Optical Investigation of the Intervalence Charge-transfer Interactions in the Three-dimensional Gold Mixed-valence Compounds $Cs_2Au_2X_6$ (X = Cl, Br or I)

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The intervalence charge-transfer (i.v.c.t.) transitions between the gold-(I) and -(III) ions in $Cs_2Au_2X_6$ (X = Cl, Br or I) have been investigated. From the polarized reflectance spectra of a single crystal of $Cs_2Au_2I_6$ and group-theory analysis, the i.v.c.t. bands have been assigned. The strongest reflectance peak was that of lowest energy, which was observed with the electric vector perpendicular to the *c* axis, and was assigned to the $Au^I(5d_{x^2-y^2}) \longrightarrow Au^{III}(5d_{x^2-y^2})$ transition in the *ab* plane. This indicates that a two-dimensional correlation between the gold ions is present in the charge-transfer interaction despite the three-dimensional perovskite structure of the compounds.

Since the discovery of high-T_C superconductors such as $La_{2-x}Ba_xCuO_4$[1] and $Ba_{1-x}K_xBiO_3$,[2] mixed-valence systems with perovskite-type crystal structures have become of great interest. In these systems, interesting physical properties such as superconductivity remarkably depend on the valence state and the crystal structure. From these viewpoints, we have systematically investigated the relationship between the physical properties and the crystal structures of $Cs_2Au_2X_6$ (X = Cl, Br or I).[3-10] The crystal structures and mixed-valence system of the above are quite similar to those of $BaBiO_3$ which is the parent compound of the superconductors Ba_{1-x}(K or Rb)$_x$BiO$_3$ and $BaPb_{1-x}Bi_xO_3$.

The salts $Cs_2Au_2X_6$ have distorted perovskite structures belonging to the space group *I*4/*mmm*, and are shown in Fig. 1.[11-13] In the crystal, all the halogens are distorted from the midpoint between neighbouring Au ions in the chains, and the linear $[Au^IX_2]^-$ and square-planar $[Au^{III}X_4]^-$ complexes occur alternately. Consequently, its structure consists of three-dimensional metal–halogen frameworks formed by elongated octahedra with Au^{III} and compressed octahedra with Au^I sharing their corners.

In these compounds, as pointed out by Robin and Day,[14] there are two relative orientations of $[Au^IX_2]^-$ and $[Au^{III}X_4]^-$ complexes, as shown in Fig. 2. In one, configuration *a*, the $\cdots X{-}Au^I{-}X \cdots Au^{III} \cdots X{-}Au^I{-}X \cdots$ network lies along the *c* axis, while in the other, configuration *b*, this network lies in the *ab* plane. However, as to which of these configurations is dominant in the charge–transfer interaction between the gold-(I) and -(III) ions has been a matter of debate. According to Robin and Day,[14] the donor and the acceptor orbitals in $Cs_2Au_2Cl_6$ are the $5d_{z^2}$ orbital of the $[Au^ICl_2]^-$ ion and the $5d_{x^2-y^2}$ orbital of the $[Au^{III}Cl_4]^-$ ion, respectively. For configuration *a*, the donor $5d_{z^2}$ and the acceptor $5d_{x^2-y^2}$ orbitals should be diagonal while for configuration *b* they must have a non-zero overlap. Consequently it was assumed that configuration *b* is dominant in the charge-transfer interaction and that the intervalence charge-transfer band (i.v.c.t. band) corresponding to the $Au^I(5d_{z^2}) \longrightarrow Au^{III}(5d_{x^2-y^2})$ transition would be polarized in the *ab* plane.

