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Structures and electronic states of gallium–acetone complexes: ab-initio DFT study

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Abstract

The structures and electronic states of acetone–metal complexes (Ac–M, where M = Ga, Al, and B) have been calculated by means of ab-initio DFT and configuration interaction (CI) calculations in order to shed light on the mechanism of the electron conductivity and doping effects. It was found that the electronic states of Ac–Ga and Ac–Al at the ground state are composed of ion-pair state expressed approximately by $(Ac^{\delta-})(M^{\delta+})$: the electron is transferred from metal to the carbonyl group, suggesting that the carbonyl compound interacting with Ga and Al behaves as an n-type semiconductor. In the case of the Ac–B complex, on the other hand, the electron on Ac is significantly transferred to the boron atom, expecting that hole is transferred in the boron-doped carbonyl compound (p-type semiconductor). In these complexes, the first electronic transition is a charge-transfer band between metal and carbonyl group. The mechanism of the electronic conductivity was discussed on the basis of theoretical results.

Keywords: Gallium–acetone complexes; Ab-initio molecular orbital; DFT; Electronic states

1. Introduction

High quality organic semiconductor with good optoelectronic properties have been received much attention because these materials are of crucial importance in novel device applications [1–3]. The organic compound having the C=O carbonyl group is one of the molecules that are commonly used in molecular device [4–6]. The compounds react easily with metal atoms such as M = Ga, In, and Al, and then new energy state, which plays an important role in electron conductivity, is formed. However, the origin of the formation of new energy state is not clearly understood.

For the carbonyl compounds binding to indium atom, perylene-3,4,9,10-tetracarboxylic dianhydride (PTCDA), 1,8-naphthalic anhydride–indium (In_2–NA), and acetone–indium (Ac–In) are known [5–8]. These carbonyl compounds possess high performance as molecular devices. The interaction between the C=O carbonyl and In atom is considered to important because it affects strongly the electronic and optoelectronic properties. Also, it is reported that a new energy state in the PTCDA is generated by the interaction with the inorganic substrate or overlayer materials such as GaAs [7], In, Al, Ti, and Sn [8]. This result is significantly important because the new energy state is located very close to the Fermi level, and therefore, it is expected that the interaction with the metal atom plays an important role in organic device properties.

In a previous study [9], we investigated theoretically the structures and electronic states of the complexes composed of carbonyl compounds and indium atoms. The In atom binds strongly to the carbonyl group: the binding energies for Ac–In, In_2NA, and In_4PTCDA were calculated to be 26, 36, and 43 kcal mol^{-1}, respectively (B3LYP/LANL2DZ level). From the configuration interaction (CI) calculations, it was suggested that the new energy state is attributed to the ion-pair state expressed by $(C{=}O)^{\delta-}(In)^{\delta+}$, and the first electro-

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nic transition is assigned to charge-transfer band between the carbonyl and metal ion.

Previous ab-initio DFT calculations [10,11] on the In_4PTCDA and Ti–PTCDA systems showed that the In atom can bind to the C=O carbonyl and a half of electron on each In atom is transferred into the carbonyl group. The orbital energies of the system calculated were in good agreement with the experiments obtained by angle-resolved ultraviolet photoelectron spectroscopy. As one of the explanations for the new energy state, it was proposed that π-type 5pz orbital of the In atom is origin for the new state. Thus, a few theoretical calculations have been carried out for In–PTCDA systems. However, detailed feature for the interaction of indium atom with the C=O carbonyl, especially at the excited states, is scarcely known.

In the present study, using ab-initio DFT method, we calculated the structures and electronic states of acetone–M (M = Ga, Al, and B) complexes in order to elucidate electronic properties and the mechanism for the electron conductivity in the several Ac–M compounds. In particular, we focus our attention on the excited states and electronic transitions of the complexes, which are significantly important in the photoexcitation, photo-emission, and electronic conductivity.

In previous works, we investigated mechanism of electron and hole conductivities in molecular devices, such as poly-vinylbiphenyl (PVB) [12] and poly silanes [13–15], by means of ab-initio DFT and ab-initio molecular dynamics (MD) methods. The origin of the conductivity was elucidated on the basis of theoretical results. In the present study, we extend these techniques to the Ac–M complexes.

