J. Phys. Chem. A **2001,** *105,* 5823−5828

ESR and Optical Properties of Copper Atoms in γ-Irradiated Organic Solutions at 77 K

Yoko Miyatake

Department of Systems and Human Science, Graduate School of Engineering Science, Osaka University,
Toyonaka Osaka, 560-8531 Japan

Hirotomo Hase* and Takeshi Saito

Research Reactor Institute, Kyoto University, Kumatori-cho, Osaka, 590-0494 Japan

Masayoshi Onishi

Department of Applied Chemistry, Faculty of Engineering, Nagasaki University,
Bunkyo-cho, Nagasaki, 852-8131 Japan

Yusuke Tajima and Mikio Hoshino

The Institute of Physical and Chemical Research, Wako-si, Saitama, 351-0198 Japan

Received: January 23, 2001; In Final Form: March 28, 2001

EtOH and MTHF solutions containing Cu^+ ions are γ-irradiated at 77 K. ESR spectra are attributed, for the first time, to Cu^0 that is produced radiation-chemically by reducing Cu^+ ions in the solutions at 77 K. A large delocalization of the unpaired spin density of Cu^0 onto ligands is deduced. No evidence for formation of the dimer cation of Cu^0 has been obtained. This is contrary to the case of Ag^0 produced in the solutions containing Ag^+ ions. The NUV absorption spectrum of Cu^0 is decomposed into five Gaussian bands that are attributed to two types of exciplexes formed between excited Cu^0 and ligands: one associates with Cu^+ ions as well as solvent molecules, the other consists mainly of solvent molecules. The exciplexes are supposed to be transferred to relaxed states followed by two emission bands, one of which is common to both solvents and the other is characteristic of the solvents. The absorption band at 255 nm is ascribed to a photoionization spectrum of Cu^0.

Introduction

Metal monocations, as denoted hereafter by M^+, are reduced in the irradiated solutions to form the metal atoms (M^0) by the following reactions:

$$S \rightsquigarrow S^+ + e^- \qquad (1)$$

$$e^- + M^+ \rightarrow M^0 \qquad (2)$$

where S and e^- stand for a solvent molecule and the electron generated by ionization of S, respectively. M^0 thus produced and trapped in solutions at low temperatures interacts with ligands and neighboring ions, so that its spectroscopic characteristics differ prominently from those in gas phase or solid rare gas matrixes.

Most previous studies of 1B metal atoms; i.e., Cu, Ag, and Au were reported on ESR[1−5] and optical properties[6−9] in rare gas matrixes where interactions of the atoms with the matrixes are certainly evidenced by such observations as splitting of absorption lines, ESR line broadening, and the excitation wavelength dependence of emission spectra with a large Stokes shift and so on.

Early studies of Ag atoms (Ag^0) produced radiation-chemically in aqueous and organic solutions were carried out by means of ESR at 77[10−12] and 4 K[13−16] and pulse radiolysis at an ambient temperature.[17] It was found that Ag^0, when first formed in ice at 4 K, is trapped in the same solvation shell that solvates the parent Ag^+ by four water molecules. On annealing to 77 K, Ag^0 is partly desolvated to give rise to a reduction of the isotropic hyperfine coupling, indicating a new solvation configuration in which one of the four water molecules reorients one hydrogen toward Ag^0.[14] The dimer cation, $Ag_2{}^+$ was found to form by the tunneling reaction between Ag^0 and Ag^+ ion at 77 K.[16−19]

The optical properties of Ag^0 were previously studied in 2-methyltetrahydrofuran (MTHF), ethanol (EtOH), and aqueous solutions.[20−22] The absorption spectra of Ag^0 in EtOH and MTHF solutions consisted of the UV and NUV bands, each of which was composed of at least two bands. These bands were ascribed to Ag^0 originating from Ag^+ ions trapped in the cavities of different degrees of solvation. Excitation with light of wavelengths in the NUV band at 400 nm gave no emission. This was interpreted as due to photoionization of Ag^0 of a reduced ionization potential. An intense emission band was observed at 590 nm by excitation with light of wavelengths in the other NUV band at 370 nm as well as two UV bands at 310 and 330 nm and was attributed to the emission from a relaxed state of the exciplex that was formed between excited Ag^0 and surrounding solvent molecules. Excitation with light of wavelengths in the two UV bands also led to an emission band at 510 nm. This band was ascribed to another exciplex formed

---

* Corresponding author. Fax: +81 724 51 2472. E-mail: hase@HL.rri.kyoto-u.ac.jp

10.1021/jp010281c CCC: \$20.00

TABLE 1: ESR Magnetic Fields and Line widths for Cu^0 Produced Radiation-chemically in EtOH and MTHF Solutions at 77 K[a]

