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The Electronic Structure and Spectrum of the Silver(I)Perchlorate-Pyridine Complex

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The absorption spectrum of the silver perchlorate-pyridine system was measured in acetonitrile and ethanol in the wavelength region of 180 mμ to 400 mμ. It was found that the solution exhibits a new shoulder in the 210 mμ region characteristic for the 1:1 complex, in addition to the absorption maxima at 196 mμ and 253 mμ which correspond, respectively, to the L_a and L_b bands of pyridine. From the concentration dependence of the absorption intensity of this shoulder, the equilibrium constant for 1:1 complex formation was determined to be 108 l/mole at 26 °C. Furthermore, we studied theoretically the electronic structure of this complex by the method of the localized orbital model, the effect of the solvation energy upon the charge-transfer configurations being taken into account. The theoretical results show that the new absorption band at 207.5 mμ has to considerably great extent the character of a charge-transfer type excitation.

Das Absorptionsspektrum des Systems $AgClO_4$-Pyridin in Acetonitril- und Äthanol-Lösung wurde im Bereich von 400 – 180 mμ vermessen. Es treten Absorptionsmaxima bei 196 und 253 mμ auf, die der L_a- bzw. L_b-Bande des Pyridins entsprechen; daneben eine Schulter bei 207 mμ als Charakteristikum des 1:1-Ag^+-Pyridin-Komplexes. Aus der Konzentrationsabhängigkeit der Intensität dieser Schulter folgt als Gleichgewichtskonstante der Komplexbildung $k = 108$ l/Mol (26 °C), aus der Temperaturabhängigkeit $\Delta H = 4{,}5$ kcal/Mol, $\Delta S = -6$ Cl in guter Übereinstimmung mit polarographischen Ergebnissen. Weiterhin wurde die Elektronenstruktur mit der Methode der Moleküle in Molekülen unter Berücksichtigung von Solvatationseinflüssen untersucht. Danach ist die neue Schulter als Ladungsübergangsbande zu klassifizieren.

Mesure du spectre d'absorption du système $AgClO_4$-Pyridine en milieu acétonitrile ou éthanol dans le domaine 400 – 180 mμ. On obtient des maxima d'absorption vers 196 et 253 mμ correspondant aux bandes L_a et L_b de la pyridine; un épaulement vers 207 mμ est caractéristique du complexe 1:1-Ag^+-Pyridine. D'après la variation de l'intensité de cet épaulement avec la concentration on obtient comme constante d'équilibre du complexe $k = 100$ l/Mol (26 °C), et à partir de la variation avec le température $\Delta H = 4{,}5$ kCal/Mol, $\Delta S = -6$ Cl, en bon accord avec les résultats polarographiques. De plus la structure électronique est étudée à l'aide de la méthode des molécules dans les molécules en considérant les effets de solvatation. On en déduit le caractère de bande de transfert de charge de cet épaulement.

I. Introduction

Thes ilver cation is known to be an electron acceptor and to form charge-transfer (abbreviated hereafter to CT) type complexes with various electron donors such as benzene [1], its derivatives [2], unsaturated aliphatic hydrocarbons [3, 4], amines, and so on. Of these, the silver cation complexes with hydrocarbons have hitherto been studied extensively from the viewpoint of CT interaction. ANDREWS and KEEFER carried out a series of experimental studies on the silver cation complexes of several aromatic hydrocarbons [2a]. They determined the formation constants for the toluene-silver cation complex by the aid of solubility measurement and measured the ultraviolet spectrum of the aqueous solution containing silver perchlorate and toluene [2b]. The silver cation-olefine complexes were investigated by LUCAS et al. [3]. They measured the distribution ratios of olefines between silver salt solution and organic solvent, and determined the formation constants of these complexes. HOSOYA and NAGAKURA found a new absorption band at 220 ~ 230 mμ for the cyclohexene-silver cation system and showed theoretically that the corresponding transition has CT character to a considerable extent [4].

On the other hand, spectrophotometric studies on the CT interaction of the silver cation with heterocyclic amines have scarcely been carried out. PEARD and PFLAUM [5] measured ultraviolet and infrared spectra of various solutions containing Ag^+ and heterocyclic amines, but they could not recognize a change of the ultraviolet absorption spectra of unidentate amines like pyridine and its derivatives by complex formation with silver cation. Recently, MULLIKEN and PERSON [6] have given theoretical consideration to the CT interaction between the silver cation and pyridine, and have predicted that the CT band of this complex might appear at 225 mμ (5.51 eV). For the purpose of finding experimentally the predicted CT band, we undertook to study spectrophotometrically the silver cation-pyridine system. Furthermore, theoretical studies have been carried out on the electronic structure of the complex.

