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First-principles study of solid iodine and bromine under high pressure

Hiroshi Miyagi^{†‡}, Kenji Yamaguchi[§], Hiroshi Matsuo[†] and
Kiichiro Mukose[†]

[†] Department of Material Physics, Faculty of Engineering Science, Osaka University, Toyonaka, Osaka 560-8531, Japan

[‡] CREST, Japan Science and Technology Corporation (JST), Japan

[§] Central Research Institute, Mitsubishi Materials Corporation, Omiya, Saitama 330-0835, Japan

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Abstract. Experiments on solid iodine under pressure are reviewed. Theoretical results obtained on solid iodine by the full-potential linear muffin-tin orbital method are reviewed. The pressure dependences of the Raman-active A_g modes of molecular solid bromine have been studied theoretically by the same method. The calculated results reproduce recent experimental results very well. After metallization, the softening of frequencies that is seen is not the same as in experiments. This contrasts with the case for solid iodine.

1. Introduction

The molecular halogens, I_2 , Br_2 , and Cl_2 , form diatomic molecular crystals under ambient conditions. These diatomic molecular solids have received much attention as regards their molecular dissociation and metallization, which are related to the metallization of high-density hydrogen. There is much interest in whether the metallization of hydrogen occurs by means of ‘band overlap’ or ‘molecular dissociation’. For a long time, since Wigner’s pioneering work, hydrogen has been regarded as the first element of the alkali group. As Ashcroft pointed out, hydrogen is regarded naturally as the first element of the halogen group. However, there are essential differences between hydrogen and the other halogens as regards the existence of core electrons and the magnitudes of quantum effects. In solid halogens, the structural transformations—band overlap and molecular dissociation—occur under lower pressure than in solid hydrogen. A particularly large number of studies have been carried on solid iodine.

1.1. Experiments on solid iodine

The metallization of solid iodine was first observed at 16 GPa; it was evident from electrical resistivity and optical reflectivity measurements [1]. Shimomura *et al* [2] carried out x-ray studies on iodine up to 20.6 GPa, and the crystal structure at this pressure is the same as that at ambient pressure: body-centred orthorhombic, D_{2h}^{18} ($Cmca$), as shown in figure 1. Hence the metallization at 16 GPa comes from the band overlap. Later, Takemura *et al* extended the studies up to 30 GPa, and found molecular dissociation at 21 GPa, where the structure transforms to a monatomic BCO one, D_{2h}^{25} ($Immm$) [3]. Furthermore, Fujii *et al* observed structural transitions at 43 GPa from a BCO to a body-centred tetragonal (BCT)

structure, D_{4h}^{17} ($I4/mmm$) [4], and from a BCT to a face-centred cubic (FCC) structure at 55 GPa [5].

Shimomura *et al* studied Raman scattering of iodine up to 21 GPa [6]. They found a softening of the librational A_g mode above 15 GPa. Below the dissociation pressure, softening of the Raman-active librational A_g and vibrational B_{3g} modes is observed.

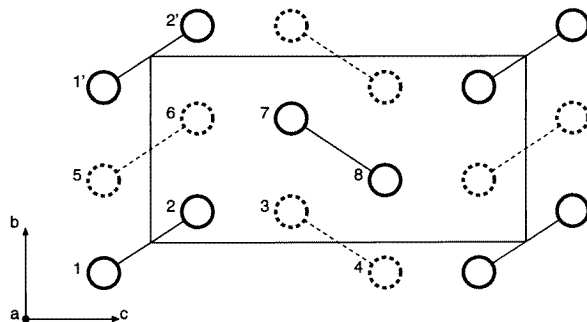


Figure 1. The crystal structure of molecular solid iodine with the space group D_{2h}^{18} ($Cmca$). The molecular axes are in the bc -plane. The molecules shown with solid lines are on the plane and those shown with broken lines are on the adjacent plane(s), which are $a/2$ above (or below) the plane shown with solid lines. For the atom numbered 2, the first-nearest neighbour is 1, the second is 7, and the third is 1'.

For several years there was disagreement between x-ray diffraction groups and Mössbauer spectroscopy groups about the crystal structure above 16 GPa—over whether it is a molecular phase or a dissociation phase. Pasternak *et al* conducted Mössbauer spectroscopy experiments on ^{129}I [7]. They asserted that the large asymmetry parameter of the electric field gradient, seen in Mössbauer experiments, cannot be explained by the molecular dissociation picture. And they proposed two new molecular phases (HP1, HP2), and considered these phases are coexisting with the low-pressure phase. Also, Pasternak *et al* observed the Mössbauer isomer shift up to 30 GPa, but they found no evidence of the transitions up to 30 GPa [8].