		ESR Transition							
		$(1, 1) \Leftrightarrow (2, 2)$		$(1, 0) \Leftrightarrow (2, 1)$		$(1, -1) \Leftrightarrow (2, 0)$		$(2, -2) \Leftrightarrow (2, -1)$	
solvent	isotope	H^b	$\Delta H_{pp}{}^c$, mT	H^b	$\Delta H_{pp}{}^c$, mT	H^b	$\Delta H_{pp}{}^c$, mT	H^b	$\Delta H_{pp}{}^c$, mT
EtOH	^{65}Cu	133.8 $(63.23)^d$	8.333 (11.5)	202.3	8.319	268.1	$-^e$	481.8 (511.98)	$-^f$ (6.9)
	^{63}Cu	149.3 (86.23)	8.941 (11.6)	217.6	8.647	278.6	−	475.0 (501.45)	− (6.7)
MTHF	^{65}Cu	139.6	7.963	207.8	10.418	268.7	−	474.6	−
	^{63}Cu	156.6	8.388	224.0	9.839	281.1	−	469.1	−

[a] The microwave frequency used for EtOH and MTHF solutions is 9.463 GHz. [b] ESR magnetic fields. [c] Line widths between peak positions of the first derivative lines. [d] The values in parentheses are reported by Zhitnikov and Kolesnikov.[4] The microwave frequency used by them was 9.459 GHz. [e] ESR lines due to two isotopes are partly masked by the spectra due to solvent radicals so that the line widths cannot be determined. [f] ESR lines due to two isotopes are situated too closely for the line widths to be determined.

between excited Ag^0, Ag^+, and solvent molecules. Excitation of the dimer cation, $Ag_2{}^+$ which absorbs light of wavelength shorter than 290 nm also gave the emission band at 510 nm.

Recently Hase and co-workers[23] have initially reported ESR characteristics of Au atoms (Au^0) produced radiation-chemically in MTHF and 10 M NaOH aqueous solutions at 77 K. The results show that the hyperfine splittings of Au^0 are smaller than those of the free Au atoms, indicating a dominant van der Waals interaction occurring between Au^0 and ligands.

Zhitnikov et al.[4] reported ESR characteristics of Cu atoms (Cu^0) that are deposited directly in various matrixes at 77 K. However, there has been no report on ESR and optical properties of Cu^0 produced radiation-chemically in organic solutions at 77 K so far, and a comparison of ESR and optical data obtained for Cu^0 in this study with those for other 1B atoms may be of interest.

Experimental Section

Reagent grade CuCl and EtOH were used as supplied. Reagent grade MTHF was distilled fractionally, and no optical absorption due to its chemical additives was observed in the region of wavelengths longer than 230 nm. EtOH and MTHF (10 mL each) first were bubbled with N_2 gas sufficiently in order to remove oxygen molecules in the solvents. CuCl was then added. The solute was dissolved in the solvents after adding hydrochloric acid (35% in content) of 0.2 and 0.05 mL for the solute concentration of 10^{-1}, and 10^{-2} M, respectively. The solutions were transferred into optical cells of 1 mm in the light path length for optical absorption measurements and ESR tubes of 4 mm in the inner diameter for emission and ESR measurements, and then immersed into liquid nitrogen.

Samples were γ-irradiated at 77 K at a dose rate of 25 kGy h^{-1}. Total dose was typically 25 kGy. After γ-irradiation, the samples were illuminated with light of wavelengths longer than 600 nm from a 500 W halogen lamp through an interference filter (Toshiba O-54) in order to photobleach trapped electrons. X-band ESR measurements were carried out at 73 K by bubbling helium gas into liquid nitrogen in an ESR Dewar to avoid bubbling of liquid nitrogen around the center part of the ESR cavity. Emission and excitation spectra were measured at 73 K with use of a Hitachi fluorescence spectrophotometer (model F-4500). A color filter of a cutoff wavelength of 440 nm was typically used for the removal of scattered excitation light in the measurements.

Results and Discussion

ESR Properties. EtOH and MTHF solutions containing Cu^+ ions of 10^{-1} M were γ-irradiated at 77 K and measured at 73 K. The ESR spectra observed are shown in Figures 1A and B. The spectra consist of four groups; two resolved pairs of lines at about 140 and 210 mT, two lines appearing on the edge of the large signal due to solvent radicals at about 300 mT and a poorly resolved doublet line appearing at about 470 mT. We ascribe the spectra to Cu^0 produced radiation-chemically in the solutions. The ESR magnetic fields and line widths of the resolved lines due to Cu^0 are listed in Table 1 where the values reported by Zhitnikov et al[4] are also listed for comparison. ESR spectra for dilute solutions containing Cu^+ ions of 10^{-2} M showed no difference in their profiles in comparison with those for the concentrated solutions. There was no change in the spectral profiles for the sample stored for 140 h in liquid nitrogen after irradiation. Furthermore, additional irradiation of the concentrated solutions with total dose as high as 100 kGy gave no difference in the spectral profiles except for a growth of the intensity of the total spectrum. Based on these results, we conclude that the dimer cation, $Cu_2{}^+$ is not formed in both of the solutions. This is in contrast to the case of Ag^0 in EtOH and MTHF solutions where ESR spectra are due to the dimer cation, $Ag_2{}^+$ was clearly observed as well as Ag^0 in γ-irradiated solutions at 77 K with dose as low as 33 kGy. In this case, the conversion from Ag^0 to $Ag_2{}^+$ amounted to about 30% for the sample stored in liquid nitrogen for 5 days.[19]

