served in radiation chemistry and high-pressure mass spectrometry.[21]

The results obtained on krypton isolated in an argon matrix are highly encouraging. They suggest that even relatively poor matrix isolation ratios such as 1:100 to 1:1000 will be adequate for mass spectrometric investigations of matrix isolated species.

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Disilver: Spectroscopy and Photoprocesses in Rare-Gas Matrices

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Abstract: We report the absorption and fluorescence spectra of Ag$_2$ molecules in Ar, Kr, and Xe matrices at 12 K. A comparison is made with the absorption spectrum of Ag$_2$ in the gas phase, and detailed assignments of the matrix absorption bands are suggested. The absorption and fluorescence spectra are indicative of strong guest-host interactions involving the A$^1\Sigma_u^+$ and C$^1\Pi_u$ states of Ag$_2$ in rare-gas matrices. The emission spectrum produced by A-X Ag$_2$ excitation is interpreted in terms of an excited-state Ag$_2$ dissociation process, involving strong stabilization of the $^2S + {}^2P$ Ag atomic fragments by matrix cage relaxation effects. Electronic relaxation of the C state of Ag$_2$ is discussed in terms of matrix cage relaxation, energy transfer to Ag atoms, and nonradiative decay to the A state.

Matrix isolation has proven to be a valuable technique for spectroscopic study of a wide variety of normally unstable metal complexes and molecular metal clusters.[1,2] In particular, matrix trapping and stabilization of silver atoms and clusters have been extensively studied.[3-7] We have recently shown that silver clusters can be formed in a highly controllable manner by photoinduced diffusion and aggregation of matrix-entrapped silver atoms.[8,9] These studies have led to broader enquiries into the nature of electronic relaxation processes of matrix-isolated silver atoms and molecules, with a view to establishing guidelines for the possible extension of the photoinduced diffusion technique to other metal and matrix systems, and to investigate the photoprocesses of matrix-entrapped silver clusters generally.[10,11] In a previous paper[12] we reported the fluorescence excitation, emission, and polarization spectra of silver atoms isolated in Ar, Kr, and Xe matrices, and proposed a qualitative model for the excited-state interactions to account for the observed optical and photolytic properties. In this paper we extend these studies to include fluorescence spectroscopy and electronic relaxation of Ag$_2$ molecules in rare-gas matrices. The first matrix fluorescence spectrum of Ag$_2$ was reported by Kolb and Leutloff.[13] We also present a more detailed analysis of our previously reported observations concerning photodissociation of matrix-entrapped Ag$_2$ molecules.[11]

Laser-induced fluorescence has been used to study the electronic spectra of a wide variety of matrix-isolated diatomic molecules, and to investigate the nature of the guest-host interactions.[14-20] It is often found that the molecular constants are perturbed only slightly in the matrix environment, and in general quite weak guest-host interactions are indicated, although the matrix may influence the electronic relaxation behavior by inducing nonradiative transitions.[21] However, it appears for the case of the excited states of Ag$_2$ that rather strong guest-host interactions are operative and that unusual electronic relaxation processes are induced by these matrix interactions.

Experimental Section

The experimental arrangement for matrix preparation and fluorescence studies has been described previously.[12] Matrices were deposited onto a NaCl optical window cooled to 12 K by means of an Air Products Displex closed-cycle helium refrigerator. Absorption spectra were re-

Table I. Ag$_2$ Absorption Maxima in Ar, Kr, and Xe Matrices at 12 K[a]

λ, nm			
Ar	Kr	Xe	gas phase
261	270	283	266
[+720 cm^{-1}]	[−557 cm^{-1}]	[−2260 cm^{-1}]	
264	275	289	
(273)	(280)	(296)	
(282)	(290)		
389	390	391	435
[+2720 cm^{-1}]	[+2650 cm^{-1}]	[+2590 cm^{-1}]	
(406)			

[a] Absorption maxima due to secondary matrix sites appear in parentheses. The shifts of the major absorption bands from the (0,0) gas-phase transition energies[22,24] are given in square brackets.

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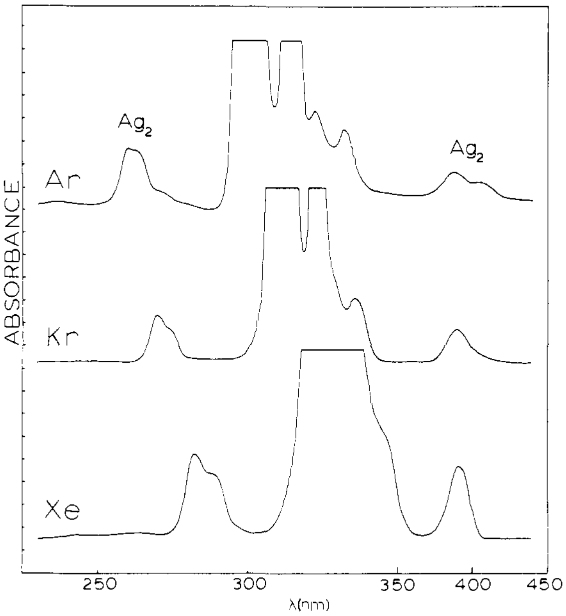

Figure 1. Absorption spectra of Ag_2 molecules isolated in freshly deposited Ar, Kr, and Xe matrices at 12 K. Ag/rare gas $\simeq 1/(2 \times 10^3)$. The strong central features are due to isolated silver atoms.

corded on a Unicam SP 8000 spectrometer, and fluorescence spectra were recorded on a Perkin-Elmer MPF 44 fluorescence spectrometer, selecting both the excitation and emission wavelengths with scanning monochromators. The fluorescence excitation and emission spectra were corrected for the frequency dependence of the excitation intensity; however, the emission spectra were not corrected for the characteristics of the analyzing monochromator and photomultiplier.