2. Computational methods

Ab-initio molecular orbital (MO) and DFT calculations were carried out using GAUSSIAN 98 program package [16]. As models of the carbonyl–metal compounds, acetone–M (M = Ga, Al and B) was chosen and a schematic structure is illustrated in Fig. 1. The geometries of Ac and Ac–M were fully optimized at the Hartree–Fock (HF), Møller–Plesset second order perturbation theory (MP2) and density functional theory (B3LYP) with the standard 6-311++G(d,p) basis set. Using the optimized geometries, the excitation energies and the electronic states were calculated by the singly excited configuration interaction (SE-CI) method. Expectation values of $\langle S^2 \rangle$ for all compounds were less than 0.765, so that the spin contamination from quartet state can be ignored throughout.

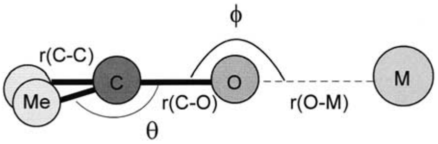

Fig. 1. Structure and geometrical parameters of Ac–M (M = Ga, Al, and B).

3. Results

3.1. Structures of acetone–M complexes

The selected optimized parameters of Ac and Ac–M at the ground state are given in Table 1. The structure of Ac–M is given in Fig. 1. All calculations gave the similar geometrical parameters. We will discuss the structure and electronic states using the results of the B3LYP/6-311++G(d,p) calculations.

In order to check the local minima for the structures of the complexes, harmonic vibrational frequencies were calculated for all complexes. All vibrational frequencies were positive, indicating that the complex lies in each local energy minimum. It was found that the C=O stretching mode of Ac (1785 cm^{-1} for free Ac) is red-shifted by the interaction with the M atoms: the vibrational frequency of the C=O stretching mode in M = Ga, Al and B are calculated to be 1320, 1335, and 1519 cm^{-1}, respectively.

For the Ac–Ga complex, Ga is bound at r(O–Ga) = 1.8712 Å from the oxygen atom of C=O carbonyl. The angle of Ga–O–C ($= \phi$) was calculated to be 176.8°,

Table 1
Selected optimized geometrical parameters of acetone (Ac), acetone radical anion (Ac^-) and acetone–M complex (Ac–M) (M = Ga, Al, and B) calculated at several levels of theory

	Value	HF	MP2	B3LYP
Ac–Ga	r (C–O)	1.3459	1.3649	1.3168
	r (C–C)	1.503	1.4965	1.4945
	r (O–Ga)	1.7942	1.8092	1.8712
	θ	117.5	117.5	119.5
	ϕ	168.9	171.2	176.8
Ac–Al	r (C–O)	1.348	1.3515	1.3382
	r (C–C)	1.5011	1.4953	1.492
	r (O–Al)	1.6903	1.7218	1.7357
	θ	117.7	118.0	119.0
	ϕ	176.6	175.3	180.0
Ac–B	r (C–O)	1.3882	–	1.3677
	r (C–C)	1.4979		1.4862
	r (O–B)	1.276		1.2845
	θ	115.4		117.3
	ϕ	145.3		180.0
Ac	r (C–O)	1.1881	1.2196	1.2114
	r (C–C)	1.5132	1.5164	1.5178
	θ	121.7	121.9	121.7
Ac^-	r (C–O)	1.2829	–	1.2164
	r (C–C)	1.5254		1.516
	θ	118.9		121.9

Basis sets used are 6-311++G(d,p) for all atoms. Bond lengths and angles are in Å and in °, respectively.

indicating that the Ga atom interacts with the oxygen atom from the C=O axis. The C=O bond length of Ac was slightly elongated by the interaction with the Ga atom (1.3168 vs. 1.2114 Å). The calculated structure of Ac–Al is significantly similar to that of Ac–Ga: the Al atom interacts collinearly with the C=O carbonyl, but the C=O bond length was much elongated (1.3382 Å). In the case of the B atom, as well as Ac–Ga and Ac–Al, the collinear structure was obtained. The C=O bond length was calculated to be 1.3677 Å, which is 0.156 Å longer than that of Ac. This bond length is close to a single bond rather than the C=O double bond. The binding energies of M to acetone calculated for Ac–Ga, Ac–Al and Ac–B are 17.9, 33.8 and 60.0 kcal mol^{-1}, respectively. These energies are comparable to that of chemical bond.

