Silver Atoms and Small Silver Clusters in Ice and Wax Matrix Supports

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Abstract: By monitoring the optical spectra of silver vapor cocondensed with water or high molecular weight paraffin wax matrices over a range of concentration and thermal annealing conditions, the isolation properties of ice and n-$C_{22}H_{46}$ and n-$C_{32}H_{66}$ waxes with respect to silver atoms and small silver clusters have been investigated and the potential usefulness of these materials as "high-temperature" matrix supports has been assessed. Four optically distinct silver atom trapping sites with quite different thermal stabilities could be distinguished in 10-12 K quench-condensed silver vapor-water vapor films. Under these conditions, cotrapped silver atoms and small silver clusters remained reasonably well isolated up to about 130 K. At higher temperatures, diffusion-aggregation processes leading to silver microcrystallites became pronounced. By contrast, the paraffin waxes were found to be poor trapping agents for silver atoms and clusters. For example, to ensure efficient atomic isolation, very low deposition rates were required. This effect might be related to the high heat of condensation and solidification behavior of the waxes. The immobilization properties of the paraffin wax films were such that pronounced silver atom diffusion occurred at temperatures as low as 30 K, resulting in larger silver clusters.

Introduction

In the field of metal atom-metal cluster chemistry[1] there has emerged a need to establish a range of high-temperature matrix media for use in the fabrication of supported catalysts.[2] The ultimate objective here is an evaluation of the catalytic properties of ultrafinely dispersed, narrow size distribution particle catalyst systems. Immobilization on oxide, zeolite, ligand silica, and polymer type supports is envisaged for these very small cluster arrays and unique catalytic activity/selectivity patterns are anticipated. The usefulness of a support material for the envisioned preparative applications can be considered to be determined by (a) the reactivity of the support toward the metal vapor on deposition and during any subsequent annealing and photolysis treatment; (b) the nature of the metal atom and metal cluster support interactions, as these will inevitably influence both the degree to which metal atom aggregation processes occur and the extent to which the spectroscopic properties of the atoms and clusters are perturbed and hence disguised in the matrix; (c) the thermal stability of metal atomic/small cluster dispersions, indicated by the temperature at which metal atom diffusion-aggregation processes become noticeable; (d) the practicability of a macroscale preparation; (e) the availability of a convenient means of extracting and dispersing the metal clusters on a support material suitable for catalyst testing.

Silver atom aggregation has been studied by metal deposition-surface diffusion, matrix annealing-bulk diffusion, and photoclustering techniques, coupled with UV-visible, Raman, ESR, MCD, EXAFS, and emission spectroscopy.[3] The optical spectra of $Ag_{1,2,3,4}$ have been studied in great detail in H_2, D_2, Ne, Ar, Kr, Xe, CH_4, and N_2 matrices.[3] Electronic assignments have been considerably aided by reference to the results of EH[3,4]/CNDO[4]/Xα[5,6] molecular orbital calculations for $Ag_{2,3,4}$. Selective cluster cryophotochemical experiments are also proving useful for testing these assignments, for performing cluster transformations, and for manipulating cluster distributions.[6]

Silver-atom trapping in ice matrices has been studied extensively by ESR spectroscopy[7,8] where the isolated atoms are usually formed by reaction of radiation-produced electrons with silver ions entrapped in frozen aqueous solutions of silver salts. These studies have largely been concerned with silver atom/silver ion solvation and desolvation phenomena and the local geometry of the silver atom trapping sites. ESR spectroscopy has also been used to investigate the cocondensation of Ag atoms with H_2O at 77 K.[7] Ice-entrapped silver atoms produced in this way were found to have ESR parameters which were very close to the gas-phase values but quite different from those of isolated silver atoms generated by reduction of Ag^+ with radiation-produced electrons. UV-visible absorption spectra of vapor-condensed ice films containing isolated Ag atoms have not been reported, although such spectra have been reported for radiation-produced silver atoms in frozen (77 K) aqueous solutions[9] and H_2SO_4 glasses.[10]