1.2. Solid bromine

On the other hand, studies of other solid halogens are few in comparison with those of solid iodine. For solid bromine, Fujii *et al* observed similar structural phase transitions in x-ray diffraction experiments [9]—that is, a molecular dissociation transition near 80 GPa. The structure of the high-pressure phase is found to be BCO, D_{2h}^{25} ($Immm$), as previously observed for solid iodine above 21 GPa. Furthermore, Fujihisa *et al* determined the pressure dependence of the atomic positions by synchrotron radiation x-ray intensity measurements, and proposed empirical scaling rules for the metallization and molecular dissociation pressures [10]. They also found a sign of metallization at around 60 GPa, where the surface of the sample begins to reflect light. Direct measurements of the electrical resistance of solid bromine under high pressure have been made by Shimizu *et al* [11]. According to their measurements, though the transition pressure to the metallic state is not clear, bromine is considered to undergo metallization in the molecular state under 80 GPa, at which point bromine enters a monatomic phase. They also found superconductivity at pressures higher than 90 GPa.

Recently Akahama *et al* reported pressure dependences of Raman-active A_g modes [12]. However, softening of the modes is not observed up to the molecular dissociation pressure of 80 GPa; this contrasts with the case for solid iodine.

2. Band-theoretical studies

The band overlap in the molecular phase has been investigated theoretically by means of both crude band calculations, by Siringo *et al* [13], and detailed band calculations by the *ab initio* pseudopotential (PP) method, by Orita *et al* [14]. The structural transformations in the monatomic phases have also been studied by the *ab initio* PP method [15, 16].

Recently, using the full-potential linear muffin-tin orbital method (FP-LMTO), Yamaguchi and Miyagi have shown that the results for the high-pressure phase reported above 24 GPa obtained by Mössbauer experiments can be explained well with the monatomic base-centred orthorhombic (BCO) phase reported from x-ray experiments above 21 GPa [17, 18]. The study succeeded in giving a consistent interpretation for the x-ray and Mössbauer experiments. Very recently, the authors studied the Raman-active A_g modes of molecular solid iodine using a frozen-phonon calculation [19]. The calculated frequencies reproduce well the experimental results from the Raman experiment.

2.1. Calculation

In the FP-LMTO method, the electronic states are described by linear muffin-tin orbitals (LMTO). The crystal space is partitioned into muffin-tin spheres (MTS) centred at every atomic position and the interstitial region. In the interstitial region, the electronic state is described by Hankel functions. The method was developed by Weyrich [20], Methfessel *et al* [21], and Savrasov [22]. The method is very complicated, so we cannot describe the detail of the method in this report; see the paper by Savrasov and Savrasov [23].

The program source of FP-LMTO used in this work was originally developed by Savrasov [22]. Here we note only the parameters which we used. We adopted the exchange–correlation potential proposed by von Barth and Hedin [24]. In the calculation for solid iodine, we used four values of κ for the valence electrons: $\kappa^2 = 0.5$ Ryd was used for 5s, 5p, and 5d states, -0.5 Ryd and -1.5 Ryd for 5s and 5p states, and -2.5 Ryd for the 4d state. Inside the MTS, the scalar-relativistic calculations are performed for valence electrons.

All of the parameters, such as the number of k -points, and the number of G -vectors in the Fourier expansion of the densities and potentials, are selected to converge total energy within 0.5 mRyd per atom. Throughout all of our calculations, the MTS radius is fixed as $2.558a_0$, which is slightly smaller than half of the bond length at zero pressure. More details of the calculation are described in [19].

In figure 1, the molecules are on the bc -plane. The structure is characterized by the orthorhombic lattice parameters, a , b , and c , and two atomic coordinates, y and z . The lattice parameters a , b , and c at each pressure are taken from the recent x-ray experimental results of Fujihisa *et al* [25]. We do not optimize with respect to the lattice parameters a , b , and c .

Though we have described the formalism of the calculation of the pressure dependence of the Raman-active A_g mode in [19], we describe it here again, because the results for solid bromine obtained recently by Akahama *et al* [12] seem to be different from the results for solid iodine.

