Emission Characteristics of Silver Atoms in γ−Irradiated Organic Solid Solutions at 77 K

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Ag^0 atoms were produced via the electron capture of Ag^+ ions in γ-irradiated solid solutions of ethanol and MTHF at 77 K. The 2-dimensional time-resolved fluorescence spectra together with the steady-state fluorescence spectra and excitation spectra were measured by photoexcitation of Ag^0 produced in the γ-irradiated solid solutions. The steady-state measurements have revealed the existence of two main emission bands at nearly 500 and 580 nm. The intensity of the 500 nm band increased and that of the 580 nm band concomitantly decreased with increasing concentration of Ag^+ in both solutions. The time-resolved observation has shown that the 500 nm band consists of three components of different lifetimes (τ). The main component with $\tau \sim 1$ μs is attributed to the exciplex $(Ag^0 \cdot Ag^+)^*$, the one with $\tau \sim 2$ μs, to the similar exciplex which is weakly coupled to solvent molecules, and the third one with $\tau \sim 3$ ns, to Ag^{0*} trapped in a large cavity where Ag^0 scarcely interacts with solvent molecules. The 580 nm band grows at about $0.5-1$ μs and decays with a long lifetime, i.e., about 50 μs in ethanol or 40 μs in MTHF. The band is attributed to the exciplex $(Ag^0 \cdot L_n)^*$, where L_n denotes n solvent molecules.

Introduction

Metal atoms produced by radiolysis of liquid and solid solutions containing the metal ions are affected strongly by surrounding solvent molecules and neighboring metal ions, so that the optical properties of them are considerably different from those in solid rare gas matrixes. Therefore, it is worthwhile to investigate physical and chemical properties of metal atoms in such environments for understanding interactions between the metal atoms and surrounding solvent molecules and neighboring metal ions, especially to elucidate the dynamical behavior of these interactions by observing the time dependence of the optical properties of the excited metal atoms leading to an equilibrium in this system.

Most previous studies have reported on the optical properties of silver atoms (Ag^0) dispersed in rare gas matrixes at low temperatures.[1−7] The existence of interactions between the "isolated" Ag^0 and the matrix even in the solid rare gas cases was evidenced by observations such as matrix-induced energy shifts, level splitting, line broadening, temperature dependence

of the absorption spectra, and excitation dependence of emission spectra with large Stokes shift. Forstmann *et al.*[3] explained the 3-fold or 4-fold splitting of the absorption spectrum in terms of the spin−orbit interaction and crystal field interaction assuming a static deformation of the gas cage and repulsion forces between the outer electrons of the metal and the matrix atoms. Furthermore, on the basis of Forstmann et al.'s arguments, Kolb *et al.*[4] interpreted the large Stokes shift of the emission spectra in terms of the transition of the excited Ag^0 forming an excimer complex with the matrix gas cage and the ground Ag^0 in a repulsion state. In contrast with them, Mitchell *et al.*[6] proposed a vibronic coupling model based on the Jahn−Teller effect in order to interpret the photolytic properties as the results of the diffusion and aggregation of Ag^0 isolated in rare gas matrixes.

On the other hand, the photophysical properties of crystalline silver halides such as AgBr and AgI, which are ionic semiconductors, have long been investigated by many researchers.[8−17] The effects of size restriction on the static and dynamic emission behavior of AgBr crystallites have been investigated.[12−14] On the basis of these photophysical experimental results, Freedhoff *et al.*[15] presented a review of quantum confinement effects in

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nanocrystals of AgBr in comparison with ones in nanocrystals of AgI. It is noteworthy that the emission spectra and the long lifetime component observed in the organic solid solutions in the present study resemble more closely those for the nanocrystalline silver halides[15,17] than those for the rare gas matrixes.

