

Long-Lived Nonmetallic Silver Clusters in Aqueous Solution: Preparation and Photolysis

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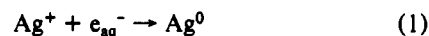
Abstract: Radiolytic reduction of Ag^+ ions in aqueous solution and reduction by sodium borohydride in the presence of polyphosphate leads to long-lived nonmetallic silver clusters besides particles of metallic silver (having a narrow plasmon absorption band at 380 nm) and quasi-metallic silver (having a blue-shifted and broadened plasmon absorption band). The best conditions for the preparation of cluster solutions are described, and a mechanism of cluster formation is discussed. The Ag_4^{2+} cluster formed in the first stages of Ag^+ ion reduction lives for many hours even in the presence of air. It is oxidized by H_2O_2 and $\text{K}_2\text{S}_2\text{O}_8$. Its great stability is explained on the basis of the oscillatory behavior of the standard redox potential of silver microelectrodes at very small agglomeration numbers as described previously.¹³ Larger clusters with sharp absorption bands at 300, 330, and 345 nm (absorption coefficients of more than $10^4 \text{ M}^{-1} \text{ cm}^{-1}$) are formed in the later stages of Ag^+ reduction. They are very sensitive toward air and thermally less stable than Ag_4^{2+} . The absorptions of these clusters are tentatively attributed to CTTS transitions. These clusters are readily photolyzed by 308-nm light to yield larger particles of quasi-metallic (ca. 360 nm) and metallic (ca. 380 nm) silver. On the other hand, illumination of the quasi-metallic particles with 366-nm light causes fragmentation to yield smaller clusters. Flash photolysis shows that 308-nm light causes electron ejection from the clusters with yields greater than 0.10, while electrons are not ejected from metallic particles. Ejection of one electron from a cluster leads to complete disappearance of its sharp absorption band. It is tentatively proposed that open-shell clusters in aqueous solution possess a sharp absorption band in the 300–345-nm range, while closed-shell clusters do not or little absorb there.

The reduction of silver ions in aqueous solution yields under certain conditions silver clusters consisting of a small number of atoms, which do not yet possess metallic properties.^{1,2} These clusters may be kept in solution for hours, enough time to study their properties and chemical reactivity. The stabilization of the clusters is brought about by sodium polyphosphate being present at low concentrations (10^{-4} – 10^{-3} M). The metal complexing properties of polyphosphates have been studied thoroughly a few decades ago.³ The conception in the present and previous work^{1,2} is to complex and thus stabilize the intermediate clusters formed in the reduction of metal ions in solution. Metal clusters are of great interest in various fields of physics and chemistry.⁴ However, their investigation has been confined to date to the gaseous and solid phase. For example, silver clusters have been observed in zeolites,⁵ rare gas matrices at low temperature⁶ and in frozen solutions.⁷ Our finding that clusters can also be observed in liquid solution at ambient temperature opens new possibilities for carrying out chemical reactions with them and studying their physico-chemical properties.

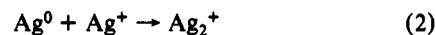
The reduction of silver ions generally leads to a yellow sol of colloidal particles several nanometers in diameter. The absorption spectrum of such a solution contains a rather narrow band peaking at 380 nm and having a half height width of about 25 nm. This band is caused by surface plasmon absorption of the electron gas in the particles, and once this band is observed one may conclude that one is dealing with particles having metallic properties. The time-resolved transition from the silver atoms to metallic colloidal particles has been studied some time ago in our laboratory by observing how the 380-nm band develops during the growth.⁸ In a transition region of growing particles (agglomeration numbers

around 10) the plasmon band develops, first peaking at shorter wavelengths (about 360 nm) and being strongly broadened.⁸ We call silver species having this displaced and broadened plasmon absorption band "quasi-metallic". The observed sharp bands below 360 nm are attributed to oligomeric silver species, which we call "clusters" and which are nonmetallic. In fact, it is known from studies of silver oligomers in rare gas matrices at low temperature that they absorb in this wavelengths range.⁶

In the present paper, the best conditions for cluster formation in the reduction of silver ions are investigated. The reduction in the previous work was carried out radiolytically, i.e., by exposing the deaerated solution to the γ -rays of a ^{60}Co source. Radiation produces hydrated electrons in aqueous solutions which are known to reduce silver ions:⁹



It is also known that the atoms thus formed rapidly are complexed by Ag^+ ions



and that the Ag_2^+ ions dimerize:



The absorption spectra of these species have also been observed (maxima at 360 nm (Ag^0), 310 nm (Ag_2^+), and 275 nm (Ag_4^{2+}).^{10b} The above reactions in the presence of polyphosphate have recently been studied using the method of pulse radiolysis.² It was found that reaction 3 is strongly accelerated by polyphosphate and that the life time of the Ag_4^{2+} species is tremendously increased. In the absence of polyphosphate, this species dimerizes within milliseconds and further agglomerations take place until the first metallic particles appear.

The radiolysis method is also used in the present preparation of cluster solutions. It has the advantage of high reproducibility and that the number of reducing equivalents generated, i.e. the number of Ag^+ ions consumed, is known within a few percent.

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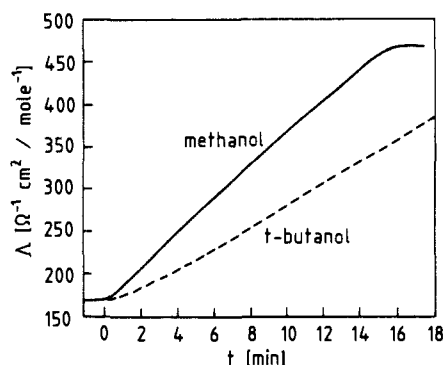


Figure 1. Conductivity as a function of γ -irradiation time in the presence of methanol and *tert*-butyl alcohol: 2×10^{-4} M AgClO_4 , 0.03 M methanol; dose rate, 1.23×10^5 rad/h; no polyphosphate.

Furthermore, as mentioned, the first elementary steps of silver ion reduction are known in detail. However, clusters were found to be formed also in the reduction of silver ions by more conventional chemicals, such as sodium borohydride. Although this method is not so reproducible, one experiment is described here in order to enable those readers who do not have access to γ -radiation to prepare silver cluster solutions.