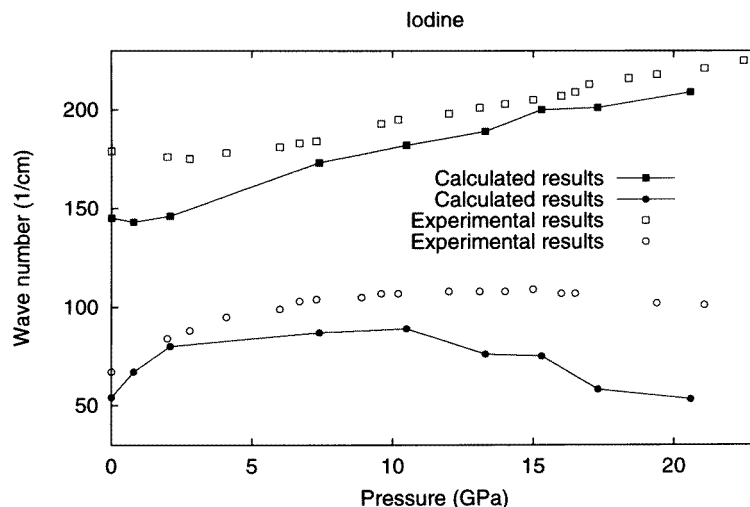


Figure 2. The pressure dependences of the Raman-active A_g modes of molecular solid iodine. Filled squares and circles denote calculated results. Open squares and circles denote experimental results [6, 26].

2.2. The Raman-active A_g mode

Because the A_g mode is the identity representation, and the molecular axis is in the bc -plane, y and z are determined as follows:

$$y = \frac{r_{\text{mol}} \sin \theta}{2b}$$

$$z = \frac{r_{\text{mol}} \cos \theta}{2c}$$

where r_{mol} is the bond length of a bromine molecule and θ is the angle of the molecular axis with respect to the c -axis.

The potential energy of the lattice is expanded in terms of the atomic coordinates in the basis corresponding to the two A_g modes:

$$U(y, z) = \frac{1}{2}\alpha(y - y_0)^2 + \beta(y - y_0)(z - z_0) + \frac{1}{2}\gamma(z - z_0)^2 + U_0.$$

Here α , β , and γ are three elements of the two-dimensional dynamical matrix, y_0 and z_0 give the equilibrium position, and U_0 is the minimum energy. On the basis of the frozen-phonon method, we obtain these parameters by fitting the potential energy, $U(y, z)$, to the calculated total energies at several points with various atomic coordinates. Phonon frequencies and normal modes are easily obtained by diagonalization of the dynamical matrix.

The pressure dependences of the calculated frequencies of the A_g modes are shown in figure 2. The low-frequency mode (LFM) has a maximum at around 10 GPa. The high-frequency mode (HFM) increases gradually with increasing pressure. The band-overlap pressure, in this calculation, is nearly 10 GPa. The softening is caused by the band overlap and the gradual molecular dissociation [19]. The pressure dependences of the atomic coordinates y_0, z_0 for the equilibrium structure are displayed in figure 3. The y_0 -value increases with increasing pressure, approaching 0.25. On the other hand, the z_0 -value remains almost unchanged, at around 0.125. The structure with $(y_0, z_0) = (1/4, 1/8)$ is the monatomic face-centred orthorhombic (FCO) structure, D_{2h}^{23} ($Fmmm$).

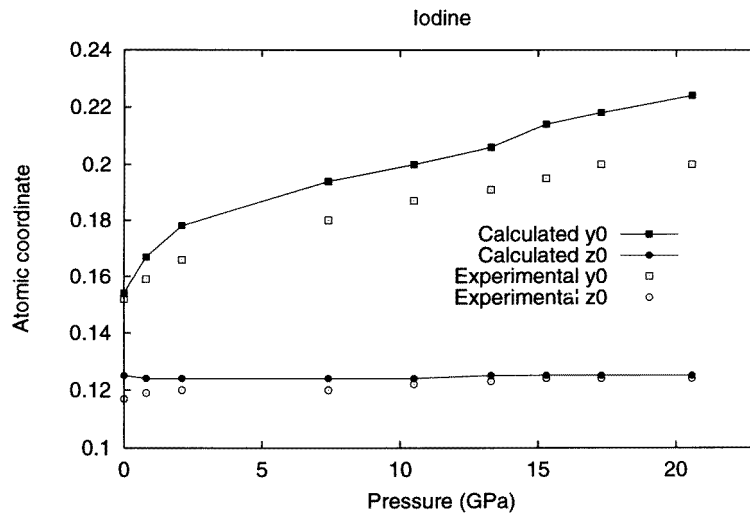


Figure 3. The pressure dependences of the atomic coordinates (y_0, z_0) of the equilibrium position for molecular solid iodine. Filled squares and circles denote calculated results. Open squares and circles denote experimental results [25].

