Silver clusters: optical absorption and ESR spectra; structure and calculation of electron transitions

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The formation of Ag_3^{2+} and Ag_4^+ clusters upon freezing out of aqueous-alcohol glassy solutions of $AgClO_4$ by γ-irradiation at 77 K was established by ESR and optical spectroscopies. The Ag_3^{2+} cluster is formed by subsequent addition of Ag^+ ions to a silver atom, and the Ag_4^+ cluster is most probably formed by the reduction of the Ag_4^{2+} cluster by alcohol radicals. The energies of optical transitions and energy gaps for the Ag_4^{m+} cluster ($m = 0$ to 3) were calculated. The absorption bands of the clusters shift to the UV region as the charge increases, which agrees with the experimental results.

Key words: silver, cluster, ESR spectra, structure, optical transitions.

It is known[1—3] that γ-irradiation of glassy aqueous or aqueous-alcohol solutions of silver salts at the temperature of liquid nitrogen results in the formation of silver atoms. Freezing out of the irradiated solutions results in the formation of clusters of various compositions up to Ag_4^{m+}. A similar phenomenon takes place upon radiation-chemical reduction of silver ions in aqueous solutions at room temperature.[4—6]

In this work, data on experimental and theoretical study of silver clusters formed upon freezing out of aqueous-alcohol solutions of $AgClO_4$ after their γ-irradiation at 77 K are presented.

Experimental

Highly pure isopropanol, ethanol, and glycerol were used. Solutions were prepared using tridistilled water. The concentration of the salt added ($AgClO_4$) was 0.05 to 0.1 mol/L. The most advantageous ratio of the aqueous-alcohol mixtures was 50 : 50 mass %, which provided the preparation of sufficiently transparent "glasses," which are necessary for optical measurements, by rapid freezing of the solutions at 77 K.

γ-Irradiation was carried out on a GUG-120 ^{60}Co source at the temperature of liquid nitrogen. Optical spectra and ESR signals were also measured at 77 K. A Specord UV VIS spectrophotometer and an RE-1306 radiospectrometer were used. Portions (~0.2 mL) of solutions for ESR studies were placed in thin tubes of special glass, which gives no noticeable ESR signal after irradiation. For spectrophotometric measurements, samples of the solution studied in special cells 1 to 2 mm in width were γ-irradiated and placed in an optical Dewar flask.

Results and Discussion

Cluster formation

According to the data of Refs. 1—3, after γ-irradiation of aqueous-alcohol solutions of $AgClO_4$ at 77 K, their ESR spectra exhibit signals of silver atoms and alcohol radicals. The optical spectrum (Fig. 1) contains an intense absorption band with a maximum at 360 nm assigned to Ag^0 atoms.[4—6] Alcohol radicals absorb in the UV range (λ_{max} = 220—240 nm), and their extinction coefficient is lower (by more than an order of magnitude) than that of Ag^0 atoms.[7] Therefore, alcohol radicals do not noticeably contribute to the observed total absorption spectrum of γ-irradiated solutions. It is noteworthy that the alcohols used (ethanol, isopropanol, or glycerol) exerted no noticeable effect on the observed ESR spectra and optical spectra of "silver" paramagnetic centers. However, the quality of the "glasses" obtained and a wider temperature range of chemical transformations of the silver clusters in the case of glycerol caused its predominant use in this work. Silver atoms are formed upon capture of thermalized electrons by Ag^+ ions, while alcohol radicals are formed due to the ion-molecular reaction of maternal positive H_2O^+ or RCH_2OH^+ ions with an alcohol molecule.[8] A temperature increase to ~150 K results in almost no change in the concentration of alcohol radicals. However, it results in the disappearance of the ESR signals of silver atoms and appearance of an intense signal of the Ag_2^+ ion, which is