Also relevant to our investigations of Ag_n clusters in wax and ice matrices are some earlier ESR experiments involving γ-irradiation of benzene or toluene matrices containing $AgClO_4$ or AgBr, leading directly to the formation of paramagnetic Ag_2^+, Ag_3^{2+}, and Ag_4^{3+} cationic clusters, presumably through $Ag^0 + Ag_n^{n+}$ diffusion-aggregation reactions.[11] Also noteworthy is a Li atom H_2O/Ar matrix ESR study which demonstrated the existence of discrete $Li(H_2O)_{1,2}$ complexes which photodecomposed under UV excitation to form LiOH and H atoms.[12]

In connection with point (e) above, we note that Klabunde[13] has reported a 77 K metal vapor/organic solvent preparation of alumina- (and silica-) supported silver and nickel microcrystallites. The latter, for example, were found to be active in catalytic hydrogenation reactions. In the present study, we have investigated the isolation properties of high molecular weight paraffin wax and ice supports in conjunction with the well-studied Ag_n (n = 1, 2, 3, 4) small cluster system.[3]

Experimental Section

Silver vapor was generated from a directly heated tantalum Knudsen cell and wax vapor came from a stainless steel Knudsen cell (wall thickness 0.015 in. and orifice diameter 0.04 in), using a four-electrode, dual quartz crystal microbalance-vacuum furnace assembly similar to that described previously.[14] Triply vacuum distilled water was employed for the ice matrix experiments and n-$C_{22}H_{46}$ and n-$C_{32}H_{66}$ (supplied by Aldrich) after extensive outgassing were used directly for the paraffin wax matrix experiments. Samples were deposited at known rates onto a sodium chloride optical window cooled to 10-12 K by an Air Products Displex closed-cycle helium refrigerator. Optical spectra were recorded on a Varian Techtron UV-visible spectrometer in the range 200-900 nm.

Silver Atoms and Clusters in Ice Matrices

A representative optical spectrum obtained when silver vapor is cocondensed with H_2O at 10-12 K under high-dilution conditions ($Ag/H_2O \simeq 1/10^4$) is shown in Figure 1C. Two

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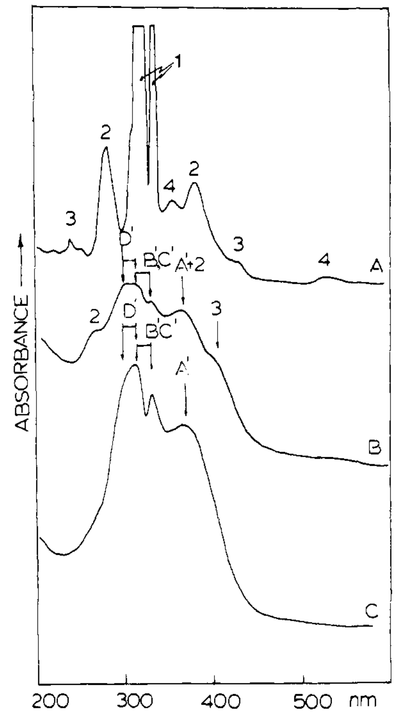

Figure 1. The optical spectra obtained on depositing silver vapor with water vapor or methane at 10-12 K: (A) silver vapor with methane at Ag/CH_4 $\simeq$ 1/10^2, (B) Ag/H_2O $\simeq$ 1/10^3, and (C) Ag/H_2O $\simeq$ 1/10^4. Throughout this paper A', B', C', and D' refer to slightly different Ag atom trapping sites in vapor-condensed ice films, and 2 = Ag_2, 3 = Ag_3, 4 = Ag_4.

well-resolved band maxima (336/316 nm), a shoulder (301 nm), and a broad, red-shifted absorption (380 nm), labeled B', C', D', and A', respectively, are reproducibly observed on deposition. Figures 1B and 2B show typical spectra obtained upon increasing the Ag/H_2O ratio to about 1/10^3 and 1/10^2, respectively, and Figure 3 shows a series of deposition/warm-up spectra obtained for a Ag/H_2O ratio of about 1/10^2. Noticeable, especially in the spectra shown in Figures 2 and 3, is the appearance of absorption bands not associated with silver atoms. These bands are attributed to silver clusters. The assignments are suggested by comparison with the known optical spectra of Ag_{1-4} in a variety of matrix materials.[3] The absorption spectrum of Ag_{1-4}/CH_4 mixtures (10-12 K) is shown in Figures 1A and 2A for the purpose of comparison.