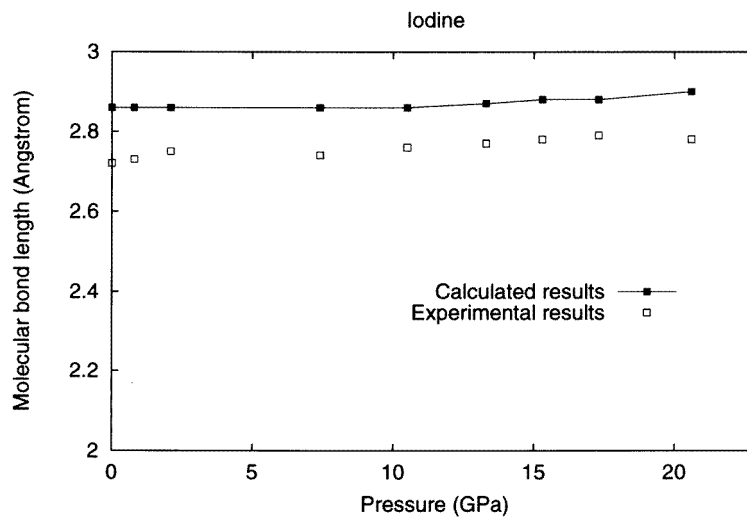


Figure 4. The molecular bond length (r_{mol}) of solid iodine versus pressure. Filled squares denote calculated results. Open squares denote experimental results [25].

The pressure dependence of r_{mol} in the equilibrium structure is shown in figure 4. The value of r_{mol} changes negligibly with pressure.

In figure 5, the angle between the eigenvector of the HFM and the c -axis is compared with the molecular axis at the equilibrium position. At low pressure, the direction of the eigenvector is nearly the same as that of the molecular axis. The HFM may be referred to loosely as a 'vibron' and the LFM as a 'libron'. However, the angle between the eigenvector of the HFM and the molecular axis increases with increasing pressure. Above the band-

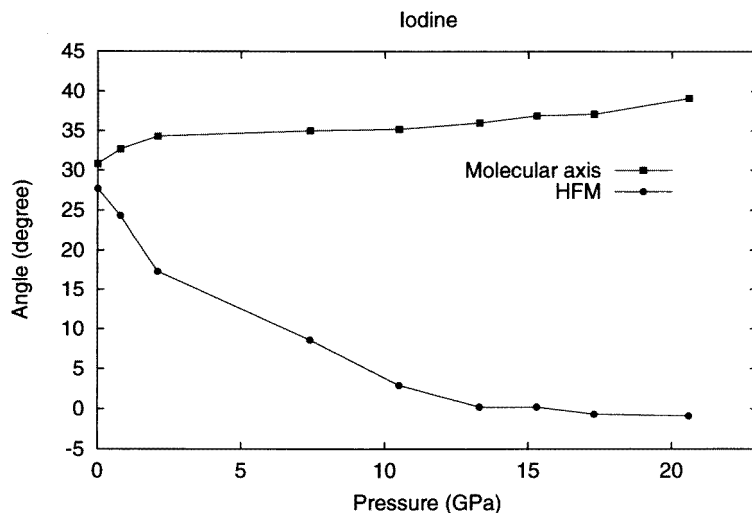


Figure 5. The pressure dependences of the direction of the molecular axis and the eigenvector of the HFM with respect to the c -axis (for solid iodine).