II. Experimental

Silver perchlorate of G. R. grade was purified by recrystallization from perchloric acid. Acetonitrile used as a solvent was refluxed first for 10 h with calciumhydride, next for half an hour with phosphoric oxide and then again with calciumhydride and was finally distilled. Ethanol was purified by the usual method [7]. Pyridine and the apliphatic amines were used after distillation.

Near ultraviolet absorption spectra were measured with a Cary recording spectrophotometer model 14 M. Vacuum ultraviolet absorption spectra below 200 mμ were measured with a vacuum ultraviolet spectrophotometer constructed in our laboratory [8].

Silver salts are known to form two kinds of coordination compounds with pyridine; namely, 1:1 and 1:2 complexes. In solution these two complexes exist in equilibrium and the 1:2 complex precipitates as white crystals by the addition of an excess amount of pyridine. We measured the spectra of the complexes under the conditions that the silver cation exists in excess in the solution. Solvents used in the present study are acetonitrile, ethanol and water. The acetonitrile solution of silver perchlorate is more transparent than the ethanol or aqueous solution. Therefore the measurements were carried out mainly with the acetonitrile solutions.

Experimental Results and Determination of Thermal Constants

The near and vacuum ultraviolet absorption spectra of acetonitrile solutions containing various amounts of the silver cation ($10^{-3} \sim 10^{-2}$ M) and a fixed concentration of pyridine (4.57×10^{-3} M) are shown in Fig. 1a. They have a band at 250 mμ; its position is almost equal to that of the absorption band of free pyridine, but its intensity increases as the concentration of the silver cation becomes higher*.

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* This increase in the intensity might be thought to be due to the effect of the ionic strength of the solution. In order to check this point, the spectrum of a solution containing sodium perchlorate instead of silver perchlorate, and pyridine was measured. The result showed that the intensity of the band near 250 mμ is equal to that of free pyridine and the effect of the ionic strength is negligibly small.

As is seen from Fig. 1, absorption intensity near 210 mμ increases with increasing concentration of the silver cation. This increment in the absorption intensity may be interpreted from two different viewpoints. One of them is that

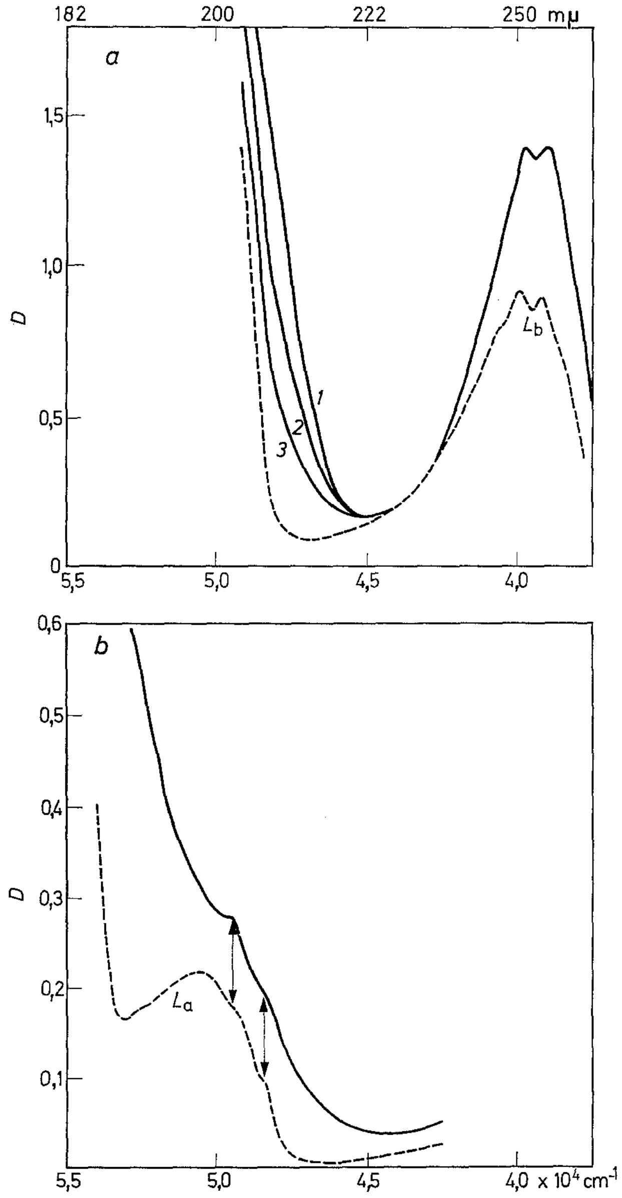

Fig. 1. The near and vacuum ultraviolet absorption spectra of $AgClO_4$ plus pyridine in CH_3CN. The dashed lines show the absorption spectrum of pyridine. a) Solutions 1, 2 and 3 contain the same amount of pyridine (4.57×10^{-3} M) and different amounts of $AgClO_4$ (1 : 3.70×10^{-2} M; 2 : 1.21×10^{-2} M; 3 : 4.48×10^{-4} M). b) The concentrations of pyridine and $AgClO_4$ are 3.02×10^{-3} M and 1.23×10^{-2} M, respectively