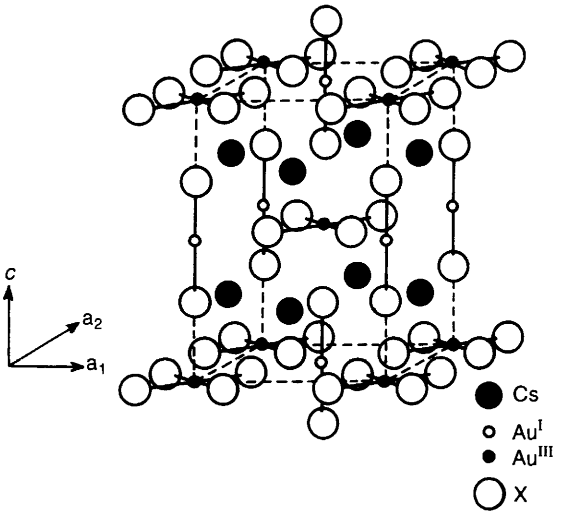
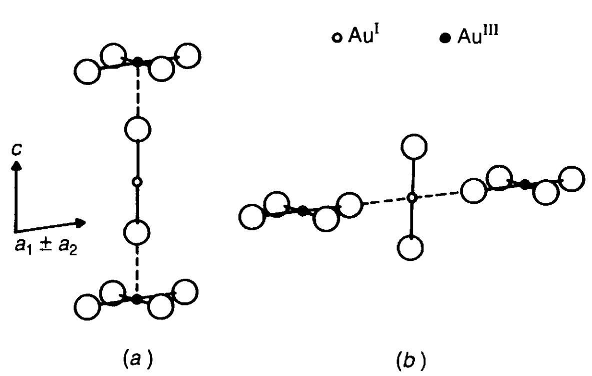


Fig. 1 Crystal structure of $Cs_2Au_2X_6$ (X = Cl, Br or I)



(*a*) (*b*)

Fig. 2 Anisotropic Au–X chains in $Cs_2Au_2X_6$

The i.v.c.t. bands in the halogen-bridged mixed-valence compounds were systematically investigated for the first time by Tsuchida and Yamada[15] who studied the dichroism of $Cs_2AgAuCl_6$ crystals under a microscope, where they appeared almost black with the electronic vector *E* of the incident light parallel to the *c* axis and yellow when perpendicular.[16] In 1962, Robin[17] preliminarily measured the dichroism of $Cs_2AgAuCl_6$ and $Cs_2Au_2Cl_6$ and reported one i.v.c.t. band with $E \parallel c$ for these compounds.

From these results, it was concluded that configuration *a* in

Fig. 2 is dominant in the charge-transfer interaction between the gold-(I) and -(III) ions.[18] However, these results were in conflict with the original assumptions of Robin and Day.[14] In addition our recent analyses of X-ray photon spectroscopy (XPS) and ^{197}Au Mössbauer measurements suggest that configuration *b* is dominant in the charge-transfer interaction.[6,7]

We have several reservations in connection with the previous optical experimental results and the assumptions of Robin and Day.[14] (*a*) The identity of the donor as the $5d_{z^2}$ orbital of the $[Au^ICl_2]^-$ ion may be incorrect and there exists the possibility that the $5d_{x^2-y^2}$ orbital of the $[Au^ICl_2]^-$ ion is the donor orbital. If so, the donor $5d_{x^2-y^2}$ of the $[Au^ICl_2]^-$ ion and the acceptor $5d_{x^2-y^2}$ of the $[Au^{III}Cl_4]^-$ ion should have a much larger overlap in configuration *b*. (*b*) The selection rule of the i.v.c.t. transition should be ideally derived from group-theory rather than from intuition. (*c*) Ideally the crystal axis of $Cs_2Au_2Cl_6$ should be determined by X-ray analysis, whether this has been done is presently uncertain. For $Cs_2Au_2X_6$, the direction of crystal growth is in disagreement with that of the presumed crystal axis, therefore a measurement to confirm the direction of the crystal axis by X-ray analysis is imperative.

In order to elucidate these entangled problems, we have investigated the absorption spectra of $Cs_2Au_2X_6$ (X = Cl, Br or I) and the polarized reflectance spectra of a single crystal of $Cs_2Au_2I_6$ quantitatively for the first time. Moreover, we have established the selection rule of the i.v.c.t. transition in $Cs_2Au_2X_6$ by using group theory for the first time. The investigation of the polarized i.v.c.t. band and group-theory analysis is one of the most powerful methods to elucidate the dimensionality of the charge-transfer interaction.