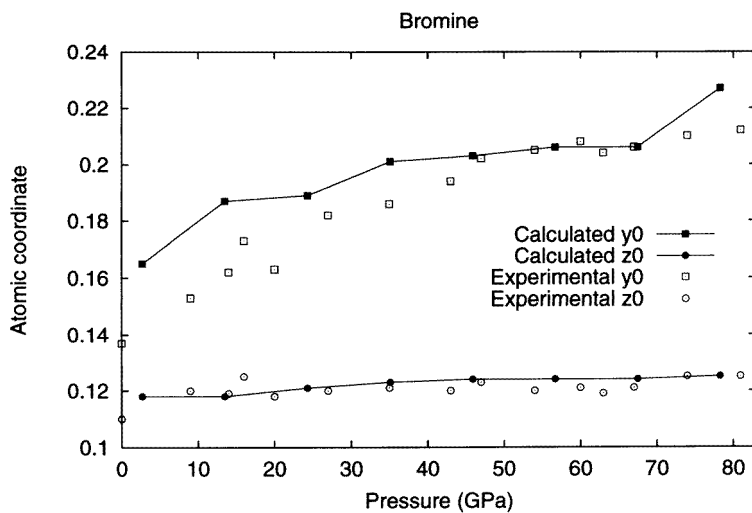


Figure 6. The pressure dependences of the atomic coordinates (y_0, z_0) of the equilibrium position for molecular solid bromine. Filled squares and circles denote calculated results. Open squares and circles denote experimental results [10].

overlap pressure (around 10 GPa) in the present calculation, the eigenvector of the HFM lies along the c -axis and that of the LFM along the b -axis.

2.3. The calculation for solid bromine

We also calculate the pressure dependence of the Raman-active A_g modes of solid bromine, using a frozen-phonon calculation. All of the calculations are carried out in the same way as for solid iodine. In the computation, 1s, 2s, 2p, 3s, 3p, and 3d electrons are regarded as

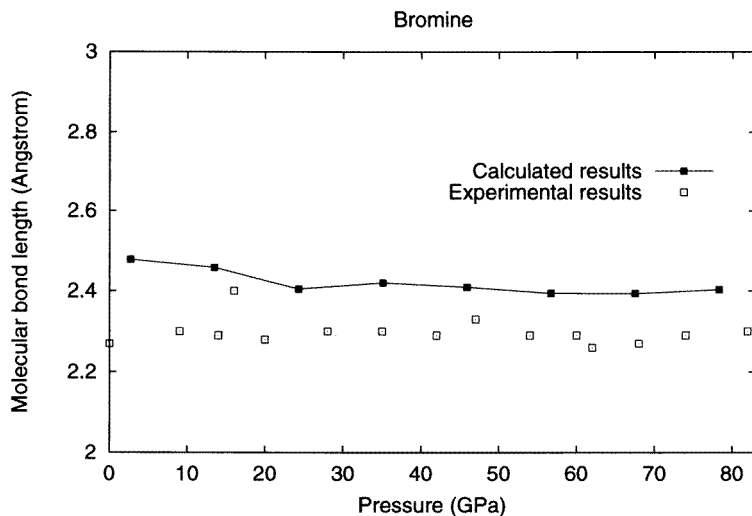


Figure 7. The molecular bond length (r_{mol}) for solid bromine versus pressure. Filled squares denote calculated results. Open squares denote experimental results [10].

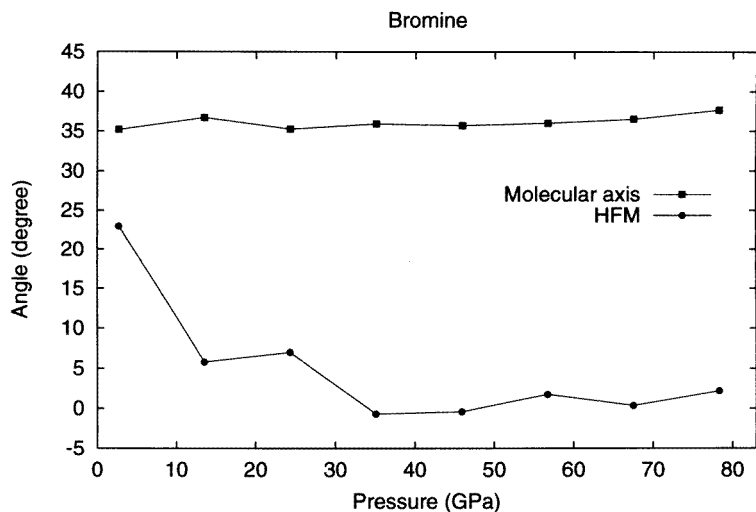


Figure 8. The pressure dependences of the direction of the molecular axis and the eigenvector of the HFM with respect to the c -axis (for solid bromine).

