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The optical absorption spectra of small Silver clusters (n=8-39) embedded in rare gas matrices

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Abstract: The optical absorption of small mass selected Ag_n-clusters (n=8-39) embedded in solid Ar, Kr and Xe has been measured. Strong absorption has been found between 3 and 4.5 eV. The absorption spectra show 1 to 3 major peaks depending on the cluster size. The width of these peaks is smaller than in gas phase photodepletion experiments of silver ions, most likely due to the low and well defined temperature of the clusters in the matrix. The results are compared to a simple model based on a Drude metal, taking into account the spillout of the electrons and allowing for a deviation of the cluster from a spherical shape. Absorption cross sections scale with the number of valence electrons.

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1. Introduction

Optical spectroscopy is certainly one of the most powerful techniques to reveal the electronic structure of small aggregates. The ideal experiment would be the direct determination of the optical absorption of free mass selected clusters at a well defined temperature. However this task is beyond the scope of experiment due to the small cluster densities which can be obtained in the laboratory. Much success has been had the photodepletion method [1] as an indirect way to measure the photoabsorption cross section. A different approach is to accumulate particles until their density is high enough to permit absorption measurements. A common way to do this is matrix isolation spectroscopy (MIS). The production of matrices containing a sufficient number of clusters (10^{14}) with well defined size has become possible now [2]. The major drawback of this technique is that the particles are not free and the interaction with the host alters the optical spectrum. It is one of the purposes of this paper to show that it is possible to extract information out of the spectra which are intrinsic to the clusters and that corresponding gas phase values can be estimated.

Charlé et al [3] measured the surface plasmon absorption of intermediate size Ag clusters. They used a gas aggregation source producing clusters with a gaussian size distribution (dispersion $\sigma/D = 0.2$). For larger clusters ($\phi \approx$ 100Å) they find excellent agreement between experiment and Mie theory using the bulk dielectric constant, which clearly reveals the influence of the d-electrons (using a Drude metal dielectric function would place the resonance at 5.2 eV, about 1.5 eV shifted with respect to the experimental value). Decreasing the mean particle size leads to a blue shift of the plasma resonance with a linear dependence on the inverse of the particle diameter. Furthermore they remark that the linewidth of the absorption increases also with the inverse of the particle diameter. The question arises now, where this linear behaviour, which has been extrapolated to small sizes, breaks down. Photodepletion measurements by Tiggesbäumker et al [4] for Ag_n^+, Ag_n^- and matrix deposition experiments by our group [5,6] (n=2-21) have shown, that very small clusters can show "giant resonances" which resemble the surface plasmon absorption peak. In order to link the data sets, we have extended our measurements up to n=39 atoms per cluster. In this size range we join the extrapolated curve proposed by Charlé, but for smaller sizes drastic deviations are found for the peak position as well as for the peak width.

2. Experimental

The production of monodispersed clusters in matrices as well as the optical detection system have been described in detail elesewhere [2, 6]. Clusters are generated by sputtering with Xe^+ (20 kV, 5-10 mA). The positively charged particles are extracted, energy filtered and fed into a quadrupole mass spectrometer which covers the mass range from 1 to 5000 amu. Cluster currents are monitored using a Faraday plate close to the deposition window. Fig 1 shows a mass spectrum obtained at 35 eV cluster deposition energy on the Faraday plate. The shaded masses have been investigated so far. In order to get an overall mass spectrum, currents have not been optimized for a particular cluster size. Multiplying the ordinate of Fig.1 by a factor of two gives a good indication of the cluster currents during deposition for sizes n>20. The charged clusters are efficiently neutralised by means of an electron cloud maintained in the deposition region[7]. In order to minimize matrix effects on the optical absorption spectra, incoming monochromatized light from a D_2 lamp is split into two halves, one containing the absorption of the matrix and the particles, the other containing information almost exclusivly from the matrix.

In order to estimate fragmentation, excitation spectroscopy is used to detect atoms and dimers [2].

