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First-principles study on molecular dissociation under metallization pressure in aromatic monomolecular crystals with iodine atoms

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Abstract

We have examined the metallization mechanism and possibility of molecular dissociation in iodanil (IA) and hexa-iodobenzene (HIB) under pressure by using first-principles calculations. We found that the metallization in IA is caused by the band overlap in the molecular phase and dissociation does not follow the metallization. In HIB, on the other hand, the band overlap mechanism is found to be less probable, which implies that a structural transformation will occur before the metallization. Both mechanisms are completely different from that for I_2 diatomic molecular crystal, and suggest essential roles of C_6 rings and O atoms.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The metallization mechanism and the relation with molecular dissociation under pressure are the most fundamental as well as important problems for molecular crystals (MC). Among these crystals, I_2 diatomic MC has been extensively studied as a prototype of the important system of H_2 MC [1], and the behaviours under pressure have been well understood [2–4]. The metallization ($P \sim 16$ GPa) is ascribed to the band overlap in the molecular phase, and the following electron occupation of the anti-bonding σ -states of the molecule leads to the molecular dissociation ($P \sim 21$ GPa).

Recently, metallization has been observed in aromatic monomolecular crystals with I atoms: iodanil ($C_6O_2I_4$; IA) and hexa-iodobenzene (C_6I_6 ; HIB) [5–7]. Since both materials contain I atoms and they have similar metallization pressures ($P \sim 33$ – 35 GPa), one may expect predominant contributions of I such as molecular orbitals originating from I or dissociated I atoms and similar metallization mechanisms for the two materials. On the other hand, contributions from the C_6 rings, and O atoms in IA, will be not negligible and may lead to different behaviours from that of I_2 diatomic MC. However, their mechanisms of metallization and possibilities of molecular dissociation under pressure have not been clarified yet.

Here we investigate these behaviours in IA and HIB under pressure using first-principles calculations. In this study, postulating a band overlap mechanism in the molecular phase as in I₂ MC [4], we calculate structures and electronic states of the molecular phases in IA and HIB under pressure. Then, comparing the results with the experimental ones already known, we discuss the metallization mechanisms and possibilities of molecular dissociation in IA and HIB.

2. Calculation method

We use a first-principles method based on density functional theory (DFT) [8] with a plane-wave basis and ultrasoft pseudopotentials [9], which is highly accurate for calculations of atomic force and stress. We calculate optimized electronic states as well as relaxed atomic coordinates at several pressures. The unit cell at each pressure is determined by the stress calculations [10]. Thus we can examine IA and HIB at the pressures where the cell parameters have not yet been determined in experiments.

The detailed calculation conditions are as follows. The cut-off energies for the wavefunction and deficit charge are 30.25 and 289 Ryd, respectively. Exchange–correlation energy is calculated by generalized gradient approximation (GGA) [11]. The first Brillouin zone is integrated by sampling 64 *k*-points. The unit cell contains 24 atoms (two molecules) and is constrained to hold the *P*2₁/*c* symmetry in most cases. The calculations include only the scalar-relativistic effect, and not spin–orbit (SO) interaction.

3. Results and discussion

First, we have calculated the relaxed structures of the molecular phases of IA and HIB at several pressures between 0 and 40 GPa. The pressure dependence of the calculated cell parameters in both materials well reproduces the experimental ones. The bulk modulus of IA (HIB) is calculated to be 12.8 (17.2) GPa, which is in very good agreement with 9.5 (14.4) GPa in experiments.

The pressure dependence of the band gap in IA shown in figure 1(a) indicates that the metallization pressure is about 25 GPa in the calculations. Considering the usual tendency of DFT to underestimate band gaps, this pressure is consistent with 33 GPa observed in experiments [5]. Thus the metallization in IA is ascribed to the band overlap mechanism in the molecular phase as observed in I₂ MC.

We also examine the band structures in IA at 0 and 29.9 GPa (figure 2). The valence band (VB) top mainly consists of non-bonding O 2p *y*-orbitals with a small contribution of I 5p *y*-orbitals, while the conduction band (CB) bottom originates from C=O π^* - and C–C π^* -orbitals. As pressure increases from 0 GPa, the dispersion of the CB bottom becomes remarkable, indicating that the interlayer interaction along the *b*-direction increases significantly for the C=O π^* -states. This increase in dispersion finally leads to the gap closing by band overlap.

The band overlap causes partial occupation of the bands originating from O 2p *y*- and C=O π^* -orbitals. This leads to only C=O π -bond breaking, and affects little the C=O σ -bonds. Consequently, C–O single bonding in each molecule and intermolecular O–O bonding will be formed in IA. Thus the molecule is expected to remain even after band overlap. This suggests that the molecular dissociation following the band overlap metallization as in I₂ MC will not occur in IA. This is consistent with persistence of the molecule up to 48 GPa observed in experiments [12]. It should be noted that the molecular phase may persist up to the pressure of the superconducting transition (52 GPa) [6], because there is no band related to molecular σ - or σ^* -orbitals around the Fermi level.

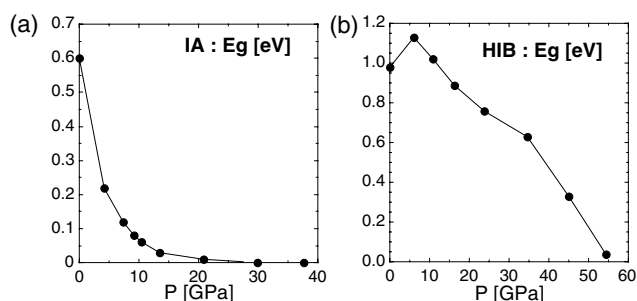


Figure 1. Pressure dependences of the band gaps in (a) IA and (b) HIB.

