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# Pressure effects on the absorption spectra of KBr:Ag$^+$

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Absorption bands $A$, $B$, and $D$ in KBr:Ag$^+$ have been investigated under hydrostatic pressure at low temperature. The pressure shifts of these bands at 85 K are $A$: $5.093+0.14p-0.012p^2$ eV, $B$: $5.343+0.05p+0.006p^2$ eV, and $D$: $5.882+0.13p-0.016p^2$ eV, where pressure $p$ is given in GPa units. The absorption intensity decreases and the half width becomes narrower under higher pressure. The pressure dependence of the peak position is analyzed by taking into consideration the ligand field interaction in addition to Drickamer's framework. The rather large blue shift is attributed to the enhancement of the ligand field under pressure, and the different shift rate (0.08 ~ 0.09 eV/GPa) between the $A(D)$ and $B$ bands results from the ligand field splitting of the $d$ electron. It is suggested that the adiabatic potential in the excited states is deformed in $Q(T_{1u})$ space. The changes of adiabatic potential in both the configuration coordinates of $Q(A_{1g})$ and $Q(T_{1u})$ are discussed.

## I. INTRODUCTION

It is well known that the Cu$^+$ and Ag$^+$ ions with a closed-shell structure of the $d^{10}$-type show unstable local structural behavior in alkali halide crystals.[1-7] This phenomenon appears to be one of the prototypes embodying the essential nature of chemical bonding, because the crystal structures of cuprous halides and silver iodide are different from alkali halides. The inconsonant crystal structure of the dopant to the matrix may give rise to the delicate balance of the ionicity and covalency around the Cu$^+$ (Ag$^+$) ion, and this balance determines whether the defect ions occupy the on-center position or the off-center position. Hydrostatic pressure moves the balance toward the stronger ionicity which is favorable to the on-center position.

This instability is classified into four types by Holland and Luty,[8] following the characteristic temperature behavior of the parity-forbidden absorption band intensity. The classification also describes the corresponding adiabatic potentials on the Cu$^+$ or Ag$^+$ ion. Various theoretical models have focused attention on the origin of the instability. Of these, a charge transfer excited state (CTE) model, in particular, described well the local structural instability in terms of admixing a charge-transfer state with $T_{1u}$ symmetry in a cubic field with a ground state.[9,10] The adiabatic potentials along the three principal directions of $\langle 001\rangle$, $\langle 110\rangle$, and $\langle 111\rangle$ were given for several different cases.

Hydrostatic pressure significantly affects the local structural instability of this type through a change of the local elastic constant, that is, a change of the adiabatic potential around the defect ion, because the defect ions are loosely bound to the ligand ions in alkali halide crystals. This has been substantiated by observations of a low-lying vibrational mode around the defect.[11-14] In the case of the shallow off-center systems such as NaBr:Cu$^+$ (Refs. 8, 15, 16), RbCl:Ag$^+$ (Ref. 8), and RbBr:Ag$^+$ (Ref. 8), hydrostatic pressure drives them to the on-center potential, and reduces the degree of anharmonicity of the potential in an anharmonic on-center system of NaCl:Cu$^+$ as well.[16] The deep off-center system of KBr:Cu$^+$ also changes to the shallow system.[17] These are analyzed by monitoring the oscillator strength of the parity-forbidden absorption bands $A$, $B$, and $D$.[4]

On the other hand, we have revealed directly the local arrangement around the Cu$^+$ ions in NaCl (Ref. 18) and NaBr (Ref. 19) by means of extended x-ray-absorption fine-structure (EXAFS) measurements. The analysis shows that the bond distance between the Cu$^+$ ion and halide ions in NaCl is rather closer to that of the alkali halide. This fact implies loose binding of the defect ion and the ligand ions corresponding to a low-lying resonance mode. In NaBr:Cu$^+$, it is likely that the cage consisting of the Cu$^+$ ion and six halide ions is deformed.

In this paper, we will present the pressure effect of the $A$, $B$, and $D$ absorption bands in KBr:Ag$^+$, which is understood to be an on-center system in the ground state. The pressure dependences of the peak positions and the absorption intensity of the $A$, $B$, and $D$ bands are discussed through the adiabatic potential change in $Q(A_{1g})$ and $Q(T_{1u})$ configuration coordinates. The ligand field interaction with $d$ electrons of the Ag$^+$ ion is explicitly taken into consideration in the analysis.

