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OPTICAL ABSORPTION SPECTRA OF AG-MICROCLUSTERS FORMED BY MATRIX TECHNIQUES

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Résumé. — Des microagrégats d'argent ont été préparés par condensation simultanée d'un faisceau d'argent monoatomique et d'un gaz noble en excès sur une cible de saphir refroidie et analysés par spectroscopie optique à transmission dans le domaine UV-VISIBLE.

En fonction des paramètres de condensation (i.e. température rapport gaz/métal, taux d'admission du gaz et gaz lui-même) les atomes du métal qui se condensent peuvent soit être isolés, soit former des mélanges d'agrégats à la surface de la matrice en train de croître. Les spectres d'absorption optique de tels mélanges présentent plusieurs bandes d'absorption distinctes dans le domaine 2 000-5 000 Å. Les bandes correspondant à l'argent monoatomique et diatomique peuvent être clairement identifiées, ce qui permet d'attribuer les autres bandes à des particules contenant plus de deux atomes d'argent.

Abstract. — Silver microclusters have been prepared by co-condensation of a monoatomic silver beam with an excess of noble gas on a cooled sapphire target and investigated by optical transmission spectroscopy in the U.V.-VIS. range. Depending on the condensation parameters (i.e. temperature, gas/metal ratio, the gas admission rate and the gas itself) the condensing metal atoms can either be isolated as single atoms or as a mixture of aggregates at the surface of the growing matrix layer.

The optical absorption spectra of such mixtures show several distinct absorption bands within the range 2 000-5 000 Å. The spectral features of monoatomic and diatomic silver can be clearly identified, allowing the remaining bands to be assigned to multimeric silver particles.

1. Introduction. — The matrix isolation of atomic species which normally exist as large aggregates is a method widely used today [1, 2]. The technique involves the co-condensation of the species with an excess of gas onto a cooled substrate. The principal features of the method are that species unstable under normal conditions can be stabilised in matrices at low temperatures, and that the formation of matrices is a continuous process, thus allowing an accumulation of species through increasing layer thickness.

Another advantage of this method has recently been emphasized in literature [3-6]. Under certain experimental conditions an aggregation of atomic or molecular fragments can be achieved. These aggregates are of great relevance to many problems in chemistry and physics, e.g. in such areas as heterogeneous catalysis, chemical synthesis, nucleation phenomena and solid state physics.

Although much work has already been carried out in the field of matrix isolation the main problem has not yet been solved satisfactorily: aggregation occurs easily, but doubt exists as to the composition and cluster size of the resulting aggregate mixtures. These two factors depend on the various condensation parameters, e.g. temperature, gas/metal ratio, gas admission rate and gas sort. It

is therefore difficult to assign clearly the numerous spectral features that are usually present in matrix absorption spectra to specific clusters. This is particularly true if molecular aggregates containing more than two atoms are present, for which the corresponding gas phase data are generally unknown.

To get a better understanding of the aggregation/isolation process [3-9] we have begun a systematic investigation of matrix spectra in the U.V.-VIS. region as a function of the various condensation parameters using Xe, Kr and Ar as matrix gases and silver as metal [12]. In this article we demonstrate the effect of varying the condensation parameters on the spectral features and show how such experiments can greatly aid in the assignment of bands to specific clusters.

2. Experimental. — The experimental apparatus used in these experiments is shown schematically in figure 1 [10, 11]. As substrate a sapphire target (area $\approx 4 \text{ cm}^2$) was used, which was in good thermal contact to the cryostat. The cryostat a combined bath and continuous flow device permitted the adjustment and regulation of temperature continuously within the range 2-300 K. Temperatures were measured with a vapour pressure thermometer