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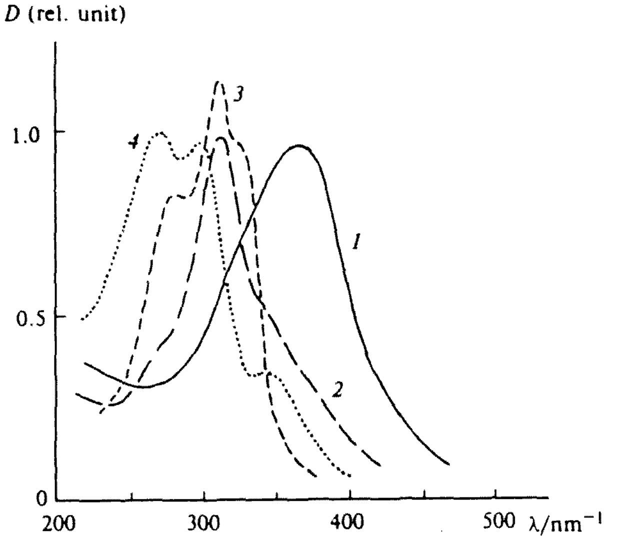

Fig. 1. Absorption spectra in an aqueous-glycerol (1 : 1) solution containing 0.1 mol L^{-1} $AgClO_4$ after γ-irradiation at 77 K (*1*) and heating to 170 (*2*), 190 (*3*), and 200 K (*4*).

caused by the reaction

$$Ag^0 + Ag^+ \rightarrow Ag_2^+. \qquad (1)$$

The latter is a triplet ESR signal with the pronounced anisotropy of the *g*-factor ($g_\perp$ = 1.985 and $g_\parallel$ = 2.000). The nuclear spins of ^{107}Ag (content 51.8 %) and ^{109}Ag isotopes are equal to 1/2, and a ratio of magnetic moments is equal to 0.885. The terminal components of the triplet can be seen in Fig. 2. Each of the components has an additional triplet splitting caused by the signals of $^{107}Ag_2^+$, $^{107}Ag^{109}Ag^+$, and $^{109}Ag_2^+$ particles formed in a ratio of ~1 : 2 : 1, whose HFS constants differ insignificantly. In the optical spectrum (Fig. 1), an intense band with λ_{max} = 300±10 nm corresponds to the Ag_2^+ cluster, which agrees well with the absorption of this ion at 310 nm in an aqueous solution at room temperature.[4–6]

A temperature increase to 170 K results in further transformation of the silver clusters. A new particle is formed, whose ESR spectrum is characterized by terminal components separated at ~57 mT (Fig. 2). Each of them has quartet splitting. Due to the peculiarities of anisotropy of the *g*-factor, this is observed most distinctly for the high-field signal, for which a ratio of intensities in the quartet is close to the binomial ratio of 1 : 3 : 3 : 1. We assign this signal to the Ag_3^{2+} cluster, which is formed in the reaction

$$Ag_2^+ + Ag^+ \rightarrow Ag_3^{2+}. \qquad (2)$$

In the central region of the ESR spectrum, two central components of the signal of this cluster overlap an intense signal of alcohol radicals. The additional quartet splitting of each of the terminal components of the signal mentioned has the same reason as that in the case of Ag_2^+, *i.e.*, it is caused by the formation of $^{109}Ag_3^{2+}$, $^{107}Ag^{109}Ag_2^{2+}$, $^{107}Ag_2{}^{109}Ag^{2+}$, and $^{107}Ag_3^{2+}$ particles with a ratio of mean statistical masses of 1 : 3 : 3 : 1. The ESR signal of this cluster was observed for the first time in toluene or alcohol matrices containing a silver salt.[9] Later, this cluster in the zeolite matrix was studied in detail.[10] The observed parameters of the signal for $^{109}Ag_3^{2+}$ ($g_\perp$= 2.014, $g_\parallel$ = 1.994, and a_{HFS} = 20.54 mT) agree well with the parameters of the ESR spectrum of the same particle in the matrices mentioned. Changes in the absorption spectrum of aqueous-alcohol solutions of $AgClO_4$ at the temperature corresponding to occurrence of reaction (2) are insignificant (Fig. 1). This correlates with the data on the optical properties of the Ag_3^{2+} cluster in aqueous solutions at room temperature. According to the data in Ref. 11, the absorption of Ag_3^{2+} is close to that of Ag_2^+: a band at 310 nm and a low-intense shoulder at 265 nm. It is noteworthy that the formation of both the Ag_3^{2+} and preceding Ag_2^+ particles occurs in the temperature range, in which almost no decay of alcohol radicals is observed.