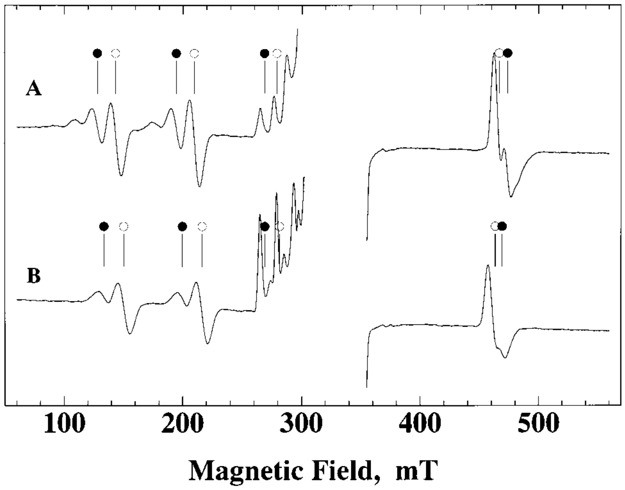

Figure 1. ESR spectra at 73 K of Cu^0 produced in γ-irradiated EtOH (A) and MTHF (B) solutions containing 10^{-1} M CuCl. Irradiation was carried out at 77 K and the dose was 25 kGy. ESR lines are identified as those due to ^{63}Cu (○) and ^{65}Cu (●).

Natural copper has two isotopes, ^{63}Cu (69%) and ^{65}Cu (31%), both of which have a nuclear spin of 3/2, and, in free state, have magnetic moments of 2.2233 and 2.3817 nuclear magnetons, respectively. Thus the ESR of Cu^0 exhibits duplicate hyperfine quartets, resulting in an eight-line spectrum. The energy levels of the hyperfine structure of the ground state, $2S_{1/2}$,

TABLE 2: Values of hfcc (*a*) and g_J of Cu^0 Produced in γ-Irradiated EtOH and MTHF Solutions Containing 10^{-1} M CuCl[a]

solvent	isotope	transition Set (F, m)[b]	*a*, GHz		$\delta(a)/a_{free}$[c], %		g_J	
EtOH	^{65}Cu	(1, 1) ⇔ (2, 2) (2, −2) ⇔ (2, −1)	6.3346	(8.046)[d]	−49.60	(−36.0)	2.0071	(2.0150)
		(1, 0) ⇔ (2, 1) (2, −2) ⇔ (2, −1)	6.3361		−49.59		2.0072	
	^{63}Cu	(1, 1) ⇔ (2, 2) (2, −2) ⇔ (2, −1)	5.9344	(7.503)	−49.42	(−36.1)	2.0024	(2.0181)
		(1, 0) ⇔ (2, 1) (2, −2) ⇔ (2, −1)	5.9338		−49.43		2.0023	
MTHF	^{65}Cu	(1, 1) ⇔ (2, 2) (2, −2) ⇔ (2, −1)	6.1534		−51.04		2.0223	
		(1, 0) ⇔ (2, 1) (2, −2) ⇔ (2, −1)	6.1494		−51.07		2.0219	
	^{63}Cu	(1, 1) ⇔ (2, 2) (2, −2) ⇔ (2, −1)	5.7246		−51.21		2.0093	
		(1, 0) ⇔ (2, 1) (2, −2) ⇔ (2, −1)	5.7237		−51.22		2.0092	

[a] The two sets of values were calculated from different pairs of lines in the same spectrum by using Breit−Rabi equations. The values of *a* and g_J are calculated by Eqs.(4), (5), and (7) using the data listed in Table 1. [b] *m* is the magnetic quantum number of the total moment of Cu atom $\mathbf{F} = \mathbf{J} + \mathbf{I}$. [c] $\delta(a) = a - a_{free}$, where a_{free} is the hyperfine coupling constant of free Cu atom: $a_{free}(^{65}Cu) = 12.568$ GHz and $a_{free}(^{63}Cu) = 11.733$ GHz. [d] The values in parentheses are reported by Zitnikov and Kolesnikov.[4]

are given by the following Breit-Rabi equation:[1,21]

$$W\left(\pm\frac{1}{2}, m\right) = -\frac{ah}{8} + g_I\beta Hm \pm \frac{ah}{2}(1 + mx + x^2)^{1/2} \quad (3)$$

where *a* is the hyperfine coupling constant; g_I is the gyromagnetic ratio of the nucleus; *m* is the magnetic quantum number of the total moment of the atom $\mathbf{F} = \mathbf{J} + \mathbf{I}$, where **J** and **I** are the moments of the electrons and of the nucleus, respectively; and $x = (g_J - g_I)\beta H/ha$, where g_J is the *g*-value of the electron shell. According to the Zeeman levels of the hyperfine structure of Cu^0,[4] four groups in ascending order of magnetic field correspond to transitions (F = 1, *m* = 1) → (2, 2), (1, 0) → (2, 1), (1, −1) → (2, 0), and (2, −2) → (2, −1), respectively. We infer that the lines due to transition (1, −1) → (2, 0) in the region of 300 mT are partly masked by the large signal that results from solvent radicals. As shown in Table 1, Zhitnikov et al.[4] reported that the lines corresponding to the first transition (1, 1) → (2, 2) appear at around 70 mT for Cu atoms which were directly deposited in EtOH at 77 K. In this study, however, no signal was observed at a magnetic field lower than 100 mT. We cannot pose any reasonable explanation for this discrepancy of the resonance magnetic field for the first transition.