a new band characteristic of the 1:1 complex formation appears near 210 mμ*. The other is that the L_a band of pyridine at 196 mμ shifts to longer wavelengths by the complex formation. In order to check the latter possibility, we measured the vacuum ultraviolet spectrum of the Ag^+-pyridine system in acetonitrile with the result given in Fig. 1b. This figure shows that the L_a band of pyridine does not show an observable shift by the interaction with the silver cation. Therefore the latter of the above-mentioned two interpretations may safely be disregarded.

In the solution containing the silver cation and pyridine, there exist the following two equilibria:

$$\mathrm{Ag^+ + Py = (Ag\,Py)^+} \qquad k_1 = \frac{\mathrm{(Ag\,Py)^+}}{\mathrm{(Ag^+)\,(Py)}} \tag{1}$$

$$\mathrm{(Ag\,Py)^+} + py = \mathrm{(Ag\,Py_2)^+} \qquad k_2 = \frac{\mathrm{(Ag\,Py_2)^+}}{\mathrm{(Ag\,Py)^+\,(Py)}}\,. \tag{2}$$

Since absorption measurements were carried out with solutions containing an excess amount of silver cation, we took account of only (1) and disregarded (2). We tried to explain quantitatively the absorption intensity increment in the 210 mμ region on the basis of equilibrium 1. In the region near 210 mμ, Ag^+, pyridine and $(Ag\,Py)^+$ all show absorption. Let us designate the initial concentrations of Py and Ag^+ as a and b, respectively, the molar extinction coefficients of Py, Ag^+ and $(Ag\,Py)^+$, respectively, as ε_a, ε_b and ε_c, and the concentration of $(Ag\,Py)^+$ as x. The observed absorbance d can be given as follows:

$$\begin{aligned} d &= \varepsilon_a(a-x) + \varepsilon_b(b-x) + \varepsilon_c\,x = (\varepsilon_a\,a + \varepsilon_b\,b) + (\varepsilon_c - \varepsilon_a - \varepsilon_b)\,x \\ &= d_0 + (\varepsilon_c - \varepsilon_a - \varepsilon_b)\,x \end{aligned} \tag{3}$$

and

$$k_1 = \frac{x}{(a-x)\,(b-x)}\,. \tag{4}$$

We actually measured the spectra of twelve solutions of different concentrations and could evaluate ε_c and k_1 from various sets of observed d values by the aid of Eqs. (3) and (4). The ε_c and k_1 values evaluated from various sets were found to be constant. The equilibrium constant k_1 was finally determined to be 108 $(\mathrm{mole/l})^{-1}$ at 26 °C. This value is well coincident with that determined by Bruehlman and Verhoek [9] from polarography experiment at 25 °C.

Fig. 2 shows the relation of $(\varepsilon_c - \varepsilon_a - \varepsilon_b)$ and ε_c versus wavelengths. On the assumption that the absorption spectrum of the complex in the 210 mμ region is the superposition of rather unaltered bands of the components and a new band, $\varepsilon_c - \varepsilon_a - \varepsilon_b$ may be regarded as the extinction coefficient of the new band characteristic of the CT interaction between the silver cation and pyridine. The curves show that the maximum of the CT band appears at 207.5 mμ and the peak molar extinction coefficient is $3.3 \sim 3.5 \times 10^3$.