There has been a limited number of optical studies on Ag^0 produced via the radiation chemical reduction of silver ions (Ag^+) in organic solutions at low temperatures except for ESR studies.[18−20] Therefore, we have been investigating the optical properties of Ag^0 produced by γ-irradiation at 4 or 77 K in aqueous, ethanol, and 2-methyltetrahydrofuran (MTHF) solutions containing Ag^+ of 0.015 M and have already reported the results of the optical absorption properties[21] and the steady-state emission and excitation spectra.[22] We observed the two intense emission bands centered at nearly 500 and 600 nm in both ethanol and MTHF solutions but no emission band in the aqueous solutions. We also reported that the excitation of the main broad absorption bands in the region of 350−450 nm did not yield any visible emissions in ethanol solutions. It was concluded that the reduction of the ionization potential of Ag^0 in aqueous and organic solutions due to the solvation energy of Ag^+ leads to the direct photoionization of the excited Ag^0 in this absorption region. We proposed the formation of fluorescent complexes consisting of excited Ag^0 and solvent molecules for the two emission bands.

To test the validity of the previous interpretation for the two emission bands and to elucidate the emission mechanism of each band, we have made further investigation of the time-resolved fluorescence spectra as well as the steady-state emission and excitation spectra, giving particular attention to the dependence of Ag^+ concentration and the solvent polarity on the emission properties.

The present study has brought us new information about the excited state involving Ag^0 and the interactions between the excited-state and neighboring Ag^+ ions as well as surrounding solvent molecules.

Experimental Section

All samples were prepared as described previously.[21,22] Either $AgNO_3$ or $AgClO_4$ of various concentrations was quickly dissolved in ethanol and MTHF at the room temperature. MTHF was first distilled fractionally and then dried over Na and K alloy. Other chemicals were used without further purification. The concentrations of Ag^+ ions ($[Ag^+]$) were 0.008, 0.08, and 0.2 M for the measurements of steady-state emission and excitation spectra, and $[Ag^+] = 0.015$ and 0.15 M for the time-resolved emission measurements.

The fresh solutions transferred into Suprasil quartz ESR tubes of 5 mm in diameter were degassed by the pump and thaw method and then cooled to 77 K by immersing them into liquid nitrogen. The γ-irradiation of the frozen samples was carried out at a dose rate of 27 kGy h^{-1} at 77 K. The total dose was typically 10 and 15 kGy for the steady-state emission and excitation spectrum measurements and for the time-resolved fluorescence spectrum measurements, respectively. To remove the trapped electrons which were produced by γ-irradiation in ethanol and MTHF solutions at 77 K, the irradiated solutions were illuminated with light of wavelength longer than 540 nm before the optical measurements. The steady-state emission and excitation spectra of Ag^0 produced in γ-irradiated solid solutions were measured at 77 K using a Hitachi fluorescence spectrometer of model F-4500. A color filter of a cutoff wavelength of 440 nm was used for the removal of scattered excitation light in the measurements.

The time-resolved emission measurements for Ag^0 produced in γ-irradiated solid solutions were carried out with a pulsed nitrogen laser of wavelength of 337 nm for the excitation light (LN120C by Laser Photonics) and C4780 picosecond fluorescence lifetime measurement system by Hamamatsu Photonics.[22,23] The nitrogen laser was operated at 13 Hz. The pulse width (fwhm) was 300 ps, and its output energy was about 70 μJ per pulse. The beam spot was less than 1 mm in diameter at the sample. Bubbles from liquid nitrogen in the dewar were prevented by bubbling helium gas continuously into it, enabling the measurements to be carried out at a stable temperature of 73 K. In the present measurements, a handmade spiral-laser-spot apparatus was used for preventing the sample from repeated irradiation with the excitation pulses at the same point of the sample for a long time. The apparatus, constructed by combining an ultraslow synchronous motor and some gears, made it possible to change the position of the laser beam spot on the sample upward or downward at the rate of 1.2 mm/turn/min. The schematic diagram of the measurement system was essentially the same as that described before[23] except for the spiral-laser-spot apparatus which was placed at the position of the target sample holder. The excitation light pulses of 337 nm were passed through a narrow band-pass filter of 6 nm in fwhm in order to avoid the stray light such as the scattered light. The excitation light was illuminated onto the surface region of the sample at half right angle in order to prevent the self-absorption of the fluorescence by Ag^0 produced in the solid solutions. The time-resolved fluorescence data were obtained as two-dimensional photoelectric images, i.e. streak images, containing the three-dimensional information of wavelength (horizontal axis = 640 pixels), arrival time (vertical axis = 480 pixels), and intensity of fluorescence (brightness = 16 bits/pixel). The time resolution is restricted by the jitter in triggering the streak camera.[24] In the present experiment, the time-resolved fluorescence measurements were carried out for various sweep full range from 10 ns to 200 μs for each sample. Since the emission is resolved into 480 channels (pixels) for the time axis, the time resolution of each time spectrum can be given by the value of the sweep full time range divided by 480. More than 50 time-resolved fluorescence spectra were analyzed for obtaining the lifetimes of both emission bands by using basically nonlinear iterative fitting methods with a multiexponential function.