The effect of warming a matrix very dilute in silver (Ag/H_2O $\simeq$ 1/10^5) is illustrated in Figure 4. Note that the bands labeled A'-D' behave very differently as the matrix is warmed and that these changes are irreversible, suggesting the existence of at least four distinct trapping sites for silver atoms in vapor-condensed ice films. Moreover, the thermal stability of the trapping sites is seen to decrease in the sequence D' > C', B' > A'.

As shown in Figure 5, silver atom site interconversions in vapor-condensed ice matrices can also be induced photolytically. Thus, site A' can be photolyzed to disappearance with concomitant growth of the thermally stable site D' (Figures 5A-D). Irradiation at 340-360 nm has the effect of partially regenerating site A', while depleting sites B' and C' (Figures 5D,E). Photolysis centered near 300 nm, corresponding to site D', apparently results in either silver atom photomobilization, similar to that observed for CH_4 and rare-gas matrices,[3] or silver atom photoinsertion into water, possibly similar to that observed for Li and other metal atoms in H_2O/rare gas matrices.[12,19]

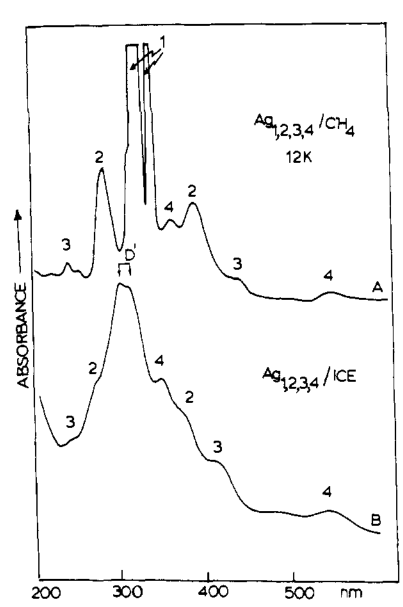

Figure 2. The optical spectra obtained on depositing (A) silver vapor with methane at 10-12 K at Ag/CH_4 $\simeq$ 1/10^2 and (B) silver vapor with water vapor at Ag/H_2O $\simeq$ 1/10^2, brief warming to 77 K (see text and Figure 3), and recooling to 10-12 K for spectral recording.

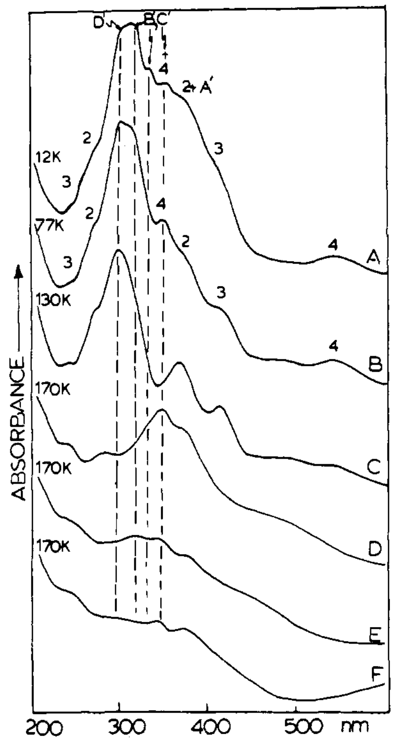

Figure 3. The optical spectra obtained on depositing silver vapor with water vapor (A) at 10-12 K and Ag/H_2O $\simeq$ 1/10^2 and (B)-(F) showing the progress of thermal annealing at 77, 130, 170, 170, and 170 K, respectively.