3.2. Electronic states at the ground state

The atomic charges on the complexes were calculated for the ground state, and the results are given in Table 2 together with that of Ac–In for comparison. The charge on the Ga atom was calculated to be +0.31 at the B3LYP/6-311++G(d,p) level (MP2 value was +0.53), indicating that a part of the electron is transferred from the Ga atom to the carbonyl group in Ac–Ga. This feature is very similar to that of Ac–In complex (charge on In is +0.41). For the Ac–Al complex, the charge on Al is slightly less than that of Ac–Ga (+0.11 vs. +0.31). Thus, it can be summarized that charges on atoms in Ac–M are expressed by In(+0.41) > Ga(+0.31) > Al(+0.11).

In the case of Ac–B, on the other hand, sign of the charge on the B atom was changed to negative (−0.46), indicating that B-doping effect is much different from those of In, Ga, and Al atoms. The back donating-like charge transfer occurs in the case of the B-doping.

The orbital energies calculated for Ac and Ac–M are illustrated in Fig. 2. Only the electron in highest occupied molecular orbital (HOMO) and singly occupied molecular orbital (SOMO) are indicated by dot in Fig. 2. Arrow indicates the energy difference between HOMO and lowest unoccupied molecular orbital (LUMO). Ac has a HOMO–LUMO band gap of 6.27 eV. This wide band gap is changed to 2.27 eV after the interaction with Ga atom. The unpaired electron is originated from the electron on the Ga atom. For Ac–Al, the band gap was calculated to be 2.74 eV, which is slightly larger than that of Ac–Ga. In the case of Ac–B, the calculated band gap (4.98 eV) was close to that of free Ac.

Table 2
Mulliken atomic charges of Ac–M complexes (M = Ga, Al, B, and In) at the ground state, calculated at the MP2/6-311++G(d,p) and B3LYP/6-311++G(d,p) levels

	MP2			B3LYP		
Ac–M	M	C	O	M	C	O
Ac–Ga	+0.53	−0.48	+0.18	+0.31	+0.14	−0.31
Ac–Al	+0.22	+0.22	−0.19	+0.11	+0.16	−0.14
Ac–B	–			−0.46	−0.02	+0.48
Ac–In	+0.57	+0.37	−0.78	+0.41	+0.37	−0.65

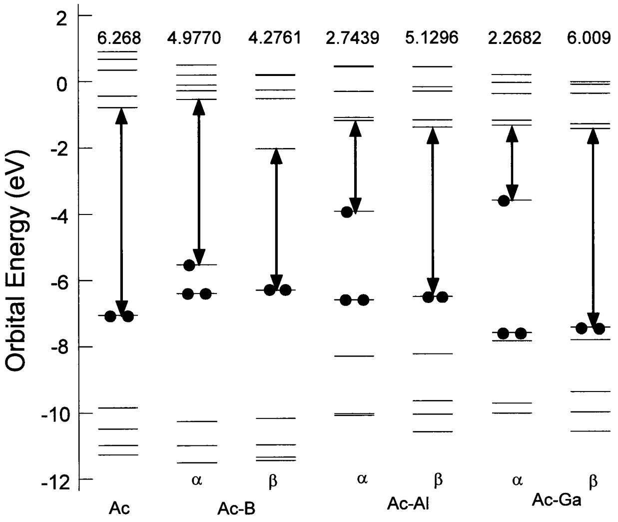

Fig. 2. Orbital energies of Ac and Ac–M calculated at the B3LYP/6-311++G(d,p) level. The circle indicates occupied electron in HOMO and SOMO.