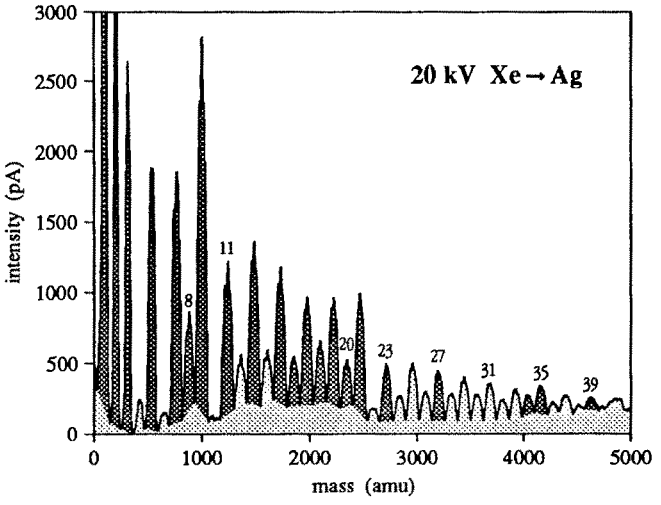

Fig 1: Mass spectrum for Ag_n^+

3. Results and discussion

The first problem one is concerned with in mass selected cluster deposition is the fragmentation F of the cluster during deposition. Excitation spectroscopy, i.e. the detection of all fluorescence light, is used to detect the atom signal which is a good estimation of F. In general we find for silver that less than 20% of the incoming clusters are fragmented. Fragmentation scales, as would be expected, with the binding energy of the cluster and decreases when the deposition energy is reduced. F tend to decrease slightly as the cluster size increases. This can be seen in Fig.2 where

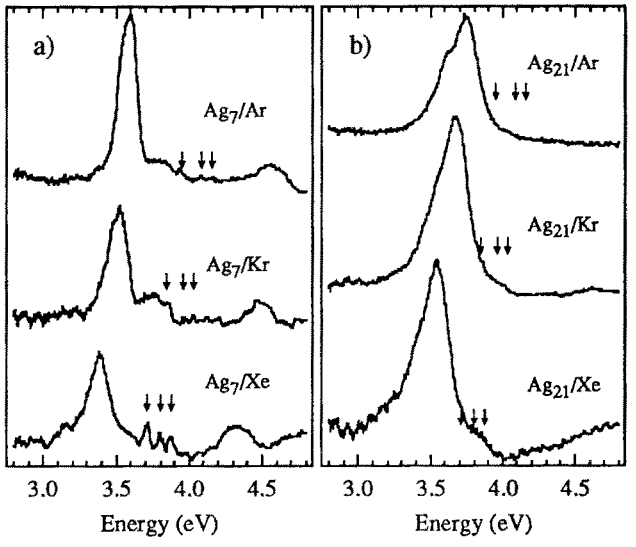

Fig 2: Absorption spectra for Ag7(a) and Ag_{21}(b) in Ar, Kr and Xe

the absorption spectra of Ag7 and Ag_{21} for three different matrix gases are shown. The atomic signal (marked by arrows) is clearly visible for Ag7 and can hardly be seen in absorption for Ag_{21}. More pronounced is the effect of the matrix gas. As the mass of the host decreases, fragmentation also decreases, which can clearly be seen by comparing the absorption spectra for Ag7/Ar and Ag7/Xe (Fig 2a.) This indicates that the momentum transfer which increases as the mass of the matrix atom increases plays a dominant role for F. A detailed discussion of the fragmentation processes is beyond the scope of this article and will be published separately [8].

Fig 2 elucidates another point which is of importance in MIS spectroscopy, namely the change of the optical response due to cluster matrix interaction. Although the resonance positions change for different matrix gases the overall form of the absorption spectra (number, width and shape of the peaks) does not change. This strongly supports our conclusion that we are really measuring the response of the particle at least for the weakly interacting inert gases. This observation is in agreement with Charlé et al [3] who finds the same resonance shift behaviour of the plasmon absorption peaks even if less inert matrices (O_2, C_2H_4) are used. We have investigated the relative shifts of the peaks as a function of the matrix gas for a selected number of clusters and find the shifts to be almost constant. As discussed in detail in [9] we estimate a matrix shift of the resonance position between Ar and gas phase to be about 0.24 eV.