Results and Discussion

Steady-State Emission and Excitation Spectra. The steady-state emission spectra were measured at 77 K for Ag^0 produced in the irradiated solid solutions of ethanol and MTHF, both of which contained Ag^+ ions of various concentrations. The spectra for ethanol and MTHF solutions are shown in Figure 1 A,B, respectively. The solid and dotted lines represent the spectra obtained with excitation light of wavelengths (λ_{exc}) of 337 and 280 nm, respectively.

The present results are consistent with those reported previously[22] for diluted ethanol and MTHF solutions of $[Ag^+] = 0.015$ M, in which the two emission bands of the shorter and longer wavelengths have been interpreted as originating from Ag^0. These bands are denoted hereafter by E_1 and E_2 bands, respectively. The peak wavelengths of the E_1 and E_2 bands were 510 and 590 nm in ethanol and 490 and 570 nm in MTHF solutions, respectively. The peak wavelengths of both emission bands in ethanol solution are shifted toward the red by 20 nm compared to those in MTHF solution. This means that the solute−solvent interaction is dominant in ethanol, which is more polar than MTHF.
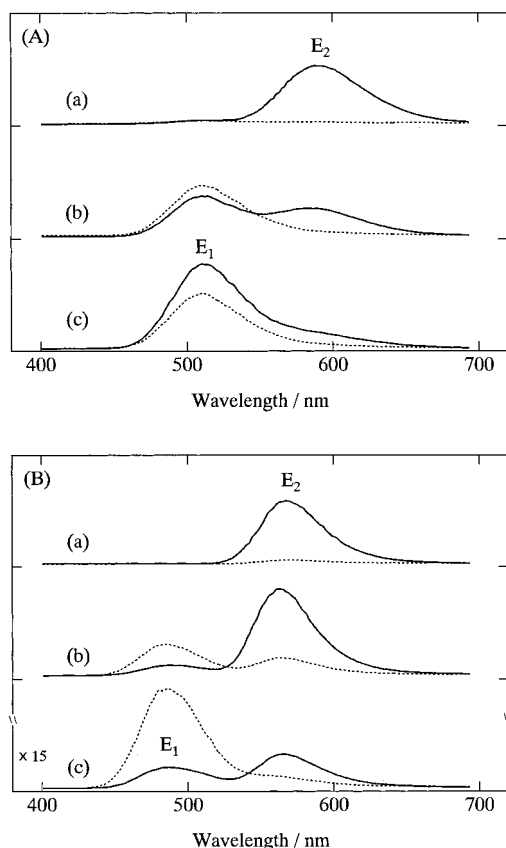
Emission Characteristics of Silver Atoms