One obtains from eq 3 the following relations for transitions (1, 1) → (2, 2), (1, 0) → (2, 1), (1, −1) → (2, 0), and (2, −2) → (2, −1), respectively:

$$h\nu = ha\left\{\frac{1}{2}(1 + x + x^2)^{(1/2)} + \frac{1}{2}(1 + x) + \frac{g_I\beta H}{ha}\right\} \quad (4)$$

$$h\nu = ha\left\{\frac{1}{2}(1 + x + x^2)^{(1/2)} + \frac{1}{2}(1 + x^2)^{(1/2)} + \frac{g_I\beta H}{ha}\right\} \quad (5)$$

$$h\nu = ha\left\{\frac{1}{2}(1 - x + x^2)^{(1/2)} + \frac{1}{2}(1 + x^2)^{(1/2)} + \frac{g_I\beta H}{ha}\right\} \quad (6)$$

$$h\nu = ha\left\{\frac{1}{2}(1 - x + x^2)^{(1/2)} - \frac{1}{2}(1 - x) + \frac{g_I\beta H}{ha}\right\} \quad (7)$$

The values of *a* and g_J can be calculated from different pairs of lines in the same spectrum. Thus, we obtain one set of the values from eqs 4 and 7, and the other from eqs 5 and 7. The two sets of values obtained for EtOH and MTHF solutions are listed in Table 2. We can obtain similar values of *a* and g_J from eqs 6 and 7, but the values are somewhat scattered owing to an uncertainty in determination of the magnetic fields of ESR lines due to transition (1, −1) → (2, 0). It is clear that the two sets of values in Table 2 are the same for each isotope in both solutions within the experimental errors. This is evidence that our assignment of the transitions is correct. Moreover, the ratio of the hyperfine coupling constants of the isotopes, $a(^{65}Cu)/a(^{63}Cu)$, obtained in this study is 1.07 for each transition, being in close agreement with the corresponding ratio of the free Cu atom. This provides another evidence for the validity of the present assignment. It is seen in Table 2 that the values of *a* reported by Zhitnikov et al. are larger than those in this study. This discrepancy results from their observation of the ESR transition (1, 1) → (2, 2) in extremely low magnetic field.

For comparison of the values of *a* of trapped and free Cu atoms, the relative shifts of the values of *a*, i.e., $\delta a/a_{free}$, where $\delta a = a - a_{free}$, are tabulated in Table 2. The very large negative shifts, i.e., −50% were deduced for both matrixes in this study. The values of the relative shifts reported previously for other 1B atoms produced radiation-chemically in organic glasses were about −13% for Ag^0 [10] and −16% for Au^0.[23] A comparison of the present result for Cu^0 with those for Ag^0 and Au^0 leads us to conclude that a larger delocalization of the spin density of Cu^0 onto ligands occurs.

As shown in Table 2, the values of g_J for Cu^0 in this study are always larger than that of the free Cu atoms: $g_{J,free} = 2.0025$.[4] It was previously reported that the *g* shift, $g_J - g_{J,free}$, is negative for Ag^0 [16] and positive for Au^0 [23] when these atoms are produced radiation-chemically in organic glasses at 77 K. The negative shift is expected to occur by an admixture of the wave function of the atom in its $2S_{1/2}$ state into the p orbital. The positive shift for Au^0 observed previously and for Cu^0 in this study is of interest. One possible explanation is that the free atom configuration of Cu, $3d^{10}4s^1$, admixes into $3d_{x^2-y^2}$ in some extent rather than 4p orbital for the systems studied.[5] Another possibility may be found in the applicability of the common Breit-Rabi treatment where the values of *a* and g_J are always evaluated from the equations derived for the case of isotropic forces of interaction between trapped atoms and ligands. It may be necessary to add an anisotropic interaction term to the Breit-Rabi equation for such cases that the spin density of trapped atoms does not delocalize uniformly onto ligands, but heterogeneously onto specific ligand molecules or