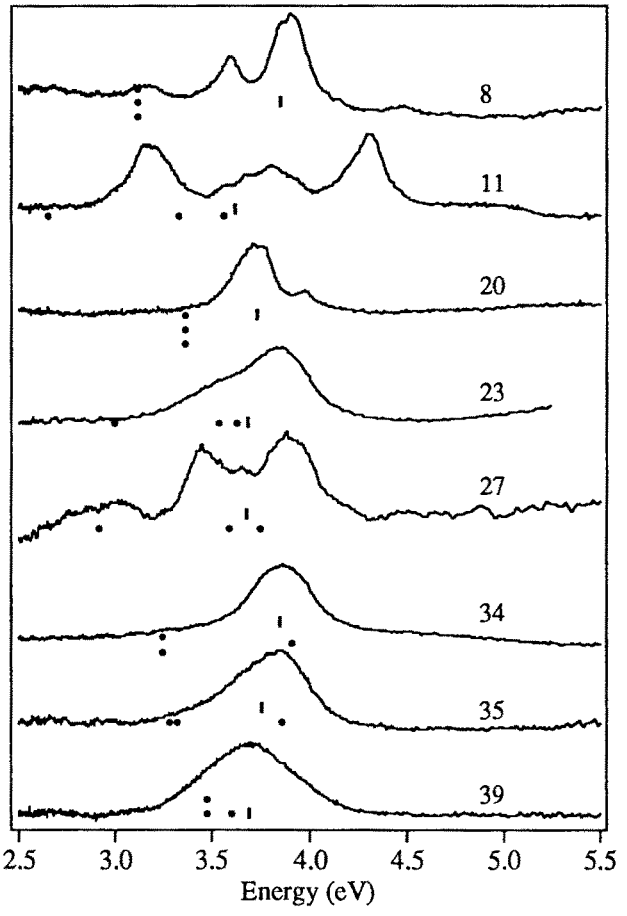

Fig 3: Absorption spectra of Ag_n/Ar, absorption spectra are rescaled to fit in the diagram, ∫ mean absorption energy, • center frequencies from the modified Mie-Drude model (see text)

Fig 3 shows the absorption spectra of Ag_n (n=8,11,20,23,27,34,35,39). The complete data set from Ag1-Ag_{21} can be found in [6], while the spectra from 23 to 39

have not been reported before. Ag_8 has a dominant absorption at 3.89 eV and a small absorption at 3.16 eV. The resonance at 3.58 eV is assigned to Ag_7 due to fragmentation. It should be noted, that Ag_8 is the only case where the fragmentation becomes an important component in the absorption spectra of the cluster sizes investigated. Clusters with an even number of electrons are more stable than those with odd numbers as reflected in the mass spectrum (Fig.1). This odd even alternation becomes less pronounced as the cluster size increases. Together with the observation that fragmentation has a tendency to decrease with increasing cluster size we conclude that fragmentation is a serious problem only for small clusters with an odd number of electrons. In contrast to the rather narrow dominant peak for Ag_8, Ag_{11} shows (neglecting fine strucure) three peaks of comparable width between 3 and 4.5 eV. Ag_{20} again is dominated by one strong absorption peak with a small satellite in the blue. Increasing the size further broadens the absorption spectra (2 nearly degenerate peaks for Ag_{23}, 2 distinct peaks for Ag_{27}) until at Ag_{34} we find again one narrow peak at 3.85 eV with a FWHM of 0.37eV. Ag_{39} finally shows one highly symmetric absorption peak but is larger than Ag_{34} (3.69 eV, FWHM=0.52 eV).

Since sophisticated calculations for the optical response of small silver clusters are not available, we compare our data to a simple model which was used by Selby et al [10] to explain the Na photodepletion data. We start from a Drude metal and calculate the optical response if we allow the electrons to spill out beyond the positive ionic background. The spillout parameter has been chosen to be t=0.75Å [11]. In addition we allow the cluster to deviate from its spherical shape and calculate the deformation parameters by minimizing the energy of a three dimensional harmonic oscillator. (for details see [1, 6]). The center frequencies of the plasmon peaks are given by the equation:

$$\omega_i = \omega_p \sqrt{\frac{Nr_s^3}{(x+t)(y+t)(z+t)}} \sqrt{\frac{1}{1+\varepsilon_m(L_i^{-1}-1)}} \qquad (1)$$

where ω_p is the bulk plasmon frequency for a free electron gas (9 eV for silver), r_s the Wigner Seitz radius, L_i geometric factors related to the depolarization effect[12], x,y,z the axes of the ellipsoid and ε_m the dielectric constant of the matrix. Note that the d-electrons are neglected . The plasmon resonances calculated from equation1 are marked as dots in Fig 3. The average resonance positions from this model are all redshifted with respect to the experimental data with a tendency to converge for larger sizes (0.7 eV for Ag_8, 0.2 for Ag_{39}). The number of absorption peaks or better the total width, which is a measure for the deformation of the particle, is fairly well reproduced in the size range 8 to 23 (see also [6]) and also for 39 but disagrees for 27, 34 and 35. This would indicate that the particles are less distorted than the model predicts. This is caused to some extend by the use of a harmonic potential which does not reproduce the subshell closing at n=34.