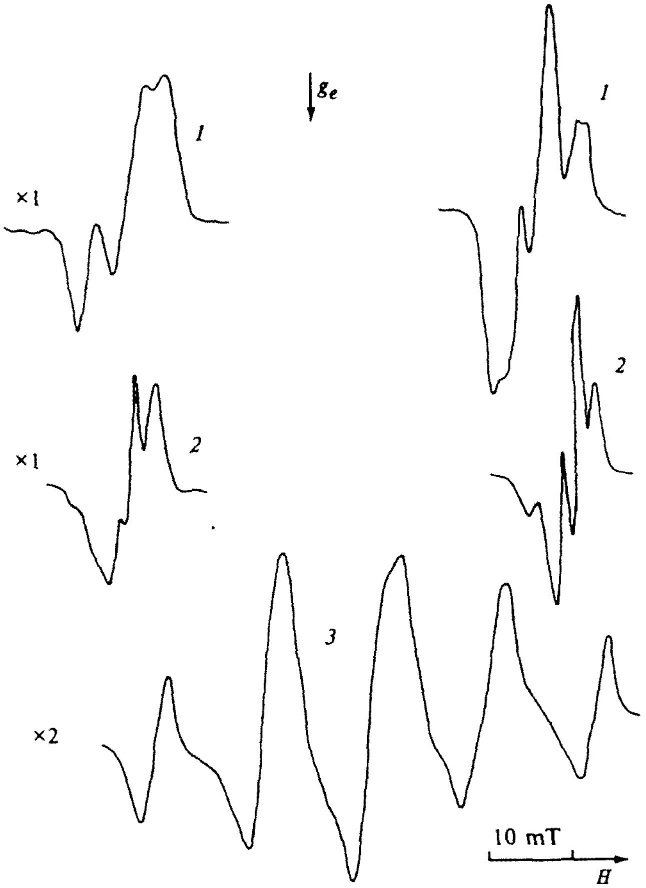

Fig. 2. ESR spectra in an aqueous-glycerol (1 : 1) solution containing 0.1 mol L^{-1} $AgClO_4$ after γ-irradiation at 77 K (*1*) and heating to 170 (*2*) and 200 K (*3*).

Melting of glassy aqueous-alcohol solutions begins at 190 K and is accompanied by a jumpwise change in mobility of alcohol radicals and silver clusters to result in a substantial change in the ESR and absorption spectra (Figs. 1 and 2). In the ESR spectrum, the signal of alcohol radicals and Ag_3^{2+} clusters disappears with simultaneous appearance of the quintet with a ratio of intensities of the components of 1 : 4 : 6 : 4 : 1, which is close to binomial one, and splitting of ~13.5 mT between them. The parameters of the hyperfine structure definitely indicate to the interaction of the unpaired electron with four approximately equivalent silver atoms. For the first time, this signal was observed by the authors of Ref. 2, and it was assigned to the Ag_4^{m+} tetramer (where m can be 1 or 3). The Ag_4^{3+} particle formed due to subsequent addition of the third Ag^+ ion to the silver atoms was preferred later.[12] However, the formation of the tetramer during the decay of alcohol radicals and the results of theoretical calculations presented above allow us to assign this signal to the Ag_4^+ particle. Overlapping bands with maxima at 260 (assigned to the Ag_4^{2+} cluster)[4—6] and 300 nm as well as a less intense band at ~350 nm appear in the optical spectrum after heating at 190 K. These changes are related to the occurrence of the following reactions:

$$Ag_3^{2+} + Ag_3^{2+} \rightarrow Ag_4^{2+} + 2Ag^+, \qquad (3)$$

$$Ag_4^{2+} + ROH \rightarrow Ag_4^+ + H^+ + RO. \qquad (4)$$

According to our data, the absorption bands with the maxima at 300 and 350 nm can be assigned to the Ag_4^+ cluster. This is indicated by the correlation between the changes in the intensities of these bands and the quintet ESR signal. Further increase in temperature by ten degrees results in nearly complete disappearance in the ESR signals, and the sample looses to a considerable extent its transparency, which prevents obtaining reliable information about absorption spectra. Only the absorption band of the Ag_4^{2+} cluster and the broad blurred absorption in the visible range with a maximum at ~400 nm caused by colloidal silver are recorded rather definitely. A gray precipitate of silver metal is formed after melting of the samples studied. It should be once more emphasized that these transformations of silver clusters are observed without basic distinctions for aqueous solutions of glycerol, isopropanol, or ethanol. Changes are mainly observed for the temperature range of transformations and quantitative ratios of paramagnetic centers.

