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Optical Spectra of Palladium Chloride

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Absorption and reflection spectra of a crystal of chain compound palladium chloride are measured in the energy range of 1–11 eV at low temperature. The structures found in the spectra and their anisotropies are discussed by referring D_{2h} molecular orbital states of d^8 metal ion in rhombic planar ligand field.

§1. Introduction

Electronic properties of metallic chain crystals have been investigated quite extensively in recent years because of their significant natures realized in a low dimensional crystal such as the Peierls instability and the charge density wave. On the contrary, little attention has been given to insulating chain crystals although a strong electron-phonon coupling is expected in them in a similar fashion to that operates in a low dimensional metallic compound.

From this point of view, we have investigated the electronic excitation and its relaxation assisted by phonon-coupling in a linear chain insulating compound Wolffram's red salt by means of optical measurements.[1] We have observed that the absorption spectrum is polarized strongly in the chain direction and have found that the electronic wave function extends in the chain direction. In Wolffram's red salt, the chlorine-bridged chain is linear and one chlorine ion is found between two platinum d^8 ions whose d_{z^2} directs along the chain due to the ligand whose plane is in perpendicular to the chain axis.

In palladium chloride, which is investigated in this study and is also a chlorine-bridged chain compound, two chlorine ions are situated between two palladium d^8 ions on the chain to form a ribbon-like structure[2] as shown in Fig. 1. Here the ligand plane surrounding a palladium ion is in parallel to the chain so that d_{z^2} would be in perpendicular to the chain axis. Thus the electronic state of this compound might be fairly different from that of Wolffram's red salt, although they are both chlorine-bridged d^8 chain compounds. In this paper, we present absorption and reflection spectra of palladium chloride and discuss its electronic structure.

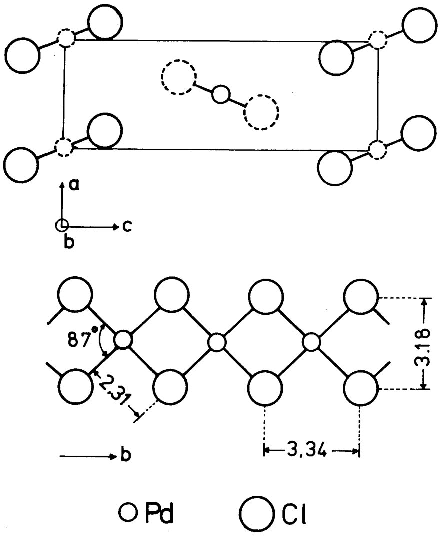

Fig. 1. Crystal structure of $PdCl_2$, taken from ref. 2.

§2. Experiments and Results

Palladium chloride, $PdCl_2$, was prepared from five nine palladium metal powder by dissolving it into aqua regia. Its powder was obtained by evaporating the solution. Thin film of $PdCl_2$ necessary for a direct measurement of absorption spectrum of high absorption coefficient was prepared by evaporating the powder onto a quartz plate as fast as

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possible to avoid a decomposition at high temperature in vacuum. For the measurement in the vacuum ultra-violet region, the substrate was a LiF plate.

Single crystals of $PdCl_2$ were grown from the powder in a sealed quartz tube whose one end, where the powder was placed, was maintained at 615–620°C and the other end at temperature lower by 60°C. In the tube, chlorine gas of 100–200 torr was introduced to serve as the carrier gas as well as to depress the decomposition. The crystals thus grown at the lower temperature end were of needle shape of a few mm long whose axes were in the chain direction *b*. Occasionally, a small but flat and thin crystal grew at the higher temperature end with typical dimensions of $0.3 \times 0.3 \times 0.03$ mm^3, whose smallest dimension is parallel to *c*. This crystal was useful for the absorption measurement of a single crystal by polarized light.

K_2PdCl_4 was prepared by dissolving $PdCl_2$ into HCl and KCl solution. Its spectrum was used for the analysis of the spectrum of $PdCl_2$. The light sources for the optical measurements were iodine lamp, hydrogen lamp or synchrotron radiation depending upon the energy range.