J. Phys. Chem. B, Vol. 102, No. 43, 1998 **8391**

Figure 1. Steady-state emission spectra measured at 77 K for irradiated ethanol (A) and MTHF (B) solutions. All samples were irradiated at 77 K by γ-rays with a total dose of 10 kGy. The solid and dotted lines represent the emission spectra for excitation light of wavelengths of 337 and 280 nm, respectively. The spectra of (a), (b), and (c) are for concentrations of Ag^+ ions of 0.008, 0.08, and 0.2 M, respectively.
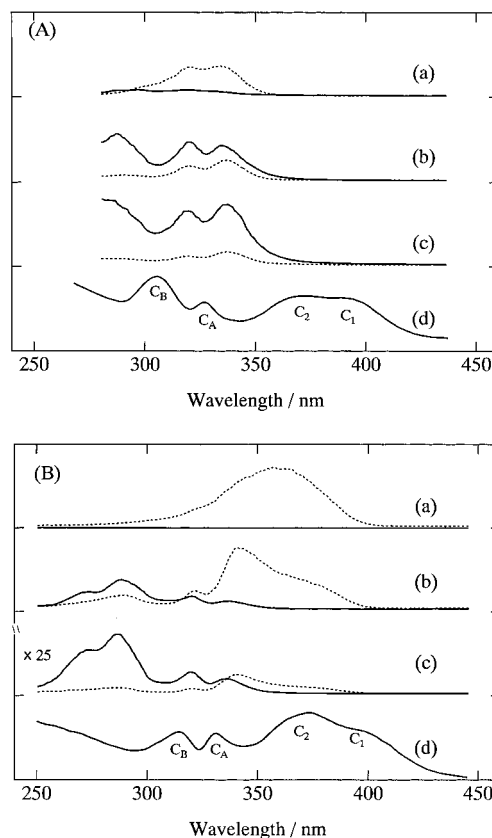

Figure 2. Excitation and absorption spectra measured at 77 K for irradiated ethanol (A) and MTHF (B) solutions. All samples were irradiated at 77 K by γ-rays with a total dose of 10 kGy. The spectra of (a), (b), and (c) are excitation spectra for concentrations of Ag^+ ions of 0.008, 0.08, and 0.2 M, respectively. The solid and dotted lines represent excitation spectra monitored at 510 and 590 nm, respectively in ethanol. For MTHF solutions, the solid and dotted lines represent excitation spectra monitored at 490 and 570 nm, respectively. The absorption spectra for concentrations of Ag^+ ions of 0.015 M are shown in (d) in both (A) and (B).

The intensity of the E_1 band increased and that of the E_2 band concomitantly decreased with increasing the concentration of Ag^+ ions in both solutions. The change in the intensity with Ag^+ concentration was more prominent in ethanol than in MTHF solution. Our recent ESR study has revealed that the spectrum due to Ag_2^+ is observed in concentrated ethanol and MTHF solutions of $AgClO_4$ ([Ag^+] = 0.15 M) after γ-irradiation at 77 K and that the spectral intensity of Ag_2^+ is stronger in ethanol than MTHF solution.[25] On the basis of the ESR result together with the concentration dependence of the emission intensity of E_1 band observed in this study, we conclude that the E_1 band consists partly of the emission of the dimer cation formed between Ag^0 and a nearby Ag^+. We denote this as ($Ag^0 \cdot Ag^+$).

In the case of $\lambda_{exc} = 280$ nm, the E_2 band almost disappeared and the E_1 band was observed almost exclusively in ethanol solution regardless of the concentration of Ag^+ ions. In MTHF solution, the E_2 band decreased in the intensity but did not completely disappear. This is consistent with the observation of the band at 290 nm in the excitation spectra of MTHF solution (see below).

The intensity ratio between the two emission bands, $I(E_1)/I(E_2)$, was larger for $\lambda_{exc} = 280$ nm than that for $\lambda_{exc} = 337$ nm in all of the solutions. This is consistent with the results of the previous study, in which the emission was measured by λ_{exc} in the region from 280 to 440 nm.[22]