Experimental Section

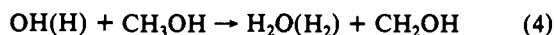
The experimental conditions for observing clusters formed by γ -radiation have been described recently.¹ The solutions contained AgClO_4 (10^{-4} – 10^{-3} M) and alcohol (0.1–1 M); sodium polyphosphate from Riedel des Haen was present at 1.2×10^{-3} M, the molarity referring to the formula $(\text{NaPO}_3)_n$. The solutions were evacuated with a water pump in a glass vessel carrying a side arm with a cuvette for optical measurements. Some vessels had a pair of Pt electrodes for the measurement of the conductivity during irradiation. The vessels were exposed to the γ -rays of a ^{60}Co source. Reagents were added after irradiation in the absence of air as described previously.¹

Photolysis experiments were carried out by using the light of a 450-W xenon lamp with a 10-cm water filter and various UV cut-off filters. Monochromatic light was used to illuminate into the various absorption bands of the clusters and to determine quantum yields.

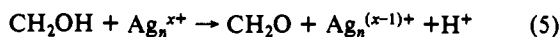
Flash photolysis was carried out with a Lambda Physik excimer laser, type EMG 201, as excitation source ($\lambda = 308$ nm). A detailed description of the laser system has been given previously.¹¹ The actinometer was potassium ferrocyanide, from which e_{aq}^- is produced with a quantum yield of 0.28 (measuring $[e_{\text{aq}}^-]$ at 700 nm using $\epsilon = 1.7 \cdot 10^4 \text{ M}^{-1} \text{ cm}^{-1}$).

Results

The Overall Reduction Rate in γ -Radiolysis. The solutions contained 0.1–1 M alcohol besides silver perchlorate and sodium polyphosphate. The alcohol serves to scavenge hydroxyl radicals and a small amount of hydrogen atoms which are produced besides hydrated electrons in the radiolysis of the aqueous solvent. In these scavenging processes, free organic radicals are formed. For example, in the presence of methanol, the hydroxy methyl radical is generated:



The radicals generally have reducing properties. They cannot transfer an electron to Ag^+ ions in solution as the standard redox potential of the system Ag^+/Ag^0 in solution is too negative (i.e., -1.8 V).^{8,10} However, as positively charged silver clusters are formed in reactions 1–3 initiated by hydrated electrons, the organic radicals may contribute to the reduction by reacting with the clusters:



The molar conductivity of the solution increases during the reduction. By measuring this increase as a function of irradiation time the yield of reduced silver can be determined. Figure 1 shows the results obtained with solutions containing methanol or *tert*-butyl alcohol as additives. Polyphosphate was absent as it disturbs the conductivity measurements by acting as a buffer. In the case

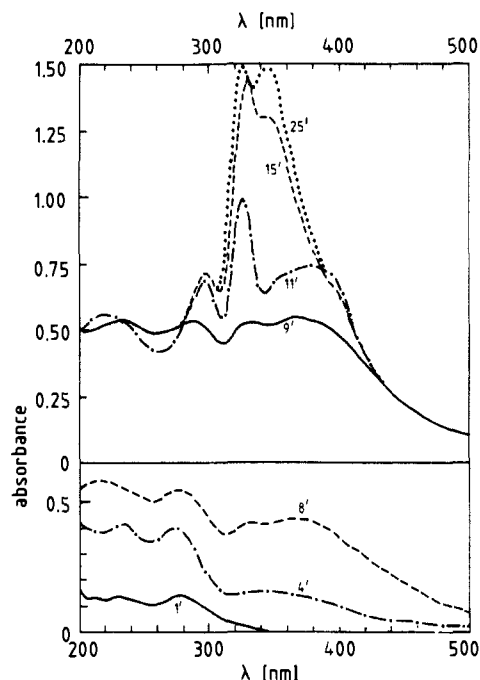


Figure 2. γ -Irradiation of a solution containing 2×10^{-4} M AgClO_4 , 1.2×10^{-3} M polyphosphate, 0.03 M CH_3OH ; initial pH, 9.0; 1.23×10^5 rad/h; rate of Ag^+ reduction, $1.25 \times 10^{-5} \text{ M} \cdot \text{min}^{-1}$.

of methanol, the conductivity increases practically linearly with time up to about 70% conversion. The curve then strives a little more slowly toward the final value of the molar conductivity which corresponds to the reduction of all the Ag^+ ions. From the slope of the curve a radiation chemical yield $G(-\text{Ag}^+)$ of 6.0 ions reduced per 100 eV absorbed radiation energy is calculated. This is the value expected for the case in which all organic radicals generated contribute to the reduction (hydrated electrons are formed with a yield $G(e_{\text{aq}}^-) = 2.7/100$ eV, hydroxyl radicals with $G(\text{OH}) = 2.7$, and hydrogen atoms with $G(\text{H}) = 0.6/100$ eV⁹). A similar curve was observed for a solution containing 2-propanol; in which the attack of OH and H radicals leads to $(\text{CH}_3)_2\text{COH}$ radicals.

In the presence of *tert*-butyl alcohol, the conductivity increases more slowly. In the beginning, the curve slightly bends toward the ordinate axis, which indicates that the radicals from *tert*-butyl alcohol are less efficient reductants. From the slope of the curve at longer times a yield $G(-\text{Ag}^+)$ of 3.8/100 eV is calculated. The final value of the conductivity was the same as in the case of the methanol-containing solution, i.e., all Ag^+ ions were finally reduced. *tert*-Butyl alcohol reacts with OH and H radicals to yield the 2-hydroxy alkyl radical $\text{CH}_2\text{C}(\text{CH}_3)_2\text{OH}$, which is known to possess less reducing power than the 1-hydroxy alkyl radicals formed from methanol and 2-propanol.¹²

Conductivity measurements were also made with silver solutions containing polyphosphate and methanol. The conductivity increase reached its final value after the same irradiation time as in the absence of polyphosphate, although this value was much lower because of the partly buffering action of polyphosphate. It is concluded that the organic radicals contribute to the reduction also in the presence of the stabilizer.

Absorption Spectra. Figures 2 and 3 show absorption spectra of silver solutions which were reduced radiolytically (Figure 2) and chemically (Figure 3).

