Light emission during the agglomeration of silver clusters in noble gas matrices

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The agglomeration of small silver clusters in noble gas matrices to form larger ones may be accompanied by the emission of light. Spectral analysis reveals that part of radiation intensity can be attributed to fluorescence from excited metal atoms, dimers and trimers the formation of which results from cluster/cluster agglomeration as a consequence of the gain in binding energy. The remaining spectral features must be assigned to excited clusters Ag_n, with $n \geqslant 4$. © *1998 American Institute of Physics.* [S0021-9606(98)01212-4]

I. INTRODUCTION

The release of the excess energy of a chemical reaction through the emission of photons (chemiluminescence) is a widely observed phenomenon which is, for example used to study the reaction dynamics of molecular collisions[1] or to generate coherent light with chemical lasers.[2] Emission of visible light proceeds via electronically excited states whose lifetime has, of course, to be comparatively long with that for the optical transitions, as is the case in reactions in which only few atoms are involved, such as $Ca+F_2 \rightarrow CaF^*+F$.[3] In reactions with metal surfaces, on the other hand, the high density of occupied and empty states opens up very efficient decay channels of electron–electron scattering so that the lifetimes drop into the femtosecond regime[4] and alternate deexcitation mechanisms such as exoelectron emission become dominant.[5] The recent observation of light emission accompanying the agglomeration of small Cu or Ag clusters in noble gas matrices was quite unexpected.[6] Spectral analysis revealed that at least part of the radiation intensity had to be attributed to fluorescence from excited metal atoms and dimers, whose formation was attributed to ejection from the coalescing clusters as a consequence of the gain in binding energy. The present paper reports on continuing experiments which were performed in order to further clarify this surprising effect.

II. EXPERIMENT

The experiments were performed by means of a cluster source operating with the gas aggregation technique[7] and depicted schematically in Fig. 1. Metal atoms are evaporated from a resistively heated Knudsen cell into an atmosphere of noble gas atoms. The latter transport the hot metal atoms into the nucleation zone (diameter about 5 cm, length 50 cm) whose walls are cooled by liquid nitrogen. There the temperature of the noble gas is reduced by collisions with the walls and that of the metal atoms by collision with gas atoms. In this way the metal vapor becomes saturated and homogeneous nucleation leading to cluster growth is initiated. By variation of the experimental parameters such as rate of evaporation, flow of carrier gas, diameter of orifices, temperature and geometry of the cooling part the mean cluster size can be varied over a wide range from monomers and dimers up to more than 10^4 atoms/cluster. After leaving the nucleation zone through an orifice into an axially oriented cryopump of high pumping speed the stationary gas pressure is lowered. As a consequence the nucleation process is terminated at this stage and a cluster/noble gas beam with a high concentration of noble gas atoms is available.

This beam is then condensed onto a cold quartz plate where the clusters embedded into the matrix can undergo migration and agglomeration processes. With the experiments to be described here the flux of deposition was very high, typically about 10^{18} noble gas atoms $s^{-1}\,cm^{-2}$ with a gas to metal ratio of about 10^2-10^3, leading to a growth rate of about 1.5 cm/h. The high condensation pressure ($p \leqslant 1$ mb) and hence high condensation rate allows us to extend by far the available temperature range for matrix preparation as compared with common experiments. The available temperature range hence extends to $\leqslant 13$ K for Ne, and $\leqslant 50$ K for Ar, and $\leqslant 70$ K for Kr.

In order to check the possibility for chemiluminescence by direct collision of two clusters an additional experimental arrangement was developed in which two beams could be directed against each other.

Optical measurements were performed by means of a monochromator coupled to a charge-coupled-device (CCD) detector system.

For determination of the cluster size distribution the cluster source was aligned with a single focusing magnetic mass spectrometer (modification of the type SM1A, Varian-MAT) equipped with an electron impact ionization source.

