the Debye–Waller factor must be introduced to give the best fit, corresponding to a large degree of spatial disorder and violent thermal vibration of the Xe atoms around the Br atom.

**Keywords:** X-ray absorption; supercritical fluids.

### 1. Introduction

Molecules in the supercritical fluid (SCF) state, *i.e.* the state beyond the critical temperature and pressure, are known to show high solubility for specific organic materials due to high kinetic energy. To study the nature of intermolecular interactions between the solute molecules and solvent in the SCF state, it is important to obtain information on the local structure around the



**Figure 1**  
Schematic diagram of the supercritical fluid sample cell for X-ray absorption measurement.

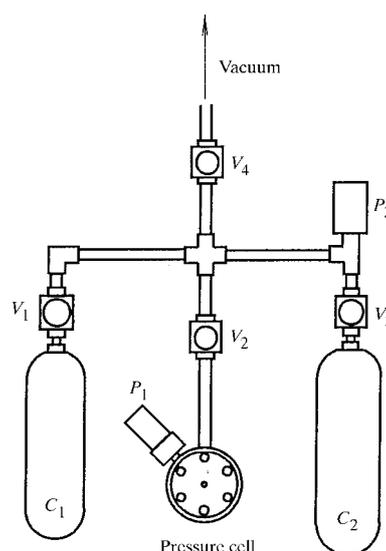
solute molecules (Nakagawa *et al.*, 1996). X-ray absorption fine-structure (XAFS) spectroscopy is an appropriate technique for this purpose. We have previously developed a cell equipped with a compact gas-handling system and succeeded in measuring the X-ray absorption of CF<sub>3</sub>Br in the SCF state (Murata *et al.*, 1995). Recently, Wallen *et al.* (1996) have developed a new system using a capillary cell made of fused silica for this purpose, and have measured the fluorescence XAFS spectra for Mn-containing molecules dissolved in supercritical CO<sub>2</sub> at a pressure of 16 MPa.

In this study, we performed X-ray absorption measurements using the same cell and gas-handling system as used previously. Liquid 1-bromonaphthalene (BrNph) and Xe were chosen as the solute material and supercritical fluid, respectively. The reasons for choosing these molecules for the present experiment are as follows. (i) The critical temperature (289.8 K) and pressure (5.85 MPa) of Xe are relatively low, giving easy control of the SCF state of Xe. (ii) From the extensive investigations of Krukoniš *et al.* (1984), it is known that naphthalene molecules can be dissolved in SCF Xe. (iii) Because of the large atomic number, the back-scattering power of Xe atoms is large. This may cause changes in the absorption spectrum due to the solute–solvent interaction in the SCF state.

In this paper the results of the Br *K*-edge XAFS measurements, together with *ab initio* theoretical calculations, are presented.

### 2. Experimental

The sample cell and the gas-handling system used in this experiment are shown schematically in Figs. 1 and 2. The X-ray path length can be controlled by changing the distance between the two beryllium windows. The cylinder C<sub>1</sub> contains Kr gas used for calibrating the distance between the windows. The SCF Xe is stored in the cylinder C<sub>2</sub>. X-ray absorption measurements were performed as follows. The X-ray absorption at the Kr *K*-edge was first measured to calibrate the X-ray path length. After removing the Kr, the cell was detached from the gas-handling system and a droplet of BrNph liquid was introduced. The cell was reconnected to the system and evacuated before introducing the Xe. Br *K*-edge



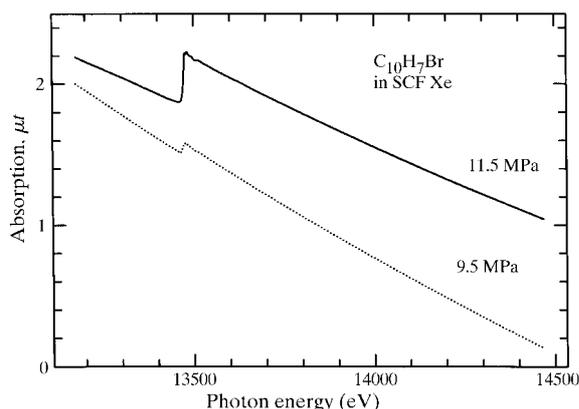
**Figure 2**  
Schematic diagram of the gas-handling system. C<sub>1</sub> and C<sub>2</sub>, P<sub>1</sub> and P<sub>2</sub> and V<sub>1</sub> through V<sub>4</sub> denote sample cylinders, pressure gauges and valves, respectively.