core electrons, and 4s, 4p and 4d electrons as valence electrons. For bromine, we use two values of κ for valence electrons: $\kappa^2 = 0.5, -0.5$ Ryd. Throughout all of our calculations, the MTS radius is fixed as $2.17a_0$, which is slightly smaller than half of the bond length at zero pressure. In the pressure regions considered, muffin-tin spheres with this radius do not overlap with each other. The lattice parameters a , b , and c at each pressure are taken from the x-ray experimental results given by Fujihisa *et al* [10]. The pressure dependence of the atomic coordinates y_0 , z_0 for the equilibrium structure are displayed in figure 6. The y_0 -value increases with increasing pressure, approaching 0.25, while the z_0 -value remains

almost unchanged, at around 0.125. The pressure dependence of r_{mol} for the equilibrium structure is shown in figure 7. The value of r_{mol} changes negligibly with pressure. In figure 8, the angle between the eigenvector of the HFM and the c -axis is compared with the molecular axis at the equilibrium position. The angle between the eigenvector of the HFM and the molecular axis increases with increasing pressure. Above about 35 GPa, the eigenvector of the HFM lies along the c -axis and that of the LFM along the b -axis. All of these behaviours of the eigenmodes are like those of solid iodine.

In figures 9, 10, and 11, we show the graphs of the density of states obtained from the present calculations for three pressures, 24.3, 35.1, and 45.9 GPa. As can be seen from the figures, metallization due to band overlap occurs near 35 GPa.

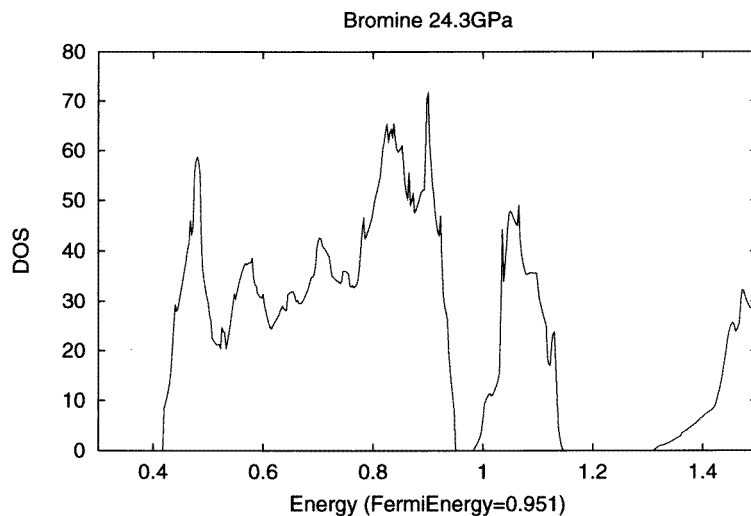


Figure 9. The density of states of bromine at the pressure 24.3 GPa.

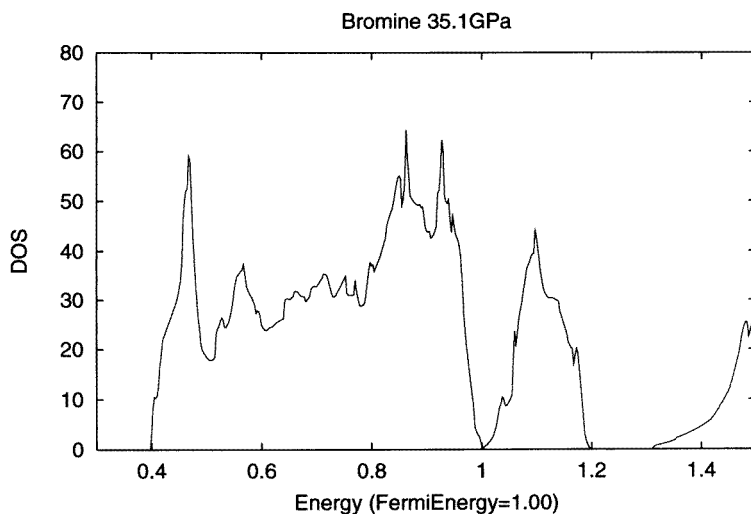


Figure 10. The density of states of bromine at the pressure 35.1 GPa.