The occurrence of multiple trapping sites of Ag atoms isolated in ice supports has been demonstrated by means of detailed ESR studies of radiation-produced Ag atoms in $AgNO_3$ ices.[8] The overall picture that emerges from these ESR studies is one of magnetically distinct, multiple trapping sites that are interconvertible by thermal and optical excitation, with little loss of Ag^0 spins up to 77 K.[8] The evidence of the present study indicates that the silver atomic trapping sites are quite different depending on the method of sample preparation, i.e., vapor condensation or reduction of silver ions in prefrozen aqueous solutions. They thus differ from the sites suggested by Kevan et al.[8] Thus, when Ag atoms are condensed with H_2O at 77 K, the observed ESR parameters are very similar to those of gas-phase Ag atoms,[7] but radiation-produced silver atoms trapped in frozen (77 K) aqueous solutions display ESR pa-

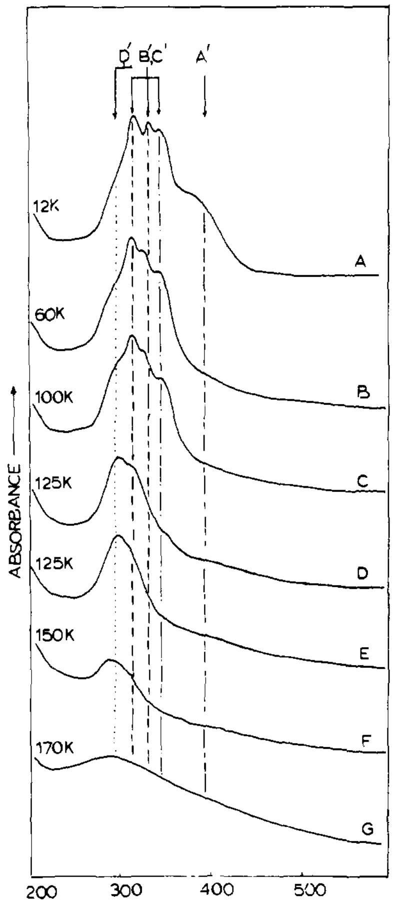

Figure 4. The optical spectra obtained on depositing silver vapor with water vapor (A) at 10-12 K and $Ag/H_2O \simeq 1/10^5$ and (B)-(G) showing the progress of thermal annealing at 60, 100, 125, 150, and 170 K, respectively.

rameters markedly different from the gas-phase values.[8] Similarly, the optical absorption spectra obtained from Ag atoms isolated in vapor-condensed ice films at 77 K (the present study) are quite different from those obtained for radiation-produced silver atoms in 77 K aqueous solids.[9] In the latter case, there is a *complete lack of absorption bands near 300 nm*, where the most intense features were observed in the present study. We note here that 10-12 K vapor-condensed ice films are likely to be amorphous,[15] while frozen aqueous solutions of the type used for generating the radiation-produced silver atoms are probably more ordered in structure. In any case, the orienting influence of the electric field of Ag^+ ions is entirely absent for the vapor-condensed samples and this influence has been shown by ESR studies[8] to be of dominant importance in determining the structures of the atomic silver trapping sites. In view of the complex phase behavior of ice, therefore, and the ordering influence of the electric field of Ag^+, it is not surprising that the spectroscopic results indicate very different silver atomic trapping sites for the different methods of sample preparation. Notwithstanding this general conclusion, it is conceivable that at least one of the A′-D′ trapping sites observed in the present study does in fact correspond with one of the A-D trapping sites observed in the ESR spectra.[8] Concurrent ESR and optical absorption studies might provide a clarification of this point.