## II. EXPERIMENT

The high-pressure equipment used here was described in Ref. 16 in detail. The cooling bath is slightly modified for conventionally achieving liquid-nitrogen temperature (LNT). The sample was refrigerated to about 85 K by liquid nitrogen, which was monitored by a copper-constantan thermocouple located near a sapphire window. An optical high-pressure cell of the piston-cylinder

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type produces a high-quality hydrostatic pressure. The quality, including the uniformity, of hydrostatic pressure produced by the optical pressure cell used here was confirmed by the sharp phase transition of rubidium halides. The pressures at the phase transition of rubidium and potassium halides were used to correct the applied pressure. This optical pressure cell is available up to about 2 GPa at LNT. However, at room temperature, the sapphire windows sometimes cracked simultaneously with the phase transition of potassium halides which is accompanied by a large and abrupt volume change.

The single crystals of KBr:Ag$^+$ with various concentrations of Ag$^+$ ions were grown by the conventional Kyropoulos method in air. Before melting the KBr powder, it was held for one day at 400 °C in order to eliminate hydroxyl ions. The crystal was processed in a cylindrical form of 5 mm diam and subsequently sliced into 1 mm thicknesses. The sample thickness reduces to 0.92 mm when subjected to 1.8 GPa pressure. Before each measurement, the samples in disk form $(5^{\phi}\times 1^{t}\ \mathrm{mm}^2)$ were annealed for 1–2 min at 50 K below the melting point, then rapidly quenched to room temperature. Consequently, the aggregation of sliver ions and the formation of fine crystals of silver halide were avoided.

The absorption spectrum at atmospheric pressure was first measured, and then the sample was subjected to a pressure ~0.5 GPa a few times to achieve good contact between the sample and the sapphire windows. Keeping a low pressure of about ~0.03 GPa, we refrigerated the samples. By this procedure, we can maintain good interface contact throughout the measurement at low temperature.

## III. RESULTS

Ag$^+$ defect systems in alkali halide crystals exhibit several absorption bands on the low-energy side of the fundamental absorption edge of host substances. These are denoted by the letters *A*, *B*, *C*, and *D*, in order of increasing energy, and assigned to be the transitions from $^1\Gamma_1^+(d^{10})$ to *A*: $^3\Gamma_3^+ + {}^3\Gamma_5^+$, *B*: $^1\Gamma_3^+$, and *D*: $^1\Gamma_5^+$ (Refs. 4, 20), which are parity-forbidden transitions. In many cases, the band *C* is not clearly observed and is not definitely assigned. The absorption intensities of the vibronically allowed transitions display strong temperature dependence in the cubic ligand field.[4] Figure 1 shows the absorption spectra under various pressures at 85 K. The tail of the strong bands (*G* and *H* bands) on the higher energy side is subtracted from the observed spectra to show clearly the intensity variation with increasing pressure. The absorption peaks shift toward the higher energy. The half widths of the bands become slightly narrower. These pressure effects are common behavior in the Cu$^+$ and Ag$^+$ defect systems in alkali halides. A weak band, which is considered to be an Ag$^+$ pair band, appears on the low-energy side of the *A* band.

The peak positions are plotted in Fig. 2 as a function of the applied pressure. The least-squares fitting of the observed shifts to the second-order polynomial of pressure is performed:

$$A \text{ band: } E_A(p) = 5.093 + 0.14p - 0.012p^2 \text{ (eV)}, \quad (1a)$$

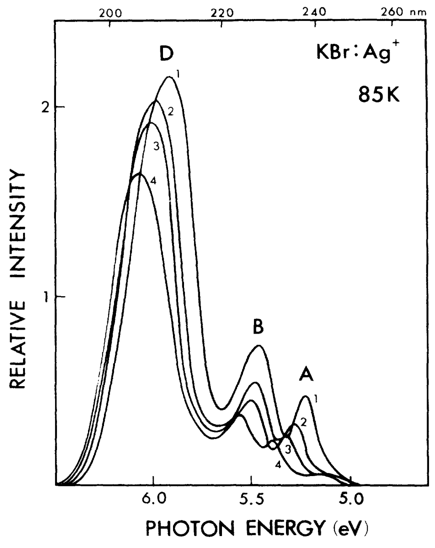

FIG. 1. The absorption spectra at 85 K under different pressures, (1) 0.06 GPa, (2) 0.5 GPa, (3) 0.8 GPa, and (4) 1.5 GPa. All observed absorption-band intensities become weaker as pressure increases, accompanying a subband which is considered to be the Ag$^+$ pair band. The corrections for decrease of the sample thickness due to the application of pressure and the formation of the Ag$^+$ pair are not made in the spectra.