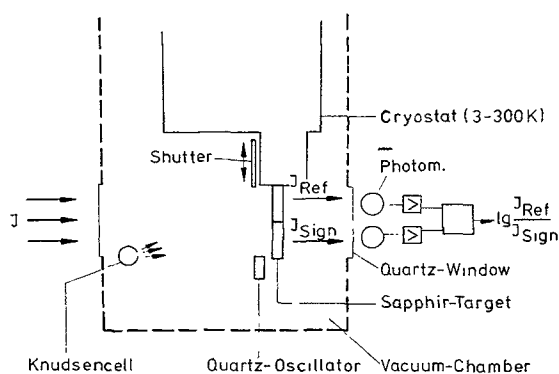


FIG. 1. — Schematic view of the experimental apparatus.

and carbon resistors. The resistor which was attached to the sapphire target directly had been calibrated separately. Noble gases of high purity were introduced into the vacuum chamber and condensed quantitatively on the sapphire target.

Silver atoms were evaporated from an electrically heated tantalum Knudsen cell. The silver evaporation rate as well as the total quantity condensed was monitored by a quartz oscillator which was located near the sapphire target. The resolution of the quartz balance was approximately 10 ng. During the formation of the matrix layer the silver atoms could condense on only half of the sapphire substrate. This was achieved by a shutter mounted on a translational-motion-feedthrough. The gas atoms, however, could condense homogeneously on the whole substrate. Light of incident intensity I was passed through both halves and the transmitted intensities measured separately by two photomultipliers. I_{REF} is the transmitted intensity of the reference beam which passed the matrix containing no silver, whereas I_{SIGN} is the remaining intensity of the beam which passed the matrix containing silver. Both these signals were fed into a logarithmic divider, yielding directly the absorbance $A = \log I_{REF}/I_{SIGN}$.

3. Results and discussion. — The yield of isolated atoms strongly depends on the condensation parameters, namely on the condensation temperature T_K , the gas/metal ratio R , the gas condensation rate \dot{m}_{GAS} and the gas itself [9, 12]. Qualitatively it is known that within the series Xe-A the yield of isolated atoms decreases with increasing T_K or decreasing R and \dot{m}_{GAS} . Hence aggregation occurs on the surface of the growing matrix layer. This effect is currently being investigated in our laboratory [12]. The nature of the gas appears to exert practically no influence on condensation at corresponding temperatures, but the gas admission rate, a parameter to which little attention has yet been paid, strongly influences the yield of isolated atoms.

Metal atoms can be isolated quantitatively under the following conditions: $T_K \leq 0.1 T_M$ (T_M : melting

point temperature of the respective matrix gas), a gas/metal ratio $R > 1000$ and a gas condensation rate $\dot{m}_{GAS} > 10^{16} \text{ cm}^{-2} \text{ s}^{-1}$ [12]. Spectra of isolated silver atoms exhibit well known absorption bands corresponding to the P←S resonance transition of silver atoms in the gas phase (see Fig. 2) [10-11, 13-14].

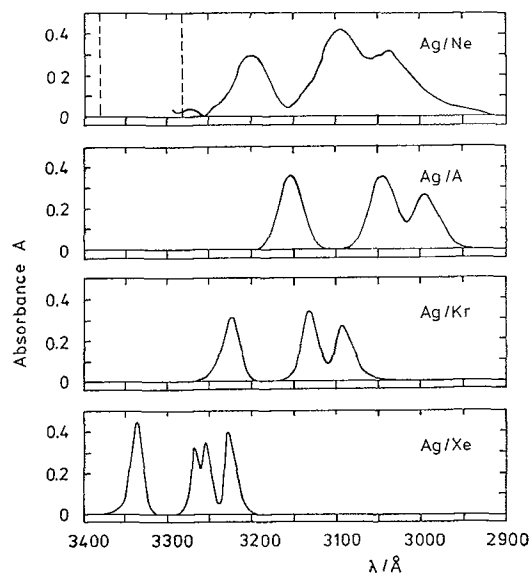


FIG. 2. — Absorption spectra of silver atoms in noble gas matrices below 10 K (solid lines) and in the gas phase (dashed lines).