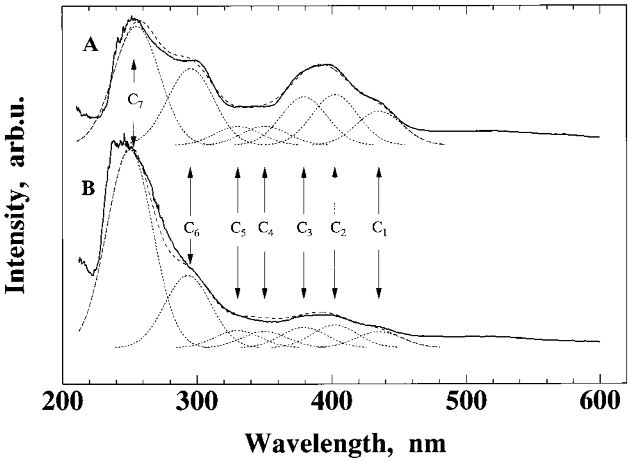

Figure 2. Optical absorption spectra at 77 K of Cu^0 produced in γ-irradiated EtOH solutions containing 10^{-1} M (A) and 10^{-2} M (B) CuCl. Irradiation was carried out at 77 K and the dose was 25 kGy. The ordinates of the spectra represent optical density in arbitrary units. The spectra are decomposed in seven Gaussian line- shapes with the same half-amplitude line width of 40 nm (dotted lines). Also shown are the envelopes (broken lines) of the Gaussian bands that have peaks at 435, 402, 379, 350, 330, 293, and 250 nm in the sequence from C_1 to C_7.

ions. In this context, the nature of interactions between the trapped atoms and ligands must be further investigated.

It is seen in Table 1 that the line width of $^{63}Cu^0$ is slightly greater than that of $^{65}Cu^0$ for each transition. The same tendency was previously reported for Cu atoms which were directly deposited in EtOH at 77 K.[4] However, these observations are contrary to the result reported by Shields[10] for $^{109}Ag^0$ and $^{107}Ag^0$: for transitions $(1, -1) \rightarrow (0, 0)$ and $(1, 0) \rightarrow (1, 1)$, the values of ($^{109}Ag^0$, $^{107}Ag^0$) are (13.1, 11.9) and (10.2, 9.1) for EtOH, and (17.2, 15.5) and (13.6, 12.2) for MTHF solutions at 77 K, respectively. It follows that the line width dependence on the hyperfine coupling constant of Cu isotopes is not as discernible as that for Ag isotopes, the latter being discussed by Shields.[10]

Optical Properties. The absorption spectra after irradiation were subtracted from those before irradiation. The difference spectra thus obtained for EtOH and MTHF solutions at 77 K are shown in Figures 2 and 3, respectively. The absorption spectra extending from 230 to 470 nm can be divided into two wavelength regions, i.e., the UV region of $230 < \lambda < 310$ nm and the NUV region of $320 < \lambda < 470$ nm. On the basis of the ESR evidence of formation of Cu^0 in this study, and also by the spectral analogy with the previous results of the optical absorption of Ag^0 in the solutions of Ag^+ ions at 77 K,[20] we attribute the difference spectra to absorption of Cu^0 formed in the solutions at 77 K.

In the previous study,[20] we reported the absorption spectra of Ag^0 in γ-irradiated EtOH and MTHF solutions containing Ag^+ ions at 77 K. We attempted to decompose the spectra of Ag^0 into several bands of Gaussian line-shapes with an arbitrary assumption of the line widths, and we interpreted successfully the optical properties of Ag^0 in the organic solutions. Now, considering the excitation spectra that show the dependence of the emission intensity upon excitation wavelengths, we assume as a matter of convenience that the absorption spectrum of Cu^0 for EtOH is decomposed into seven bands with Gaussian line-shapes with the same half amplitude line width of 40 nm. They are labeled by C_1(435 nm), C_2(402 nm), C_3(379 nm), C_4(350 nm) and C_5(330 nm) bands in the NUV region and C_6(293 nm) and C_7(250 nm) bands in the UV region. For MTHF solution, we assume that the C_1 band is not distinguished and that the C_2, C_3, C_4, and C_5 bands shift toward the red up to about 45 nm, i.e., C_2(445 nm), C_3(418 nm), C_4(367 nm), and C_5(335 nm), while C_6 and C_7 bands are nearly at the same wavelengths as those for EtOH, C_6(294 nm) and C_7(256 nm), as shown in Figure 3. The envelope spectra that are reproduced by the Gaussian bands from C_1 to C_7 are in good accordance with the observed spectra, as the case illustrated in Figures 2 and 3 demonstrates. In a solid Ne matrix, four absorption lines due to Cu atoms appear in the region of 304−315 nm.[25−27] In the gas phase, the corresponding two lines appear around 325 nm.[28] These lines are assigned to the transitions from Cu ($3d^{10}4s\ 2S_{1/2}$) to Cu*($3d^{10}4p\ 2P_{1/2}$) and Cu*($3d^{10}4p\ 2P_{3/2}$). Since the UV bands, i.e., C_6 and C_7 bands, observed in this study appear in the same wavelength region as in the solid Ne matrix, we infer that the bands are due to Cu^0 trapped in cavities which are as large as those in solid rare gases.