Figure 2 is the absorption spectrum of $PdCl_2$ at 4.2 K measured by using the evaporated film. The absolute value of the absorption coefficient was estimated by normalizing the optical density of evaporated film to the absorption coefficient determined in a single crystal at the energy of low absorption coefficient. Although $PdCl_2$ is highly anisotropic in the crystal structure, no anisotropy is found in the spectrum of evaporated film probably because of the random orientation of micro-crystals in the film. We note that the absorption coefficient of the peak *A* in this figure is so low that the direct measurement was not possible to be made with the film. The intensity and the shape of the peak *A* in the figure are estimated as the mean of the anisotropic absorptions measured in a single crystal as given in Fig. 3 assuming the random orientation of micro-crystals in the film. The details of the anisotropic spectra in Fig. 3 will be described in the later part. One observes that the peak *A* of low absorption coefficient of the order of $10^2\,\mathrm{cm}^{-1}$ is at the lowest energy. As the energy increases, the absorption increases and gives the structures *B* and *C*. They are followed by the structures *D*-*J* at higher energy where the absorption coefficient is of the order of 10^4–$10^5\,\mathrm{cm}^{-1}$. In the vacuum ultra-violet region, large peaks *K* and *L* with high absorption coefficients are observed.

The spectrum in Fig. 2 is represented approximately by a superposition of Gaussian absorption bands with their peaks at the energies of *A*-*J*. Particularly the bands *A* and

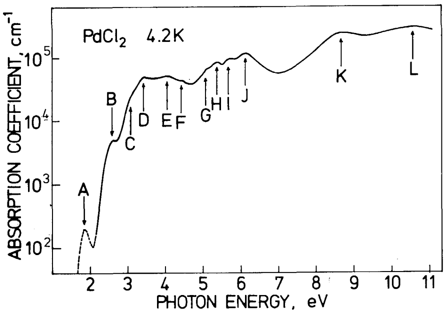

Fig. 2. Absorption spectrum of $PdCl_2$ at 4.2 K. The measurement was made on an evaporated thin film composed of micro-crystals oriented randomly.

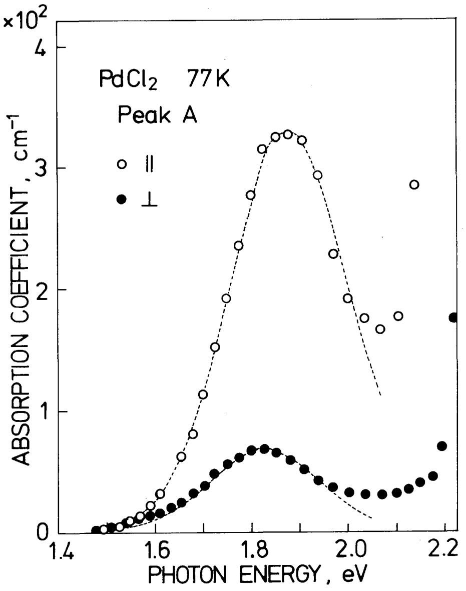

Fig. 3. Absorption spectra of a single crystal of $PdCl_2$ at 77 K in the vicinity of the peak *A*. Incident light is polarized in parallel (//) to and in perpendicular (⊥) to the chain. Dotted lines are Gaussian functions.

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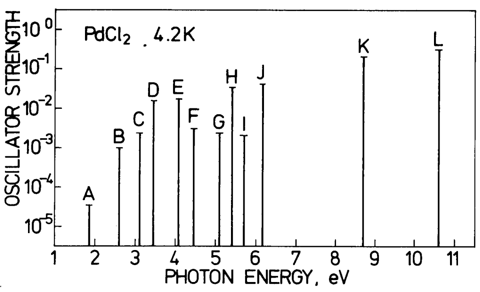

Fig. 4. Oscillator strengths of the structures in the spectrum in Fig. 2.

B at low energy are represented by Gaussian shapes nicely. At higher energy, the spectrum is represented by Gaussian shape bands not as good as that of low energy. In Fig. 4, the oscillator strengths of the structures are given. They are estimated from the spectrum in Fig. 2 by assuming the Gaussian shape so that the accuracy decreases as the energy of the structure increases. We note that the accuracies of the small structures *F*, *G* and *I* are quite poor because of the presence of neighbouring large structures.