III. RESULTS

As will be outlined below and as reported before,[6] the agglomeration of clusters of Ag or Cu in a noble gas matrix leads to the emission of visible light which can readily be recognized by the naked eye. By contrast, experiments in which two beams were colliding with each other yielded no detectable optical signal. The two beams had fluxes of about 10^{14} metal atoms $s^{-1}\,cm^{-2}$ each, and the scattering volume contained about 10^{10} atoms. If the collisional events would

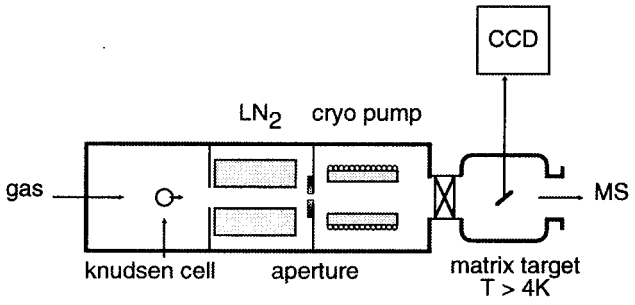

FIG. 1. Schematic drawing of the experimental set up: gas aggregation cluster source and matrix cryostat. The port where the mass spectrometer can be attached is also indicated.

have been associated with noticeable chemiluminescence, optical detection would have been readily possible.

A hint on the size of metal clusters which are responsible for the effect of chemiluminescence is obtained from inspection of the mass spectra reproduced in Fig. 2 representing the size distributions in the cluster beams. These contain essentially monomers and dimers ($n=1$ and 2), and then with growing intensity particles with $n \geqslant 10$, while there is a gap

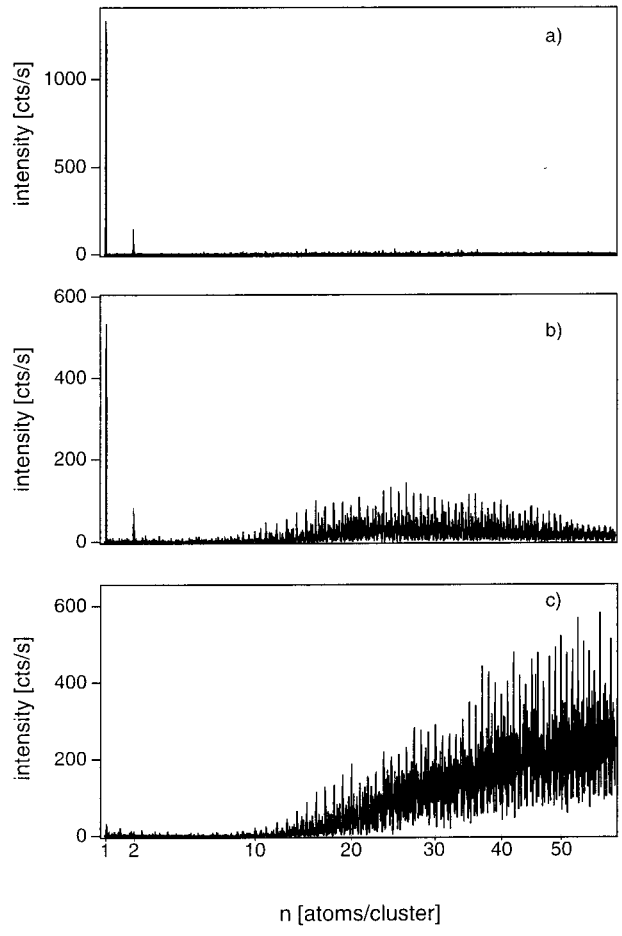

FIG. 2. Mass spectra of Ag clusters for three different neutral size distributions at an electron impact energy of 100 eV. The mean size increases from top to bottom. Beside singly charged also doubly and triply charged species are present.

in intensity (caused by the processes leading to cluster formation) for $3 \leqslant n \leqslant 10$. If a beam consisting essentially of monomers and dimers was condensed into a matrix at temperatures low enough to isolate these species subsequent warming up lead to migration and agglomeration associated with luminescence. Continuous luminescence was also observed during the deposition at temperatures high enough to allow migration and agglomeration of the condensing species. No light emission was, however, observed if the deposited clusters were larger ($n \geqslant 20$) and if monomers and dimers were missing. These findings suggest that chemiluminescence is essentially caused by clusters in the intermediate size range, viz. $3 \leqslant n \leqslant 20$. These species have first to be formed by agglomeration of monomers and dimers in a matrix and are not created by direct collision of two beams.