XAFS of a pure liquid sample of BrNph and of a 2 mol% solution of BrNph in hexane were also measured.

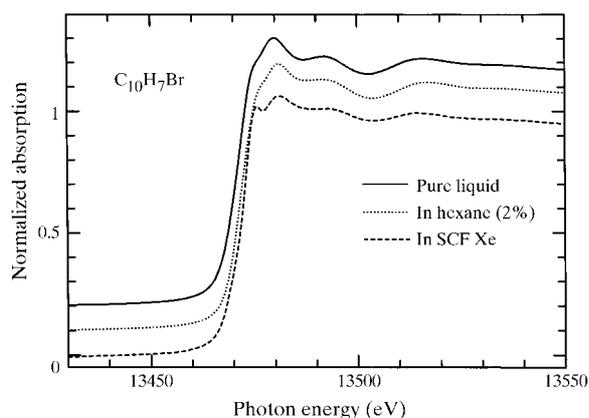
X-ray absorption measurements at the Kr and Br *K*-edges were performed at the BL-7C XAFS station in the Photon Factory (Nomura & Koyama, 1991). The storage ring was operated with a positron energy of 3.0 GeV and a stored current of 250–350 mA. Harmonic rejection was achieved by detuning the first crystal of the monochromator to about 60%.

### 3. Results and discussion

Fig. 3 shows the Br *K*-edge XAFS spectra of BrNph dissolved in SCF Xe at 298 K. The X-ray path length was about 600  $\mu\text{m}$ . No edge-jump was observed when the Xe pressure was below 9.0 MPa. A small jump appears at a pressure of 9.5 MPa. The edge height gradually increased as the Xe pressure was increased. This is evidence for the dissolution of the sample in the SCF Xe at high pressure. The estimated concentration of the sample dissolved in the SCF Xe at 11.5 MPa is about 2%, which is consistent with the value obtained by Krukoniš *et al.* (1984). Fig. 4 shows the normalized X-ray absorption near-edge structure (XANES) spectra of the pure liquid BrNph sample, the 2 mol% solution in hexane and the sample dissolved in SCF Xe. The spectra of the pure liquid and that dissolved in hexane appear to be identical, whereas the spectrum of the sample dissolved in SCF Xe is different. This difference is caused by the different environments



**Figure 3**  
X-ray absorption spectra of BrNph dissolved in supercritical fluid Xe.



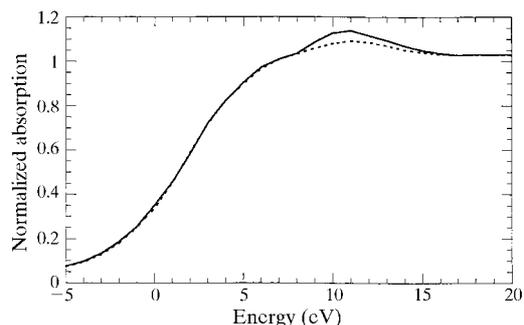
**Figure 4**  
XANES spectra of pure BrNph liquid (solid line), BrNph dissolved in hexane (dots) and BrNph dissolved in supercritical fluid Xe (dashed line).

around the Br atom in the samples. To our knowledge, this is the first direct observation of the molecular interaction between solute molecules and a supercritical-fluid solvent.