Results and Discussion

1. Absorption and Fluorescence Spectra. The two major bands in the absorption spectrum of Ag_2 in Ar, Kr, and Xe matrices are illustrated in Figure 1. As described later, these bands correlate with the A–X and C–X systems of Ag_2 observed in the gas phase.[22-24] The higher-energy band shows a poorly resolved double-peak structure in all cases, and a progressive red shift from Ar to Kr to Xe matrices, while the lower-energy band shows broad structure only in Ar matrices, and approximately constant energy for the heavier rare gases. There is a notable lack of resolved vibrational structure in all cases, even though the gas-phase spectra show vibrational spacings that are relatively large (~ 160 cm^{-1})[22-24] compared to the resolution of our instrument.

The absorption band profiles illustrated in Figure 1 were found to undergo changes as a result of either photoinduced dimerization of the isolated silver atoms or thermally induced processes when the matrices were annealed. The most pronounced changes occurred for the higher-energy bands, which in all cases developed additional maxima red shifted from the principal band. The behavior of these additional red-shifted peaks during photoinduced clustering of the silver atoms, and during subsequent thermal annealing, strongly suggests that they arise from secondary matrix trapping sites for the Ag_2 molecules. With the exception of Ar matrices, no pronounced secondary trapping site effects were observed for the lower-energy absorption bands near 390 nm. The exception in the case of Ar matrices is clearly visible in Figure 1. The wavelengths of the various Ag_2 absorption maxima are listed in Table I, together with the observed gas-matrix shifts for the major absorption bands. Note that the lower-energy band shows a large and comparable blue shift from the gas-phase value in all three matrices, while the shift of the higher-energy band is more strongly matrix dependent, and changes from blue in Ar to red in Kr and Xe, relative to the (0,0) gas-phase transition energy.

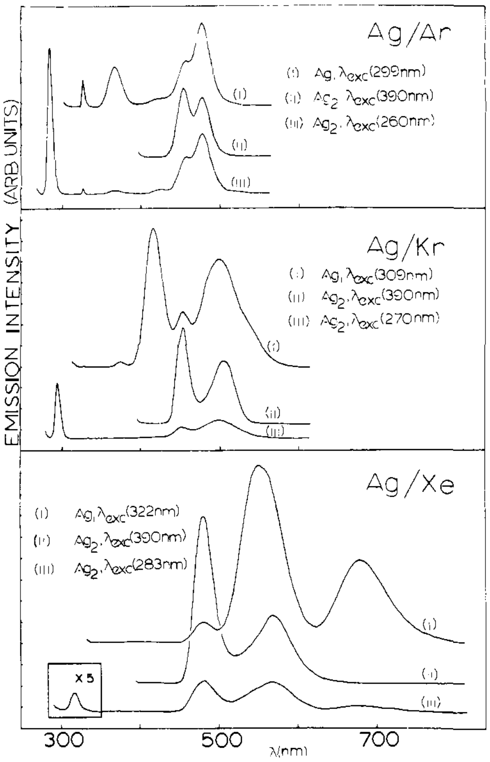

Figure 2. Fluorescence spectra of Ag atoms and Ag_2 molecules isolated in freshly deposited Ar, Kr, and Xe matrices at 12 K, corrected for excitation intensity at the indicated excitation wavelengths. Ag/Ar,Kr $\simeq 1/(2 \times 10^3)$, Ag/Xe $\simeq 1/(1 \times 10^3)$. Relative amplifier gain settings within each panel as follows: Ag/Ar 299 nm (×1), 390 nm (×1), 260 nm (×10); Ag/Kr 309 nm (×1), 390 nm (×1), 270 nm (×3); Ag/Xe 322 nm (×1), 390 nm (×1), 283 nm (×1).

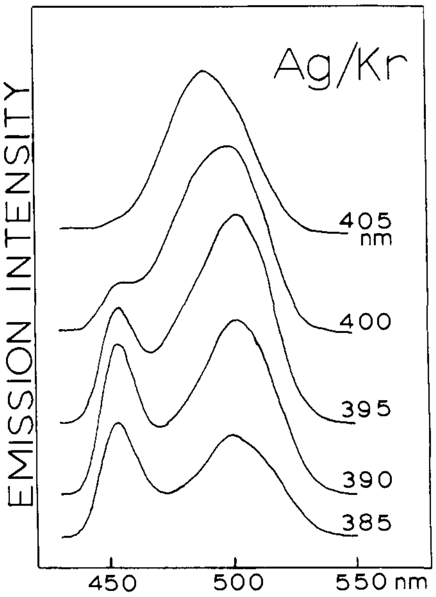

Figure 3. Fluorescence spectra of Ag_2 molecules isolated in solid Kr at 12 K, showing the dependence of the emission profile on the excitation wavelength. Ag/Kr $\simeq 1/(2 \times 10^3)$.