In this paper, we report the i.v.c.t. bands in $Cs_2Au_2X_6$ (X = Cl, Br or I) and assign these bands by using group theory. Moreover, we discuss the dimensionality of the charge-transfer interaction between the gold-(I) and -(III) ions in $Cs_2Au_2X_6$.

Experimental

The compounds $Cs_2Au_2X_6$ (X = Cl, Br or I) were prepared as described previously.[5,6] Single crystals of $Cs_2Au_2I_6$ were recrystallized by a diffusion method using a H-type tube and 55% hydroiodic acid as the solvent. The bases of the two arms of the H-tube were kept at 45 and 20 °C, respectively for one month. Single crystals of dimensions up to 3 × 2 × 1 mm were obtained at the low temperature arm.

For the solid-state absorption spectra, powdered samples of $Cs_2Au_2X_6$ (X = Cl, Br or I) were dispersed in CsCl, KBr and CsI pellets, respectively. Their absorption spectra were measured at 4.2 K with a JASCO CT-100 spectrometer using a tungsten lamp as the light source. A lock-in amplifier system working with HTV R376 and R316 photomultipliers and a PbS photoconductive cell was used for detection. The data were collected with a NEC 9801VX0 computer linked to the lock-in amplifier. Solution electronic spectra were measured at room temperature with a Hitachi model 356 double beam spectrometer.

Polarized reflectance spectra of the single crystal of $Cs_2Au_2I_6$ were measured at room temperature for the (110) and (001) faces, with a JASCO CT-100 spectrometer, a tungsten lamp as the light source and a Glan–Thompson prism for polarizing light. The (110) and (001) faces of $Cs_2Au_2I_6$ were confirmed by using a four-circle X-ray diffractometer. The sample was irradiated with polarized monochromatic light. The electric vector was aligned parallel to the *ab* plane and the *c* axis. Only as grown surfaces were measured and the sample dimension was 3 × 2 × 1 mm. Absolute reflectivities were calibrated with an aluminium mirror. The detector, amplifier and computer system for the reflectance spectra was the same as that for the solid-state absorption spectra.

Results and Discussion

Fig. 3 shows the solid-state absorption spectra of $Cs_2Au_2X_6$ (X = Cl, Br or I) dispersed in alkali-metal halide pellets at 4.2 K, together with solution spectra in ethanol at room temperature. In each of the mixed-valence compounds, two strong absorption bands appear in the visible/near-infrared region, which are not observed for the corresponding component complex ions. Therefore, these two bands can be assigned to i.v.c.t. transitions from Au^I to Au^{III}. The i.v.c.t. band is a common feature of the class-II mixed-valence compounds classified by Robin and Day.[14]

As shown in Fig. 3, the energy of both the i.v.c.t. bands is in the order $Cs_2Au_2Cl_6 > Cs_2Au_2Br_6 > Cs_2Au_2I_6$, indicating that the energy difference between the electronic states of Au^I and Au^{III} becomes smaller from X = Cl to I. This behaviour is consistent with the results of XPS[6] and ^{197}Au Mössbauer[7] spectroscopy studies. An absorption band at higher energy than the two i.v.c.t. bands can be assigned to a ligand-to-metal charge-transfer transition (l.m.c.t.) from the halogen p_π orbital to the $Au^{III}(5d_{x^2-y^2})$ orbital. The peak positions of i.v.c.t.(1), i.v.c.t.(2) and the l.m.c.t. in $Cs_2Au_2X_6$ (X = Cl, Br or I) are listed in Table 1.

In $Cs_2Au_2X_6$, the energy order of the 5d orbital of Au^I in the compressed octahedron Au^IX_6 is $5d_{z^2} > 5d_{x^2-y^2} > 5d_{yz,zx} > 5d_{xy}$ and all five 5d orbitals are doubly occupied in the ground state. On the other hand, for Au^{III} in the elongated octahedron $Au^{III}X$, the energy order is $5d_{x^2-y^2} > 5d_{z^2} > 5d_{xy} > 5d_{yz,zx}$ and only the $5d_{x^2-y^2}$ orbital is unoccupied. Therefore, the