The absorption bands in the matrix spectra in the region 3 000-3 400 Å are shifted to higher energies compared to the gas phase lines of Ag and this shift increases from Xe to A but decreases again for Ne. Furthermore the matrix spectra show a substantial broadening of the absorption bands and additional level splitting. These effects which are due to the influence of the surrounding matrix atoms can generally be expected also for small aggregates. We discuss them in detail elsewhere [10, 11].

Changing one of the above parameters in the reverse direction increases the chance of metal cluster formation. Figure 3 shows a spectrum after the onset of metal clustering as the gas/metal ratio reaches values below 1 000. The change in R is achieved by increasing the silver rate at constant temperature and fixed gas condensation rate. New absorption bands appear symmetrical to the characterized absorption lines of isolated silver atoms, namely a single band at lower energies and an only partially resolved doublet on the high energy side. The matrix layer had been formed at about 7 K in 137 s with a gas/metal ratio of 670 : 1 and a gas condensation rate of about $10^{16} \text{ cm}^{-2} \text{ s}^{-1}$. The total amount of condensed silver is $1.5 \times 10^{16} \text{ cm}^{-2}$; i.e. roughly only one monolayer.

These additional lines always showed the same relative intensity under the various experimental

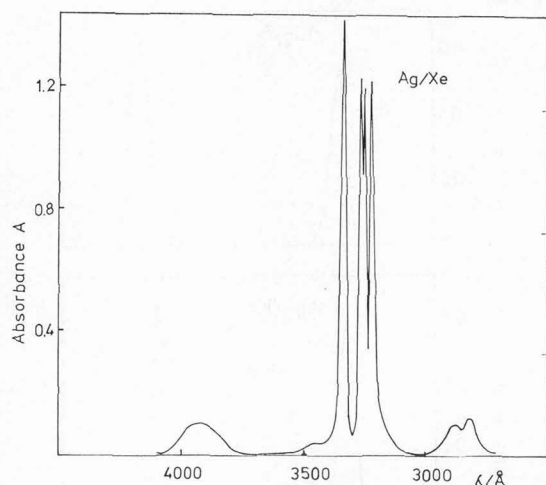


FIG. 3. — Absorption spectrum of monomeric and dimeric silver particles in a Xenon matrix formed at about 7 K. $\dot{m}_{Xe} = 7.2 \times 10^{16} \text{ cm}^{-2} \text{ s}^{-1}$, $\dot{m}_{Ag} = 1.1 \times 10^{14} \text{ cm}^{-2} \text{ s}^{-1}$, $m_{Ag} = 1.5 \times 10^{16} \text{ cm}^{-2}$.

conditions. It can therefore be concluded that these bands correspond to the same species. Under the given experimental conditions a statistical formation of molecular aggregates can be assumed. This results from a comparison between experimental data on the yield of isolated atoms [12] and theoretical predictions of Behringer [7], which show a relative good correspondence. Using these arguments we have attributed the additional absorption bands in figure 3 to dimeric silver. Furthermore a comparison with gas phase data for Ag_2 [15] shows a good agreement between the matrix bands and the $A \leftarrow X$, $B \leftarrow X$ transitions of gaseous Ag_2 .

A further decrease of the gas/metal ratio to a value $R = 257$ (cf. Fig. 4) by increasing the silver