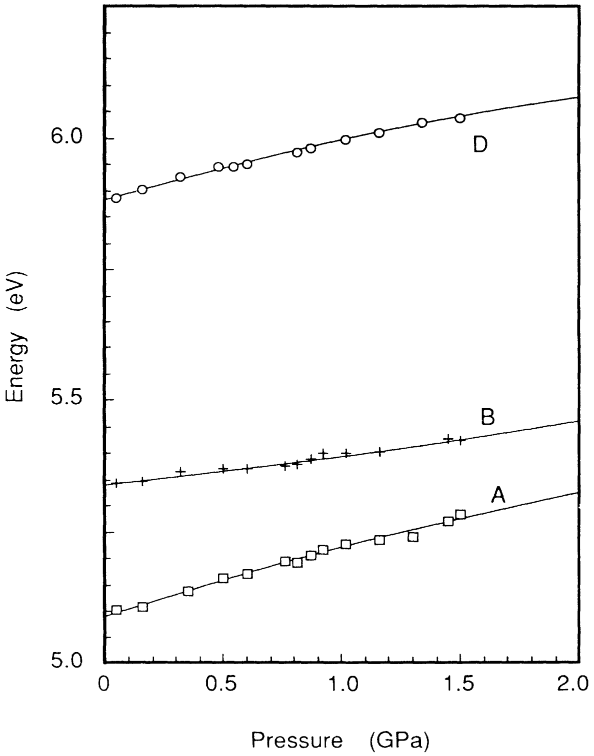

FIG. 2. The peak shift of the absorption bands *A*, *B*, and *D* as a function of pressure. The bands *A* and *D* shift at the same rate within experimental error, while the band *B* displays a small shift. The solid lines are fitted with a least-squares method to the second-order polynomial.

$$B \text{ band: } E_B(p)=5.343+0.05p+0.006p^2 \text{ (eV)} , \tag{1b}$$

$$D \text{ band: } E_D(p)=5.882+0.13p-0.016p^2 \text{ (eV)} , \tag{1c}$$

where the pressure is given in GPa units. The linear coefficients of the $A$ and $D$ bands are the same within experimental error. The small quadratic coefficients suggest nearly the same force constants for the ground state and the excited state. The negative sign means that the force constant is weaker in the excited state than in the ground state, as described in Sec. IV.

## IV. DISCUSSION

To discuss the pressure dependence of the quantities such as peak position, half width, and absorption intensity, we consider a complex consisting of the Ag$^+$ ion and six Br$^-$ ions. The Cartesian coordinates of the complex [Ag$^+$Br$_6^-$] are reduced to normal coordinates of $Q_1(A_{1g})$, $Q_{2,3}(E_g)$, $Q_{4-6}(T_{1g})$, $Q_{7-9}(T_{2g})$, $Q^1_{10-12}(T_{1u})$, $Q^2_{13-15}(T_{1u})$, $Q^3_{16-18}(T_{1u})$, and $Q_{19-21}(T_{2u})$. The relevant normal coordinates are $Q(A_{1g})$ and the three kinds of $Q(T_{1u})$, because the hydrostatic pressure (which transforms as $A_{1g}$ symmetry) affects the peak position and the half width of the absorption bands in the $Q(A_{1g})$ space. Furthermore, the absorption intensity of vibronically allowed transitions is related to the $Q(T_{1u})$ space, and also to the $Q(A_{1g})$ space, through a third-order anharmonic coupling. [One of the $Q(T_{1u})$'s involves the Ag$^+$ ion in the off-center displacement.] We discuss individually the adiabatic potential in the $Q(A_{1g})$ and $Q(T_{1u})$ spaces.

### A. Adiabatic potential in the $Q(A_{1g})$ coordinate

As in the present case where the defect ions have $d$ electrons in the outermost shell, the ligand field has a quite different influence from that consisting of $p$ electrons such as the Tl$^+$ ion. The ligand field in cubic symmetry merely lifts up the $p$-electron energy, but for the $d$ electron it causes energy splitting. Therefore, we include the ligand field interaction in Drickamer's framework[21,22] to analyze the pressure shift of the absorption bands.