The results described above allow for an assessment of the trapping efficiency of silver/water vapor condensed films. At low concentrations ($Ag/H_2O \simeq 1/10^5$), isolation of atomic silver predominates and the presence of a number of distinct trapping sites of widely varying thermal stabilities can be recognized. At temperatures above approximately 125 K, diffusion-aggregation processes become important, probably as a result of the occurrence of exothermic phase changes in the ice films.[15b] In the context of the present study, it is encouraging that a metal atomic dispersion can actually be stabilized in a weakly interacting support material at the relatively high temperature of 125 K (cf. Ag/THF at 77 K, ref 13). As illustrated in Figure 3, silver clusters in the size range Ag_2-Ag_4 can be isolated at higher Ag/H_2O concentrations ($\sim 1/10^2$). These silver atomic/cluster dispersions are stable to about 130 K; at higher temperatures the optical spectra indicate that silver atom diffusion-aggregation processes seem to lead to silver microcrystallites.[3,17] Further studies relating to the size distribution and spectroscopic properties of these ice-entrapped silver cluster species would be worthwhile, as would methods for extracting these small silver clusters onto conventional, room-temperature supports for catalyst testing.

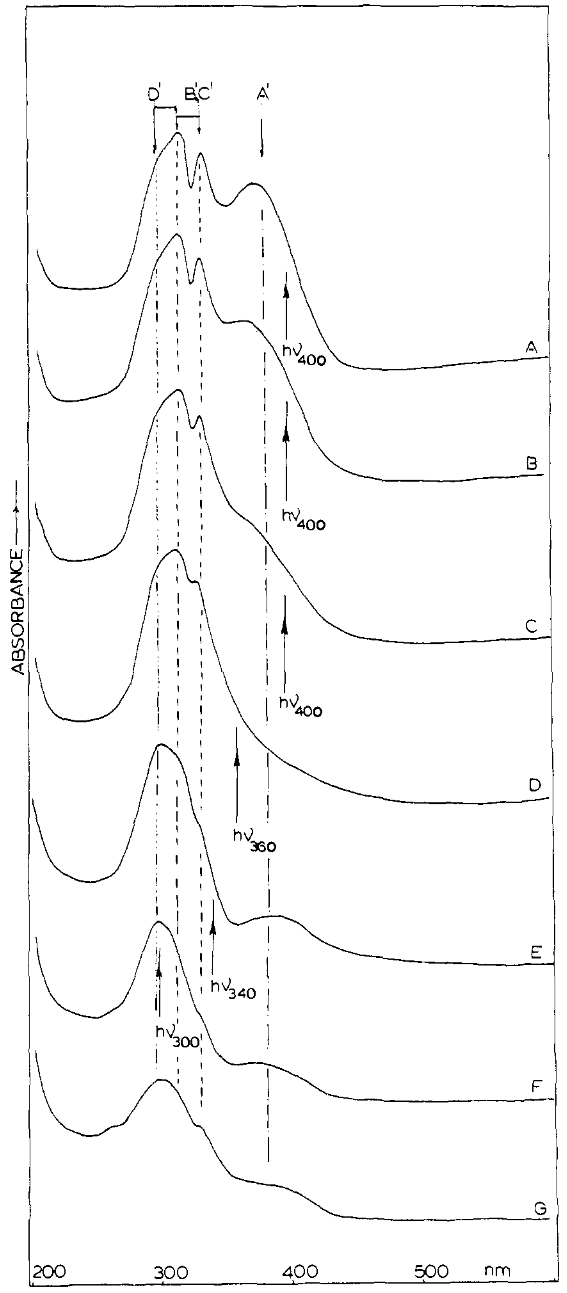

Figure 5. The optical spectra obtained on depositing silver vapor with water vapor (A) at 10-12 K and $Ag/H_2O \simeq 1/10^4$ and (B)-(G) showing the progress of a series of 30-s, narrow-band (20-nm band pass) irradiations (500-W xenon lamp-monochromator assembly with 10-cm water filter) at 400, 400, 400, 360, 340, and 300 nm, respectively.