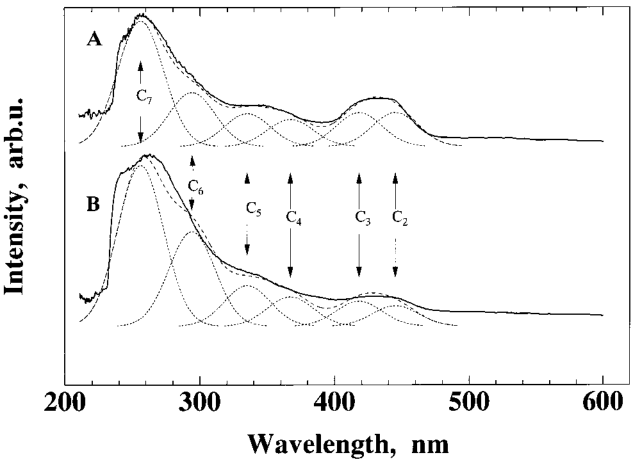

Figure 3. Optical absorption spectra at 77 K of Cu^0 produced in γ-irradiated MTHF solutions containing 10^{-1} M (A) and 10^{-2} M (B) CuCl. Irradiation was carried out at 77 K and the dose was 25 kGy. The ordinates of the spectra represent optical density in arbitrary units. The spectra are decomposed in six Gaussian line shapes with the same half-amplitude line width of 40 nm (dotted lines). Also shown are the envelopes (broken lines) of the Gaussian bands that have peaks at 445, 418, 367, 335, 294, and 256 nm in the sequence from C_2 to C_7.

The NUV bands in this study, bands from C_1 to C_5, are characteristic of Cu^0 in organic solutions at 77 K, because there is no absorption at any wavelengths longer than about 330 nm for Cu atoms in both gas phase and rare gas matrixes. As evidenced by ESR results in this study, interaction between Cu^0 and ligands is so strong even in the ground states that about 50% of the unpaired spin density of Cu^0 delocalizes onto ligands. An attractive, van der Waals interaction between Cu^0 and ligands may differ from site to site, perturbing the atomic energy levels in various degrees. Consequently, the absorption spectrum of Cu^0 may consist of several bands, being broadened and shifted depending on solvents in comparison with those in the gas phase and rare gas matrixes. In the same way as the case of Ag^0 in these solvents,[22] we ascribe the bands from C_1 to C_5 to exciplexes formed between excited Cu^0 and ligands. It follows from Figures 2 and 3 that the ratio of the optical densities of the C_2 and C_3 bands to those of the C_4 and C_5 bands for the concentrated Cu^+ solutions is greater than that for the dilute solutions. This suggests that the exciplexes responsible for the C_2 and C_3 bands associate in part with Cu^+ ions in their structures. Since the absorption energies of the C_1, C_4, and C_5 bands depend on solvents, we infer that the respective exciplexes consist mostly of solvent molecules.

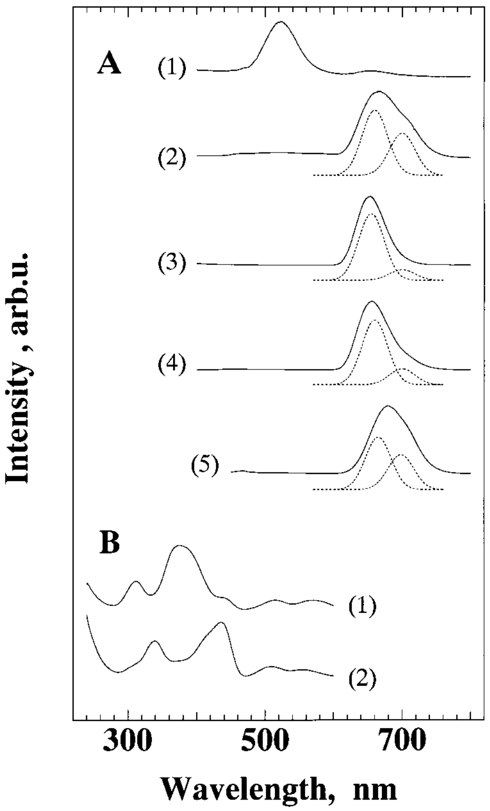

Figure 4. Emission (A) and excitation (B) spectra at 73 K of Cu^0 produced in γ-irradiated EtOH solution containing 10^{-1} M CuCl. Irradiation was carried out at 77 K and the dose was 25 kGy. In the emission spectra, the wavelengths of light used for excitation are (1) 250, (2) 330, (3) 380, (4) 400, and (5) 440 nm. The emission spectra are decomposed in two bands at 650 and 700 nm, as represented by dotted lines. The excitation spectra are recorded for the emission wavelengths of 650 (1) and 700 nm (2). All of the ordinates represent emission intensity in arbitrary units.