The total absorption cross section scales with the number of valence electrons per cluster. Approximately 89% of the dipole-oscillator strength, as determined by the dipole sum rule [13] including matrix correction, is exhausted by the measured transitions. Note that the simple model predicts peak intensity ratios of 1:1:1 for ellipsoids and 2:1 for spheroids. Although the relative intensities follow the oblate and prolate deformation, the quantitative agreement for the peak ratios is rather poor. If we compare the mean resonance frequencies we find a link to the extrapolated values of Charlé et al [3] for cluster sizes n=30-40 (energy difference smaller than 0.05 eV) but a drastic deviation for smaller sizes (redshifted to the extrapolated curve). Table 1 compares the extrapolated values of Charlé et al to the present data.

cluster size	<hω>	Charlé et al extrapolated
8	3.85	4.12
11	3.62	4.03
20	3.73	3.86
23	3.69	3.84
27	3.68	3.82
34	3.85	3.79
35	3.76	3.76
39	3.69	3.74

Table I: Comparison of mean resonance positions from our data with extrapolated values from Charlé et al [3]

In addition, the general trend of our measurements is fairly well described by a simple s-electron metal, introducing an electron spillout parameter t. We propose that the optical response for small Ag clusters (n<23) is dominated by the s-electrons, and tends to redshift with decreasing cluster size as a result of the spillout of the s-electrons beyond the positive ionic background. In the size range n>23 the influence of the d-electrons becomes more and more important until at particle diameters of about 100Å the optical response is completely described by the bulk dielectric constant in the framework of Mie theory.

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References

1. for a review see: de Heer, W.A., Rev. Mod. Phys. 1993
2. Harbich,W., Fedrigo, S., Meyer, F., Lindsay, D.M., Lignieres,J., Rivoal ,J. C.and Kreisle, D., J. Chem. Phys. **93** (1990) 8535.
3. Charlé, K. P., Schulze,W., Winter, B., Z. Phys. D **12** (1991) 471.
4. Tiggesbäumker, J., Köller, L., Lutz, H.O. Meiwes Broer, K. H. "From clusters to crystals", Eds. P. Jena, S.N. Khanna, B.K. Rao (Kluwer Academic publishers, Boston 1992), Tiggesbäumker, J., Köller, L., Lutz, H.O. Meiwes Broer, K. H., Chem. Phys. Lett. **190** (1992) 42. and private comm.
5. Harbich, W., Fedrigo ,S., Buttet, J., Chem. Phys. Lett. **195**, 613, (1992)
6. Fedrigo, S., Harbich, W., Buttet,J.,submitted to Phys.Rev. B
7. Lindsay, D. M., Meyer,F. and W. Harbich, Z. Phys. D **12**, (1989) 15.
8. Fedrigo, S., Harbich, W., Buttet,J., to be published
9. Fedrigo, S., Harbich, W., Buttet, J., Clusters and Fullerenes, Eds., V. Kumar, T.P. Martin and E. Tosatti, World Scientific (1992)
10. Selby, K., Vollmer, M., Masui, J., Kresin, V., de Heer, W.A. and Knight, W. D., Phys. Rev. B **40** (1989) 5417.; Selby, K., Kresin, V., Masui, J., Vollmer, M., de Heer, W.A., Scheidemann, A., Knight, W.D., Phys. Rev. B **43** (1991) 4565.
11. Lang, N.D., Kohn,W., Phys.Rev.B 7 (1973) 3541.
12. see for example Bohren, C.F., Huffman, D.R.; *Absorption and scattering of light by small particles,* (J. Wiley , New York, 1983)
13. Jackson, J.D., Classical electrodynamics (Wiley, New York, 1962)