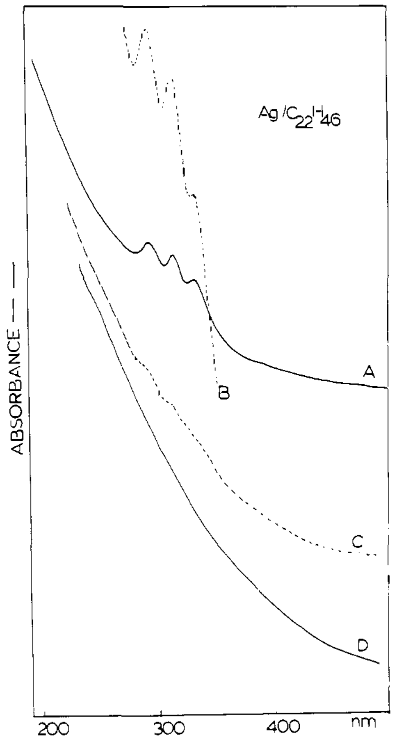

Figure 6. The optical spectra obtained on depositing silver vapor with n-$C_{22}H_{46}$ vapor (A) at 10-12 K and Ag/n-$C_{22}H_{46}$ $\simeq$ $1/10^4$, (B) an expansion of (A) showing the $^2S \rightarrow {}^2P$, spin-orbit and vibronic threefold splitting of matrix isolated atomic silver[3] and (C), (D) showing the progress of brief thermal annealing at 30 and 40 K.

Paraffin Wax Matrix Supports

Methane and short-chain alkanes have been explored as "weakly interacting" matrix media as alternatives to the noble gases.[16] The initial objectives in the present investigation of silver/paraffin wax codepositions were to establish the conditions under which silver atoms could be isolated and to determine the temperature range over which diffusion-aggregation events became pronounced. Samples of n-$C_{22}H_{46}$ and n-$C_{32}H_{66}$ were chosen as representative of high molecular weight paraffins.

A four-electrode furnace was employed with dual quartz crystal mass monitors for controlling the silver and wax vapor deposition rates, from tantalum and stainless steel Knudsen cells, respectively. A lengthy series of cocondensations was necessary to establish optimum isolation conditions in these paraffin wax supports, as the anticipated flow conditions based on previous experiences with Ag/CH_4 matrices turned out to be quite inappropriate for immobilizing Ag atoms in either n-$C_{22}H_{46}$ or n-$C_{32}H_{66}$. The problem apparently arose from the high heat of condensation and solidification behavior[18] of the wax (compared to, say, CH_4), causing excessive Ag atom surface diffusion-clustering during the actual deposition process. In order to efficiently isolate atomic silver we were obliged to employ extremely slow depositions of the wax (at least an order of magnitude less than with, for example, methane) with the appropriate proportion of silver vapor to maintain the 0.1-0.01% metal concentration necessary for efficient atomic isolation. Only under these extremely low-flow, high-dispersion conditions was it possible to establish the atomic spectrum of silver in the n-$C_{22}H_{46}$ wax (Figures 6A,B).

The divergence in the isolation properties of paraffin waxes from the trends noted for the shorter chain alkanes (increasing isolation efficiency with increasing chain length[16]) was found also in the observed thermal stabilities of the Ag/wax dispersions. Thus, while the short-chain alkanes appeared to follow the reasonably successful Tamman predictive diffusional temperature of $0.3T_{\mathrm{mp}}$, bulk diffusion of silver atoms in the paraffin wax supports was observed at temperatures as low as 30 K (Figure 6C). This observation is not surprising in view of the likelihood that 10-12 K vapor-condensed wax films are highly disordered or glassy, with very open structures allowing for diffusion at relatively low temperatures.[18]