The temporal development of the absorption spectrum of a solution, which contained methanol as additive, in Figure 2 may be compared with Figure 2 in ref 1, where the spectra of a solution containing 2-propanol are shown. In principle, one observes the same features. At short times (lower part of figure), two UV bands at 235 and 275 nm appear and very little absorption is present around 380 nm where metallic silver absorbs. However, at longer

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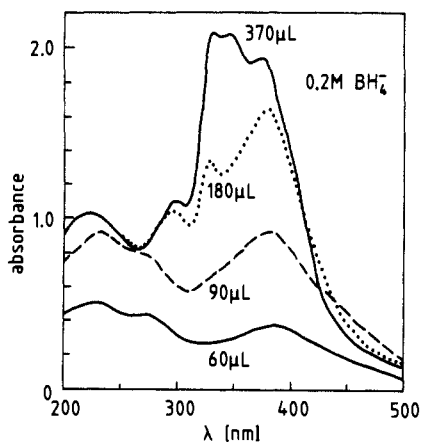


Figure 3. Development of the absorption spectrum in the reduction of Ag^+ by NaBH_4 .

times the absorption in the 300–500 nm range becomes relatively stronger. The upper part of the figure shows what happens at irradiation times longer than 9 min. Rather suddenly two new bands, i.e., at 300 and 330 nm, appear, and the bands at 235 and 275 nm vanish. Upon further reduction, a band at 345 nm develops. After 19 min, all the silver ions are reduced. At longer times, changes still occur. In fact, the spectrum after 20 h contains mainly the plasmon absorption band of colloidal silver metal.

As in the previous work,¹ the bands at wavelengths substantially shorter than that of the plasmon absorption band are attributed to small silver clusters having nonmetallic properties. The structure Ag_4^{2+} has previously been assigned to 275-nm peak.² The comparison with Figure 2 in ref 1 shows that in the presence of 2-propanol less cluster absorption is produced with respect to metallic colloid absorption, although the rate of reduction was the same in both cases. This indicates that the nature of the organic radicals formed in reaction 4 strongly influences the distribution of the reaction products.

Figure 3 shows the development of the spectrum upon reduction by addition of NaBH_4 . Various amounts of a freshly prepared 0.2 M solution of NaBH_4 in water were added to 100 mL of a solution containing 2×10^{-4} M AgClO_4 and 1.2×10^{-3} M polyphosphate, the initial pH being 9.0. The preparation occurred under argon. One can see that all the bands at shorter wavelengths developed which were observed in the radiolytic reduction. However, the contribution of metallic silver (absorption band at 380 nm) is greater than in the radiolysis experiments of Figure 2. We have not tried to optimize the conditions for the chemical reduction of Ag^+ . Small quantities of silver clusters were also formed when CO or H_2 was bubbled through alkaline solutions of Ag^+ and polyphosphate. These reduction reactions are very slow.

On the other hand, the composition of the solution used in the γ -irradiation experiments of Figure 2 was at an optimum. Solutions having an initial pH much different from 9.0 or having higher silver ion concentrations also acquired absorption bands at wavelengths shorter than that of the plasmon absorption. However, the contribution of these bands to the total absorption was smaller, since relatively more metallic silver was formed.

In solutions containing *tert*-butyl alcohol as OH scavenger the 275-nm band of Ag_4^{2+} developed more strongly than in the presence of methanol. Figure 4 shows the absorption spectrum at various times. After 11 min, a pronounced 275-nm band is present and rather little absorption occurs in the 300–400 nm range. At longer times, the long wavelength absorptions become relatively much stronger and a weak cluster band appears at 330 nm.

Thermal Decay of the Clusters. The changes occurring upon aging at room temperature are shown in Figure 5. The cluster solution was made by irradiating a solution for 18 min, i.e., up to almost complete reduction of the Ag^+ ions. Upon aging at room temperature, the 345-nm band decreased more rapidly than the 330- and 300-nm bands. After 6 h, new maxima appeared at 360

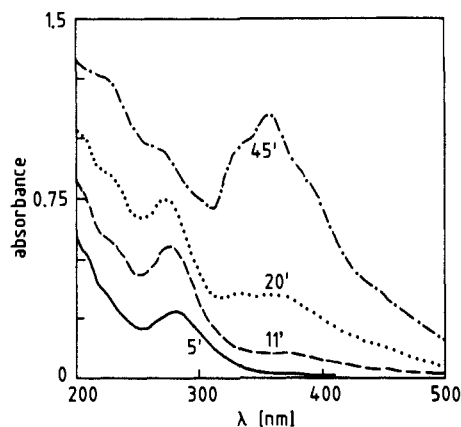


Figure 4. Spectra of a 5×10^{-4} M AgClO_4 solution containing 0.5 M *tert*-butyl alcohol after different irradiation periods: polyphosphate, 1.2×10^{-3} M.

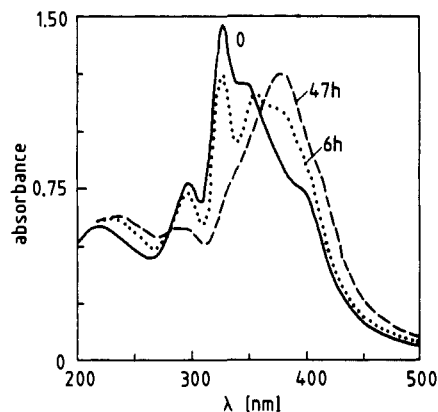


Figure 5. Thermal aging at ambient temperature. Spectrum of a solution after various times. Solution as in Figure 2: 18-min γ -irradiation.

and 380 nm. After 45 h, the 380-nm band of metallic silver dominated the spectrum, only very weak shoulders or maxima still being present at shorter wavelengths. These observations are interpreted as the thermal conversion of clusters to larger metallic particles. The fact that the bands at 300, 330, and 345 nm disappeared with different rates indicates that clusters with different stabilities were present, i.e., the bands belong to different clusters.

Similar experiments were carried out with a solution which had been prepared by γ -irradiation for only 15 min, i.e., which contained more unreduced silver ions after irradiation. Under these circumstances, the thermal decay of the cluster bands was about 3 times faster than in the absence of Ag^+ ions in the experiments of Figure 5. It is therefore concluded that the clusters are destabilized by the presence of excess silver ions. This conclusion is corroborated by experiments in which the solution was completely reduced and 5×10^{-5} M Ag^+ ions added subsequently. The decay of the absorption bands was also accelerated under these conditions.