Similar measurements were carried out at 0 °C with the results given in Fig. 3. Fig. 3 is a diagram of $D - D_0 = (d - d_0)l$ (l is the length of the optical path.) used for the analysis of the observed spectra. This figure, in which results measured at 26 °C are also given for the purpose of comparison, shows that the absorption

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* In the ethanol solution of the silver-pyridine complex, a new band appears at about 220 mμ more clearly than in the acetonitrile solution.

intensity in the 210 mμ region measured at 0 °C is greater than that at 26 °C. This intensity change with temperature was found to be reversible. From the analysis of the results at 0 °C, the equilibrium constant was determined to be 226 (mole/l)$^{-1}$. The temperature dependence of the equilibrium constant makes it possible to evaluate the enthalpy and entropy changes due to complex formation. The result is as follows:

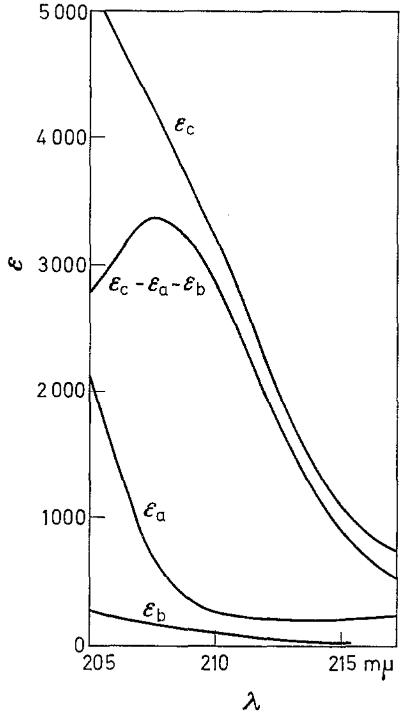

Fig. 2. The molar extinction coefficient-wavelength curves; ε_a: molar extinction coefficient for pyridine, ε_b: molar extinction coefficient for silver cation, ε_c: molar extinction coefficient for pyridine-silver cation complex

$$\Delta H = -4.5 \text{ kcal/mole}\ , \qquad \Delta S = -5.8 \text{ e.u.}$$

These values are in good agreement with those obtained by the aid of polarography [9]: namely,

$$\Delta H = -4.6 \text{ kcal/mole}\ , \qquad \Delta S = -6.2 \text{ e.u.}$$

III. Theoretical

The new absorption band at 210 mμ may be regarded as the CT band from the pyridine molecule to the silver cation. In order to study this point theoretically, we carried out a calculation of the electronic structure of the pyridine-silver complex.

Since the geometrical structure of this complex has not yet been determined, we assumed the bond length between the silver cation and nitrogen atom of pyridine as 2.40 Å from the distances between the metal cation and the ligands in

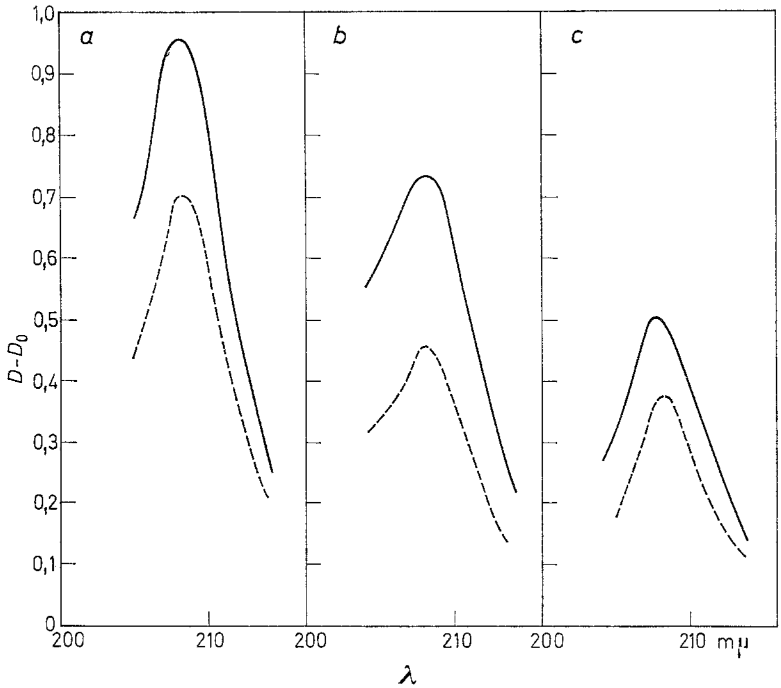

Fig. 3. The $D - D_0$-wavelength curves at 0 and 26 °C. ——— at 0 °C; ------ at 26 °C. a) $[Ag^+] = 1.232 \times 10^{-2}$ M, $[Py] = 5.68 \times 10^{-3}$ M; b) $[Ag^+] = 6.16 \times 10^{-3}$ M, $[Py] = 5.68 \times 10^{-3}$ M; c) $[Ag^+] = 8.21 \times 10^{-3}$ M, $[Py] = 3.02 \times 10^{-3}$ M

such complexes as Co^{2+}-pyridine ($r_{Co-N} = 2.12$ Å), Cu^{2+}-pyridine ($r_{Cu-N} = 2.02$ Å) [10] and Ag^+-dioxane ($r_{Ag-O} = 2.46$ Å) [11] which have hitherto been reported. In actual calculation, we took 6 π electrons and 2 nonbonding electrons of the nitrogen atom for pyridine and 10 d electrons for the silver cation and adopted the method of localized orbital model (molecules in molecule method or method of composite system). That is to say, we considered the configurational interaction among the ground, CT and locally-excited configurations which are brought about by putting 18 electrons into the appropriate orbitals of the components pyridine and silver cation. The procedure is similar to that used for the calculations of olefine-silver cation complexes [4].