We develop the potential of the ligand field to the second order of the normal coordinate of $Q(A_{1g})$, which is the relevant one for the pressure shift of the absorption bands:

$$H_{\text{en}}[r,\ R,\ Q(A_{1g})]=V_0(r,R_0)+V_1(r,R_0)Q(A_{1g}) + V_1'(r,R_0)Q^2(A_{1g}) , \tag{2}$$

where

$$V_0(r,R_0)=6Ze^2/R_0+B(R_0) , \tag{3}$$

$$V_1(r,R_0)=\partial H_{\text{en}}/\partial Q(A_{1g})|_{Q=0} , \tag{4}$$

and

$$V_1'(r,R_0)=\partial^2 H_{\text{en}}/\partial Q^2(A_{1g})|_{Q=0} , \tag{5}$$

in which $r$ is the electron coordinate, $R_0$ the equilibrium position of the ligand ions, $V_0$ the ligand field potential at $R_0$, $B(R_0)$ gives the ligand field splitting of the fivefold degenerate level of the $d$ electron, and $V_1$ and $V_1'$ represent the coupling strength for linear and quadratic electron-nucleus interaction, respectively, in the $Q(A_{1g})$ space.

For the ground state denoted by $\Psi_g(r,R)$ which has total symmetry for the sake of a filled ($d^{10}$) electron configuration, the adiabatic potential is

$$\begin{aligned} U_g[R_0^g,Q(A_{1g})]={}&E_g(R_0^g)+\langle \Psi_g(r,R_0^g)|V_1'(r,R_0^g)|\Psi_g(r,R_0^g)\rangle Q^2(A_{1g}) \\ &+\{\partial^2 U(R_0^g)/\partial Q^2(A_{1g})\}Q^2(A_{1g})=E_g(R_0^g)+\omega_g^2 Q^2(A_{1g}) \end{aligned} \tag{6}$$

around an equilibrium position $R_0^g$ in the ground state. Here, $E_g(R_0^g)=\varepsilon_g+A[=\langle \Psi_g(r,R_0^g)|(6Ze^2/R_0^g)|\Psi_g(r,R_0^g)\rangle]$, $\varepsilon_g$ is the electron energy in free ions, $U(R_0)$ the bare potential between the ions constituting the complex, and $\omega_g^2$ a force constant. On the other hand, the adiabatic potential at the optically excited state denoted as $\Psi(\Gamma,r,R)$ is

$$\begin{aligned} U_e[\Gamma,R_0^g,Q(A_{1g})]={}&E_e(\Gamma,R_0^g)+\langle \Psi(\Gamma,r,R_0^g)|V_1(r,R_0^g)|\Psi(\Gamma,r,R_0^g)\rangle Q(A_{1g}) \\ &+\langle \Psi(\Gamma,r,R_0^g)|V_1'(r,R_0^g)|\Psi(\Gamma,r,R_0^g)\rangle Q^2(A_{1g})+\{\partial^2 U(R_0^g)/\partial Q^2(A_{1g})\}Q^2(A_{1g}) \\ ={}&E_e(\Gamma,R_0^g)+\Delta(\Gamma)Q(A_{1g})+\omega^2(\Gamma)Q^2(A_{1g}) , \end{aligned} \tag{7}$$

where

$$E_e(\Gamma,R_0^g)=\varepsilon_e(\Gamma)+A'(=\langle \Psi(\Gamma,r,R_0^g)|(6Ze^2/R_0^g)|\Psi(\Gamma,r,R_0^g)\rangle)+B(R_0^g),$$

$\varepsilon_e$ is the excited electron energy in free ions, $\Gamma$ indicates the character of the different excited states, and $\omega^2(\Gamma)$ is a force constant in the $\Gamma$ excited state. Note that the linear term of $Q(A_{1g})$ does not vanish in the excited states. This implies that the ligand ions relax to different equilibrium positions from that in the ground state for the respective excited states.