Figure 2A,B shows the excitation spectra measured at 77 K for irradiated ethanol and MTHF solid solutions containing Ag^+ of various concentrations, respectively, together with the absorp-

tion spectra (d). The excitation spectra were obtained by monitoring the emission at the peak wavelengths of the E_1 and E_2 bands. The broad absorption bands observed in the wavelength region of 350−450 nm for both the solutions are decomposed into two bands, which are denoted by the C_1 (400 nm) and C_2 (370 nm) bands in Figure 2. These bands were assigned to Ag^0 originating from Ag^+ ions in the cavities of different degrees of solvation in the previous study.[21] The other main bands are observed in the region of 300−340 nm, i.e. the C_A(330 nm) and C_B(310 nm) bands. Since the peak wavelengths of C_A and C_B bands are very close to those of Ag^0 in solid rare gases,[6] the bands were assigned to Ag^0 trapped in larger cavities.[21] For ethanol solution, as shown in Figure 2A, the threshold wavelength of the excitation spectra is 360 nm for both emission bands. This means that the excitation of C_A and C_B bands gives rise to the emissions of both the E_1 and E_2 bands in irradiated ethanol solutions. On the other hand, the threshold wavelengths for MTHF solutions are 360 and 400 nm for the emission monitored at the peak wavelengths of the E_1 and E_2 bands, respectively, as shown in Figure 2B. Thus for MTHF solutions the E_1 band is caused by the excitation of the C_A and C_B bands, while the E_2 band is caused by the excitation of the C_2 band as well as the C_A and C_B bands. Note that the C_1 band does not contribute to any emission. This has been interpreted as due to the bound−free transition of Ag^0 of a reduced ionization potential for the C_1 band.[22] The excitation
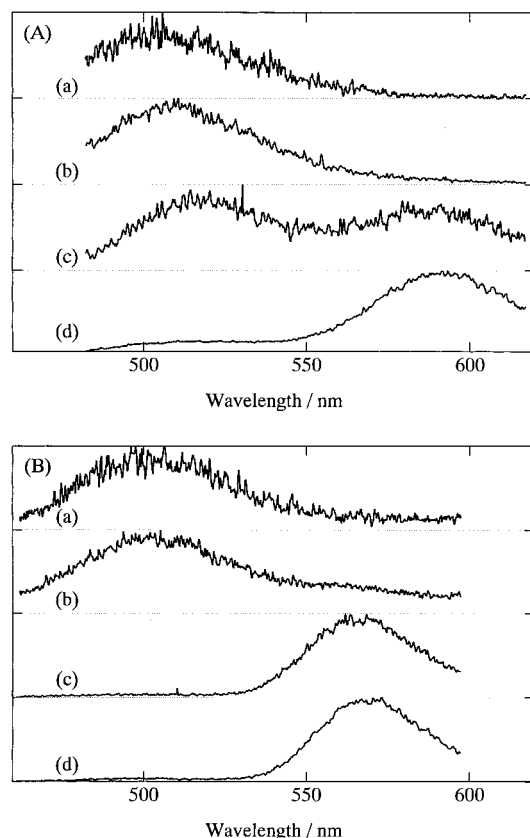
Figure 3. Typical wavelength profiles of the time-resolved fluorescence spectra measured at 73 K after irradiation at 77 K by γ-rays with the total dose of 15 kGy for ethanol (A) and MTHF solution (B), respectively. The concentration of Ag^+ ions in both solutions was 0.015 M. The spectra correspond to the wavelength distribution of all the photons received during the sweep full times of 10 ns (a), 100 ns (b), 20 μs (c), and 200 μs (d).

Figure 4. Typical fluorescence decay profiles measured at 73 K for a MTHF solid solution which was γ-irradiated at 77 K with a total dose of 15 kGy. The concentration of Ag^+ ions was 0.015 M. The fluorescence decay profiles were obtained with a sweep full range of 100 ns for the E_1 band (A) and 200 μs for the E_2 band (B).

spectra for $[Ag^+] = 0.08$ and 0.2 M in Figure 2A,B show that the excitation with the light at 280–290 nm efficiently yields the E_1 band in these solutions.

Time-Resolved Emission Spectra. The time dependence of the emission intensities of Ag^0 produced in γ-irradiated ethanol and MTHF solid solutions of $[Ag^+] = 0.015$ and 0.15 M was measured by photoexcitation with $\lambda_{exc} = 337$ nm at 73 K. The typical wavelength profiles of the time-resolved emission spectra for ethanol and MTHF solutions are shown in Figure 3A,B, respectively.