Experiments on the thermal decay of the Ag_4^{2+} cluster, which absorbs at 275 nm, are shown in Figure 6. This cluster is much more stable than the above clusters absorbing at 300, 330, and 345 nm. Elevated temperatures are therefore necessary to make the cluster decay rapidly. Figure 6 shows the absorption spectrum after various times of aging at 70 °C. One can see that the disappearance of Ag_4^{2+} is accompanied by the formation of colloidal silver absorbing in the 350 to 500-nm range. Note that the maximum of the absorption band of the colloid is at 360 nm, i.e., at a wavelength shorter than that of the regular plasmon absorption band. It is concluded that not all the larger particles formed from Ag_4^{2+} have fully metallic character. Figure 7 shows an Arrhenius plot of the rate of decay. From the slope of the straight line obtained an activation energy of 80 $\text{kJ}\cdot\text{mol}^{-1}$ is calculated. Probably, detachment of a cluster from the stabilizer

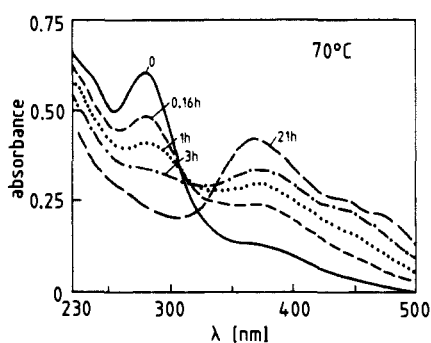


Figure 6. Absorption spectrum of a solution containing *tert*-butyl alcohol before and after various times of aging at 70 °C. Solution as in Figure 4 prepared by 11-min γ -irradiation. The larger silver particles present after the complete decay of the 275-nm band also absorb at this wavelength. This was taken into account in the calculation of the rates of disappearance in Figure 7.

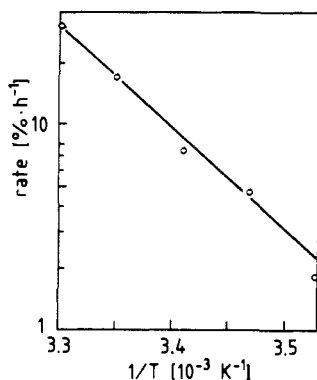


Figure 7. Arrhenius plot of the rate of thermal decay of Ag_4^{2+} . Solution as in Figure 6. The rates are initial rates and are given in $\% \cdot \text{h}^{-1}$ as the initial absolute cluster concentration was not known.

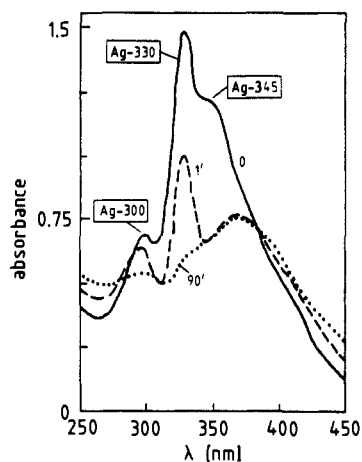


Figure 8. Spectrum after preparation of a solution (0) and 1 and 90 min after addition of air. Solution as in Figure 2: 15-min irradiation.

chain is the first step, followed by cluster-cluster interactions in solution. If the first step is rate determining, the activation energy would have to be interpreted as the energy to detach a cluster from the chain.

Reaction with Oxygen and Hydrogen Peroxide. Figure 8 shows that the 300- and 330-nm bands rapidly disappeared when the irradiated solution was exposed to air. To make the decay relatively slow, air was admitted in this experiment at a pressure of only 80 mbar (corresponding to an O_2 concentration in the solution of 2.1×10^{-3} M). The decay of the 345-nm band was much faster than that of the 330- and 300-nm bands. In order to investigate this in more detail, the experiment of Figure 9 was performed, in which the spectra of a cluster solution were taken before and at various time periods after admission of air by using a Bruins Instruments spectrophotometer, type Omega 10, which allows

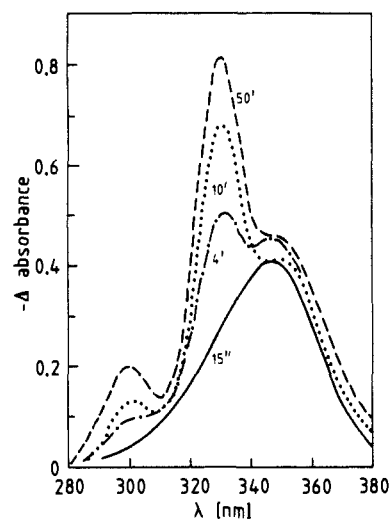


Figure 9. Absorbance change of the solution of Figure 7 at various times after the addition of air.

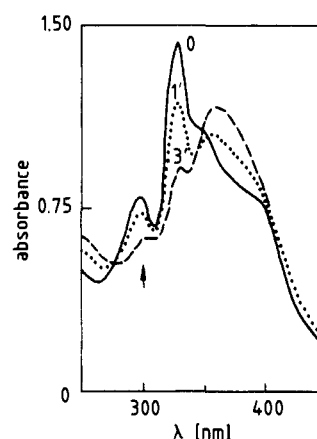


Figure 10. Spectrum of a cluster solution before (0) and after illumination with 308-nm light. The solution was made by a 15-min irradiation of $2 \cdot 10^{-4}$ M AgClO_4 , 0.03 M methanol, and $1.2 \cdot 10^{-3}$ M polyphosphate.

scanning a spectrum within milliseconds. The spectra obtained were subtracted from that before air admission. The difference spectra shown in the figure describe the bleaching of the various bands. It is seen that 15 s after admission of air practically only the broad 345-nm band had disappeared. At longer times, the 330-nm band started to disappear and then finally the 300-nm band did so, still more slowly. The fact that the three bands show different sensitivities toward oxygen indicates that they belong to different cluster species.

In contrast to the thermal decay of the cluster absorption bands there is no significant increase in absorption at longer wavelengths when oxygen is added. This is in fact expected if the decay is due to the reoxidation of the clusters and not to their thermally catalyzed growth to form larger metallic particles. Quite similar observations were made when 1×10^{-4} M H_2O_2 was added to a cluster solution.

The reactivity of the Ag_4^{2+} cluster toward oxygen was studied by exposing a solution which had been made as described in Figure 4 (11-min irradiation) to air. It turned out that this did not influence the rate of the thermal decay. It thus has to be concluded that this cluster has an extraordinarily positive redox potential. The cluster was reactive toward hydrogen peroxide, although the oxidation rate was smaller by about an order of magnitude than that of the clusters absorbing in the 300–345-nm range. Addition of 10^{-4} M $\text{K}_2\text{S}_2\text{O}_8$ to a Ag_4^{2+} cluster solution led to a more rapid oxidation.