3.3. Electronic states at the excited states

Excitation energies and charges on atoms of Ac–M complexes are summarized in Table 3. The first excita-

Table 3
Excitation energies (E_{ex} in eV) and charges on atoms of Ac–M complexes (M = Ga, Al, and B) calculated at the MP2+CIS/6-311++G(d,p)//B3LYP/6-311++G(d,p) level of theory

	Ground		Excited state		
	Atom	State	1st	2nd	3rd
Ac–Ga					
E_{ex}/eV		0.0	2.89	3.52	4.01
Charge	Ga	+0.53	−0.17	+0.11	+0.24
	C	+0.18	+0.31	+0.32	+0.33
	O	−0.48	−0.20	−0.36	−0.43
Ac–Al					
E_{ex}/eV		0.0	3.32	4.59	4.63
Charge	Al	+0.24	−0.50	+0.15	+0.27
	C	+0.21	+0.23	+0.49	+0.26
	O	−0.20	+0.08	−0.19	−0.27
Ac–B					
E_{ex}/eV		0.0	5.33	5.43	5.44
Charge	B	−0.43	−0.35	−0.51	−0.43
	C	+0.04	+0.12	−1.73	+0.20
	O	+0.52	+0.41	+0.48	+0.72

tion energy in Ac–Ga was calculated to be 2.89 eV, which is significantly lower than that of Ac (5.2 eV). This implies that doping of Ga affects strongly the energy gap of the carbonyl compounds. Also, it is predicted that the absorption band is largely red-shifted after the doping. The similar tendency was obtained for Ac–Al and Ac–B.

The charges on the Ga atom in Ac–Ga for the ground and first excited state were calculated to be +0.53 and −0.17, respectively, indicating that the electronic excitation is a charge transfer transition between Ga and C=O carbonyl. The first excited state is composed of van der Waals character. From these results, it can be concluded that the first electronic transition in Ac–Ga is attributed to the charge-transfer band between Ga^+ and Ac^-, which is expressed by

$$(\mathrm{Ga})^{\delta+}(\mathrm{Ac})^{\delta-}\ \text{(ion-pair state)} + h\nu \\ \rightarrow (\mathrm{Ga})(\mathrm{Ac})\ \text{(vdW state)}$$

This feature is very similar to that of In_4PTCDA. The energy level corresponding to the ion-pair state would be appeared as a new energy level.

4. Discussion

4.1. Summary of the present study

In the present study, ab-initio DFT and CI calculations have been carried out for the Ac–M complexes (M = Ga, Al and B). The results can be summarized as follows: (1) these atoms have an ability to form a strong bond with C=O carbonyl; (2) the ground state of the complexes for M = Ga is an ion-pair state expressed by $(\mathrm{Ga}^{\delta+})(^{\delta-}\mathrm{O{=}C}<)$, and the new energy state appearing at UV and visible spectra is attributed to the ion-pair state; (3) the Al atom binds to the carbonyl group and makes a chemical bond; (4) in the case of the B atom, electron-back donation from C=O to B occurs and ion-pair $(\mathrm{B}^{\delta-})(^{\delta+}\mathrm{O{=}C}<)$ is formed (this bond is very strong). For the excited state, the ion-pair state is changed to vdW interaction.

Potential energy curves for the formation of the ion-pair is schematically illustrated in Fig. 3. The Ac and M have a neutral state (Ac+M) at the dissociation limit, as shown in lower curve. At closer points, a van der Waals complex (Ac–M) would be formed. This state is crossed with the excited state (ionic state) expressed by $Ac^- + M^+$ at further closer point. After that, the ion-pair is formed. The potential energy curves are crossed, but these states become avoided crossing interaction.

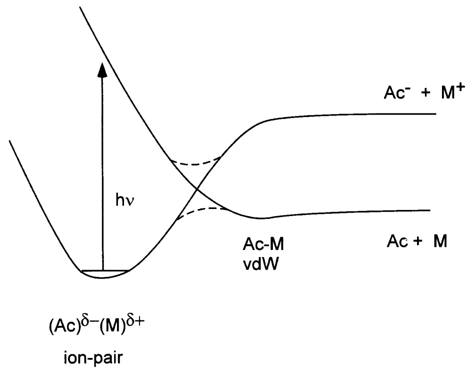

Fig. 3. Potential energy curves for the formation of ion-pair of acetone (Ac) and M atoms.