For the above adiabatic potentials, the hydrostatic pressure $p$ works to change those equilibrium positions as described by Drickamer, Frank, and Slichter.[21] Adding the pressure work $pQ(A_{1g})$ to Eq. (6) and assuming the pressure-independent force constant, we obtain a new equilibrium position, $Q_n(A_{1g})=Q(A_{1g})+p/(2\omega_g^2)$, or $R_n^g=\{(R_0^g)^3+p/(2\omega_g^2)\}^{1/3}$ in the ground state, where the positive sign of pressure work means compression. Thus, the absorption peak energy under pressure can be represented as follows:

$$\begin{aligned}\delta E(\Gamma,p)&=U_e[\Gamma,R_n^g,Q_n(A_{1g})=0]-U_g[R_n^g,Q_n(A_{1g})=0]\\&=\Delta\varepsilon(\Gamma)-\{\Delta(\Gamma)/(2\omega_g^2)\}p\\&\quad+\{[\omega^2(\Gamma)-\omega_g^2]/(4\omega_g^4)\}p^2\ ,\end{aligned}\tag{8}$$

where all the pressure-independent terms are included in $\Delta\varepsilon(\Gamma)$. The linear term of pressure in Eq. (8) originates from the linear electron-nucleus interaction $\Delta(\Gamma)Q(A_{1g})$ in Eq. (7). The coefficient $\Delta(\Gamma)/(2\omega_g^2)$ denotes a volume change. Within the harmonic oscillator approximation, the absorption bands shift in a quadratic form of the hydrostatic pressure, in agreement with observations.

From the observed blue shift of the $A$, $B$, and $D$ absorption bands [Eqs. (1a)–(1c)], the negative value of $\Delta(\Gamma)$ can be deduced. The negative $\Delta(\Gamma)$ corresponds to the more spread equilibrium position in the excited states than in the ground state. From the observed shifts and under the assumption of equal force constants in the ground and excited states,[23] we can estimate the equilibrium positions in each excited state; $\delta Q(A_{1g})=\Delta(\Gamma)/[2\omega^2(\Gamma)]=22.4$ Å$^3$ for the $A$ band ($\Gamma={}^3\Gamma_3+{}^3\Gamma_5$), 8.0 Å$^3$ for the $B$ band ($\Gamma={}^1\Gamma_3$), and 20.8 Å$^3$ for the $D$ band ($\Gamma={}^1\Gamma_5$). Here it should be noted that the dimension of $Q(A_{1g})$ is (length)$^3$ because we define the pressure work not as $pQ^3$, but $pQ$.

Now we direct our attention to the pressure dependence of the ligand field strength in a straightforward way. As is well known, the ligand field lets a $\Gamma_3^+$ state lower by $6Dq$ [$Dq=(Ze^2\overline{r}^4)/(6R_0^5)$ in a point charge approximation] and a $\Gamma_5^+$ state raise by $4Dq$,[24] where the splitting direction is inverted because of the electron configuration of $d^9s$ (complementary state of a $ds$ electron configuration) in the excited state. The energy splitting diagram of the Ag$^+$ ion in a cubic field is schematically depicted in Fig. 3. The absorption bands $A$ (${}^3\Gamma_3^+ + {}^3\Gamma_5^+$) and $D$ (${}^1\Gamma_5^+$) originate from the same initial state $\Gamma_5^+$, and the band $B$ (${}^1\Gamma_3^+$) originates from a $\Gamma_3^+$ state. Therefore, the same contribution from the ligand field is expected for the $A$ and $D$ bands under hydrostatic pressure. The same blue-shift rate of the absorption bands means the same strength of the linear electron-nucleus interaction. An electron-electron interaction and a spin-orbital interaction are not so strongly influenced by the pressure application. The difference (0.08 ~ 0.09 eV/GPa) in the blue shift between the $A$ ($D$) and $B$ bands may be practically attributed to the pressure change in the ligand field splitting term. In the form developed by the normal coordinates, this is reflected in the different equilibrium positions within Drickamer's expression. The blue shift of the entire spectrum observed here gives a relationship of $\partial A'/\partial p > \partial A/\partial p$, indicating that the electron wave functions in the excited states are more strongly affected by the change in the equilibrium position of the ligand ions.

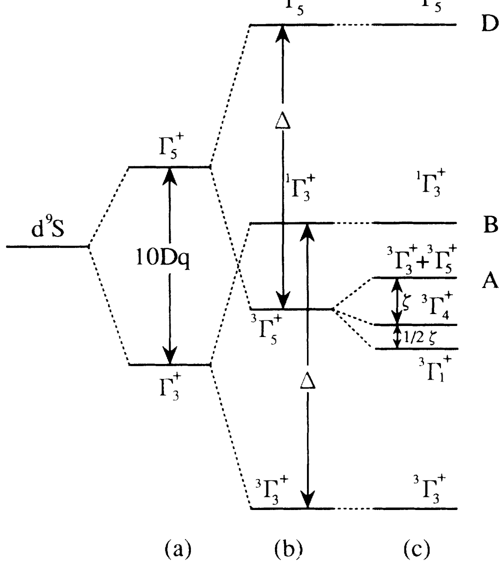

FIG. 3. Electronic energy splitting scheme in the cubic field. Stage (a) shows the ligand field splitting $10Dq$. Stage (b) the electron-electron interaction $\Delta$, and stage (c) the spin-orbital splitting $\zeta$. The capital letters $A$, $B$, and $D$ denote the corresponding absorption bands.