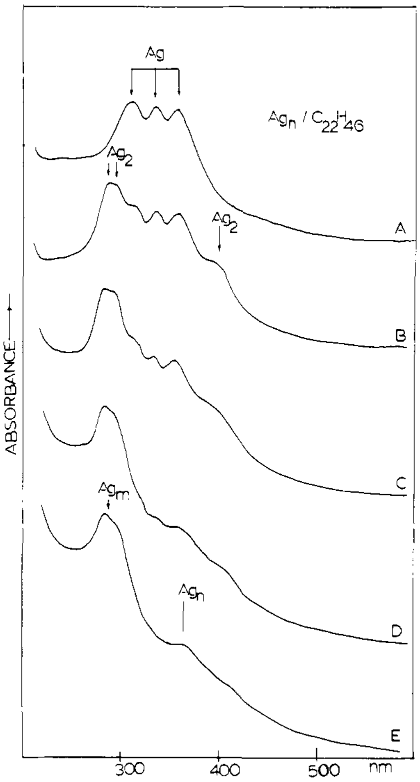

Figure 7. The optical spectra obtained on depositing silver vapor with n-$C_{22}H_{46}$ vapor at 10-12 K: (A) Ag/n-$C_{22}H_{46}$ $\simeq$ $1/10^4$, (B) Ag/n-$C_{22}H_{46}$ $\simeq$ $1/10^3$ showing trapped Ag and Ag_2, and (C)-(E) showing the progress of annealing (B) at 30, 40, and 80 K, respectively, leading to larger silver clusters and microcrystallites.[3,17]

Table I. Optical Spectra of Ag Atoms and Ag_2 Dimers in Methane and High Molecular Weight Paraffin Wax (n-$C_{22}H_{46}$, n-$C_{32}H_{66}$) Matrices (nm)

CH_4 (10-12 K)[3d]	n-$C_{22}H_{46}$ (10-12 K)	n-$C_{32}H_{66}$ (10-12 K)	assignment[3]
380	390	390	Ag_2
333	357	360	Ag
320	334	338	Ag
310	312	315	Ag
278	298	300	Ag_2
	284	284	Ag_2

The ability to trap and retain Ag/Ag_2/wax mixtures on deposition at 10-12 K is shown in Figure 7, which illustrates part of a typical Ag/n-$C_{22}H_{46}$ concentration study (Figures 7A,B). Silver atom and silver dimer lines are quite easily identified and correlated with only slight frequency shifts to the values found for Ag/Ag_2 in solid CH_4 (Table I).[3] These data follow the trend with increasing alkane chain length found previously for V/V_2/n-C_nH_{2n+2} for n = 1-10[16] (i.e., red shifting toward the gas-phase transition energies with increasing chain length). Representative portions of Ag/Ag_2/n-$C_{22}H_{46}$ and Ag/Ag_2/n-$C_{32}H_{66}$ warm-up studies are depicted in Figures 7C-E and 8B,C, both showing marked Ag atom diffusion at temperatures near 30 K, with growth of silver microcrystallites[3,17] becoming apparent around 50-80 K (Figures 7E and 8C).

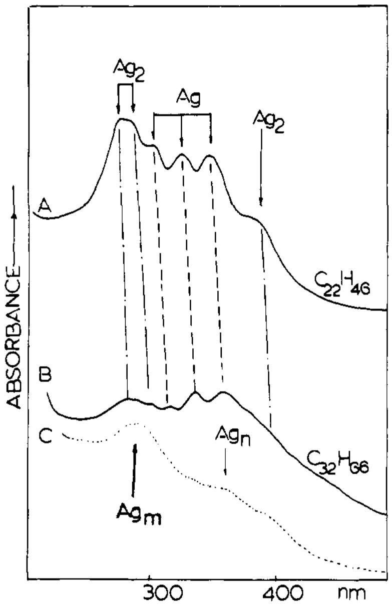

Figure 8. The optical spectra obtained on depositing silver vapor with (A) n-$C_{22}H_{46}$ and (B) n-$C_{32}H_{66}$ at Ag/wax $\simeq 1/10^3$ showing the coexistence of Ag/Ag_2 and (C) displaying the progress of thermal annealing of Ag/Ag_2/n-$C_{32}H_{66}$ at 30–35 K to yield higher clusters and microcrystallites.[3,17]

It is interesting to note the similarity of the Ag/Ag_2/alkane data to that for Ag/Ag_2 isolated in highly dipolar ice matrices (Figure 1, Table I). Similar observations were reported by Zhitnikov et al.[7] in an ESR study of Ag atoms condensed in polar and nonpolar media at 77 K.

The results of the present study show that very small, naked metal clusters cannot be stabilized in high molecular weight paraffin wax supports close to room temperature. Instead, pronounced diffusion–agglomeration processes dominate at very low temperatures, although it is likely that the metal aggregates so formed are still extremely small and therefore of interest to those concerned with the catalytic properties of metal clusters.

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