The two emission bands, i.e. E_1 and E_2, observed in the steady-state emission measurements were also observed in both the time-resolved emission spectra of the solutions. The red shifts of the E_1 and E_2 bands in ethanol and MTHF are the same as those observed in the steady-state measurements. The ratio of the intensities of the two emission bands, $I(E_1)/I(E_2)$, changes with time. This is shown in Figure 3. It is clear that the intensity ratio of the two emission bands obtained for sweep full range of 200 μs becomes almost equal to that for the steady-state measurement for both solutions.

The E_1 band disappears after about 20 μs for ethanol but not later than 20 μs for MTHF. Note that the E_2 band is not observed before 100 ns for both solutions. This means that the E_2 band appearance is delayed relative to the E_1 band and that the lifetime of the E_2 band is long enough to be distinguished from that of the E_1 band. The E_2 band is at first observed about 0.8–1 μs after the arrival of the excitation light pulses for both solutions. However, it is difficult to determine the rise time of the E_2 band precisely because of the difficulty of measurements
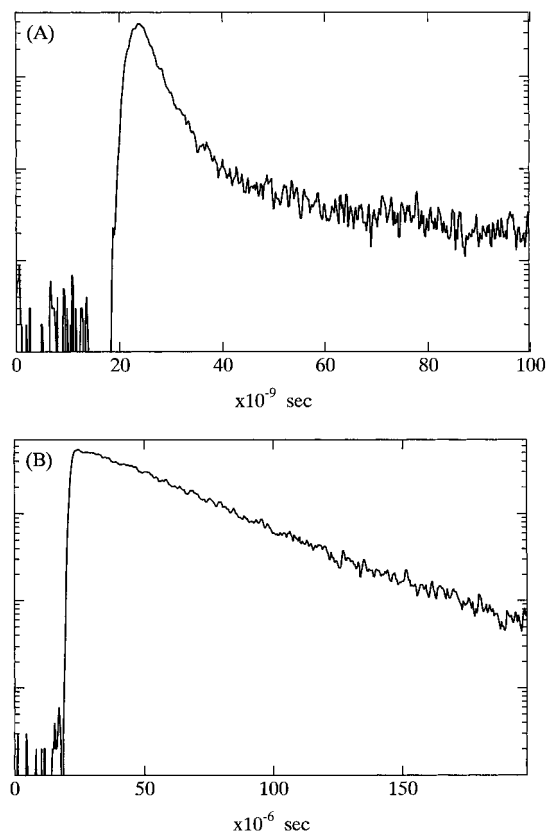
for the sweep full range of 1 or 5 μs with good accuracy.[24] In the present study, it suffices to say that the rise time of the E_2 band is between 0.5 and 1 μs.

The typical time profiles of the E_1 and E_2 bands for MTHF solid solution are shown in Figure 4A,B, respectively. It is clearly shown in the decay profiles of Figure 4 that the E_1 band consists of several components of lifetimes and that the E_2 band consists of a single component of the lifetime which is longer than that of the E_1 band. The same is true for the ethanol solution. The lifetime analysis for the E_1 band was carried out by three steps: At first, the time profiles for the sweep full range of 20 μs were analyzed by two exponential functions to determine the two longer components, which are denoted by τ_{long} and τ_{middle}. The results obtained in this time range were confirmed by those for the sweep full range of 50 μs. Next, the time profiles for the sweep full range of 100 ns were analyzed by two exponential functions again in which the longer component, τ_{middle}, was fixed. Thus the shorter component was determined. This is denoted by $\tau_{short'}$. The results obtained in this time range were also confirmed by those for the sweep full ranges of 50 and 20 ns. As the final step, the shortest component of the E_1 band, (denoted by τ_{short}, was determined by the iterative deconvolution method with one exponential function for the time profiles of the sweep full range of 10 ns. It turned out that the values of τ_{short} thus determined were equal to those of $\tau_{short'}$ within the experimental errors. Thus we conclude that the E_1 band consists of three components. It is noted that the emission intensity of the component of τ_{middle} is dominant and amounts to ca. 80–90% of the total emission intensity. The lifetime of the E_2 band was obtained by assuming a single-exponential function for the time profiles of the sweep