### B. Adiabatic potential in the $Q(T_{1u})$ coordinate

A parity-forbidden transition, such as in the present case, becomes partially allowed through an admixture with the opposite-parity states induced by odd motion or odd deformation of the defect ion and its ligand ions. This admixture occurs both in the ground state and in the excited state. The transition probability in this case is approximately represented as follows:[24]

$$f_{\Gamma\Gamma'}(v)=\frac{2}{3}\frac{m}{e^2}\frac{v}{h}\left[\frac{2}{\delta\Omega}\right]^2 M_{\Gamma\Gamma'}\sum_i\langle Q_i(T_{1u})\rangle^2\ ,\tag{9}$$

and is proportional to the mean-square displacements $\sum\langle Q_i(T_{1u})\rangle^2$. Here, $\delta\Omega$ is the mean value of the transition energy, $v$ the incident-photon frequency, and $M_{\Gamma\Gamma'}$, the dipole matrix element.

As seen in Fig. 1, the intensities of the $A$ (${}^3\Gamma_3^+ + {}^3\Gamma_5^+$), $B$ (${}^1\Gamma_3^+$), and $D$ (${}^1\Gamma_5^+$) absorption bands decrease in different ways. The intensity decrease results from smaller $\sum\langle Q_i(T_{1u})\rangle^2$ under pressure. The Ag$^+$ ions in KBr are located at the on-center position in the ground state, and then the temperature dependence of the oscillator strength of the $A$, $B$, and $D$ bands exhibits rather the hyperbolic contangent-type for the transition partially allowed by the vibration.[25] Hence, the static deformation around the defect ion and its ligand ions from the cubic symmetry is considered to be small in the ground state. However, while the hydrostatic pressure is exerted equally upon the transition strength of all the bands in the ground state, the different rate of decrease in strength indicates that the deformed configuration occurs in the excited states and its deformation is changed by hydrostatic pressure through the third-order anharmonic couplings,

$\alpha Q_i(T_{1u})Q_j(T_{1u})Q(A_{1g})$, in the respective excited states.[26,27] The lifetime of an emission band in KBr:Ag$^+$ is considerably shorter than in other Ag$^+$ and Cu$^+$ defect systems in alkali halides.[28] Together with the above fact, the enormous increase in the lifetime of the emission band with pressure implies that in the relaxed excited state (which is different from the optically excited state[29]) the configuration of complex [Ag$^+$Br$_6^-$] may have a rather large deformation. Therefore, the deformation of the optically excited state is deduced to be also large, resulting in the large decrease of the absorption intensity under pressure.

## V. CONCLUSION

We measured the absorption spectra of KBr:Ag$^+$ under various hydrostatic pressures at 85 K. It was found that the absorption bands $A$, $B$, and $D$ shift to the higher energy side, the half width becomes narrow, and the absorption intensity is weakened by pressure increases. The absorption bands $A$ and $D$ shift at almost the same rate, and the band $B$ more slowly than these. Following Drickamer's expression, the shifts $\delta Q(A_{1g})$ of the equilibrium positions in each excited state from that in the ground state are evaluated as 22.4 Å$^3$ for the $A$ excited state, 8.0 Å$^3$ for the $B$ excited state, and 20.8 Å$^3$ for the $D$ excited state. We have discussed these experimental results by considering the ligand field interaction with the $d$ electron of the Ag$^+$ ion. The rather large blue shifts are attributed to the ligand field enhancement under pressure, and the different shift rates between the $A$ ($D$) and $B$ bands result from the ligand field splitting of the $d$ electron, which is changed at the rate of 0.08 ~ 0.09 eV/GPa.

The lowering of intensity at higher pressure is attributed to the hardened force constant in $Q(T_{1u})$ space through the third-order anharmonic coupling. The adiabatic potentials in the excited states are considered to be deformed from the cubic symmetry.

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