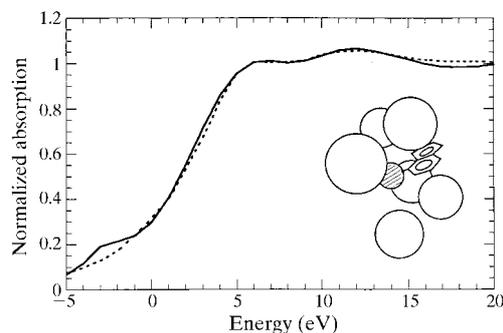
*Ab initio* full multiple-scattering calculations (Fujikawa, 1993) were made to reproduce the measured XANES spectra. Fig. 5 shows the experimental and calculated spectra of BrNph dissolved in hexane. The agreement is fairly good except for the height of the second peak. Fig. 6 shows the calculated and experimental spectra for BrNph in SCF Xe, together with the configuration of the Xe atoms. The Br atom of BrNph is placed at the centre of an f.c.c. lattice formed of Xe atoms, two of which are located above and below one of the benzene rings of BrNph. The distance between Br and Xe atoms is about 5 Å. On introducing a large value of the Debye–Waller factor (0.2 Å), the calculated spectrum was in good agreement with the experimental spectrum. The configuration of placing two Xe atoms above and below the benzene ring is consistent with the model used to explain the experimental result of the jet cluster of anthracene dissolved in SCF Xe (Kettley *et al.*, 1985). The large value of the Debye–Waller factor means that there is large degree of spatial disorder and violent thermal oscillation of the Xe atoms, properties which are characteristic of a supercritical fluid.

### 4. Conclusions

The *in situ* measurement of the Br *K*-edge XAFS of 1-bromonaphthalene dissolved in supercritical Xe was achieved. The



**Figure 5**  
The comparison of the experimental (dashed line) with the *ab initio* full multiple-scattering calculation (solid line) XANES spectra of BrNph liquid dissolved in hexane.



**Figure 6**  
The comparison of the experimental (dashed line) with the *ab initio* full multiple-scattering calculation (solid line) XANES spectra of BrNph dissolved in SCF Xe. A Debye–Waller factor of 0.2 Å was used in the calculation. The configuration of the Xe atoms around the BrNph molecule is also shown. The hatched circle represents the Br atom located at the centre of an f.c.c. lattice of Xe atoms.

absorption spectrum of the sample in SCF fluid Xe shows remarkably different features compared with that of a pure sample, indicating the interactions between the solute Br atom and the SCF Xe solvent. *Ab initio* full multiple-scattering calculations can reproduce the spectrum features qualitatively. A large value of the Debye–Waller factor, corresponding to violent thermal vibration of Xe atoms around the Br atom, must be introduced to obtain the best fit.

This research project has been performed with the approval of the Photon Factory Advisory Committee (Proposal No. 96-G-173).

#### References

- Fujikawa, T. (1993). *J. Phys. Soc. Jpn*, **62**, 2155–2165.
- Kettley, J. C., Palmer, T. F. & Simons, J. P. (1985). *Chem. Phys. Lett.* **115**, 40–46.
- Krukonis, V. J., McHugh, M. A. & Seckner, A. J. (1984). *J. Phys. Chem.* **88**, 2687–2689.
- Murata, T., Nakagawa, K., Kimura, A., Otoda, N. & Shimoyama, I. (1995). *Rev. Sci. Instrum.* **66**, 1437–1439.
- Nakagawa, K., Otoda, N., Kimura, A., Nurdiawati, D., Tanaka, K., Kimura, K. & Ejiri, A. (1996). *J. Electron Spectrosc. Relat. Phenom.* **78**, 415–418.
- Nomura, M. & Koyama, A. (1991). *X-ray Absorption Fine Structure*, edited by S. S. Hasnain, pp. 666–669. London: Ellis & Horwood.
- Wallen, S. L., Pfund, D. M., Fulton, J. L. & Yonker, C. R. (1996). *Rev. Sci. Instrum.* **67**, 2843–2845.