The π-electron molecular orbitals of pyridine calculated by NISHIMOTO and MATAGA [12] were used. Now let us represent the six π orbitals and the nonbonding orbital of pyridine by 1 (−14.318 eV), 2 (−11.435 eV), 3 (−10.763 eV), 4 (−1.577 eV), 5 (−1.290 eV), 6 (1.638 eV) and n, and the five d orbitals of silver cation by d_1, d_2, d_3, d_4 and d_5. The wave function of the ground configuration can be given by the following equation:

$$\left| 1\bar{1}2\bar{2}3\bar{3}n\bar{n}d_1\bar{d}_1d_2\bar{d}_2d_3\bar{d}_3d_4\bar{d}_4d_5\bar{d}_5 \right| .$$

In addition to the ground configuration, the locally excited configurations (LE) corresponding to 2 → 4, 3 → 5, 2 → 5 and 3 → 4 transitions in the pyridine molecule and $4d_i \rightarrow 5s$ transitions in the silver cation, the CT configurations corresponding to

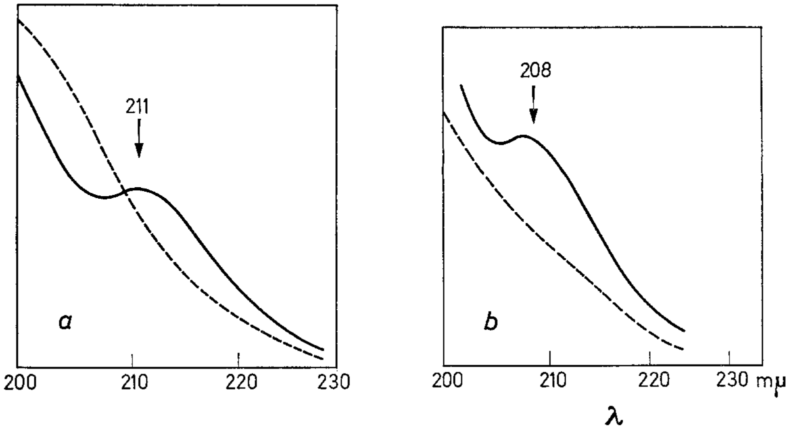

Fig. 4. The ultraviolet absorption spectra of acetonitrile solutions containing some aliphatic amines and silver perchlorate. - - - - - - Amine [a) diethylamine, b) n-propylamine]; ——— complex

$n \rightarrow 5s, n \rightarrow 5p_i, 2 \rightarrow 5p_i, 2 \rightarrow 5s, 3 \rightarrow 5p_i$ transitions, and the back CT configurations corresponding to $d_{zx} \rightarrow 4$, $d_{xy} \rightarrow 5$, $d_{zx} \rightarrow 5$, $d_{xy} \rightarrow 4$, $d_{z^2} \rightarrow 4$, $d_{yz} \rightarrow 5$ and $d_{x^2-y^2} \rightarrow 4$ transitions were taken into account.

In calculating the energies of the CT and back CT configurations, we must consider the solvation energy of the silver cation in acetonitrile. This is because the difference Δ in the solvation energy between the ground configuration and the CT configuration may be considerably large. For the purpose of estimating the Δ value, we measured the spectra of the systems containing the silver cation as electron acceptor and various aliphatic amines as electron donor. It may be expected that the Δ value can roughly be estimated from the transition energies of CT bands observed with these systems if the ionization potentials of the donors are known.