Peculiarities of cluster formation mechanism

Two temperature ranges of transformations of the silver clusters can be distinguished. The first of them (up to ~170 K) is associated with the formation of Ag_2^+ and Ag_3^{2+} clusters and, in our opinion, corresponds to "freezing out" of the mobility of Ag^0 atoms and Ag^+ ions. The second range (at ~190 K) is caused by melting of glass and results in the formation of Ag_4^{2+} and Ag_4^+ tetramers.

The existence of two structural phase transitions for glassy aqueous and aqueous-alcohol solutions has previously been established.[13] The first of them is caused by "freezing out" of the rotational mobility of molecules and initiates disappearance of ions and radicals stabilized in intermolecular traps due to solvating forces: certain orientation of dipoles of polar water or alcohol molecules (for example, solvated electron, H atom, and others). The second structural transition is caused by the phase transition of the substance from the metastable glassy state to the crystalline or liquid state. The translational mobility of molecules of the substance along with that of ions and radicals incorporated into the matrix is "frozen out" in the temperature range of this transition. The temperature ranges of transformation of the silver clusters established in this work rather exactly correspond to the temperatures of the structural phase transitions of the aqueous-alcohol glasses studied.[13]

Reduction potentials of the radicals formed in the case of ethanol ($CH_3\dot{C}HOH$, $E^0 = -1.1$ V), isopropanol ($(CH_3)_2\dot{C}OH$, $E^0 = -1.5$ V),[14] and, likely, glycerol ($CH_2(OH)-\dot{C}(OH)-CH_2(OH)$) are insufficiently high for reduction of Ag^+ ions, because $E^0(Ag^+/Ag^0) = -1.8$ V. However, the potential of the silver clusters increases as the change and number of atoms composing the cluster increase. For example, even $E^0(Ag_2^+/2Ag^+) \le -1.44$ V, and $E^0(Ag_2^0/2Ag^+) \le 0.5$ V.[6]

According to the published data,[11] in liquid aqueous solutions the disappearance of the Ag_3^{2+} clusters is accompanied by the formation of the Ag_4^{2+} ion (λ_{max} = 265 nm) in reaction (3). Taking into account the stabilizing role of the Ag^+ ions in the Ag_4^{2+} cluster, its potential should be considered more positive than $E^0(Ag_2^0/2Ag^+)$ and, thus, it should be efficiently reduced by alcohol radicals. In fact, the absorption bands, which can be assigned to the Ag_4^{2+} (~260 nm) and Ag_4^+ (bands at 300 and 350 nm) are present in the optical spectrum of the solution at 190 K (Fig. 1).

Calculation of optical transitions for Ag_4^{m+} clusters

Optical transitions for Ag_4^{m+} clusters (where m = 0 to 3) were calculated for two possible structures: square and tetrahedron. The values of energies of one-electron levels were obtained by the X_α wave scattering method. The Ag—Ag distances ranged from 4.8 to 5.2 atomic units (au) according to the known interatomic distances in the Ag_2 (4.72 au) and Ag_6 (5.22 au) clusters.[15] It is established that the experimental results are in the best agreement with the square structure of all Ag_4^{m+} clusters; therefore, the results of calculations for this structure are presented in Table 1. The designations (−) and (+) correspond to the transitions forbidden and allowed by symmetry, respectively. For each electron transition, its type and correspondence to atomic orbitals (s or p)

Table 1. Optical transitions of Ag_4^{m+} clusters, λ (nm)