Emission Characteristics of Silver Atoms

J. Phys. Chem. B, Vol. 102, No. 43, 1998 **8393**

TABLE 1: Lifetimes Obtained for the E_1 and E_2 Bands of Ethanol and MTHF Solid Solutions at 73 K[a]

	[Ag$^+$], M	τ_{short}, ns	E$_1$ band		E$_2$ band
			τ_{middle}, μs	τ_{long}, μs	τ, μs
EtOH	0.015	2.9(0.9)	0.9(0.2)	2.2(0.5)	56(1.3)
	0.15	2.9(0.6)	0.9(0.4)	2.2(0.3)	64(2.5)
MTHF	0.015	2.1(0.3)	0.8(0.1)	2.2(0.3)	36(1.9)
	0.15	2.3(0.1)	0.8(0.1)	2.3(0.1)	41(0.4)

[a] The values in parentheses are statistical errors.

full range of 200 and 100 μs. Table 1 lists the results of the lifetime analyses for both emission bands for ethanol and MTHF solid solutions of [Ag$^+$] = 0.015 and 0.15 M. The lifetimes of the E$_2$ band depend on the solvent; they are shorter for MTHF solutions than for ethanol solutions by about 20 μs. It follows that the E$_2$ band is attributed to the entity that is strongly associated with solvent molecules. The long lifetime and the large Stokes shift of the E$_2$ band for ethanol solution lead us to infer that the E$_2$ band is the emission of an exciplex formed between an excited Ag^0 and surrounding solvent molecules, denoted by (Ag^0·L$_n$)*, where L$_n$ represents n solvent molecules. It takes 0.5−1 μs for the exciplex to be transferred to the emission state. The E$_2$ band did not shift with time in both solid solutions. This implies that the band is due to emission after the interaction between Ag^0 and L$_n$ is completely relaxed. At present we are unable to explain the appearance of the E$_2$ band about 1 μs after the E$_1$ band and to specify the precursor of the emitting species responsible for the E$_2$ band. Our results also show that the lifetimes of the E$_2$ band depend on the concentration of Ag$^+$ ions; they are longer for the higher Ag$^+$ concentrations in both solutions. This suggests that long-range interactions between Ag^0 and Ag$^+$ contribute to the E$_2$ band to some extent.

On the other hand, neither solvent nor Ag$^+$ concentration affected the lifetimes of any of the three components of the E$_1$ band. As shown in Figure 3, however, the peak wavelength of the E$_1$ band for ethanol shifts toward the red by about 13 nm between 10 ns and 20 μs but not for MTHF. This time dependence in ethanol suggests that at least one component of the E$_1$ band is attributed to (Ag^0·Ag$^+$)*, which is weakly coupled to solvent molecules. It follows that the shift of the E$_1$ band with time is explained in terms of the component which is transferred by the internal conversion from an excited transient state to a relaxed equilibrium state in association with solvent molecules, followed by the emission. We infer that this component is the one with τ = 2.2−2.3 μs (τ_{long}).

By analogy with the lifetimes in the nanosecond time region for Ag^0* in solid rare gas matrixes,[6] we ascribe the emission with τ = 2.1−2.9 ns (τ_{short}) to Ag^0* trapped in a large cavity in which Ag^0 interacts very weakly with the surrounding solvent molecules. Finally, the increase in the intensity of the E$_1$ band, which consists of the three components with different but constant emission lifetimes, with increasing [Ag$^+$] leads us to the conclusion that the remaining, main component with τ = 0.8−0.9 μs (τ_{middle}) is attributed to the exciplex (Ag^0·Ag$^+$)*. The mechanism for the proposed species corresponding to the E$_1$ and E$_2$ bands is schematically illustrated in Figure 5.