Photoexcitation of the Ag_2 absorption bands produces intense luminescence, as illustrated in Figure 2 for Ar, Kr, and Xe ma-

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Table II. Properties of Ag_2 Emission Bands in Ar, Kr, and Xe Matrices at 12 K

matrix	excitation λ, nm	emission λ, nm	spectral shift, 10^3 cm^{-1}	polarization[a]
Ar	261	284	3.10	+0.22
		326		
		365		
		420		
		455		
		478		−0.12
	389	455	3.73	+0.11
		478	4.79	+0.08
Kr	270	295	3.14	+0.18
		370[b]		
		420[b]		
		454		−0.02
		500		−0.03
	390	454	3.61	+0.07
		504	5.80	+0.05
Xe	283	315	3.59	
		480		−0.03
		570		−0.01
		680		
	391	480	4.74	+0.08
		570	8.03	+0.03

[a] Degree of polarization defined as $P = (I_{\parallel} - I_{\perp})/(I_{\parallel} + I_{\perp})$, corrected for instrumental factors.[27] Estimated experimental uncertainty is ±0.05. [b] Very weak bands.

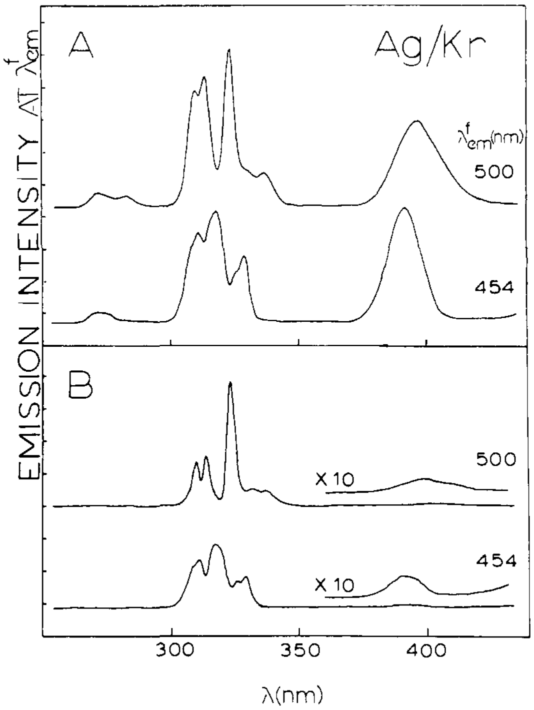

Figure 4. Fluorescence excitation spectra of Ag/Kr matrices at 12 K, obtained by scanning the excitation monochromator with the emission monochromator fixed at the indicated wavelengths. Spectra corrected for wavelength dependence of excitation intensity. (a) Ag/Kr ≃ 1/(2 × 10^3); (b) Ag/Kr ≃ 1/(5 ×10^4). The excitation (absorption) features near 320 nm are due to isolated silver atoms.[12]

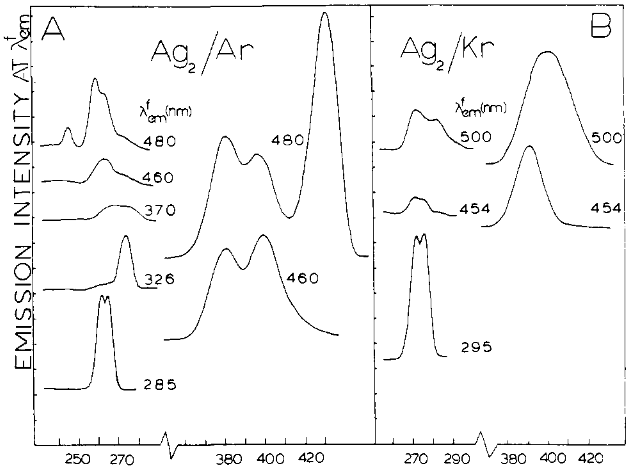

Figure 5. Fluorescence excitation spectra showing Ag_2 excitation profiles in Ar and Kr matrices at 12 K. These spectra were obtained by scanning the excitation monochromator over the Ag_2 absorption bands with the emission monochromator fixed at the indicated wavelengths. Ag/rare gas ≃1/(2 × 10^3).

trices. The emission bands are quite broad, exhibit large spectral shifts, and in all cases are devoid of resolved vibrational structure. Also shown in Figure 2 are the emission spectra produced by excitation of the high-energy component of the respective Ag *atomic* absorption band.[12] Note that with the exceptions of the highest-energy emission bands at 284–315 nm each of the bands produced by Ag_2 excitation can be correlated with a band in the Ag atomic emission spectrum. The correspondence is exact in the case of Ar matrices, while for Kr and Xe matrices there are slight shifts between the lowest-energy Ag and Ag_2 emission maxima. However, these latter emission bands were found to undergo significant shifts depending on the Ag[12] or Ag_2 excitation wavelength. This is illustrated for the case of Ag_2 in Kr matrices in Figure 3. As can be seen in Figure 2, the emission bands produced by the long-wavelength Ag_2 excitation are in all cases also produced by the high energy excitation. Selected properties of the Ag_2 emission bands are listed in Table II for the three rare-gas matrices.