Cluster	Experiment			Calculation			
	ΔE/eV	λ/nm	Ref.	λ/nm	Transition	Type of transition	Atomic orbitals
Ag_4^0	$\Delta E(1e_g-1b_{1g}) = 1.8\div2.0$	300 (Ar)	16, 17	220—262	(−)	$1a_{1g}-1b_{1g}$	s—p
		350 (Ar)	16, 17	326—331	(+)	$1a_{1g}-1a_{1g}$	s—p*
		330 (aq)	6	405—409	(+)	$1e_g-1e_u$	s—p
		490 (Ar)	16, 17	438—460	(−)	$1e_g-2a_{1g}$	s—p
				550—577	(−)	$1e_g-1b_{2g}$	s—p
				553—690	(−)	$1e_g-1b_{1g}$	s—p
Ag_4^{1+}	$\Delta E(1e_g-1b_{2g}) = 1.9\div2.1$			225—250	(−)	$1a_{1g}-1b_{2g}$	s—p
		300 (aq)	4, 6	300—310	(+)	$1a_{1g}-1a_{1u}$	s—p*
		~300 (aq) (77 K)	*				
		360 (aq)	4, 6	360—370	(+)	$1e_g-1e_u$	s—p
		~360 (aq) (77 K)	*	370—410	(−)	$1a_{1g}-1e_g$	s—p
				545—560	(−)	$1e_g-1b_{1g}$	s—p
				580—645	(−)	$1e_g-1b_{2g}$	s—p
Ag_4^{2+}	$\Delta E(1a_{1g}-1e_g) = 3.2\div3.7$	265 (aq)	4, 6	270—293	(+)	$1a_{1g}-1a_{1u}$	s—p*
		~270 (aq) (77 K)	*	335—390	(−)	$1a_{1g}-1e_g$	s—p
Ag_4^{3+}	$\Delta E(1a_{1g}-1e_g) = 3.6\div3.9$			260—277	(+)	$1a_{1g}-1a_{1u}$	s—p*
				316—348	(−)	$1a_{1g}-1e_g$	s—p

* Data of this work.

are indicated. The symbol (*) marks the type of transition that, as can be expected, is the most intense. This is transition $1a_{1g} \rightarrow 1a_{1u}$. The energy gap ΔE characterizes the difference in energies of the last occupied and first unoccupied molecular levels. The experimental values of positions of absorption bands of charged Ag_4^{m+} clusters in aqueous solutions and in the matrix of inert gases are also presented in Table 1. Good agreement between the results of calculation and the experimental data for the Ag_4^+ and Ag_4^{2+} tetramers is observed for the series of experiments in aqueous media. We have already mentioned that the authors of Ref. 12 assigned the quintet ESR signal of the silver tetramer to Ag_4^{3+}. The results of this study do not confirm this interpretation. The absorption band of the Ag_4^{3+} cluster, if it exists, should be in a deeper UV range than the band of Ag_4^{2+}, *i.e.*, at wavelengths less than 265 nm. However, it was not observed in the experiment performed or upon pulse radiolysis of aqueous solutions at room temperature.[11] It is most likely that this particle is not formed at all due to strong Coulomb repulsion.

Silver clusters most likely exist as aqua complexes. Therefore, the appearance of forbidden transitions due to a decrease in symmetry could be expected. However, no distinct manifestation of such transition was established. Low-lying free molecular levels participate in the interaction with water molecules and are low active in electron transfer. This should especially concern the highly positively charged Ag_4^{2+} and Ag_4^{3+} clusters, in which the values of energies of the $1e_g$ and $1a_{1g}$ levels are more negative than those in clusters with charges equal to 0 or +1. Transitions $1a_{1g} \rightarrow 1a_{1u}$ are active and can be well observed. They are characterized (as other transitions of the same type) by the shift of the absorption band to the UV range as the charge of the cluster increases. As can be seen, the ΔE value increases as the charge of the cluster increases. On going from Ag_4^0 and Ag_4^+ to Ag_4^{2+} and Ag_4^{3+}, the change in ΔE is jumpwise, which is caused by the presence of the occupied $1e_g$ orbital in the first of them and only of the $1a_{1g}$ orbital in the second clusters. The experimental ΔE value for Ag_4^0 is equal to 1.9 eV,[18] and the calculated value is 2.1 eV.[19] Our calculations give the value of 1.8 to 2.0 eV for the square configuration at the distance of 4.8 to 5.2 Å between the atoms. It is noteworthy that ΔE is equal to 2.7 to 3.1 eV for the tetrahedral structure.

In aqueous solutions at room temperature metal nucleation is the result of subsequent coalescence of silver clusters. Thus, the product of aggregation of the Ag_4^{2+} clusters is a more complex cluster (presumably, Ag_8^{2+}),[20] which is a precursor of silver sols formed. At low temperatures, more exactly, in viscous media due to restriction of mobility of large clusters, the process of their subsequent enlargement can be predominantly related to reduction of adsorbed Ag^+ ions by more mobile organic radicals and molecules-reducing agents. The results obtained in this work testify to a certain extent in favor of this mechanism. The Ag_4^{2+} clusters are the centers of growth of metal nuclei. Undoubtedly, this directly concerns the mechanism of the photographic process, and such clusters are hidden centers of images.

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