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HIGH PRESSURE XAS ON BROMINE IN THE DISPERSIVE MODE

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Résumé

Br₂ a été étudié sous haute pression par spectroscopie d'absorption X en dispersion d'énergie jusqu'à 57,5 GPa. Les avantages du montage en dispersion d'énergie sont présentés. Les résultats de XANES et d'EXAFS sur le bromure sont discutés en termes de dépendance avec la pression de la longueur de la liaison moléculaire et du potentiel interstital moyen.

Abstract

High pressure energy dispersive x ray absorption spectroscopy has been performed on Br₂ up to 57.5 GPa. The advantages of the energy dispersive set up are presented. The XANES and EXAFS results on bromine are discussed in terms of bond length and average interstitial potential pressure dependence.

Introduction

The dissociation of diatomic molecules under high pressure, due to the increasing charge transfer from the intramolecular to the intermolecular bond, has been investigated by different experimental techniques: resistivity measurement (1), Raman spectroscopy (2), x ray diffraction (3,4,5). Through the halogen series, only the iodine dissociation has been observed (3). For bromine and chlorine, using a scaling law between the halogens and the volume variation with pressure, the transition from a molecular to a monoatomic phase has been predicted respectively at 58 ± 6 GPa and 140 ± 30 GPa. All the data on halogens leave the question still open, whether or not the bond length changes with pressure prior the transition. X ray absorption spectroscopy is particularly suited to address this issue. We present preliminary results of energy dispersive x ray absorption spectroscopy on solid bromine under high pressure, using the diamond anvil cell technique.

Experiment

The pressure was generated by a classical Bell and Mao type diamond anvil cell with "Drukker standard" diamonds (Ø = 4 mm). Bromine was loaded in the hole (Ø = 150 μm, 30 μm thick) of a stainless steel gasket without any pressure transmitting medium. In order to measure the pressure (6) a ruby chip was added to the sample. The luminescence of the ruby, excited by the 488 nm line of an air cooled argon laser (40 mw), was recorded outside the hutch using a single monochromator. The mount of the cell, with centering pins, was specially built to put back the cell, after pressure measurements, at the same place, better than 10 μm. The cell was placed on a three axes translator, motor driven from outside the hutch.
The energy dispersive port of LURE (ORSAY) (7) presents important advantages to perform high pressure experiments:

(i) The x ray beam is focused which is very important according to the small size of the sample.
(ii) All the data are obtained at once in a very short time. This makes easier the alignment of the cell in the beam and also prevents for some of the distortions of the spectrum due to a possible deformation of the gasket.
(iii) The stability of the beam is excellent because of the lack of any mechanical movement during data collection.
(iv) The acquisition time is very short: for a frame, we need only 800 ms. Six frames are sufficient to obtain data on the XANES part of the spectrum. For EXAFS up to 100 frames were added to improve statistics.

Though the x ray beam goes through the anvils, we see only a Bragg peak of the diamonds in the preedge part of the spectrum. Some glitches due to the extra Bragg reflection of the curved crystal were also observed in the spectrum, unfortunately very near the position of the E2 peak (figure 1). Although the x ray beam was focused, the size of the spot was a little bit bigger than the gasket hole so a part of the beam goes directly through the gasket and the spectra were slightly distorted. The main consequence was that only a small energy band pass was available to collect significant data. The energy calibration was made using NaBr as a standard. Thus we choose the NaBr threshold as an arbitrary origin.

Previous measurements of liquid bromine (8) show that the achieved energy resolution in our experiment is not at the top. This may be due to the attempt to collect a wide energy band pass for EXAFS data which leads to a larger radius of curvature and a detector position close to the focus.

Results and discussion

In figure 1, we show the spectra at the lowest pressure (4.8 GPa) and the highest pressure (57.5 GPa) performed on solid bromine. In both spectra we can see the shape resonance peak (E1) which means that even at 57.5 GPa, bromine is still a molecular crystal. Comparing the two spectra we note that E1 and E2 peaks are shifted to higher energy by 4 and 9 eV. We note also that the peaks broaden and decrease in intensity with increasing pressure. The energy position E of the peaks is related to the bond length R according to the relation (E-E0)R² = constant where E0 is the true energy origin (average interstitial potential) (9).

If we compare the solid bromine spectrum at 4.8 GPa to the liquid spectrum (fig. 2), we observe that the peaks are shifted by 5 eV. Since we don't expect a dramatical
change in the molecular bond length with solidification and also since \( E_1 \) remains almost constant up to 20 GPa (fig. 4), we attribute the shift of the peaks energy to a shift of the origin due to the change in the interstitial potential when you go from liquid to solid state. The Fourier transform of the liquid spectrum using \( E_0 = -12 \) eV and the Fourier transform of the solid one using \( E_0 = -5 \) eV (a 5 eV shift of the energy origin) give about the same bond length (fig. 3) which is consistent with the position of the shape resonance in both phases.

To interpret the results on solid bromine with increasing pressure we can do two alternative hypothesis:

(i) The energy origin \( E_0 \) is constant with pressure in the solid phase. In this case the shift to higher energy of \( E_1 \) and \( E_2 \) peaks (fig. 4) is entirely due to a decrease of the bond length and then we can determine its variation versus the applied pressure (fig. 3). The Fourier transforms of the spectra (fig. 5) show also a decrease of the bond length with increasing pressure in agreement with the first procedure (fig. 3). According to this line of reasoning, at 57.5 GPa we obtain a variation of 13 % in the bond length, which is unexpected.

(ii) The bond does not vary with pressure. In this case the shift of the \( E_1 \) peak is entirely due to a shift of the energy origin which can be explained by an increasing delocalisation of the binding electrons. But, the \( E_2 \) peak should have the same shift which is not the case and if we do a Fourier transform of the solid bromine spectra, we obtain a decrease of the bond length with increasing pressure which is also unfounded.

In fact we think that both parameters, \( E_0 \) and \( R \) change with pressure. To fit their variation we need to compare the results of the XANES and the EXAFS treatments. The quality of the present EXAFS data is too poor to get a reliable partition of the two effects (distorted spectra lead to a Fourier transform calculated in a small k range).
Conclusion

We have shown that XAS can be performed at very high pressure and that the energy dispersive method is very well adapted to such an experiment. To obtain better data on the EXAFS part of the spectrum, some improvements are needed (better focus of the beam, harmonic rejection). To interpret the results of solid bromine both XANES and EXAFS are necessary, since both $E_0$ and $R$ can be pressure dependent. A theoretical support is also needed to really understand the data.

Références

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