Anisotropic absorption of the peak *A* measured with a single crystal at 77 K is shown in Fig. 3. Here the incident light is polarized in parallel to the chain direction *b* (//) and in parallel to *a* (⊥). One finds that the intensity of the // spectrum is almost five times larger than the ⊥ spectrum. Also, the peak energy of the former is higher by 0.05 eV than the latter.

To investigate the anisotropy of the optical spectrum in the higher energy region, reflection spectra were measured at 77 K and the results are given in Fig. 5. Since the crystals are so small that the accuracy of the reflection spectrum is not as good as the absorption spectrum. We observed a strong anisotropy in the whole spectral range. In the inset, enlarged spectra in the vicinity of the peak *B* are shown. An energy shift of ~0.05 eV of the peak *B* was observed in the reflection spectra for // and ⊥ polarized lights, in a similar way to the peak *A* in absorption spectrum. It is noted that the spectrum in Fig. 2 and the oscillator strengths in Fig. 4 are the average of the // and ⊥ values.

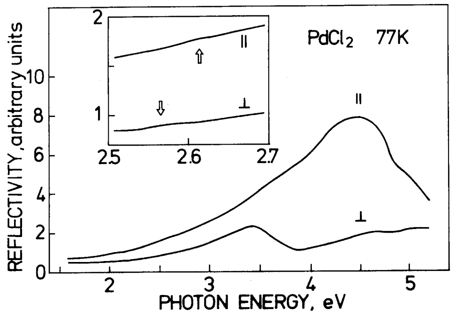

Fig. 5. Reflection spectra of single crystal of $PdCl_2$ at 77 K. Incident light is polarized in parallel (//) to and in perpendicular (⊥) to the chain. The inset is enlarged spectra in the vicinity of 2.6 eV.

In Fig. 6, the energies of the structures found in the absorption and reflection spectra are summarized. Temperature dependence of the absorption spectrum is small. The peak *A* shifts from 1.857 eV at 4.2 K to 1.875 eV at 77 K for // polarization. Though the intensities and the shapes of the bands *A*, *B* and *C* change little between 4.2 K and 77 K and they are broadened and become intense at room temperature.

Figure 7 shows the absorption spectrum of the aqueous solution of K_2PdCl_4. The spectrum is believed to be due to the electronic transitions in a square planar $PdCl_4^{2-}$ ion.[3] In this figure, the absorption intensity is ex-

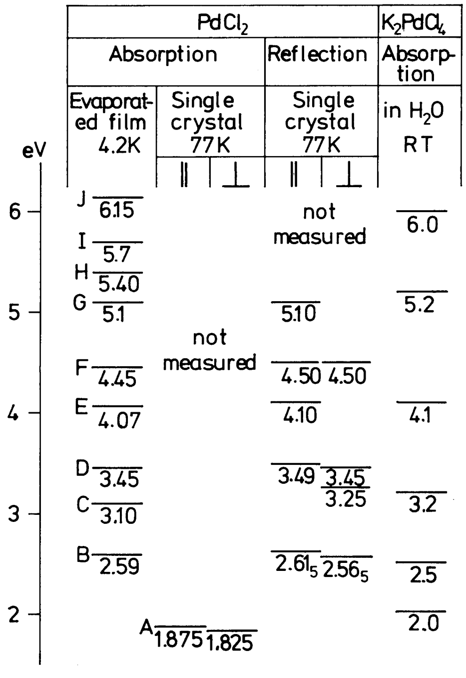

Fig. 6. Energies of the structures found in the spectra of $PdCl_2$ and K_2PdCl_4.

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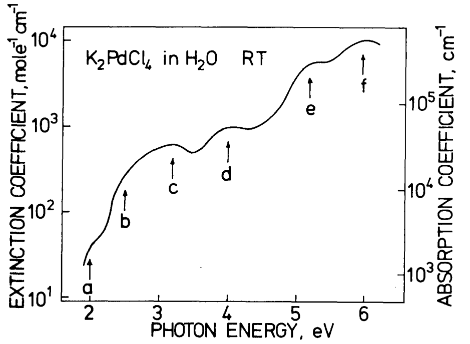

Fig. 7. Absorption spectrum of K_2PdCl_4 dissolved in H_2O. The definition of the absorption coefficient is given in the text.

pressed in terms of an extinction coefficient. The absorption coefficient shown in this figure is that of $PdCl_4^{2-}$ ion in H_2O when the Pd concentration is equal to that found in solid $PdCl_2$ whose specific gravity is 4.2.[2] This spectrum would be informative to the analysis of the $PdCl_2$ spectra because $PdCl_4^{2-}$ is a unit structure of the $PdCl_2$ chain. The energies of the structures in this spectrum are also given in Fig. 6.