Figure 4 shows fluorescence excitation spectra for the two long-wavelength emission bands in Kr matrices, under conditions of relatively high (Figure 4A) and very low (Figure 4B) Ag_2 density. Figure 4A verifies that Ag *and* Ag_2 excitation produce the 454 nm and 500 nm emission bands, while Figure 4B shows that these bands can be produced by atomic Ag excitation in matrices containing only trace quantities of Ag_2. As discussed later, these are important observations for the interpretation of the Ag_2 emission spectra. Similar results were obtained for the long-wavelength emission bands in Ar matrices, and for the 570-nm band in Xe matrices. However, the 480-nm Xe-matrix band could be produced by atomic Ag excitation only in rather concentrated matrices (Ag/Xe ≈ 1/10^3), and was produced only by Ag_2 excitation in more dilute matrices (Ag/Xe ≈ 1/10^4).

The fluorescence excitation spectra for all of the emission bands produced by Ag_2 excitation in Ar and Kr matrices are collected in Figure 5. Note that the Ag atomic excitation peaks[12] are not shown in these spectra. It can be seen that the excitation profiles for the various emission bands are markedly different within both matrices. These spectra clearly show the Ag_2 absorption bands to be made up of several overlapping components, where the different components favor specific bands of the emission spectrum. The composite nature of the absorption bands is particularly evident in the case of Ar matrices (Figure 5A). With the exceptions of the 245 and 440 nm maxima appearing in the upper traces of Figure 5A, all of the excitation maxima shown in Figure 5 can be correlated exactly with the major and secondary Ag_2 absorption maxima listed in Table I. The 245- and 440-nm bands are due to Ar-entrapped Ag_3 molecules, and will be discussed in a separate paper. The spectra for Xe matrices were found to be similar to those for Kr matrices, and are therefore not included in Figure 5.

The Ag_2 emission spectra were found to be quite sensitive to the conditions of matrix preparation, including the mode of Ag_2 formation (dimerization during matrix formation or photoinduced dimerization of isolated silver atoms), thermal annealing, total silver concentration, and matrix temperature. A similar sensitivity was found for the emission spectra of silver atoms in rare-gas matrices.[12] The changes observed in the Ag_2 emission spectra consisted mainly of relative intensity variations. For example, in all three rare-gas matrices the two components of the emission

Table III. Known Spectroscopic States of Ag_2[a]

designation	T_e, cm^{-1}	ω_e, cm^{-1}	assignment[b]
X	0.0	192.0	$^1\Sigma_g^+(O_g^+)$
A	22996.4	154.6	$2\sigma_g \rightarrow 2\sigma_u$, $^1\Sigma_u^+(O_u^+)$
B	35838.6	151.8	$2\sigma_g \rightarrow 2\pi_u$, $^3\Pi_u(l_u)$
C	37631.6	171.0	$2\sigma_g \rightarrow 2\pi_u$, $^1\Pi_u(l_u)$
D	39014.5	168.2	$2\sigma_g \rightarrow 2\pi_u$, $^3\Pi_u(O_u^+)$
E	40159.9	146.1	$1\pi_g \rightarrow 2\sigma_u$, $^1\Pi_u(l_u)$

[a] References 22-24. A description of a H ← X transition of Ag_2 lying in the vacuum UV region is included in ref 22. [b] Reference 11. The assignments for the B and C states are uncertain, and may be reversed.[26]

band produced by the low-energy Ag_2 excitation (see Figure 2) were found to undergo pronounced relative intensity variations, depending on the mode of Ag_2 formation. A similar sensitivity was found in all cases for the relative intensity of the highest-energy Ag_2 emission band. A direct correlation could often be established between the form of the emission spectra and the relative intensities of the absorption components corresponding to the major and secondary Ag_2 trapping sites. This is not surprising in view of the excitation spectra illustrated in Figure 5, which show that the various emission bands are produced in different proportions by excitation of the distinct Ag_2 trapping sites. The intensity profiles of the emission spectra were also found to be sensitive to the matrix temperature. The most pronounced temperature effects were observed for the high-energy Ag_2 excitations, where in all cases the long-wavelength emission bands were favored over the short-wavelength band at higher temperatures. Intensity variations were typically 10% over a temperature range between 15 and 35 K, and were reversible in all cases. A final matrix variable concerns the effects of the total silver concentration. As for the Ag atomic emission spectra,[12] pronounced concentration quenching effects were found in the range Ag/rare gas > 10^{-2} for the Ag_2 spectra.

2. Ag_2 Spectroscopy and Photoprocesses. Five distinct band systems have been identified in the gas-phase absorption spectrum of Ag_2 in the near-UV region.[22-24] The appearance of the systems designated C–X and D–X indicates that they represent $\Delta\Omega > 0$ and $\Delta\Omega = 0$ transitions, respectively, while the $\Delta\Omega$ character of the remaining bands is uncertain. SCF-Xα-SW molecular orbital calculations for the ground and low-lying excited states of Ag_2[11] suggest the band assignments listed in Table III. The gas-phase data show that four of the band systems are of comparable intensity, and the D–X system is very weak.[25] In addition, the spectra show strongly allowed $(v',v'') = (0,0)$ transitions and red-degraded bands in all five systems, indicating that the equilibrium bond distances are only slightly longer in the excited states than in the ground state.