Photolysis. Figure 10 shows the spectrum of a cluster solution before and after illumination with 308-nm light. Probably all the silver species present have some absorption at this wavelength. It is seen that the absorptions of the clusters at 300, 330, and 345

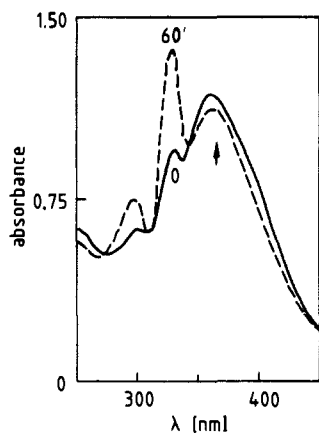


Figure 11. Illumination by 366-nm light of the solution obtained in Figure 2 after 3 min. Spectrum before (0) and after 1-h illumination.

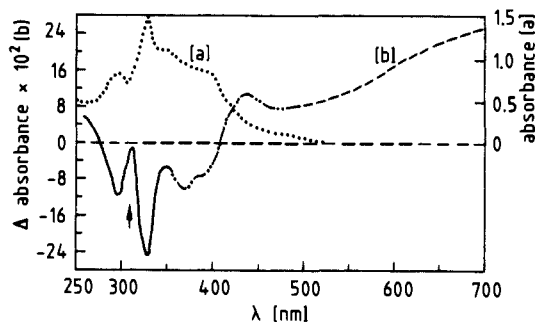


Figure 12. Flash photolysis of a cluster solution: (a) absorption spectrum of the solution and (b) difference spectrum immediately after the laser flash. Laser dose: 400 μM absorbed photons. Solution as in Figure 2.

nm decrease, the rate of decrease increasing in the given order. At the same time there is an increase in the absorptions at wavelengths around 360 nm and at longer wavelengths, where quasi-metallic and metallic particles of silver absorb. Obviously, the conversion of clusters into larger particles is catalyzed by light. The quantum yield for the disappearance of the 330-nm cluster was calculated in an approximate manner by using an absorption coefficient of $2 \cdot 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ (see Discussion) and the total absorbed photon flux at 308 nm. The value of 0.05 clusters destroyed per absorbed photon obtained in this way is certainly a lower limit as it was tacitly assumed that the product of photolysis does not absorb at 330 nm and that all absorbed photons were absorbed by the 330-nm cluster only. The quantum yield could well be greater by a factor of 3.

The solution obtained after the 3-min illumination with 308-nm light in Figure 10 was now further illuminated with 366-nm light which is absorbed by the quasi-metallic particles. Figure 11 shows how the spectrum changed after 1 h. It is seen that the absorptions of the larger particles decrease and that the 300- and 330-nm cluster bands appear. It thus seems that 366-nm light has an effect opposite to that of 308-nm light (Figure 10): larger particles are photofragmented to yield smaller clusters. The quantum yield for this process, however, is much smaller than for the photocatalyzed growth at 308 nm as much longer illumination times were required.

Flash Photolysis. The results of 308-nm flash photolysis experiments are shown in Figures 12 and 13. Curve a in Figure 12 shows the absorption spectrum of the solution with the typical 300- and 330-nm cluster bands and the absorptions around 360 nm by almost metallic and at longer wavelengths by metallic particles.

Curve b is the difference spectrum recorded immediately after the 30-ns flash. It is divided into three parts. At long wavelengths (---), a strong absorption is present which decays in the microsecond range. In the presence of 0.1 M acetone in the solution this absorption did not occur. The absorption has all the characteristic features of that of the hydrated electron. It thus is

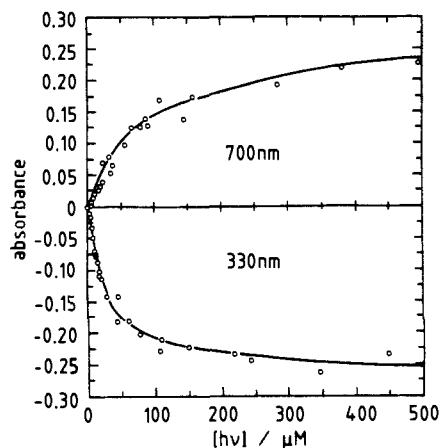


Figure 13. Absorption of hydrated electrons generated and decrease in 330-nm cluster absorption as functions of the laser dose (expressed as concentration of absorbed photons). Solution as in Figure 2.

concluded that illumination of small silver species leads to the emission of electrons into the aqueous solvent.

The short wavelengths part of the difference spectrum (—) contains sharp negative absorption bands at the wavelengths where the clusters in the absorption spectrum (curve a) have their maxima. It is concluded that the electron ejection from the clusters leaves behind silver species which do not possess sharp absorption bands. In the middle part of the difference spectrum (---) positive and negative signals are seen. They appear at the wavelengths where the metallic and quasi-metallic particles absorb. The signals are attributed to a shift to longer wavelengths of the plasmon absorption band as a consequence of electron ejection from larger particles. This electron ejection leads to a change in the charge of the particles. The shift of the plasmon absorption band with changing charge on silver particles will be described in more detail in a forthcoming paper. All the above signals were stable after the flash in the 10^{-4} s range investigated.

In Figure 13, the 700-nm absorption of hydrated electrons generated and the decrease in the 330-nm cluster absorption band are plotted as functions of the laser dose, the latter being expressed as concentration of absorbed 308-nm photons. Both curves have a linear part at low doses and strive toward a limiting value at larger ones. From the slope of the curve for e_{aq}^- in Figure 13 at low doses where less than 30 μM photons were absorbed one calculates a quantum yield of 0.10 ejected electrons per photon absorbed. This yield is certainly a lower limit as part of the 308-nm light absorbed was absorbed by the large silver particles present in the solution from which electrons were not ejected.

To show that ejection from large metallic particles practically does not occur, flash experiments were performed with a silver solution the spectrum of which contained only the narrow plasmon absorption band at 380-nm. Within the detection limits of our equipment no absorptions due to hydrated electrons were found. One must therefore conclude that photoelectron ejection from metallic particles either does not take place or occurs with such a low quantum yield that detection is not possible.

Experiments were also carried out with a solution containing quasi-metallic particles. The solution was prepared radiolytically and heated for 21 h at 70 °C as described in Figure 6. Hydrated electrons were found after the laser flash, the quantum yield being as low as 0.007.