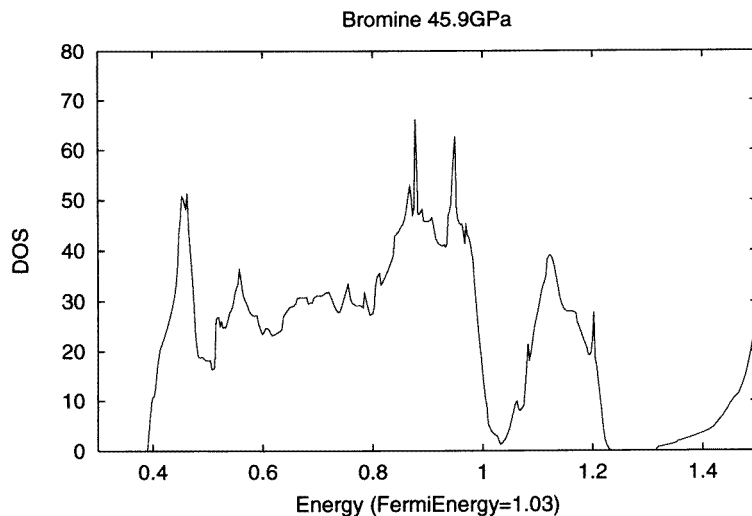


Figure 11. The density of states of bromine at the pressure 45.9 GPa.

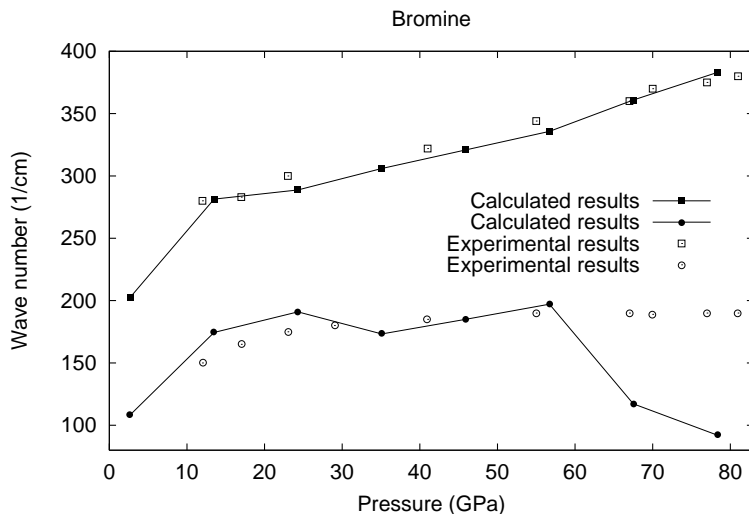


Figure 12. The pressure dependences of the Raman-active A_g modes of molecular solid bromine. Filled squares and circles denote calculated results. Open squares and circles denote experimental results [12].

On the other hand, the pressure dependences of the calculated frequencies of the A_g modes are shown in figure 12. The HFM increases gradually with increasing pressure.

Under pressure less than 60 GPa, the agreement between the calculated frequencies and observed ones is much better than that for solid iodine. Softening of the LFM above the calculated metallization pressure (35 GPa) is not seen. But considerable softening is seen under pressures above 60 GPa. In this pressure region, the discrepancy between calculation and experiments is noticeably large. This might be associated with fitting error due to anharmonicity.

3. Conclusions

In this report, we review experiments on solid iodine and bromine. We review mainly our theoretical results obtained by the FP-LMTO method for solid iodine, which succeeded in explaining consistently many experimental results obtained for solid iodine under pressure, such as the pressure dependence of the Raman-active A_g modes, and the Mössbauer experimental results.

We made calculations for the Raman-active A_g mode of solid bromine in the molecular phase. Softening of the LFM is not seen after metallization (at 35 GPa) up to 60 GPa, as in experiments. The agreement of the calculational results and experiments is excellent up to 60 GPa. But, under pressures above 60 GPa a discrepancy between calculations and experiments is seen. The origin of the discrepancy is not clear at the present stage. This discrepancy might come from fitting error due to anharmonicity. The qualitative difference between the cases of solid iodine and bromine, we need more detailed analysis of the dispersion curve.

We are looking forward to obtaining experimental data on other quantities for solid bromine, chlorine, and fluorine, such as have been obtained for solid iodine.

Lastly, we note that the dissociation transition in solid hydrogen is estimated, by the scaling rule [10], to occur at $r_s = 1.19$, where r_s is the radius (in atomic units) of the sphere with the volume per electron.

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