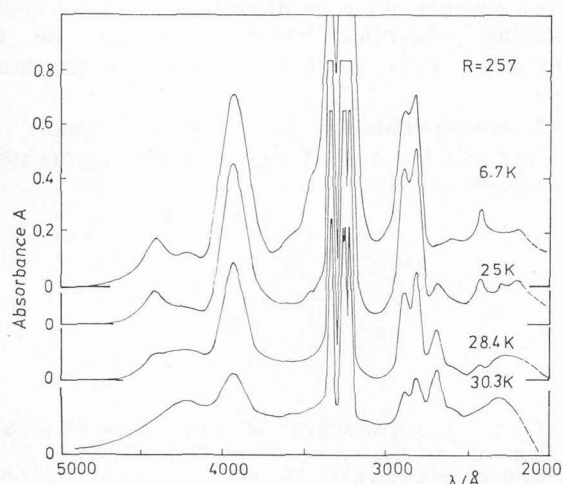


FIG. 4. — The influence of the temperature of formation on the xenon matrix spectra. $\dot{m}_{Xe} = 7.2 \times 10^{16} \text{ cm}^{-2} \text{ s}^{-1}$, $\dot{m}_{Ag} = 2.8 \times 10^{14} \text{ cm}^{-2} \text{ s}^{-1}$; $m_{Ag} = 5.9 \times 10^{16} \text{ cm}^{-2}$.

deposition rate results in an increase in the intensity of bands due to dimeric silver. In addition two new bands of the same relative intensity appear symme-

trical to the dimer bands together with a broad back-ground absorption in the whole region 2 000-5 000 Å. By statistical arguments, i.e. a decrease of R favours the formation of larger particles, and by comparison with gas phase data — where a progression of bands at about 5 000 Å due to a polyatomic silver molecule has been reported [15] — we conclude that both these bands belong to trimeric silver. The development of the broad back-ground absorption indicates that larger particles are formed.

The clustering discussed so far was achieved only by changing the silver evaporation rate with other parameters fixed. The temperature and the evaporation rate were chosen such that the growth of particles was as closely related as possible to a purely statistical growth mechanism thus assisting in the assignment of the spectral bands. If the temperature and the gas admission rate are changed, further additional bands appear, the assignment of which to specific clusters is not yet possible. Figure 4 shows the influence of the temperature on the matrix spectra. Altering the substrate temperature in the range 6.7-30.3 K results in the growth of a band near the doublet of dimeric silver. Furthermore it can be seen that the quantity of molecular aggregates Ag_1 - Ag_3 decreases and hence larger aggregates of unknown size must be formed, the mixture of which shows a broad spectrum. For even higher temperatures the bands due to the small molecular aggregates disappear totally.

Changing the gas/metal ratio by decreasing the gas condensation rate by about one order of magnitude results in the appearance of several new bands and also in the growth of a broad nearly featureless band. This band shows a broad maximum at about 3 500 Å and the onset of another band below 3 000 Å (cf. Fig. 5).

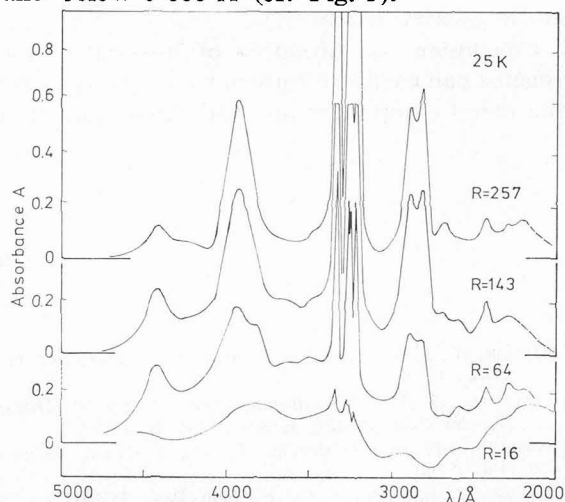


FIG. 5. — The influence of the gas/metal ratio R , which is changed by decreasing the gas rate, at 25 K on the xenon matrix spectra. $\dot{m}_{Ag} = 2.8 \times 10^{14} \text{ cm}^{-2} \text{ s}^{-1}$, $m_{Ag} = 5.9 \times 10^{16} \text{ cm}^{-2}$, $\dot{m}_{Xe} = 7.2 \times 10^{16} - 4.5 \times 10^{15} \text{ cm}^{-2} \text{ s}^{-1}$.