Table 1 Energy positions (cm^{-1}) of the intervalence charge-transfer band in the absorption spectra of $Cs_2Au_2X_6$ (X = Cl, Br or I) in alkali-metal halide pellets at 4.2 K

Compounds	i.v.c.t.(1)	i.v.c.t.(2)	l.m.c.t.
$Cs_2Au_2Cl_6$	16 500	21 500	28 000
$Cs_2Au_2Br_6$	13 000	19 500	23 500
$Cs_2Au_2I_6$	10 500	16 300	19 500

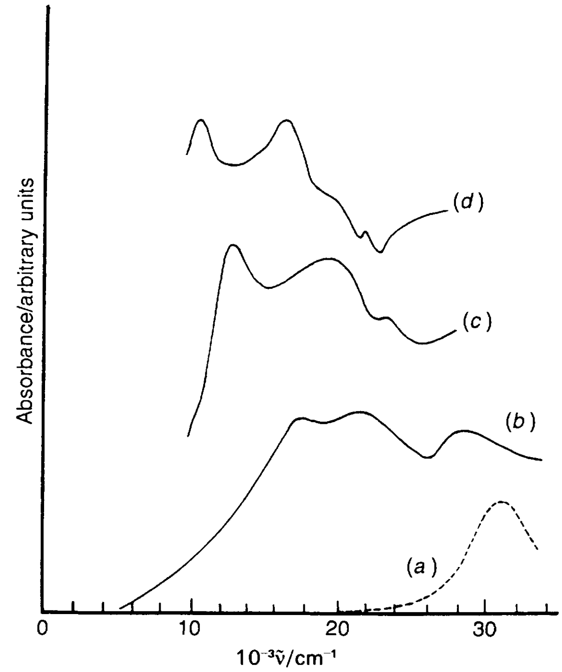


Fig. 3 Absorption spectra of $Cs_2Au_2X_6$ (X = Cl, Br or I). (*a*) Absorption spectrum of $Cs_2Au_2Cl_6$ in ethanol solution at room temperature, (*b*) solid-state spectrum of $Cs_2Au_2Cl_6$ in a CsCl pellet at 4.2 K, (*c*) solid-state spectrum of $Cs_2Au_2Br_6$ in a KBr pellet at 4.2 K and (*d*) solid-state spectrum of $Cs_2Au_2I_6$ in a CsI pellet at 4.2 K

lowest energy transition in the i.v.c.t. bands of $Cs_2Au_2X_6$ is expected to be the transition from the $Au^I(5d_{z^2})$ orbital to the $Au^{III}(5d_{x^2-y^2})$ orbital. As pointed out by Robin and Day,[14] the $5d_{z^2}$ orbital of Au^I and the $5d_{x^2-y^2}$ orbital of Au^{III} are orthogonal to each other in the *c* direction, while those orbitals in the *ab* plane have non-zero overlap. However, the overlap is considered to be very small. Therefore, it is considered that the charge transfer interaction between the gold-(I) and -(III) ions in $Cs_2Au_2X_6$ is mainly attributed to the larger overlap between the donor $5d_{x^2-y^2}$ orbital of Au^I and the acceptor $5d_{x^2-y^2}$ orbital of Au^{III} through the p orbitals of the bridging halogen X, and the i.v.c.t. band of lower energy [i.v.c.t.(1)] corresponds to the $Au^I(5d_{x^2-y^2}) \longrightarrow Au^{III}(5d_{x^2-y^2})$ transition. However, in order to establish firmly the assignment of the i.v.c.t. transition, it is indispensable to investigate the polarized reflection spectra of a single crystal of $Cs_2Au_2X_6$.

The single-crystal reflectance spectra of $Cs_2Au_2I_6$ are shown in Fig. 4. The reflectance for $E \perp c$ is remarkably stronger than that for $E \parallel c$ in the lower energy region. In particular, the strongest reflectance peak at 10 500 cm^{-1} is observed only for $E \perp c$, which implies that this reflection peak corresponds to the i.v.c.t. from the $Au^I(5d_{x^2-y^2})$ orbital to the $Au^{III}(5d_{x^2-y^2})$ orbital within the Au–X networks of the *ab* plane.