Figure 14 finally shows the results of experiments in which a silver salt solution containing methanol was γ -irradiated for various time periods and subsequently flashed with the 308-nm laser to detect the hydrated electrons ejected. With increasing irradiation time, the contribution of clusters decreased and that of metallic and quasi-metallic particles increased as already pointed out in Figure 2. It is seen that the yield decreases with increasing irradiation time, i.e., as larger clusters and metallic particles are present. After the 21-h irradiation further destruction of the remaining clusters was achieved by adding acid to the solution and subsequent thermal aging. The solution finally obtained had

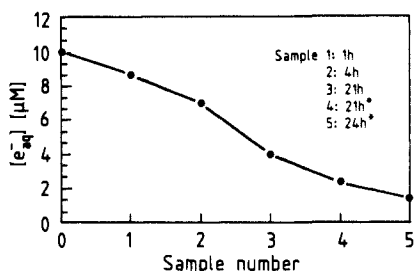


Figure 14. Photoelectron ejection from various silver solutions. The solution was prepared as in Figure 2 by 1-h irradiation. Further samples were obtained by additional irradiation up to 21 h. HClO_4 (10^{-3} M) was now added to facilitate the thermal decay of the remaining clusters. This solution was investigated immediately after HClO_4 addition and after 24-h aging. Laser dose as in Figure 12. All solutions had practically the same absorbance at the 308-nm laser wavelength.

a plasmon absorption band much wider than for purely metallic particles. The yield of hydrated electrons from this solution was less than 20% that of the original cluster solution at similar doses, showing that ejection from quasi-metallic particles can still occur but that ejection from solutions containing the cluster absorption bands is much more efficient.

Discussion

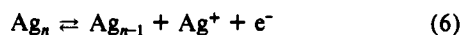
Reduction by Free Radicals: Redox Potential Considerations.

The development of the various reduced silver species in γ -irradiated solutions containing alcohols depends on the nature of the alcohol. In fact, as the alcohol acts as a scavenger of OH radicals, it is the nature of the organic radicals formed that influences the course of silver ion reduction. The standard redox potential of the system Ag^+/Ag^0 (where Ag^0 is a free silver atom in solution) is so negative (-1.8 V^{10}) that organic radicals do practically not react with silver ions. Their contribution to the reduction is possible through electron transfer to clusters (eq 5), which are formed as a consequence of reduction of Ag^+ by hydrated electrons (eqs 1–3).

In the case of 1-hydroxy alkyl radicals, such as CH_2OH and $(\text{CH}_3)_2\text{COH}$ formed in the presence of methanol and 2-propanol, respectively, all the radicals generated participate in the reduction process. However, the product distribution is not the same in the two cases. In the methanol-containing solution, silver clusters are relatively more abundant than in the 2-propanol-containing solution.

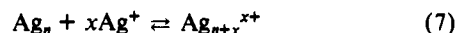
In solutions containing *tert*-butyl alcohol, the 2-hydroxy alkyl radical $\text{CH}_2\text{C}(\text{CH}_3)_2(\text{OH})$ is formed. The lower yield of Ag^+ ion reduction (Figure 1) indicates that this radical contributes to the reduction with little efficiency. In fact, in the beginning of reduction (concave range of the dashed curve in Figure 1) the reduction yield is rather small. Larger silver clusters have first to be accumulated until this radical is able to reduce Ag^+ ions on them. In the previous pulse radiolysis experiments it had already been observed that the yield of silver reduction was much lower in the presence of *tert*-butyl alcohol than in the presence of a primary or secondary alcohol.²

In order to understand why different product distributions result when different organic radicals are generated, one has to consider both the reduction potentials of the radicals and the potentials of the clusters. The latter may be regarded as microelectrodes; equilibria of the type



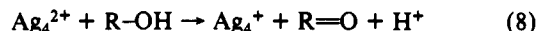
have been discussed previously for various values of n .^{8,13,14} In general, the potential becomes more positive with increasing agglomeration number n ($n = 1$, $E^\circ = -1.8 \text{ V}$; $n \rightarrow \infty$, $E^\circ = 0.799$

V). Possibly, complexation equilibria

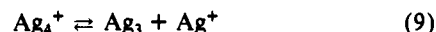


are superimposed. If Ag_{n-1} in eq 6 is more strongly complexed than Ag_n , the potential of the equilibrium of eq 6 is shifted to a more negative value. The reduction potential of the radicals $(\text{CH}_3)_2\text{COH}$ and CH_2OH are -1.8 and -1.0 V , respectively.¹⁵ The 2-hydroxy alkyl radical $\text{CH}_2\text{C}(\text{CH}_3)_2(\text{OH})$ has less reducing power than the two 1-hydroxy alkyl radicals.¹²

The following general reaction scheme explains the observed phenomena: the reduction of Ag^+ ions by hydrated electrons rapidly leads to long-lived Ag_4^{2+} clusters strongly adsorbed on the polyphosphate chains.² The organic radicals, which cannot reduce Ag^+ , reduce Ag_4^{2+} :



Ag_4^+ is a form of trimeric silver:



In the pulse radiolysis² and the γ -radiolysis experiments it was observed¹ that a band at 300 nm appears when the band of Ag_4^{2+} at 275 nm becomes weaker. One therefore is inclined to attribute the 300-nm band to trimeric silver, Ag_4^{2+} , because of its great positive redox potential (see below), can probably accept an electron from the strong reducing radicals $(\text{CH}_3)_2\text{COH}$ and CH_2OH with the same efficiency. Upon further irradiation, the radicals continue reducing Ag_4^{2+} clusters (which are still formed by reactions 1–3); however, as larger clusters are accumulated, they may also reduce Ag^+ ions on these larger clusters:



Kinetically, this reaction may occur in two steps: transfer of an electron to the cluster to form Ag_n^- , followed by reaction Ag_n^- with Ag^+ to yield Ag_{n+1} . A second kinetic path could consist of the addition of Ag^+ to Ag_n (see eq 7) and e^- transfer from the radical to Ag_{n+1}^+ formed. n could be as low as 3.

If the larger clusters are uncharged or only slightly complexed by Ag^+ ions, their potential is more negative than that of Ag_4^{2+} .¹³ This means that the radicals cannot so easily transfer an electron as in the case of Ag_4^{2+} . The efficiency of Ag^+ reduction (eq 10) will now be noticeably greater for $(\text{CH}_3)_2\text{COH}$ than for CH_2OH because of the substantial difference in redox potential between these two radicals. Rapid reactions of type 10 lead to larger and larger particles. It thus is understandable that fewer clusters and more metallic particles are formed in 2-propanol solution, in which the stronger reducing radical is generated, than in the presence of methanol. The $\text{CH}_2\text{C}(\text{CH}_3)_2(\text{OH})$ radical formed in the presence of *tert*-butyl alcohol has so little reducing power that it has already difficulties to rapidly reduce Ag_4^{2+} clusters. This explains why this cluster can be accumulated especially readily in solutions containing *tert*-butyl alcohol.