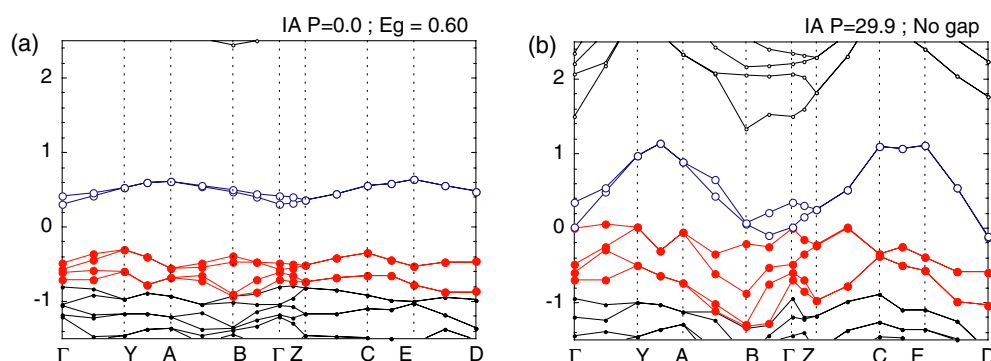


Figure 2. Band structures of IA at (a) 0 GPa and (b) 29.9 GPa in eV. The Fermi level is set as the origin. Filled and open circles show the valence band top and conduction band bottom respectively.

As to HIB, the band structures at 0 and 34.5 GPa are shown in figure 3. The VB top consists of lone I 5p y -orbitals, while C–I π^* - and C_6 -ring π^* -orbitals construct the CB bottom. Assuming band overlap in the molecular phase, electron occupation of the $C_6\pi^*$ -bands will reduce the C_6 ring planarity, leading to formation of a three-dimensional C network. Besides the occupation of C–I π^* -bands causes C–I dissociation. Thus the molecular dissociation will follow the metallization as in I_2 MC.

However, the calculated metallization pressure following this mechanism is about 56 GPa as shown in figure 1(b), which is much larger than the experimental one. This difference can be partly ascribed to the neglect of SO interaction. For I_2 MC, Orita *et al* [4] reports that the SO interaction reduces the band gap by 0.27 eV. Since C atoms are contained in addition to I in HIB, the effect of SO interaction will be smaller than in I_2 MC. Even if we consider a 0.3 eV decrease of the band gap, the metallization pressure is still larger than 46 GPa. These findings suggest that the metallization mechanism in HIB is different from the band overlap in the molecular phase.

Charge transfer from one molecule to another, as observed in many organic molecular conductors such as BEDT-TTF salts, will also be less probable because HIB is a monomolecular crystal. In fact, calculations without symmetry constraints do not differentiate between the two molecules in the unit cell. Thus we suggest another mechanism: a structural transformation occurring before the metallization. The possible transformations are those into a metallic molecular phase or a phase with dissociated I atoms. Since dissociated I atoms are actually

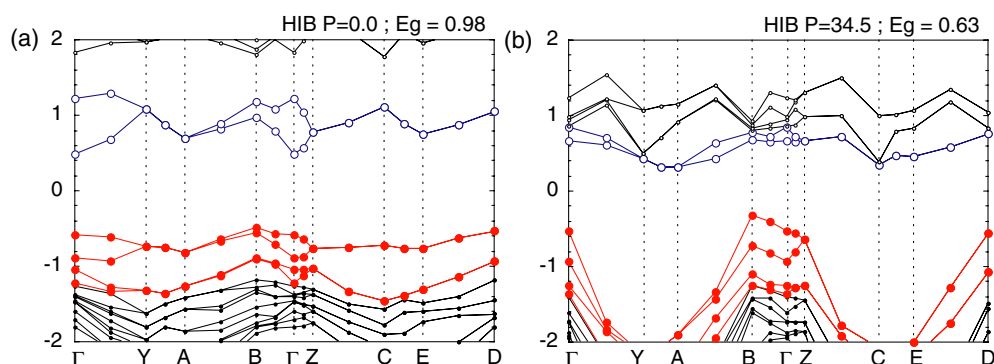


Figure 3. Band structures of HIB at (a) 0 GPa and (b) 34.5 GPa in eV. The Fermi level is set as the origin. Filled and open circles show the valence band top and conduction band bottom, respectively.

observed at 4 GPa upon unloading in experiments [13], we speculate that the latter is more probable. Establishment of this speculation is left for future work.

4. Conclusions

We have calculated structures and electronic states of the molecular phases in IA and HIB. The metallization pressure of IA is calculated to be about 25 GPa, which is consistent with the value 33 GPa from experimental results. The metallization in IA occurs by the band overlap mechanism in the molecular phase. When the band overlap occurs, the C=O π^* - and O 2p γ -bands are partially filled. This indicates that the molecular dissociation does not follow the metallization, contrary to the case for I₂ MC. In HIB, the band overlap in the molecular phase occurs at around 56 GPa in the calculations, which cannot explain the experimental metallization pressure even if SO interactions are included. This suggests that metallization in HIB is not caused by the band overlap in the molecular phase, and that a structural transformation will occur before the metallization. The transformed phase will be a metallic molecular phase or a phase with dissociated I atoms. In consequence, both mechanisms are completely different from that for I₂ MC, and suggest essential roles of C₆ rings and O atoms are indicated.

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