In actuality, triethylamine, diisopropylamine, diethylamine, isopropylamine, n-propylamine and *tert*-butylamine were used as electron donor. The results of the Ag^+-diethylamine and Ag^+-n-propylamine systems taken as examples are shown in Fig. 4. As is clearly seen from this figure, these systems exhibit new absorption bands due to the CT interaction between electron donor and acceptor. The transition energies ν_{CT} corresponding to the peaks of these bands are shown in the second column of Tab. 1. By varying the concentration of the silver cation and amines, it became clear that the new peaks are due to the [Ag Amine]$^+$ complex, and the

Table 1. *The absorption spectra of silver-amine complexes in acetonitrile and the solvation energy of the silver cation.* ($c = -0.30$)

amine	ν_{CT}	I_n [11]	β	Δ
$N(C_2H_5)_3$	5.74 eV	7.50 eV	−0.456 eV	5.67 eV
$NH(iso\text{-}C_3H_7)_2$	5.85 eV	7.73 eV	−0.463 eV	5.55 eV
$NH(C_2H_5)_2$	5.88 eV	8.01 eV	−0.471 eV	5.26 eV
$NH_2(t\text{-}C_4H_9)$	6.02 eV	8.64 eV	−0.494 eV	4.59 eV
$NH_2(iso\text{-}C_3H_7)$	5.96 eV	8.72 eV	−0.490 eV	4.79 eV
$NH_2(n\text{-}C_3H_7)$	5.96 eV	8.78 eV	−0.493 eV	4.65 eV

Table 2. *The matrix elements of the configuration interaction calculation*
[Symmetry a_1; $c = -0.30$ for $\beta(n, s)$, $\beta(n, p_z)$ and $\beta(d_{z}^{2}, n)$; $c = -0.8$ for the other β's]

Ground	0									
LE(2 → 4)	−0.886	6.79								
LE(3 → 5)	0.741	−0.380	6.54							
CT($n \to s$)	−0.721	0	0	$0.017 + \Delta$						
CT($n \to p_z$)	−0.810	0	0	0	$3.66 + \Delta$					
CT($2 \to p_x$)	−0.852	0.577	0	0	0	$8.22 + \Delta$				
LE($d_z^2 \to s$)	0	0	0	0.513	0	0	5.71			
BCT($d_{zx} \to 4$)	0.320	0.237	0	0	0	0	0	$11.22 - \Delta'$		
LE($d_{x^2-y^2} \to s$)	0	0	0	0	0	0	0	0	5.71	
BCT($d_{xy} \to 5$)	0	0	0	0	0	0	0	0	0	$12.09 - \Delta'$
	Symmetry b_1									
LE(3 → 4)	5.41									
LE(2 → 5)	0.806	6.61								
CT($3 \to p_x$)	0.770	0	$7.54 + \Delta$							
BCT($d_{zx} \to 5$)	0	0.237	0	$12.09 - \Delta'$						
LE($d_{yz} \to s$)	0	0	0	0	5.71					
CT($n \to p_y$)	0	0	0	0	0	$3.66 + \Delta$				
BCT($d_{xy} \to 4$)	0	0	0	0	0	0	$11.22 - \Delta'$			
	Symmetry b_2									
CT($2 \to s$)	$4.48 + \Delta$									
LE($d_{zx} \to s$)	0.237	5.71								
CT($n \to p_x$)	0	0	$3.66 + \Delta$							
CT($2 \to p_z$)	0	0	0	$8.22 + \Delta$						
CT($3 \to p_y$)	0	0	0	0	$7.54 + \Delta$					
BCT($d_z^2 \to 4$)	0	0	0	0	0	$11.22 - \Delta'$				
BCT($d_{yz} \to 5$)	0	0	0	0	0	0	$12.09 - \Delta'$			
BCT($d_{x^2-y^2} \to 4$)	0	0	0	0	0	0	0	$11.22 - \Delta'$		

[Ag Amine$_2$]$^+$ complex has in this region a tail of an absorption band with the maximum < 200 mμ. The details of this point are described in the Appendix.

Now let us try to evaluate the Δ value by combining the observed ν_{CT} given in Tab. 1 with the following formulae derived easily by considering the interaction between the ground and the CT configurations on the assumption of neglecting the overlap integral:

$$\nu_{CT} = \sqrt{E_{CT}^2 + 8\beta^2} \tag{5}$$

$$E_{CT} = I_n - A_{Ag} + \Delta \, . \tag{6}$$

Furthermore, the core resonance integral β was calculated by the following equation [15]:

$$\beta = cS(I_n + I_{\mathrm{Ag}})/2\ , \tag{7}$$

where c is a parameter and several values from -0.22 to -0.48 were taken in the present calculation. In Eq. (6), I_n and A_{Ag} are the ionization potential of the lone pair electron of amine [13] and the electron affinity of the silver cation (7.57 eV), respectively. S in Eq. (7) is the overlap integral between the appropriate orbitals belonging to the nitrogen atom and the silver cation. On the assumption that the distance between Ag^+ and N is 2.40 Å in all the complexes, we evaluated $S(n, 5s)$ as 0.20 [14]. By introducing the observed ν_{CT} values into Eq. (5), we can evaluate Δ's for the complexes. They depend on the selected value of the parameter c. The values for $c = -0.3$ are listed in Tab. 1.