Therefore, the absorption band i.v.c.t.(1) in the dispersed pellets of $Cs_2Au_2X_6$ can be assigned to the $Au^I(5d_{x^2-y^2}) \longrightarrow Au^{III}(5d_{x^2-y^2})$ transition. From the qualitative energy diagram of the gold 5d orbitals (see Fig. 7), it is considered that the reflectance peak at 14 500 cm^{-1} for $E \parallel c$ corresponds to the i.v.c.t. from the $Au^I(5d_{yz,zx})$ orbitals to the $Au^{III}(5d_{x^2-y^2})$ orbital. The reflectance of this band is weak, which is consistent with the small overlap between those orbitals. It is also considered that the reflectance peak at 16 000 cm^{-1} for $E \perp c$ corresponds to the i.v.c.t. from the $Au^I(5d_{xy})$ orbital to the $Au^{III}(5d_{x^2-y^2})$ orbital. Therefore, the rather broader absorption band [i.v.c.t.(2)] in the dispersed pellets of $Cs_2Au_2X_6$ presumably consists of two overlapping i.v.c.t. bands. One is the rather weak absorption [i.v.c.t.(2a): $Au^I(5d_{yz,zx}) \longrightarrow Au^{III}(5d_{x^2-y^2})$] at lower energy, and the other is the stronger absorption [i.v.c.t.(2b): $Au^I(5d_{xy}) \longrightarrow Au^{III}(5d_{x^2-y^2})$] at higher energy.

We next investigated the selection rule of the i.v.c.t. transitions in $Cs_2Au_2X_6$ by group theory.

In the group theoretical treatment, we consider an isolated cluster consisting of seven complexes, namely a linear $[Au^IX_2]^-$ complex surrounded by six square-planar $[Au^{III}X_4]^-$ complexes (cluster **a**) or a square-planar $[Au^{III}X_4]^-$ complex surrounded by six linear $[Au^IX_2]^-$ complexes (cluster **b**), as shown in Fig. 5. A similar cluster model has been used by Peters *et al.*[19] in order to explain the selection rule of the i.v.c.t. bands in $K_2PtBr_4{\cdot}2H_2O$ containing octahedral $Pt^{IV}Br_6$ defects. They have succeeded in explaining the mixed-valence electron-transfer transition involving a $Pt^{IV}Br_6$ impurity defect by analysing the selection rule of the i.v.c.t. in a cluster $[Pt^{IV}Br_6]^{2-}[Pt^{II}Br_4]^{2-}{}_2$.

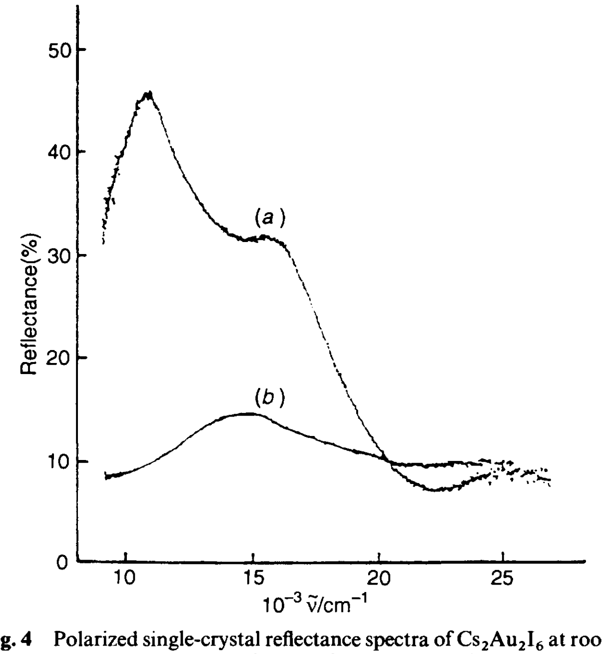


Fig. 4 Polarized single-crystal reflectance spectra of $Cs_2Au_2I_6$ at room temperature or $E \perp c$ (*a*) and $E \parallel c$ (*b*), *E* denotes the vector of the incident light

The overall symmetry of our present cluster is D_{4h}. It is sufficient to consider only one type of cluster, since we have confirmed that the selection rule of i.v.c.t. in the cluster **a** is equal to that of i.v.c.t. in cluster **b**.