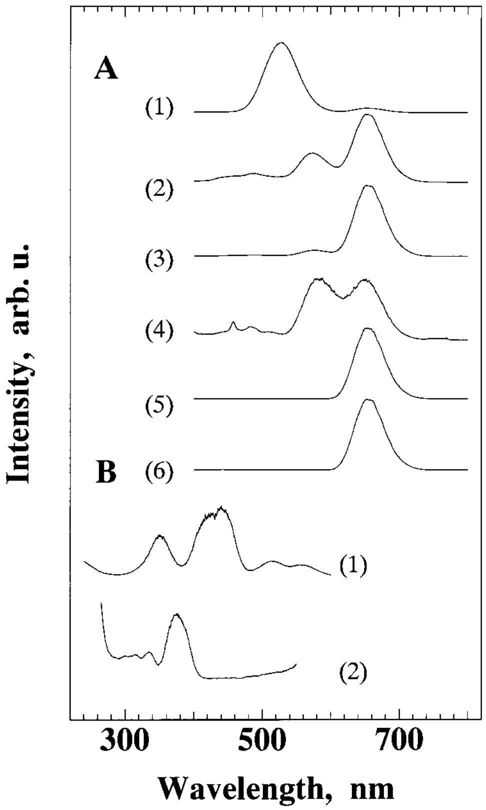

Figure 5. Emission (A) and excitation (B) spectra at 73 K of Cu^0 produced in γ-irradiated MTHF solution containing 10^{-1} M CuCl. Irradiation was carried out at 77 K and the dose was 25 kGy. In the emission spectra, the wavelengths of light used for excitation are (1) 250, (2) 310, (3) 340, (4) 380, (5) 420, and (6) 440 nm. The excitation spectra are recorded for the emission wavelengths of 660 (1) and 570 nm (2). All of the ordinates represent emission intensity in arbitrary units.

Exciting the irradiated samples with light of wavelengths in the region of their prominent absorption bands yielded emission spectra in the visible region, as shown in Figures 4A and 5A, respectively. Also shown are the respective excitation spectra in Figures 4B and 5B. The emission spectra for EtOH seem to consist of two bands with peaks at 650 and 700 nm. From the excitation spectra for the emission at 650 and 700 nm, it seems that the emission band at 650 nm originates mainly from excitation in the C_2, C_3, and C_6 bands of the absorption spectrum, whereas the band at 700 nm originates mainly from the C_1 and C_5 bands and partly from the C_4 band. The emission band at 650 nm accompanied by the emission band at 700 nm in a small extent was also observed for the excitation in the C_6 band. The emission spectra for MTHF exhibit two main bands at 570 and 660 nm. The excitation spectra monitored at these wavelengths imply that the emission band at 570 nm is mainly caused by excitation in the C_4 and C_5 bands, whereas the band at 660 nm is caused by excitation in the C_2 and C_3 bands. Both of the emission bands at 570 and 660 nm were observed by excitation in the C_6 band for MTHF.

It is noted that the emission band at around 650 nm with the half-amplitude line width of 50 nm is common to both EtOH and MTHF solutions, although the C_2 and C_3 bands that are responsible mainly for the emission band are red shifted for MTHF compared to the case of EtOH. On the basis of the previous discussion on the exciplexes of Ag^0,[22] we infer that the exciplex states of Cu^0 for the C_2 and C_3 bands are initially determined by interaction among Cu^+ ion, solvent molecules, and excited Cu^0, resulting in differences of the absorption energy. The exciplex state may be converted internally to emission states in which interaction between excited Cu^0 and the ligands is relaxed, being followed by the emission at around 650 nm. The other type of exciplex that gives rise to the C_1, C_4, and C_5 bands seems to consist mainly of excited Cu^0 and solvent molecules, and consequently the emission energy will be affected by the constituent molecules of solvent. The excitation spectra for the emission at 650 nm indicate that the emission state is also populated by the excited states of Cu^0 trapped in cavities that are as large as those in solid rare gas matrixes.

As represented in Figures 4A and 5A, excitation at 250 nm, which is the peak wavelength of the C_7 band, yielded an intense emission band at 520 nm for samples before irradiation, but its intensity was much reduced after irradiation. Since a broad absorption band extends from about 270 nm to the shorter wavelengths for samples before irradiation, we infer that Cu^+ ions associate with ligands to form an ion−ligand complex or ion pairs,[29,30] which are supposed to absorb light in the UV, and that the emission band at 520 nm is due to these complexes. The reduction in the intensity of the emission band at 520 nm after irradiation seems to be a consequence of the conversion of Cu^+ ions to Cu^0. We infer that Cu^0 trapped in cavities that are as large as those in solid rare gas matrixes does not emit fluorescence but is photoionized by absorbing light of wavelengths in the C_7 band. Thus the C_7 band is regarded as a photoionization spectrum. In the case of Ag^0 in EtOH, the band at 400 nm (3.48 eV) was identified as the photoionization spectrum. The value of the ionization potential of Ag^0 in EtOH is reduced by the solvation energy in comparison with the value in gas phase, being calculated to be 3.2 eV with the estimated value of the solvation energy of $-$ 4.6 eV.[22] The value is close to the energy of the band at 400 nm. Since the solvation energy of Cu^0 in EtOH is estimated to be $-$ 2.4 eV, the ionization potential of Cu^0 in EtOH would be 5.6 eV. This value is suggestive of the energy of the C_7 band.