As described earlier, the absorption spectrum of Ag_2 in rare-gas matrices shows two major bands in all cases. In addition, there is a much weaker band at higher energy ($\simeq$230 nm) also associated with Ag_2.[11] These assignments are supported by matrix concentration studies, together with photoinduced clustering[8,9] and photodissociation[11] experiments. The lowest-energy absorption band (see Figure 1) can be unambiguously associated with the A–X system observed in the gas phase. We have already noted the absence of resolved vibrational structure, and the large and comparable gas-matrix blue shift of this band in Ar, Kr, and Xe matrices. These observations are indicative of strong guest–host interactions in the excited state. As further discussed below, the Ag_2 emission spectra and photodissociation results are similarly indicative of strong guest–host interactions.

The assignment of the strong Ag_2 matrix absorption band at higher energy (261 nm/Ar, 270 nm/Kr, and 283 nm/Xe) is not obvious, because the gas-phase data show three separate band systems in this energy range (B, C, D–X), of which two are quite strong and one (D–X) is very weak. We feel that the matrix absorption results are best interpreted in terms of a single Ag_2 transition in this region, and that the most likely assignment is $C^1\Pi_u - X^1\Sigma_g^+$.[26] Although the high-energy matrix absorption bands exhibit several distinct maxima, as shown in Figures 1 and 5, the red-shifted maxima are believed to arise from secondary Ag_2 trapping sites in the various matrices, as previously mentioned, and not from distinct electronic transitions. Support for this site-splitting proposal is derived from the Ag_2 emission spectra, as described later. The excitation profiles for the highest-energy Ag_2 emission bands in the three rare-gas matrices provide a clue for the interpretation of the high-energy absorption band. As shown in the lower traces of Figure 5, these excitation bands show a highly symmetrical doublet structure in Ar and Kr matrices. The form of the corresponding excitation band in Xe matrices is analogous. The twofold splitting of these excitation profiles is reflected in the doublet structure of the absorption bands, as shown in Figure 1. (Note that this doublet structure should be distinguished from the major band/red-shifted band matrix site-splitting effect mentioned above.) The splitting between the doublet components (578 cm^{-1} in Ar, 673 cm^{-1} in Kr, and 1206 cm^{-1} in Xe) is too large for vibrational structure, and the equal intensities of the two narrow and symmetrical components in all cases, together with the observed splittings in comparison with the gas-phase data (Table III), argue against an interpretation in terms of distinct B–X and C–X electronic transitions. Similarly, the observation that both excitations yield identical emission spectra in all cases tends to refute the idea that B–X and C–X transitions are involved. The doublet structure of the absorption bands was found to be essentially invarient under a variety of matrix conditions, including photoinduced silver-atom dimerization and thermal annealing.[28] Thus it is unlikely that the splitting is caused by matrix site effects. We feel that crystal-field effects in a $^1\Pi_1$ state could account for the observed doublet structure if we assign the matrix absorption band as $^1\Pi_u \leftarrow {}^1\Sigma_g^+$. This seems a reasonable explanation, because the excited-state degeneracy would be lifted in a crystal field having D_{2h} symmetry, which represents the most symmetrical arrangment of a homonuclear diatomic molecule occupying a divacancy in a rare-gas lattice. The significance of the MCD measurements of Grinter et al.[29] on Ag_2 molecules in Ar matrices is somewhat uncertain in this context, because of suspected Ag_2/Ag_3 band overlap problems.[30] Additional MCD experiments involving Ag_2 in Kr and Xe matrices would be very useful.

Having associated the higher-energy Ag_2-matrix absorption band with the gas-phase C–X system, we must now consider why the B–X transition does not appear in the matrix spectra, even though its intensity is comparable to that of the C–X system in the gas-phase measurements. We note that a strongly allowed ($^1\Pi_u$ or 1_u) ← ($^1\Sigma_g^+$ or O_g^+) transition and a weak or nonexistent ($^3\Pi_1$ or 1_u) ← ($^1\Sigma_g^+$ or O_g^+) transition is consistent with a (Λ,S) or Hund's case a coupling scheme, whereas comparable intensities for these transitions implies a Hund's case c situation. Our interpretation of the matrix absorption spectra therefore implies that Ag_2 in rare-gas matrices is best described in terms of (Λ,S) coupling, while Hund's case c is appropriate for Ag_2 in the gas phase. Although we cannot rationalize this apparent difference in detail, it seems plausible that crystal-field effects imposed by the matrix could influence the spin-orbit coupling through partial quenching of the orbital angular momentum.

It was noted previously that in all three rare-gas matrices there is a striking similarity between the emission spectra produced by the Ag_2 and Ag atomic excitations (see Figure 2). In view of the exact coincidence of emission-band maxima and the similar appearance of the emission profiles for 299-nm Ag and 390-nm Ag_2 excitation in Ar matrices, there is not doubt that both excitations produce the same emission bands. Similarly, the exact or near-

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(26) There is an ambiguity in the assignment of the B and C states of Ag_2 observed in the gas phase, since either a $^3\Pi_1$ or a $^1\Pi_1$ C state would satisfy the observation $\Delta\Omega > 0$ for C ← X. For convenience of discussion we have arbitrarily assigned the B and C states as shown in Table III.