§3. Discussion

The structures found in the absorption spectrum in Fig. 2 can be classified into four groups by taking into account the oscillator strength given in Fig. 4. The first group is the peak *A* whose oscillator strength is of the order of 10^{-5}. The structures *B* and *C* are the members of the second group whose oscillator strengths are of the order of 10^{-3}. The structures *F*, *G* and *I* might belong to this group but it is not certain because of their poor accuracies. The third group consists of the structures *D*, *E*, *H* and *J* and their oscillator strengths are of the order of 10^{-2}. The oscillator strength of the fourth group is of the order of 10^{-1} and *K* and *L* are its members.

As shown in Fig. 1 each palladium ion is surrounded by four chlorine ions in the chain so that the electronic state of $PdCl_2$ will be described in the lowest order approximation by a localized molecular orbital state of $PdCl_4^{2-}$ where Pd^{2+} is in a D_{4h} crystalline field due to the four tetragonally coordinated Cl^- ions. This approximation can be supported by the similarity of the spectrum of $PdCl_2$ in Fig. 2 to that of $PdCl_4^{2-}$ in Fig. 7. One finds that the energies of the structures and their intensities in both the spectra are almost in one to one correspondence, although, in the latter spectrum, the structures are broader and some of the structures found in $PdCl_2$ are missing.

The molecular orbital of D_{4h} square planar d^8 metal complex and its absorption spectrum have been discussed by Gray *et al.*[3] and by Fenske *et al.*[4] Since the four Cl^- around Pd^{2+} in $PdCl_2$ are coordinated not exactly in square planar but in slightly rhombic planar, their molecular orbital is modified to satisfy the D_{2h} symmetry to describe the electronic state of $PdCl_2$. In Fig. 8, the symmetries of the derived Bloch functions of D_{2h} at $k=0$ and $k=\pi/b$ are given. At these particular

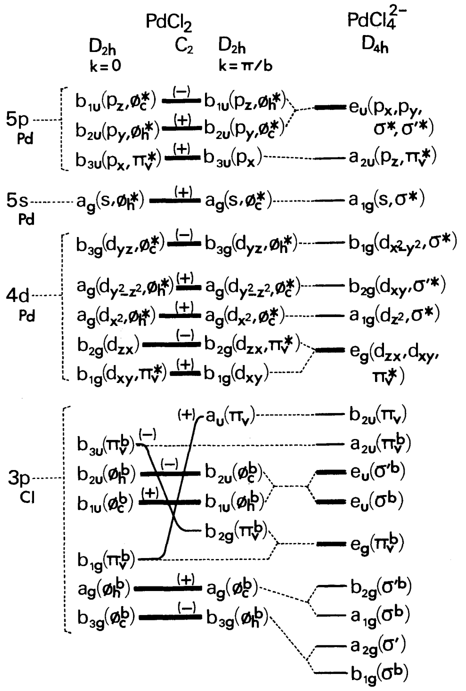

Fig. 8. The correspondence between the orbitals of the bands of $PdCl_2$ and the molecular orbitals of $PdCl_4^{2-}$. In $PdCl_2$, the point group is D_{2h} at $k=0$ and $k=\pi/b$ in the Brillouin zone, while it is C_2 at other points. The bold lines represent the band states which have same symmetries at $k=0$ and $k=\pi/b$, while the full lines represent the band states which have different symmetries. The dotted lines show the correspondence between the band states of D_{2h} and the molecular orbital states of D_{4h}.