Conclusion

Formation of Cu^0 in γ-irradiated EtOH and MTHF solutions containing Cu^+ ions was evidenced by ESR spectra at 73 K. The negative shift of the hyperfine coupling constant of Cu^0 indicated a large delocalization of the spin density of Cu^0 onto ligands. The dimer cation of Cu^0 has not been observed. This is contrary to the case of Ag^0 produced in the solutions containing Ag^+ ions. The NUV spectrum of Cu^0 was decomposed into five components and attributed to two different types of exciplex of Cu^0: one associates with Cu^+ ions as well as solvent molecules and the other consists mainly of solvent molecules. It was inferred that the exciplexes were transferred to relaxed states followed by two emission bands; one was at 650 nm, being common to both solvents, while the other was at 700 nm for EtOH and 570 nm for MTHF, respectively. The absorption band at 255 nm was ascribed to a photoionization spectrum of Cu^0.

Acknowledgment. Y. Miyatake acknowledges that this work has been carried out on her leave from Osaka University under the program of the Ministry of Education, Culture, Sports, Science and Technology, “Naichi Kenkyuin Seido”.

References and Notes

(1) Zhitnikov, R. A.; Kolesnikov, N. V.; Kosyakov, V. I. *Sov. Phys. JETP* **1963**, *16*, 839.

(2) Zhitnikov, R. A.; Kolesnikov, N. V.; Kosyakov, V. I. *Sov. Phys. JETP* **1963**, *17*, 815.

(3) Zhitnikov, R. A.; Kolesnikov, N. V. *Sov. Phys. JETP* **1964**, *19*, 65.

(4) Zhitnikov, R. A.; Kolesnikov, N. V. *Sov. Phys.-Solid State* **1965**, *6*, 2645.

(5) Kasai, P. H.; McLeod, D., Jr. *J. Chem. Phys.* **1971**, *55*, 1566.

(6) Schulze, W.; Kolb, D. M.; Gerischer, H. *J. Chem. Soc., Faraday Trans. 2* **1975**, *71*, 1763.

(7) Kolb, D. M.; Leutoloff, D. *Chem. Phys. Lett*. **1978**, *55*, 264.

(8) Mitchell, S. A.; Farrell, J.; Kenny-Wallace, G. A.; Ozin, G. A. *J. Am. Chem. Soc*, **1980**, *102*, 7702.

(9) Ozin, G. A. *Faraday Symp. Chem. Soc*. **1980**, *14*, 7.

(10) Shields, L. *J. Chem. Phys.* **1966**, *44*, 1685.

(11) Bales, B. L.; Kevan, L. *J. Phys. Chem*. **1970**, *74*, 1098.

(12) Bales, B. L.; Kevan, L. *J. Chem. Phys*. **1971**, *55*, 1372.

(13) Kevan, L.; Hase, H.; Kawabata, K. *J. Chem. Phys.* **1977**, *66*, 3834.

(14) Kevan, L. *J. Chem. Phys*. **1978**, *69*, 3444.

(15) Ichikawa, T.; Kevan, L.; Narayana, P. A. *J. Phys. Chem*. **1979**, *83*, 3378.

(16) Anson, S. W. L.; Kenvan, L. *J. Phys. Chem.* **1980**, *84*, 2862.

(17) Ershov, B. G.; Janata, E.; Henglein, A. *J. Phys. Chem*. **1993**, *97*, 339.

(18) Shields, L.; Symons, M. C. R. *Mol. Phys*. **1966**, *11*, 57.

(19) Matsuura, K.; Hase, H.; Arai, S.; Miyatake, Y.; Hoshino, M. *Bull. Chem. Soc. Jpn*. **1999**, *72*, 363.

(20) Hase, H.; Arai, S.; Isomura, A.; Terazawa, N.; Miyatake, Y.; Hoshino, M. *J. Phys. Chem.* **1996**, *100*, 11534.

(21) Hase, H.; Miyatake, Y.; Hoshino, M.; Taguchi, M.; Arai, S. *Radiat. Phys. Chem.* **1997**, *49*, 59.

(22) Miyatake, Y.; Hase, H.; Matsuura, K.; Taguchi, M.; Hoshino, M.; Arai, S. *J. Phys. Chem. B* **1998**, *102*, 8389.

(23) Hase, H.; Miyatake, Y.; Miyamoto, Y. *Chem. Phys. Lett.* **2000**, *326*, 299.

(24) Breit, G.; Rabi, I. I. *Phys. Rev*. **1931**, *38*, 2082.

(25) Brewer, L.; King, B. *J. Chem. Phys*. **1970**, *53*, 3981.

(26) Forstmann, F.; Kolb, D. M.; Leutloff, D.; Schulze, W. *J. Chem. Phys.* **1977**, *66*, 2806.

(27) Kolb, D. M.; Rotermund, H. H.; Schrittenlacher, W.; Schroeder, W. *J. Chem. Phys.* **1984**, *80*, 695.

(28) Moore, C. E. *Atomic Energy Levels*; National Bureau of Standards; U.S. Government Printing Office: Washington, DC, 1958.

(29) Antonyak, O. T.; Vishnevskii, V. N.; Pidzyruino, N. S.; Tokarivskii, M. V. *Izv. Vyssh. Zaved., Fiz.* **1974**, 124.

(30) Simonetti, J. S.; McClure, D. S. *Phys. Rev. B* **1977**, *16*, 3887.