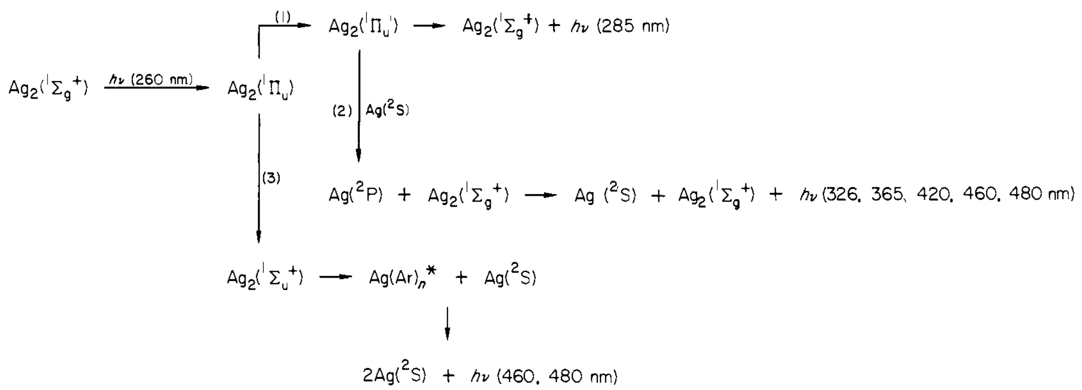
(27) T. Azumi and S. P. McGlynn, *J. Chem. Phys.*, **37**, 2413 (1962).

(28) In the case of Ar matrices, photoinduced clustering of silver atoms leads to distortion of the doublet structure due to Ag_2/Ag_3 band overlap.

(29) R. Grinter, S. Armstrong, U. A. Joyasooriya, M. McCombie, D. Norris, and J. P. Springall, *Symp. Faraday Soc.*, **14**, 94 (1980).

(30) S. A. Mitchell and G. A. Ozin, unpublished results, 1980.

Scheme I



to-exact coincidences in Kr and Xe matrices support the general conclusion that the origin of the emission bands produced by the lower-energy Ag_2 excitations in the three rare-gas matrices is the same as that of the emission bands produced by the corresponding Ag atomic excitations. It is important to note at this point that the emission bands can be produced by Ag atomic excitation in the virtual absence of Ag_2, as previously mentioned. The only exception to this statement is the 480 nm/Xe emission band. Thus the excitation spectra illustrated in Figure 4B for Kr matrices show that the 454-nm and 500-nm emission bands are produced by Ag atomic excitation in the presence of only trace quantities of Ag_2. These results for Kr matrices, together with similar results for Ar and Xe matrices, rule out the possibility that the emission bands are produced by Ag atomic excitation through energy transfer to Ag_2 molecules, as suggested by Kolb and Leutloff.[13] We conclude that all of the long-wavelength (>320 nm) emission bands illustrated in Figure 2 are associated with silver atoms, and that these same emission bands can be produced by excitation of both major Ag_2 absorption bands.

The large spectral shifts of the emission bands of Ag atoms in rare-gas matrices are caused by "cage" relaxation of the matrix trapping sites about the optically excited (^2P) Ag atoms. We have shown that the excitation dependence and overall structure of the emission spectra can be rationalized by considering a model involving Jahn-Teller instability in the excited state of the silver atom–rare-gas complexes, and vibronic coupling involving a cage vibrational mode of E_g symmetry.[12] In view of these considerations, the conclusions described in the previous paragraph suggest that lattice relaxation about the $A(^1\Sigma_u^+)$ state of Ag_2 leads to excited-state dissociation and stabilization of the atomic fragments by cage relaxation about a ^2P Ag atom. In this way, photoexcitation of the A–X transition of Ag_2 produces emission bands characteristic of Ag atoms. It is reasonable to expect that an excited-state dissociation would produce a ^2P silver atom, because the $A(^1\Sigma_u^+)$ state of Ag_2 correlates with a $5p^1\ ^2P + 5s^1\ ^2S$ separated atom limit.[23] We note that the large blue shift of the A–X matrix absorption band of Ag_2, and the smaller and more matrix-dependent shift of the C–X band, implies that the A excited state is strongly destabilized in the matrix. Thus a dissociative relaxation involving strong stabilization of the atomic fragments may be favorable energetically. The observation of net photodissociation of Ag_2 in rare-gas matrices by excitation of the A–X absorption band[11] is consistent with this proposal. Although the intensity of the emission bands produced by Ag_2 excitation suggests that the fluorescence quantum yield is near unity, absorption measurements show the quantum yield for permanent dissociation to be much lower. Thus the dominant process apparently involves a dissociation–emission–recombination sequence. This is consistent with simple energy and cage effect[20,31] considerations, from which we expect a significant barrier to net dissociation. Finally, the typical value of +0.1 (Table II) for the polarization ratio of the emission bands produced by A–X Ag_2 excitation argues against an interpretation in terms of a simple $A^1\Sigma_u^+ \rightarrow X^1\Sigma_g^+$ molecular transition, since a value near +0.5 would be expected for this case.[32] As described below, polarization ratios closely approaching the ideal value were observed for the highest-energy Ag_2 emission bands. Thus the observed polarization ratios provide indirect support for the excited-state dissociation proposal. A slight preference of the emitting axis toward parallel rather than perpendicular orientations relative to the absorbing axis could account for the small positive values of the polarization ratio observed for these bands (Table II). However, further discussion of the observed value of +0.1 must await the development of a more detailed model for the Ag_2–cage interactions.