The Stability of Ag_4^{2+} . The pulse radiolysis studies have shown that this cluster is rapidly formed and complexed in solutions containing polyphosphate.² In these experiments, no instability of the cluster could be detected in the time range available up to 1 s. In the present γ -irradiation experiments it was found that the cluster lives for many hours at ambient temperature even in the presence of air.

We would like to explain the high stability of Ag_4^{2+} by the oscillatory behavior of the E° vs n dependence at small values of n in the equilibria of eq 6. As shown previously, the dimeric silver microelectrode, $\text{Ag}_2 \rightleftharpoons \text{Ag}^0 + \text{Ag}^+ + e^-$, has an extraordinarily high potential of about 0 V, i.e., more positive than those for $n = 1$ ($E^\circ = -1.8 \text{ V}$) and $n = 3$ ($E^\circ = -0.9 \text{ V}$).¹³ An oscillatory behavior of the ionization potential has also been reported more recently in photographic plate experiments.¹⁶ Ag_4^{2+} is a complexed form of dimeric silver (eq 7) its potential being even more

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positive than that of naked Ag_2 . Under these circumstances it can be rationalized that this cluster is not attacked by O_2 . Only reagents of stronger oxidation power, such as H_2O_2 or $\text{K}_2\text{S}_2\text{O}_8$, react with Ag_4^{2+} .

Absorption and Structure of Clusters. Unfortunately, we do not see a possibility to assign cluster structures to our observed absorption bands by using the data accumulated in studies of silver clusters in solid matrices. It seems that in all this work the assignment of absorptions to monomeric and dimeric silver species is quite clear-cut, while the assignment of absorptions to larger clusters are less reliable. The sharp bands observed in noble-gas matrices were attributed to internal electronic transitions in Ag^0 (297–315 nm in argon; 322–328 nm in xenon) and Ag_2 (390 and 260 nm in argon) and larger species.^{6a} Ag^0 in water at ambient temperature absorbs around 360 nm,¹⁷ i.e., at wavelengths significantly longer than in noble gas matrices. The absorption of Ag_2^+ occurs around 310 nm,^{17,10b} in frozen solution at 303 nm,⁷ and that of Ag^0 in frozen solution lies between 320 and 400 nm, depending on conditions. The Ag_2^+ species in zeolites absorbs at 340 nm,⁵ i.e., at wavelengths much longer than in aqueous systems. These examples show that the matrix often has a strong influence which makes it difficult to compare the results from various fields of cluster research.

While our assignments of the Ag^0 and Ag_2^+ absorptions are in good agreement with those of other authors, we do not see a possibility to correlate our observed cluster bands at 300, 330, and 345 nm (Figure 2) with any structures postulated for larger clusters in the frozen solution and zeolite work. Naturally, one may ask whether our cluster bands are produced by strong cluster–polyphosphate complexes. Strong complexes are conceivable only if the clusters carry positive charges, i.e., are strongly complexed by Ag^+ ions (eq 7). However, even in the case of the cluster Ag_4^{2+} the absorption is not changed by polyphosphate, and in the case of the clusters absorbing at 300, 330, and 345 nm it is probable that they are either naked or carry little positive charge as they are still present after the complete reduction of the Ag^+ ions in solution. We have most recently succeeded in observing the 300- and 330-nm bands with lifetimes of seconds in pulse radiolysis experiments on Ag^+ solutions free from polyphosphate.¹⁸ In these solutions, the bands appear at the same wavelengths as in the presence of polyphosphate.

As it had first been observed in the early pulse radiolysis studies,⁸ Charle et al.^{6a} have found that the plasmon absorption band of colloidal silver particles is broadened and slightly blue-shifted with decreasing particle size. One could raise the question whether the sharp bands at much shorter wavelengths observed in the present work are plasmon absorptions of extremely small agglomerates. However, many effects could not be explained in this way: For example, the sharpness of the bands would not be understandable and the fact that ejection of just one electron is accompanied by the complete disappearance and not by a shift of the band.

Absorption coefficients of clusters have not yet been reported in the literature. The clusters absorbing at 300, 330, and 345 nm must have coefficients on the order of $10^4 \text{ M}^{-1} \text{ cm}^{-1}$. This can be concluded on the basis of the following considerations: In Figure 2, the increase in the absorbance of the 330-nm band is 0.50 in going from 9 to 11 min. During this time, $2.4 \times 10^{-5} \text{ M}$ reducing species were generated. Thus, a value of ϵ of $0.50 / 2.4 \cdot 10^{-5} = 2 \cdot 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ is calculated. However, this value is only a lower limit as the reducing radicals generated had produced not only the 330-nm cluster but also other clusters. Similarly, in the photoelectron ejection experiments of Figure 12 one finds that the decrease in the cluster absorptions is approximately equal to the increase in hydrated electron absorption at 700 nm, where e_{aq}^- has a specific absorption of $1.7 \cdot 10^4 \text{ M}^{-1} \text{ cm}^{-1}$.¹⁹ From this fact one must conclude that the specific absorption of the clusters

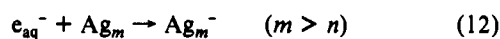
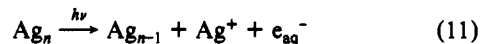
is on the same order of magnitude as that of the hydrated electron.

Another important conclusion can be drawn from the photoemission experiments in Figures 12 and 13. The negative absorption bands accompanying the ejection are also observed at low laser intensities where the concentration of ejected electrons is smaller than the cluster concentration (i.e., where no more than one electron could have been removed from a cluster). The fact that the ejection of *one* electron is sufficient to remove the cluster absorption band, without producing new bands, means that the remaining cluster does not absorb there or absorbs very little. Similarly, it was observed in the preceding pulse radiolysis studies that addition of one electron to a precursor caused the sharp absorption band to appear without bleaching of any of the bands already present.² The conclusion is that there exist clusters having electron numbers z and possessing a sharp absorption band, while the corresponding $z - 1$ and $z + 1$ numbered clusters do not absorb strongly. This raises the question whether open and closed electron shell clusters have significantly different absorption coefficients, possibly the open shell clusters (z : odd number) possessing the strong and sharp bands in the 300–345-nm range.