Finally we summarize the results obtained for the identified aggregates and show the influence of the matrix gas on these species. Figure 6 shows the

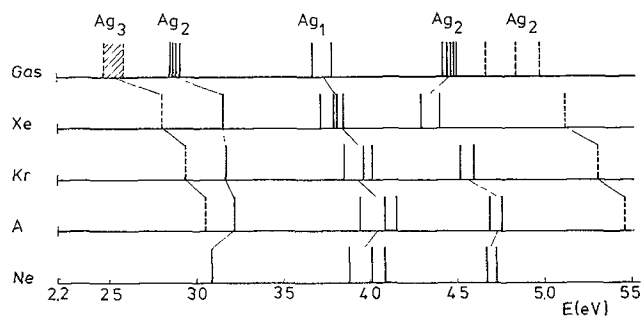


FIG. 6. — The peak maxima of the absorption bands of Ag_1 - Ag_3 in the gas phase and in Xe, Kr, A and Ne matrices. The results for Ag_3 are to be taken as preliminary.

peak maxima of Ag_1 , Ag_2 and Ag_3 in the gas phase and in different matrices. The Ne data are to be taken as preliminary. As already mentioned the progression of bands at 2.5 eV (5 000 Å) in the gas phase formerly attributed [15] to a polyatomic silver molecule can be assigned to Ag_3 . Furthermore one of the three transitions attributed to dimeric silver at about 5 eV (2 600-2 400 Å) [15] also possibly belongs to Ag_3 . All these bands shift to higher energies in the sequence Xe to A, but move back again for Ne. Furthermore we note that with respect to the gas phase transitions of Ag_2 there exist shifts to lower as well as to higher energies. Another interesting fact is that the energy difference between the Ag_2 -transitions is smallest for Xe and increases continuously from Xe to Ne, at which point it nearly equals the gas phase value. Figure 7 shows the spectra of dimeric silver in different matrices. The relative oscillator strength of these bands is approximately 1.5.

4. Conclusion. — Mixtures of molecular metal aggregates can easily be formed by co-condensation of the metal component and the matrix gas under

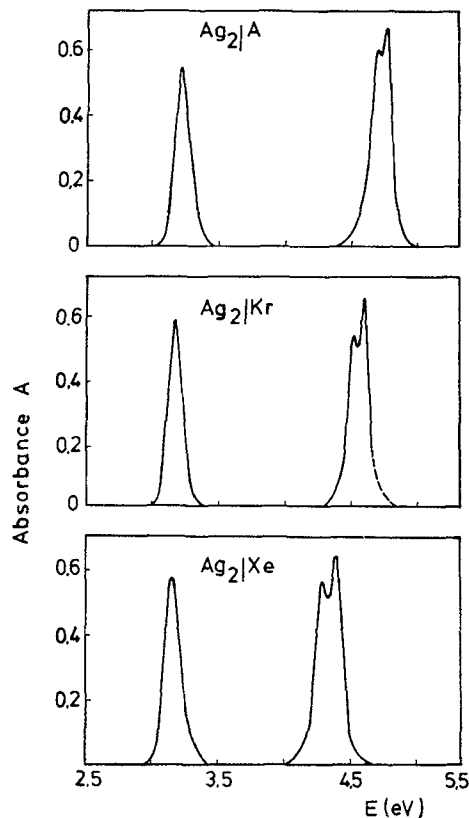


FIG. 7. — The absorption spectra of dimeric silver in Xe, Kr and A matrices.

suitable experimental conditions. It is difficult to assign the numerous features usually present in such matrix spectra clearly to specific clusters. However a systematic study of the influence of the various condensation parameters and a comparison with gas phase data allowed the assignment of the absorption bands to clusters containing up to three atoms. Further work is necessary to identify the remaining absorption bands which are due to multimetric silver particles of more than three atoms.

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