There are several features of the spectra produced by the low-energy Ag_2 excitations which remain unclear in terms of the above interpretation. For example, the emission spectrum consists of two strong bands in all cases, and in Kr and Xe matrices there are slight shifts between the lowest-energy maxima produced by the Ag and Ag_2 excitations, as shown in Figure 2. In addition, it is unclear why the 480-nm Xe-matrix band is not produced by atomic Ag excitation except under rather concentrated conditions. The presence of two components in the Ag_2/Ar emission spectrum is probably due to matrix site-splitting effects, of the kind responsible for the splitting of the corresponding band in the Ag atomic emission spectrum.[12] In Kr matrices, the presence of two bands in the Ag_2 emission spectrum may arise because two distinct electronic transitions are possible in this case. In the model for the Ag atomic emission properties it was proposed that two different transitions occur in emission, and that these involve excited states derived from the $^2P_{1/2}$ and $^2P_{3/2}$ spin–orbit components of atomic silver.[12] The 390-nm excitation of Ag_2 in Kr matrices is at higher energy than both of these Ag "atomic" emission bands, so that both transitions are energetically feasible in this case. In Ar matrices, however, only one of the emission transitions is accessible. Note that Figures 3 and 5B show the relative intensities of the 454-nm and 500-nm Ag_2/Kr emission bands to be strongly dependent on the excitation energy. This is consistent with the interpretation given above, in terms of the accessibility of the two relaxed $Ag(^2P)$ states following Ag_2 excitation. This interpretation may not be appropriate for Xe matrices, however, because both the 480-nm and 570-nm Ag_2/Xe emission bands are apparently associated with the same Ag "atomic" emission transition.[12] It therefore seems that matrix site-splitting effects are somehow involved in this case. Finally, we note that slight shifts between the Ag and Ag_2 emission maxima may arise from the presence in the case of the Ag_2 excitations of a nearby ground-state Ag atom, derived from the excited-state Ag_2 dissociation.

The occurrence of a variety of lattice relaxation and internal conversion processes can be inferred from the emission spectra for the high-energy Ag_2 excitations in the three rare-gas matrices. As shown in Figure 2, these excitations yield emission bands characteristic of Ag atoms, as in the case of the A–X Ag_2 excitations, as well as additional emission bands at higher energy than the Ag absorption bands. Although the details of the electronic relaxation processes are unclear, the initial and final

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states are at least reasonably well-defined, as outlined in Scheme I for the case of Ar matrices.

The presence of an intense Ag_2 emission band at higher energy than the Ag atomic absorption band in each of the three rare-gas matrices, as shown in Figure 2, is indicative of an important $Ag_2(C^1\Pi_u)$ relaxation pathway involving either a radiationless transition to a lower-lying excited state of Ag_2 or a matrix cage relaxation process within the $C^1\Pi_u$ state. It is unlikely that vibrational relaxation of Ag_2 is involved, because on the basis of the gas-phase data we expect that the C-X matrix absorption band is comprised mainly of transitions to the $v = 0$ and $v = 1$ vibrational levels of the C state. It is important to note that the Ag_2 matrix absorption spectra (Figure 1) do *not* show features at the wavelengths of the emission bands. Our interpretation of the absorption spectra in terms of only one electronic transition in this spectral region, as previously described, suggests that the emission bands are caused by cage relaxation within the $^1\Pi_u$ state of Ag_2. This relaxation pathway is represented by process 1 of Scheme I where $^1\Pi_u'$ denotes the cage-relaxed $^1\Pi_u$ state. Matrix cage relaxation processes of this type have not been previously observed in the fluorescence spectra of diatomic molecules in rare-gas matrices. However, we feel that a precedent in the case of Ag_2 is plausible in view of the clear evidence for strong guest–host interactions in the case of the A state of Ag_2, as described earlier. The alternative interpretation, involving a nonradiative transition to a lower-lying excited state of Ag_2 (presumably the ($^3\Pi_1$ or 1_u) B state), and subsequent emission via a different electronic transition ($B \rightarrow X$), is doubtful because there is no corresponding band in the absorption spectrum, as would have been expected in view of the significant intensity of the emission bands. We therefore prefer the cage-relaxation mechanism, although we cannot rule out the possibility of a B–X transition. Note that a radiationless transition to the B state would involve intersystem crossing. Hence a measurement of the radiative lifetime would be helfpul in identifying the emitting state. The polarization results (Table II) are in agreement with our interpretation in terms of relaxed $C \rightarrow X$ emission, although they do not exclude the possibility of a $B \rightarrow X$ transition. For Ar and Kr matrices we find $P = +0.20 \pm 0.05$, compared to the ideal value of $P = +0.14$ expected for a Π–Σ transition.[32] The origin of the small deviation from the ideal value is uncertain, although it is likely that crystal field effects in the $^1\Pi_u$ state, as described earlier, are important. Further discussion of this point must await the development of a more detailed model for the crystal-field effects, including the nature of the proposed matrix cage relaxation about the $^1\Pi_u$ state.