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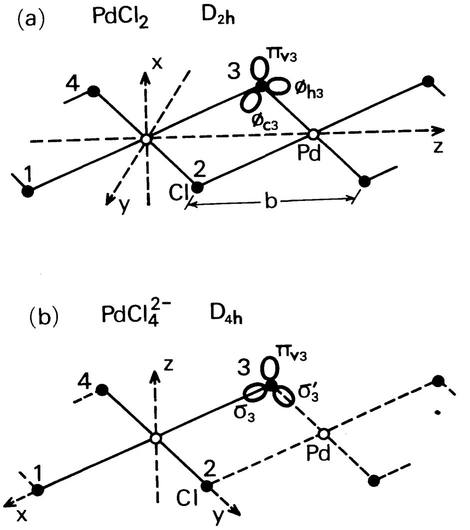

Fig. 9. Schematics of a single chain of $PdCl_2$ in (a) and a complex of $PdCl^{2-}$ in (b). Different coordinates are chosen each other.

points the states of the same symmetry mix each other, whereas at other points in the Brillouin zone, where the point group is C_2, mixings are realized between same (+) and (−) parity states. In this figure, the molecular orbital states of $PdCl_4^{2-}$ in D_{4h} symmetry are also shown with their relations to the band states. The coordinates used in Fig. 8 are shown in Fig. 9.

The d orbitals d_{x^2}, d_{yz}, $d_{y^2-z^2}$, d_{xy} and d_{zx} in the coordinate system of $PdCl_2$ given in Fig. 9 correspond to d_{z^2}, $d_{x^2-y^2}$, d_{xy}, $(d_{yz}+d_{zx})/\sqrt{2}$ and $(d_{yz}-d_{zx})/\sqrt{2}$ of usual expressions of $PdCl_4^{2-}$, respectively. We note that the energies of these five d orbitals are all different in D_{2h} and they combine with respective chlorine orbitals to form molecular orbitals. In Fig. 9(b), the orbitals which are π-like in one $PdCl_4^{2-}$ radical are represented as σ' orbitals, because they are σ-like to the neighbouring Pd ion in $PdCl_2$ chain shown by the broken lines. The ϕ_h and ϕ_c orbitals which direct to z and y in $PdCl_2$ are the mixtures of the σ and σ' orbitals in $PdCl_4^{2-}$. The ϕ and π orbitals in Fig. 8 are given as follows:

$$\phi_c(a_g)=(\phi_{c1}-\phi_{c2}-\phi_{c3}+\phi_{c4})/2,$$

$$\phi_h(a_g)=(\phi_{h1}+\phi_{h2}-\phi_{h3}-\phi_{h4})/2,$$

$$\phi_c(b_{3g})=(\phi_{c1}+\phi_{c2}-\phi_{c3}-\phi_{c4})/2,$$

$$\phi_h(b_{3g})=(\phi_{h1}-\phi_{h2}-\phi_{h3}+\phi_{h4})/2,$$

$$\pi_v(b_{2g})=(\pi_{v1}-\pi_{v2}-\pi_{v3}+\pi_{v4})/2,$$

$$\pi_v(b_{1g})=(\pi_{v1}+\pi_{v2}-\pi_{v3}-\pi_{v4})/2,$$

$$\pi_v(b_{3u})=(\pi_{v1}+\pi_{v2}+\pi_{v3}+\pi_{v4})/2,$$

$$\pi_v(a_u)=(\pi_{v1}-\pi_{v2}+\pi_{v3}-\pi_{v4})/2,$$

$$\phi_c(b_{2u})=(\phi_{c1}-\phi_{c2}+\phi_{c3}-\phi_{c4})/2,$$

$$\phi_h(b_{2u})=(\phi_{h1}+\phi_{h2}+\phi_{h3}+\phi_{h4})/2,$$

$$\phi_c(b_{1u})=(\phi_{c1}+\phi_{c2}+\phi_{c3}+\phi_{c4})/2,$$

$$\phi_h(b_{1u})=(\phi_{h1}-\phi_{h2}+\phi_{h3}-\phi_{h4})/2.$$

We assume the energy levels of the molecular orbitals in the band of $PdCl_2$ to be arranged in the same order as that given to $PdCl_4^{2-}$ ion.[3,4] Since Pd^{2+} ion is $4d^8$ and Cl^- ion is $2p^6$, the highest and vacant orbital among the orbitals originating from Pd $4d$ in the $PdCl_2$ chain is $b_{3g}(d_{yz}, \phi_c^*, \phi_h^*)$, as is often the case of a square planar ligand field, because its wave function is in the direction of the Pd–Cl bonds. Other four states, $a_g(d_{y^2-z^2}, \phi_c^*, \phi_h^*)$, $a_g(d_{x^2}, \phi_c^*, \phi_h^*)$, $b_{2g}(d_{zx}, \pi_v^*)$ and $b_{1g}(d_{xy}, \pi_v^*)$ are all filled. The last two states, b_{2g} and b_{1g}, are the result of the splitting of degenerate orbital e_g of D_{4h} symmetry. The energy ordering of the orbitals might be changed by forming $PdCl_2$ chain because of a possible contribution of neighbouring Pd ions in the chain. Since the ordering of d orbitals is quite sensitive to the ligand ions, it is not easy to predict theoretically whether the order of the d orbitals in Fig. 8 still holds in $PdCl_2$ chain.

Let us first discuss the structures A, B and C found in the lowest energy region of the absorption spectrum. Since their oscillator strengths are low and 3.5×10^{-5}, 1.0×10^{-3} and 2.3×10^{-3}, respectively, they are not due to dipole-allowed transitions. They will be transitions between levels originating mostly from Pd $4d$ states because the splitting between d levels are small compared with the ones between d and p levels or between p levels. This interpretation would be supported by the fact that, almost at the same energies and with the same intensities of A, B and C, structures a, b, and c are observed in $PdCl_4^{2-}$ spectrum which have been assigned to d-d transitions in $PdCl_4^{2-}$.[3,4]

Among the three absorptions, A is very much weaker than the other two and we assign it to the triplet transition associated with its singlet

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absorption B. This is because the ratio of the measured oscillator strength of A to B is about 1/30 and is close to the theoretically expected value of 1/20 which is estimated by taking 0.17 eV as the spin-orbit coupling constant ζ of Pd d-electron$^{5)}$ and 0.78 eV as the energy separation ΔE between A and B and by using $(k\zeta/\Delta E)^2$ as the ratio of oscillator strength of triplet to singlet where k is taken as unity. Further, the energy difference is 0.05 eV between $A(//)$ and $A(\perp)$ while it is $\sim$0.05 eV between $B(//)$ and $B(\perp)$, suggesting that A and B originate from the same orbital state.

A conclusive argument on the exact electronic states associated with the absorptions B and C, which we have assigned to spin-allowed d-d type transitions, is difficult to draw. However, the similarity between the spectra of $PdCl_2$ and $PdCl_4^{2-}$ ions would suggest that the order given in Fig. 8 would be applicable to $PdCl_2$. Then B and C will be the transitions to $b_{3g}(d_{yz}, \phi_c^*, \phi_h^*)$ from $a_g(d_{y^2-z^2}, \phi_c^*, \phi_h^*)$ and from $a_g(d_{x^2}, \phi_c^*, \phi_h^*)$ respectively assisted perhaps by odd parity stretching modes B_{2u} and B_{1u} (E_u of D_{4h}) of chlorine vibration which couple most strongly to the electronic states. This interpretation would be supported by the enhancement of these peaks between 77 K and room temperature which suggests their transitions being phonon-assisted.

One might say that the absorption B and so its triplet absorption A consist of two transitions, from $b_{2g}(d_{zx}, \pi_v^*)$ and from $b_{1g}(d_{xy}, \pi_v^*)$ to $b_{3g}(d_{yz}, \phi_c^*, \phi_h^*)$, and the energy splitting of $B(//)$ and $B(\perp)$ and also of $A(//)$ and $A(\perp)$ will be due to the energy difference between b_{2g} and b_{1g}. But this is not the case because, if it is so, both the absorption B and the absorption A must be doubly peaked in disagreement with the experimental results. Further, the above two transitions are allowed only for x-polarized light under the assistance of stretching vibrations B_{2u} and B_{1u} while the absorptions A and B are much more intense for $E//b$ $(b=z)$ than for $E//a$ $(a\cong x)$.