Reasons were given above that the 300-nm absorption band is caused by trimeric silver. If our conclusion about open and closed shell species is valid, one could be inclined to attribute the 330-nm band to pentameric and the 345-nm band to heptameric silver. This does not exclude that closed shell clusters are formed. They simply are not noticeable in the 300–345-nm range. Still larger clusters begin to acquire metallic character as they first develop a broad plasmon band around 360 nm and later the sharp band at 380 nm of truly metallic particles. That open and closed shell silver clusters in aqueous solution have substantially different absorption spectra has not yet been discussed in the literature. Our proposal can be regarded only as tentative to rationalize the observations; further experiments concerning this problem are required.

The question arises as to the nature of the optical transition that produces the rather sharp bands in the 300–345 nm range. As electrons are so efficiently ejected under illumination one is inclined to attribute the bands to charge-transfer-to-solvent transitions. The present photoejection experiments were limited to using 308-nm laser light where all the silver species seem to absorb. It is highly desirable to carry out experiments on the ejection yield as a function of the wavelength of the exciting light in the range of the cluster bands in order to see whether illumination into these bands also leads to ejection. Experiments of this type are in preparation.

Photolysis. The detection of hydrated electrons in the laser flash photolysis experiments corroborates the mechanism of photoinduced cluster growth proposed previously:¹



An electron is photoejected from a small particle Ag_n (eq 11). The hydrated electron formed reacts with a larger particle Ag_m of metallic or quasi-metallic character (eq 12). Ag_m^- finally combines with the Ag^+ ion generated in the reaction of eq 11. An alternative path could consist in the reaction of the Ag^+ ion produced in the reaction of eq 11 with Ag_m , followed by neutralization of Ag_{m+1}^+ formed by the hydrated electron. It should also be taken into account that, in solutions of low Ag^+ concentration, the hydrated electrons might be converted into H atoms, $e_{\text{aq}}^- + \text{H}^+ \rightarrow \text{H}$, before reacting with a silver species. The H atoms react with methanol, $\text{H} + \text{CH}_3\text{OH} \rightarrow \text{H}_2 + \text{CH}_2\text{OH}$, and the CH_2OH radicals would then be the reducing species in the above mechanism instead of e_{aq}^- .

The nonmetallic silver clusters have a great quantum yield, $\phi > 0.10$, for photoelectron ejection. Metallic colloidal particles (sharp plasmon absorption band at 380 nm) do not show photoelectron ejection within the detection limits of our equipment. Colloidal metallic silver particles thus behave similarly to compact

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silver electrodes from which photoelectron ejection at 0 V occurs with a quantum yield below 10^{-4} .²⁰ However, quasi-metallic particles (broad plasmon absorption band around 360 nm) still eject an electron upon illumination although the quantum yield of 0.007 is clearly lower than for the nonmetallic clusters. We thus see a gradually changing ability to photoject an electron

with decreasing size of silver particles in the transition range from bulk material to atoms.

The photofragmentation of almost metallic particles to yield small clusters (Figure 11) is possibly also an event following ejection of an electron. However, further experiments are required to investigate this question in more detail.

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Registry No. AgClO₄, 7783-93-9; NaBH₄, 16940-66-2; Ag⁺, 14701-21-4; Ag, 7440-22-4; CH₃OH, 67-56-1; O₂, 7782-44-7; H₂O₂, 7722-84-1; *tert*-butyl alcohol, 75-65-0.

Picosecond Time-Resolved Resonance Raman Scattering and Absorbance Changes of Carotenoids in Light-Harvesting Systems of Photosynthetic Bacterium *Chromatium vinosum*

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Abstract: The excited electronic states of carotenoids in light-harvesting systems of photosynthetic bacteria are examined by picosecond laser spectroscopy. Picosecond changes in absorbance and in the intensity of resonance Raman bands are observed for carotenoids (mainly rhodopin and spirilloxanthin) in *Chromatium vinosum*. These data are obtained with picosecond transient absorption and picosecond time-resolved resonance Raman spectroscopies utilizing a two laser (8 ps pulses), pump-probe instrumental configuration. Following 560 nm pump laser excitation, sample absorbance between 573 and 650 nm initially increases and subsequently decays with a fast (6 ± 0.5 ps) and two slow (~ 80 ps and >200 ns) components. The initial rise and the fastest decay component reflect, respectively, the formation and relaxation of the excited 2^1A_g state of the carotenoids. The slow decay constants both reflect the decay of excited triplet state carotenoids although the 80-ps component remains to be fully characterized. The intensities of the RR bands assignable to the ground 1^1A_g state of the carotenoids decrease by more than 30% during the laser excitation and then increase with a rate of 6 ps, reflecting the depletion of the 1^1A_g state followed by its repopulation due to the relaxation of the 2^1A_g state. The transient populations of excited triplet states in carotenoids are observed through picosecond time-resolved resonance Raman spectra containing several new resonance Raman bands, at 1475, 1260, 1171, 1124, and 1007 cm^{-1} .

In photosynthetic bacteria, light energy absorbed by carotenoids and bacteriochlorophylls (BChls) located in the light-harvesting pigment-protein complexes is transferred to photosynthetic reaction centers.^{1,2} This light-harvesting function of the carotenoid is critical to the efficient utilization of light energy in the primary charge separation reaction. In addition, carotenoids in both the light-harvesting complexes and reaction centers protect BChls from photochemical damage caused by light and oxygen.³ The participation of electronically excited states, such as the first excited singlet and triplet states, of the carotenoids are fundamental to both types of processes. Accordingly, a detailed understanding of the light-harvesting and photoprotective processes requires detailed investigations of the rates of these processes and the molecular vibrations that underlie them in electronically excited-state carotenoids.

Excited-state carotenoids, in both in vitro and in vivo preparations, have been examined by transient absorption and resonance Raman (RR) spectroscopies in a variety of previous studies.⁴⁻²¹ Of importance here is that the main optical transition (near 480 nm in β -carotene and 520 nm in chromatophores from *Chromatium vinosum*) from the ground 1^1A_g (S_0) state populates the excited 1^1B_u state. The 1^1B_u state rapidly crosses to the excited 2^1A_g state, which lies energetically nearby. The 2^1A_g state is populated only from the 1^1B_u state since the $1^1A_g \rightarrow 2^1A_g$ optical transition is formally forbidden, with an indirectly estimated rate

constant of $<1 \times 10^{12} \text{ s}^{-1}$.^{15,16} The 2^1A_g state of in vitro β -carotene decays to the ground state in 8.4 ps as observed by ground-state

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