Photoexcitation of the high-energy Ag_2/Ar or Kr absorption band in the region of the red-shifted maxima (273 nm/Ar and 280 nm/Kr) produces emission spectra similar to those illustrated in Figure 2, except that the highest-energy emission band is displaced to lower energy in both cases. The displacement is similar in magnitude to that of the red-shifted absorption maxima from the major absorption bands. These results are consistent with the assignment of the red-shifted maxima as being due to secondary trapping sites of Ag_2, as discussed above. These secondary sites apparently undergo cage relaxation processes similar to those of the major trapping sites, and hence yield emission bands showing similar spectral shifts, which therefore appear at lower energy.

The narrow band at 326 nm in the Ag/Ar emission spectrum is believed to be due to the $(4d^95s^2)^2D_{5/2} \rightarrow (4d^{10}5s^1)^2S_{1/2}$ transition of atomic silver, which occurs following $^2P \leftarrow {}^2S$ excitation as a result of a multiphonon relaxation process.[12] The presence of this same band in the Ag_2/Ar emission spectrum is accounted for in Scheme I by process 2, which depicts energy transfer from the optically excited Ag_2 molecules to ground-state Ag atoms. Energy transfer could be allowed by either a radiative or nonradiative mechanism, because the high-energy Ag_2 emission band overlaps to some extent the Ag absorption band. An essentially complete overlap occurs in the case of the red-shifted emission band produced by excitation of the secondary Ag_2 trapping site. The observation that the 326-nm emission band is produced almost exclusively by this excitation, as shown in Figure 5A, provides strong support for the energy-transfer proposal. We note that the alternative to an energy-transfer mechanism involves excited-state dissociation of Ag_2 to form $Ag(^2D_{5/2}) + Ag(^2S_{1/2})$, which seems very unlikely in view of the fact that in the gas phase the $^2D_{5/2} + {}^2S_{1/2}$ separated atom limit is at considerably higher energy than the low-lying vibrational levels of the $C^1\Pi_u$ state of Ag_2.[22] There is no evidence for stong stabilization of $Ag(^2D_{5/2})$ in rare-gas matrices, such as there is for $Ag(^2P)$. It is likely that energy transfer is also responsible for the presence of the 365-nm and 420-nm Ag-cage emission bands in the Ag_2/Ar emission spectrum. However, the much stronger 460-nm and 480-nm emission bands are believed to arise by a different mechanism, as described below. Energy transfer to silver atoms also seems to be involved in the cases of the very weak 370-nm and 420-nm Ag_2/Kr emission bands, and the moderately strong 680-nm Ag_2/Xe band. The relative weakness of the high-enegy Ag_2/Xe emission band at 315 nm, compared to the corresponding bands in Ar and Kr matrices, together with the relatively high intensity of the 680-nm Ag_2/Xe emission band, is understandable because the Ag_2 emission band/Ag absorption band overlap is most pronounced in Xe matrices, and this could lead to more efficient energy transfer.

The 460-nm and 480-nm emission bands produced by the high-enegy Ag_2 excitation in Ar matrices appear very intense in comparison with the weak bands arising from energy transfer to Ag atoms. The appearance of these same bands in the emission spectrum produced by A–X Ag_2 excitation, as shown in Figure 2, suggests that the C state of Ag_2 may relax by nonradiative decay to the A state, and thereby produce emission bands characteristic of the A–X Ag_2 excitation. This relaxation mechanism is represented by process 3 in Scheme I, in which $Ag(Ar)_n{}^*$ denotes a cage-relaxed ^2P Ag atom produced by dissociative relaxation of $Ag_2(A^1\Sigma_u{}^+)$, as previously discussed. Similar processes are indicated in the cases of Kr and Xe matrices.

The slightly negative values of the polarization ratios observed for these bands (Table II) suggest that perpendicular orientations of the emitting axes relative to the absorbing axes are on average slightly favored over parallel orientations.[32] It is hoped that future studies will permit a more detailed interpretation of these results, and lead to a fuller understanding of Ag_2 relaxation processes in matrices.

Conclusions

The absorption and fluorescence spectra of Ag_2 in Ar, Kr, and Xe matrices are clearly indicative of strong guest–host interactions involving the $A^1\Sigma_u{}^+$ and $C^1\Pi_u$ states of Ag_2. The absorption spectra show large gas-matrix energy shifts and intensity perturbations, extreme phonon broadening of vibronic structure, and evidence of crystal-field effects in the $^1\Pi_u$ state. Photoexcitation of the A–X absorption band of Ag_2 produces intense emission bands characteristic of Ag atoms, as a result of an excited-state dissociation process involving strong stabilization of the $^2S + {}^2P$ atomic fragments by matrix cage relaxation effects. Although quantitative measurements are yet to be completed the brightness of the emissions leads us to conclude that the quantum yield for Ag_2 photofragmentation fluorescence is fairly high, but the *net* Ag_2 photodissociation yield is much lower, probably because of matrix cage recombination effects. The electronic relaxation processes of the C state of Ag_2 are thought to include matrix cage relaxation within the C state, resulting in relaxed emission or energy transfer to Ag atoms, and nonradiative decay to the A state with subsequent relaxation by the dissociative mechanism.

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