We decided to analyse cluster **a** (Fig. 5). The symmetries of the $5d_{z^2}$, $5d_{x^2-y^2}$, $5d_{xy}$, and $5d_{yz,zx}$ orbitals of the linear $[Au^IX_2]^-$ complex in cluster **a** are represented as A_{1g}, B_{1g}, B_{2g} and E_g, respectively. The eigenfunctions of the lowest unoccupied orbitals, $5d_{x^2-y^2}$, of the six $[Au^{III}X_4]^-$ complexes in cluster **a** are the linear combinations of these six $5d_{x^2-y^2}$ orbitals shown in Fig. 6. Linear combinations of the $5d_{x^2-y^2}$ orbitals of the six $[Au^{III}X_4]^-$ complexes in cluster **a** have symmetries of A_{1g}, 2 × B_{1g}, B_{2u} and E_u.

When the representation of the $Au^{III}(5d_{x^2-y^2})$ eigenfunction in cluster **a** is in agreement with the representation of the direct product between the 5d orbital of Au^I and the electric vector of

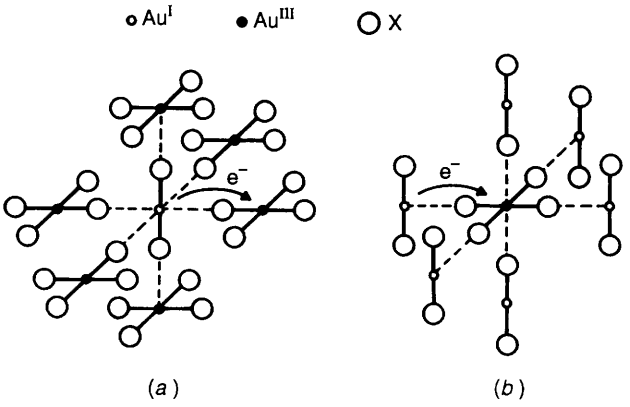


Fig. 5 Configurations of (*a*) the $[Au^IX_2]^-[Au^{III}X_4]^-{}_6$ cluster and (*b*) the $[Au^{III}X_4]^-[Au^IX_2]^-{}_6$ cluster

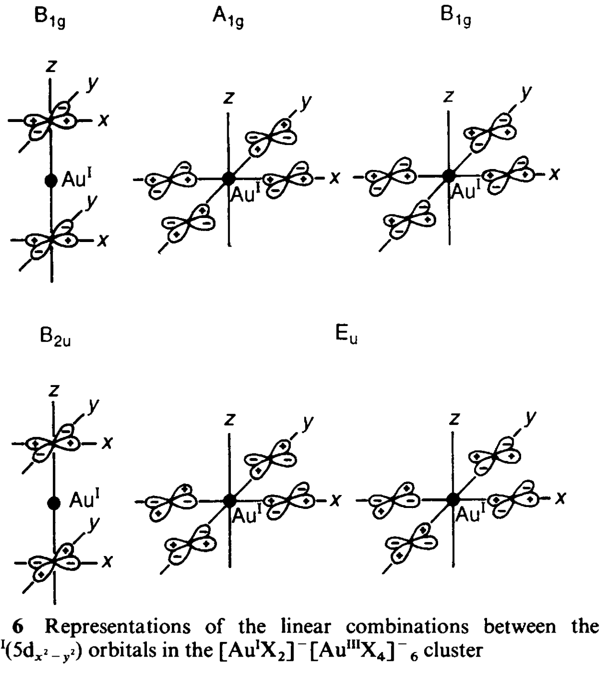


Fig. 6 Representations of the linear combinations between the $Au^{III}(5d_{x^2-y^2})$ orbitals in the $[Au^IX_2]^-[Au^{III}X_4]^-{}_6$ cluster

Table 2 Direct product between the representations of the $Au^I(5d)$ orbitals and the electric vectors of the incident light. Here, the symmetry of the gold(I) site is D_{4h}