The assignment of B to $a_g(d_{y^2-z^2}, \phi_c^*, \phi_h^*)\rightarrow b_{3g}(d_{yz}, \phi_c^*, \phi_h^*)$ given above is consistent with the anisotropic absorption intensity of A, which is the triplet of B. These two transitions are allowed for both y- and z-polarized lights under the assistance of vibrations of B_{2u} and B_{1u} and forbidden for x-polarized light. So the intensity of the transitions for x-polarized light must be negligibly small. The absorptions for y- and z-polarized lights must be almost equal as far as we are concerned with molecular orbitals of $PdCl_4^{2-}$, because the angle of Cl–Pd–Cl is 87° so that the ligand configuration is close to D_{4h} symmetry. As is shown in Figs. 1 and 8, the a-axis makes an angle of 24.4° with the x-axis. According to the above assignment for A, we can calculate the intensity of $A(//)$ as to be 5.85 times as large as that of $A(\perp)$, while the experimental value is 5.2 as is seen in Fig. 3. Thus the above transition between local molecular orbital states of $PdCl_4^{2-}$ is enough to explain the optically anisotropic nature of A shown in this figure.

To explain the origin of the different energy of the peak A (and B) measured by // polarized light from that by $\perp$ polarized light, as is seen in Figs. 3 and 5, however, the local molecular states mentioned above are not sufficient. It might be due to the difference in strength between an intra-chain interaction along z and an inter-chain interaction in perpendicular to z. If we take into account the electron transfer interaction between neighbouring Pd ions by mixing of an electron transfer excited state and the ground state,$^{6)}$ the energy decrease of the ground state and energy increase of the electron transfer state due to the intra-chain interaction would be larger than those due to the inter-chain interaction. This is because the mixing would be much larger than that between the chains. That the energy of the peak A (and B) measured by // polarized light is higher than that measured by $\perp$ polarized light would support this interpretation. Further investigation will be needed to clarify it.

The peaks higher in energy than the peak C have high oscillator strength of the order of 10^{-2}–10^{-1} and they must be dipole-allowed transitions. There are two possible allowed transitions in this energy range. When one views from atomic orbitals of Pd and Cl in $PdCl_2$, the first one is the transition from chlorine $3p$ to palladium $4d_{yz}$. The second one is that from palladium $4d$ to palldium $5p$. The first one would have a lower oscillator strength than the second one because the

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first one has an inter-atomic nature while the second one has an intra-atomic nature. Thus we assign the peaks *D* and *E* and perhaps *F* to the transitions from chlorine 3*p* to palladium $4d_{yz}$ and *H* and *J* to the transitions from palladium 4*d* to palladium 5*p*.

Let us discuss the transition from chlorine 3*p* to palladium $4d_{yz}$ from the view point of molecular orbital. The molecular orbitals associated mainly with chlorine 3*p* in $PdCl_2$ are $a_u(\pi_v)$, $b_{3u}(\pi_v^b)$, $b_{2u}(\phi_c^b, \phi_h^b)$ and $b_{1u}(\phi_c^b, \phi_h^b)$. The orbital a_u does not mix with palladium state and is purely chlorine state. The b_{2u} and b_{1u} are the levels split from e_u of D_{4h} and their separation would be small. Among the transitions from these four states to a vacant $b_{3g}(d_{yz}, \phi_c^*, \phi_h^*)$, the transition from a_u, b_{1u} and b_{2u} are allowed by the light polarized in *x*-, *y*- and *z*-direction respectively while that from b_{3u} is forbidden. At the energy of the peak *D*, a peak is observed in ⊥ reflection spectrum given in Fig. 5. This would suggest that the transition responsible for the absorption *D* would be either $a_u \rightarrow b_{3g}$ or $b_{1u} \rightarrow b_{3g}$. If the latter transition is the case, there should be a *z*-polarized absorption responsible for $b_{2u} \rightarrow b_{3g}$ in close in energy to the absorption *D* because b_{1u} and b_{2u} are split from e_u of D_{4h}. However, the absorption *D* is well separated from *E* and *F* and so we suggest that the absorption *D* is likely to originate from $a_u \rightarrow b_{3g}$. Then the absorption *E* and its neighbouring *F* would be due to the other two transitions. A strong reflection by the // light in this energy range might suggest that the transition $b_{2u} \rightarrow b_{3g}$ will be dominant in this energy range.

As for the peaks *H*, *I* and *J*, a reflection spectrum of single crystal by polarized light in this energy range was not measured and it is difficult to assign each peak separately. It can only be said that they are likely due to the transitions associated with the transition from palladium 4*d* to palladium 5*p*. The absorptions *K* and *L* must be allowed transitions but their origins are not clarified.

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