According to Tab. 1, the Δ values increase gradually in the order of primary amine < secondary amine < tertiary amine. For the case of pyridine, it may be reasonable to take the value for $\mathrm{N(C_2H_5)_3}$, for example $\Delta = 5.67$ eV for $c = -0.3$, because these two molecules are similar to each other in the point that they have no hydrogen atom directly connected to nitrogen. The energies of CT configurations given in Tab. 2 were evaluated by introducing the observed or calculated ionization potentials and electron affinities of appropriate orbitals into Eq. (6).

The matrix elements necessary for the configuration interaction calculation are given in Tab. 2, being classified into the irreducible representations of C_{2v}. The notation BCT denotes a back CT configuration. Δ' in Tab. 2, the stabilization energy due to the solvation for the back CT configuration was tentatively evaluated as $\frac{3}{4}\Delta$ [4]. In the evaluation of the matrix elements given in Tab. 2, the zero-differential overlap approximation was adopted [16] and two-center Coulomb repulsion integrals of the $(pp \mid qq)$ type were evaluated by the aid of the uniformly charged sphere model [16]. In the present calculation, the core resonance integral β was estimated by Eq. (7), the parameter c being taken to be different for σ and π type interactions. That is to say, the value of c was assumed to be changeable in the range from -0.22 to -0.48 for $\beta(n, 5s)$, $\beta(n, 5p_z)$ and $\beta(n, d_{z^2})$, and to be -0.8 for the other β values. The smaller $|\ c\ |$ value for σ type interactions were adopted for the $n, 5s$; $n, 5p_z$; $n, d_z{}^2$ combinations, because the overlap integrals for these combinations are generally overestimated so far as we used the single Slater AO's.

IV. Results and Discussion

The calculated energies and wave functions for the ground and lower excited states are shown in Tab. 3 for the case of $c = -0.3$ for σ type interaction β and $\Delta = 5.67$ eV. This Δ value seems to be reasonable or at least not to be absurd, in view of the fact that the solvation energy of the silver cation in aqueous solution amounts to 5.56 eV [17]. The transition energies and oscillator strengths calculated from the state energies and wave functions shown in Tab. 3 are given in Tab. 4. In this table, the observed values are also shown for the purpose of comparison. The depenpence of the transition energies upon c are graphically shown in Fig. 5.

The present calculation shows that the sum of contributions of the CT configurations to the ground state amounts to 2% and brings about the energy stabilization of about 9 kcal/mole. In comparison with the observed stabilization energy

Table 3. *The calculated energies and wave functions of the lower excited states of the pyridine-silver cation complex* [Δ = 5.67 eV., $c = -0.30$ for $\beta(n, s)$, $\beta(n, p_z)$ *and* $\beta(d_{z^2}, n)$; $c = -0.8$ *for the other* β's]

symmetry a_1

	ground	CT($n \rightarrow s$)	LE($d_{z^2} \rightarrow s$)	LE($2 \rightarrow 4$)	LE($3 \rightarrow 5$)	CT($n \rightarrow p_z$)	BCT($d_{zx} \rightarrow 4$)	energy (eV)	observed
Ψ_0^A =	0.976	+0.117	−0.010	+0.112	−0.098	+0.081	−0.046	W_0^A = −0.39	−0.20
Ψ_1^A =	0.079	−0.684	+0.723	+0.037	−0.034	+0.016	−0.020	W_1^A = 5.23	5.77
Ψ_2^A =	0.001	−0.040	−0.040	+0.627	+0.750	−0.000	−0.198	W_2^A = 6.22	6.11
Ψ_3^A =	−0.060	+0.713	+0.688	−0.032	+0.110	−0.016	+0.037	W_3^A = 6.24	

symmetry b_1

	LE($3 \rightarrow 4$)	LE($2 \rightarrow 5$)	BCT($d_{zx} \rightarrow 5$)	CT($3 \rightarrow p_x$)	energy (eV)	observed
Ψ_1^B =	0.894	−0.439	+0.036	−0.083	W_1^B = 4.94	4.70
Ψ_2^B =	0.432	+0.870	−0.231	−0.053	W_2^B = 6.94	

of 4.5 kcal/mole, the calculated value seems rather too large. However, the observed stabilization energy includes the contributions of the steric repulsion, van der Waals attraction, solvation energy change and so on, besides of the CT force. In view of the fact that the solvation energy generally exerts a great effect upon the stabilization energy observed for the system in polar solvent, it may be

Table 4. *The calculated and observed transition energies and oscillator strengths*

Transition	Transition energy (eV)		Oscillator strength	
	cacld.	obsd.	cacld.	obsd.
$W_1^B \leftarrow W_0^A$	5.33	4.90	0.09	0.05
$W_1^A \leftarrow W_0^A$	5.62	5.97	0.04	0.03
$W_2^A \leftarrow W_0^A$	6.61	6.31	0.16	—
$W_3^A \leftarrow W_0^A$	6.63		0.05	—

meaningless to compare directly the calculated stabilization energy due to CT interaction with the observed one.