Orbital	$\vec{E} \parallel c$: A_{2u}	$\vec{E} \perp c$: E_u
$Au^I(d_{z^2})$ A_{1g}	A_{2u}	E_u
$Au^I(d_{x^2-y^2})$: B_{1g}	B_{2u}	E_u
$Au^I(d_{xy})$: B_{2g}	B_{1u}	E_u
$Au^I(d_{yz,zx})$: E_g	E_u	$A_{1u} + A_{2u}$ $+ B_{1u} + B_{2u}$

Table 3 Selection rule of the intervalence charge-transfer transitions in $Cs_2Au_2X_6$ (X = Cl, Br or I)

	$\vec{E} \parallel c$	$\vec{E} \perp c$
i.v.c.t. along the *c* axis	$Au^I(d_{x^2-y^2}) \longrightarrow Au^{III}(d_{x^2-y^2})$	$Au^I(d_{yz,zx}) \longrightarrow Au^{III}(d_{x^2-y^2})$
i.v.c.t. in the *ab* plane	$Au^I(d_{yz,zx}) \longrightarrow Au^{III}(d_{x^2-y^2})$	$Au^I(d_{z^2}) \longrightarrow Au^{III}(d_{x^2-y^2})$ $Au^I(d_{x^2-y^2}) \longrightarrow Au^{III}(d_{x^2-y^2})$ $Au^I(d_{xy}) \longrightarrow Au^{III}(d_{x^2-y^2})$

the incident light, the i.v.c.t. transition from Au^I to Au^{III} is allowed. The direct products between the representations of the 5d orbital of Au^I and the electric vector of the incident light are listed in Table 2. Comparing Fig. 6 and Table 2, the selection rule of the i.v.c.t. from Au^I to Au^{III} in cluster **a** is determined, and allowed transitions are given in Table 3 and Fig. 7. The schematic energy levels of the compressed Au^IX_6 and the elongated $Au^{III}X_6$ octahedra in $Cs_2Au_2X_6$ are based on extended-Hückel molecular orbital calculations.

Considering the energy diagram of the 5d orbitals of Au^I and Au^{III} and the overlapping integral between these orbitals, the i.v.c.t. bands are assigned to the following transitions: i.v.c.t.(1), $Au^I(5d_{x^2-y^2}) \longrightarrow Au^{III}(5d_{x^2-y^2})$; i.v.c.t.(2a), $Au^I(5d_{yz,zx}) \longrightarrow Au^{III}(5d_{x^2-y^2})$ and i.v.c.t(2b) $Au^I(5d_{xy}) \longrightarrow Au^{III}(5d_{x^2-y^2})$.

As shown in Fig. 7, the lowest i.v.c.t. band corresponds to the $Au^I(5d_{z^2}) \longrightarrow Au^{III}(5d_{x^2-y^2})$ transition, but the overlap between these orbitals is small. A weak band corresponding to this i.v.c.t. transition would be observed on the lower energy side of the i.v.c.t.(1) band for the $E \perp c$ polarization. Recently, Kitagawa *et al.*[20] have observed a weak shoulder at *ca.* 6500 cm^{-1} in the single-crystal reflectance spectra in $Cs_2Au_2I_6$ for $E \perp c$ polarization. This weak shoulder seems to correspond to the $Au^I(5d_{z^2}) \longrightarrow Au^{III}(5d_{x^2-y^2})$ transition.

From the fact that the i.v.c.t.(1) band corresponding to the $Au^I(5d_{x^2-y^2}) \longrightarrow Au^{III}(5d_{x^2-y^2})$ transition is remarkably increased for $E \perp c$ polarization, one concludes that the charge-transfer interaction between the $5d_{x^2-y^2}$ orbitals of the gold-(I) and -(III) ions in the *ab* plane is dominant. This result is consistent with the results of XPS[6] and ^{197}Au Mössbauer spectroscopy.[7]