4.2. Doping effects on the electronic states

The model for the Ga- and B-doping effects on amorphous solid and crystalline of the carbonyl compound is proposed on the basis of the present calculations. A schematic illustration for the model is given in Fig. 4. Upper a lower figures indicate the changes of the molecular orbitals of the carbonyl compound by the interaction with Ga and B atoms, respectively. It should be noted that the band structure is formed by accumulation of the carbonyl compounds.

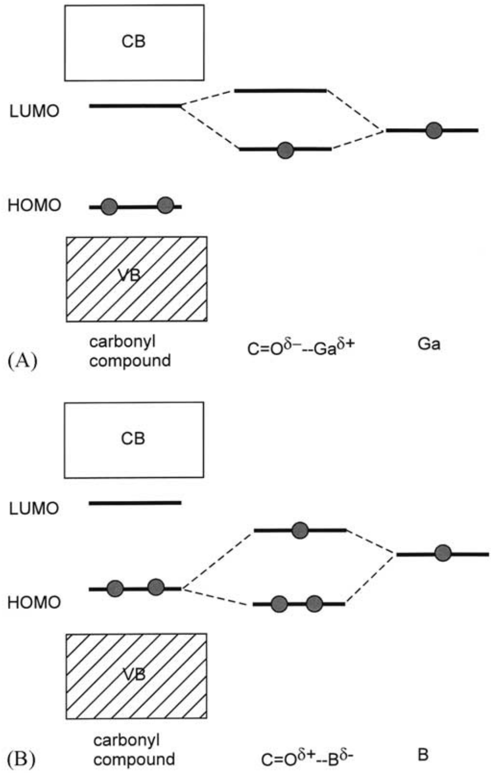

Fig. 4. Model for the band structure for amorphous solid of the metal–carbonyl compounds. (A) M = Ga; and (B) M = B. The orbitals except for HOMO and LUMO are illustrated by band structure as boxes. The solid circle indicate an electron in HOMO or atomic orbital of metal.

In the case of the interaction of solid of carbonyl compounds with Ga atom, the orbital of Ga (4p atomic orbital) interacts strongly with the lowest unoccupied molecular orbital (LUMO) of Ac because the energy level of Ga(4p) is close to LUMO. Once the interaction occurs, the energies of two orbitals (i.e. LUMO and 4p of Ga) are shifted each other, and then an unpaired electron on the Ga atom is transferred to the carbonyl group. This electron transfer results in the formation of the ion-pair state $(Ga^{\delta+})(^{\delta-}O{=}C<)$. The electron would move easily on the carbonyl compound. Thus, the doping of Ga makes the carbonyl compound to n-type semiconductor.

On the other hand, it is predicted that the interaction with the boron atom causes the electron-back donation from C=O to B atom because the energy level of the atomic orbital of the B atom is close to highest occupied molecular orbital (HOMO). As a result of the interaction, the ion-pair state $(B^{\delta-})(^{\delta+}O{=}C<)$ is formed. A hole thus formed would move on the carbonyl compound and its molecular crystal. However, this interaction in Ac–B is stronger than that of Ac–Ga. From these results, it can be concluded that the interaction with metal atoms (Ga and In) leads to the n-type semiconductor, while that with B atom makes p-type semiconductor in carbonyl compound. Boron is usually used as dopant to silicon [17], amorphous carbon [18], and polymers [19]. The present calculations predict that the carbonyl compound is activated by doping of boron.

4.3. Additional comments

We have introduced several approximations to calculate the structures and electronic states of the complexes. Firstly, we used singly excited CI calculations to obtain the electronic states at the excited states. This method is convenient to obtain the excited states. However, more accurate wave function would be required to obtain more accurate excitation energies and charge distribution. Second, acetone molecule was employed as model of carbonyl compounds. To obtain more detailed feature for the ion-pair state, one may need variety of carbonyl compounds. Such calculations are now in progress. Despite the several assumptions introduced here, the results enable us to obtain valuable information on the mechanism of the electron conductivity of M-carbonyl compounds.

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