It is revealed from the calculated wave functions that the lowest excited singlet state, W_1^B, has the character of local excitation within pyridine and the $W_1^B \leftarrow W_0^A$ transition band corresponds to the L_b band of pyridine. This theoretical conclusion is completely reasonable from the similarity in the intensity and shape between the observed 250 mμ band of the complex and that of pyridine itself. The calculated transition energy is greater by 0.43 eV than the observed one.

The second lowest excited singlet state, W_1^A, is mainly composed of CT($n \rightarrow s$) and LE($d_{z^2} \rightarrow s$) configurations. The observed 210 mμ band may safely be assigned to the $W_1^A \leftarrow W_0^A$ transition from the comparison of the calculated and observed values concerning transition energies and oscillator strengths. The third longest wavelength band of the complex which appears at 180 mμ corresponds to the

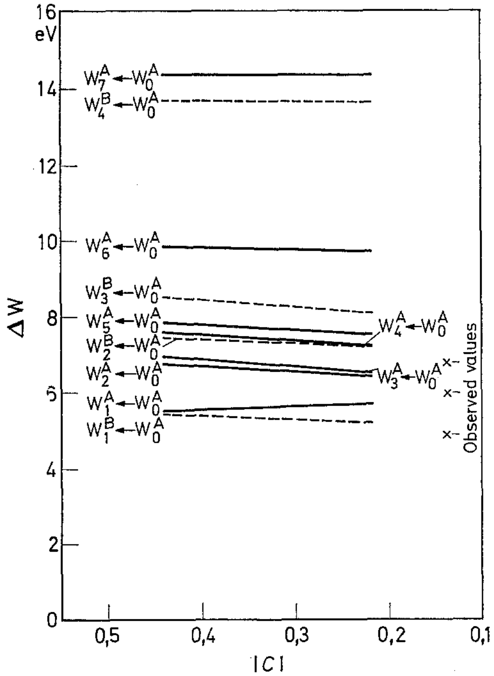

Fig. 5. The dependence of the transition energies ΔW (eV) upon c for the σ type interaction. - - - - - - for b_1 symmetry states, ——— for a_1 symmetry states

overlapped transitions of $W_2^A \leftarrow W_0^A$ and $W_3^A \leftarrow W_0^A$. From the wave function of the W_2^A state given in Tab. 3, the $W_2^A \leftarrow W_0^A$ transition is known to have the character of the local excitation (L_a band transition) within the pyridine. On the other hand, the $W_3^A \leftarrow W_0^A$ transition may be regarded as a CT($n \rightarrow s$) transition.

Appendix

We will discuss the absorption peaks observed with silver cation-aliphatic amine complexes, taking the Ag^+–$NH(C_2H_5)_2$ system as an example. As for this system, the equilibrium constants for the 1:1 and 1:2 complex formations were determined to be $\log k_1 = 2.98$ and $\log k_2 = 3.22$, respectively, by the aid of electrometric measurement [18]. Considering both equilibria, the concentrations of free Ag^+, free $NH(C_2H_5)_2$, $[Ag\,NH(C_2H_5)_2]^+$ and $[Ag\,(NH(C_2H_5)_2)_2]^+$ were evaluated for several solutions with different initial concentrations of $AgClO_4$ and $NH(C_2H_5)_2$. From the comparison of the evaluated concentrations of $[Ag\,NH(C_2H_5)_2]^+$ and $[Ag\,(NH(C_2H_5)_2)_2]^+$ with the observed absorption intensity in the 200—220 mμ region, it was derived that the $[Ag\,NH(C_2H_5)_2]^+$ complex has an absorption maximum at 211 mμ and the $[Ag\,(NH(C_2H_5)_2)_2]^+$ complex shows in this region only an tail of the absorption with the maximum below 200 mμ. Since the equilibrium constants for the pyridine-Ag^+ system are smaller than those of Ag^+–$NH(C_2H_5)_2$ system, under the present experimental conditions, the existence of the 1:2 complex can safely be disregarded.

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