In connection with our results for the i.v.c.t. transition in $Cs_2Au_2X_6$, previous optical studies for $Cs_2Au_2Cl_6$ should be mentioned. According to Robin,[17] the absorption spectra of $Cs_2Au_2Cl_6$ showed the i.v.c.t. band as a rather weak but distinct feature at 15 500 cm^{-1} as well as a stronger absorption band at 23 500 cm^{-1}, with opposite polarization. He assigned the former band to an i.v.c.t. transition from the $Au^I(5d_{z^2})$ orbital to the $Au^{III}(5d_{x^2-y^2})$ orbital, and the latter to a ligand-to-metal charge-transfer transition which was also observed at 23 500 cm^{-1} for the $[Au^{III}Cl_4]^-$ ion. Therefore, he concluded that the high energy band at 23 500 cm^{-1} must be polarized in the $[Au^{III}Cl_4]^-$ plane (*i.e.* *ab* plane), and that the low energy band at 15 500 cm^{-1} should be the i.v.c.t. band polarized along the *c* axis. By analogy with the polarized reflectance spectra of the single crystal of $Cs_2Au_2I_6$, the low energy band at 15 500 cm^{-1} in $Cs_2Au_2Cl_6$ should be observed with the electric vector perpendicular to the *c* axis.

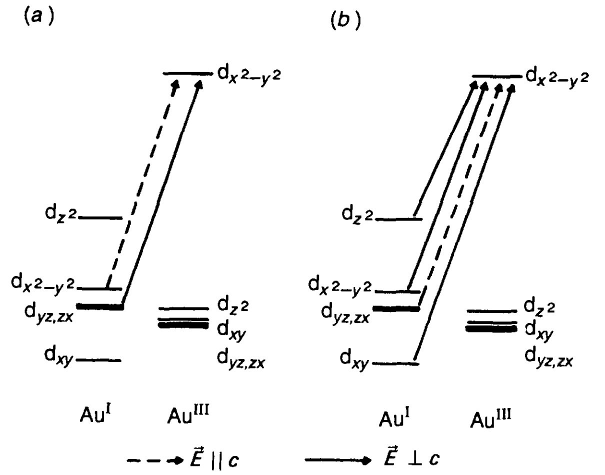


Fig. 7 Selection rules of the i.v.c.t. transitions in $Cs_2Au_2X_6$. (*a*) Along the *c* axis and (*b*) in the *ab* plane; $\vec{E}$ denotes the electric vector of the incident light. The schematic energy levels of the compressed Au^IX_6 and the elongated $Au^{III}X_6$ octahedra in $Cs_2Au_2X_6$ are derived from extended-Hückel molecular orbital calculations

Recently, Tanino *et al.*[21] measured the reflectance spectra of polycrystalline $Cs_2Au_2Cl_6$ under high pressure at room temperature. They observed strong i.v.c.t. bands in the visible region. That at *ca.* 2 eV (*ca.* 16 100 cm^{-1}), which we denote as i.v.c.t.(1), was assigned as polarized parallel to the *c* axis. According to them, this low energy band decreased in energy with increase in pressure. From this, they suggested that the electronic properties of $Cs_2Au_2Cl_6$ under high pressure were strongly anisotropic with metallic character only along the *c* axis. However, considering the *ab* polarization of the i.v.c.t.(1) band in the single crystal of $Cs_2Au_2I_6$, we propose that the charge-transfer interaction between the gold-(I) and -(III) ions in $Cs_2Au_2Cl_6$ is two-dimensional.

Conclusion

We have succeeded in establishing the polarization of the i.v.c.t. bands and the dimensionality of the charge-transfer interactions in $Cs_2Au_2X_6$. Three i.v.c.t. bands were observed for each of $Cs_2Au_2X_6$ (X = Cl, Br or I). From the polarized reflectance spectra of $Cs_2Au_2I_6$ and group theoretical analysis, the strongest reflectance peak at the lowest energy region can be assigned to the intervalence charge-transfer transition from the $Au^I(5d_{x^2-y^2})$ orbital to the $Au^{III}(5d_{x^2-y^2})$ orbital within the Au–X networks in the *ab* plane. This indicates that a two-dimensional correlation between the gold ions is present in the charge-transfer interaction despite the three-dimensional perovskite structure of the compounds.

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