The excitation by light in the shorter wavelength region, e.g. λ_{exc} = 280 nm, has been found to give rise to no emission in both the solid solutions for the low concentrations of Ag$^+$ ions.[22] This has been interpreted as due to the direct photoionization of Ag^0 by the light of λ_{exc} = 280 nm. However, in the present study the E$_1$ band has been observed for both the solid solutions in the case of high concentrations of Ag$^+$ ions. This is explained by assuming the reaction of electron transfer from the photoionized Ag^0 to the coupled Ag$^+$: (Ag^0·Ag$^+$) → (Ag$^+$·Ag^0)*.
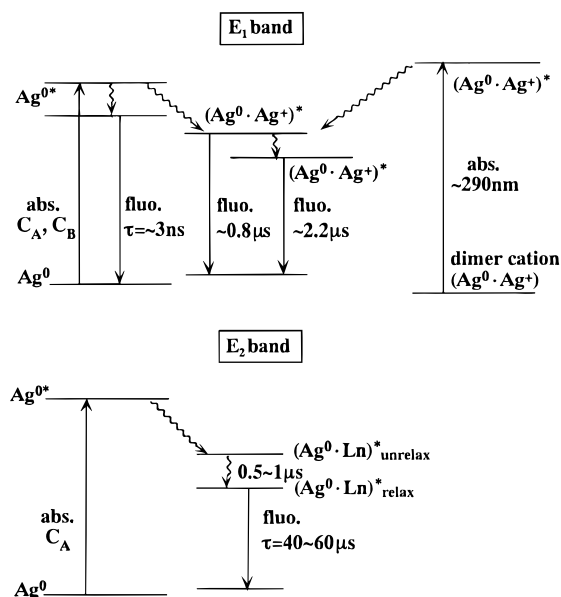

Figure 5. Schematic representation of the absorption (abs.) and emission (fluo.) mechanism of the proposed species corresponding to the E$_1$ and E$_2$ bands.

Finally, it is of great interest that not only the fluorescence spectra but also the lifetimes of the emission bands obtained in the organic solutions in this study are similar to those of nanocrystalline silver halides[15,17] rather than those in the rare gas matrixes. Since our recent ESR study has shown evidence that Ag$_2^+$ is formed by Ag^0 and Ag$^+$ which are in very close proximity to each other,[25] it may be inferred that a quasinano-crystalline configuration of Ag$^+$ ions is partly formed in the organic solid solutions. However, this hypothesis needs to be further inspected.

Conclusion

The fact that the excitation of the broad absorption band due to Ag^0 in the wavelength region of 350−450 nm did not give any emissions in ice and solid ethanol is evidence of the photoionization of Ag^0 as proposed in the previous study.[22] On the contrary, the E$_1$ (λ_{max} = 490−510 nm) and E$_2$ (λ_{max} = 570−590 nm) bands were observed by the excitation of the C$_A$ (λ_{max} = 330 nm) and C$_B$ (λ_{max} = 310 nm) bands. These indicate that the degree of solvation of Ag$^+$ ions dominates the nature of the excited state of Ag^0. It is concluded that Ag^0 in its excited state in ethanol and MTHF solid solutions is strongly coupled with matrix molecules to compose an exciplex (Ag^0·Ln)*, followed by a simultaneous relaxation to an emissive state after 0.5−1 μs, giving rise to the E$_2$ band. The E$_1$ band consists of three components with different lifetimes; the main component with τ = 0.8−0.9 μs is assignable to the emission due to exciplex (Ag^0·Ag$^+$)*. The component with τ = 2.2−2.3 μs is ascribed to (Ag^0·Ag$^+$)* coupled weakly with solvent molecules, and the emission originates from an equilibrium state which is populated from an unrelaxed Franck−Condon state. The third component with τ = 2.1−2.9 ns is due to Ag^0*, which is less affected by solvent molecules and Ag$^+$ ions.

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