While various spurious effects which might be responsible for luminescence in a matrix, such as energy supply by electrons and ions or chemical reaction (e.g., oxidation) with impurities had already been ruled out in our previous work, still another possible source of luminescence was checked with the present experiments: Ultrasonic irradiation of metal carbonyls dissolved in oil was found to produce light emission (''sonoluminescence'') from electronically excited metal atoms.[8] This effect was attributed to acoustic cavitation, namely the formation, growth, and implosion of bubbles, by which extremely high temperatures were created leading to formation of excited metal atoms. The occurrence of a similar effect by the coalescence of two metal clusters within a noble gas matrix appears to be very unlikely. If it takes place it should, however, manifest itself also in the production of excited ''spectator'' species. For this purpose a small concentration of Br_2 was added to the gas flow. These molecules are known to exhibit noticeable emission with vibrational progression between 770 and 890 nm (Ref. 9) at elevated temperatures, but the results of corresponding measurements were completely negative. Any substantial local increase of the temperature by cavitation effects causing the formation of electronically excited metal atom fragments can safely be ruled out.

If a beam containing essentially Ag monomers and dimers in Ar [cf. Fig. 2(a)] is deposited onto a cold (~20 K) quartz substrate after a short induction period at first a weak luminescence is observed which rapidly grows in intensity and is at first of blue–violet color, but then continuously shifts to red with progressing growth of the layer whereby also the temperature is continuously rising. Spectral resolution (Fig. 3) demonstrates that this is essentially due to light emitted in two bands centered at 476 nm (blue) and at 619 nm (red), apart from emission in the near infrared around 1000 nm which will be discussed in some more detail later. With higher flux or at higher temperature the relative intensities vary in favor of the 619 nm band, thereby accounting for the gradual shift from violet to red of the color. These two bands had already been reported in our previous communication,[6] and that at 476 nm had been attributed to the radiative decay of Ag_2^* species. Most likely the band at 619 nm has to be assigned to the decay of excited trimers Ag_3^*, as will be discussed further below.

Without question the two bands have to be attributed to

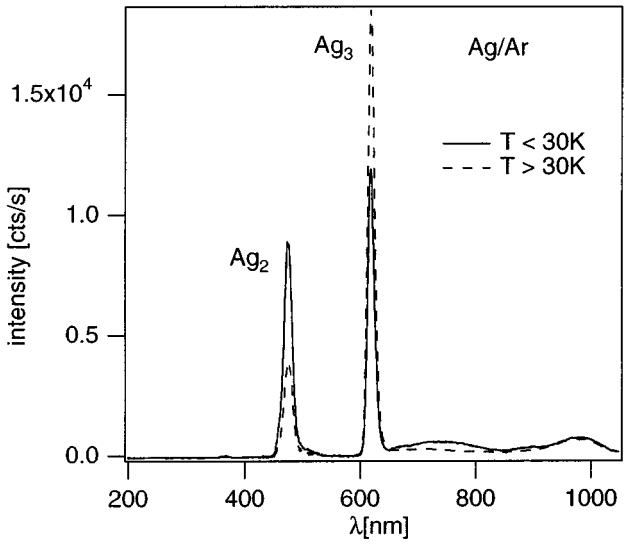

FIG. 3. Luminescence spectra during the condensation of silver atoms and dimers at matrix temperatures below and above 30 K. The intensity is not corrected for detector sensitivity. The actual intensity of the infrared band at ~1000 nm is larger by at least a factor of 10.

two different species whose relative abundance is governed by external parameters: Higher temperatures favor the production of the 619 nm species, while at a given temperature a higher concentration of metal atoms in the beam leads to an increase of the relative intensity of the 476 nm band. This suggests the coagulation process which causes the formation of Ag_2^* species involves larger clusters.

Analogous experiments were performed also with Ne and Kr as matrix gases, and apart from the discussed main bands further (but much weaker) emissions were observed down to about 250 nm wavelengths. Figure 4 shows a series of representative emission spectra from Ag clusters in Ne, Ar, and Kr matrices. With Ne the interaction is so weak that even vibrational resolution of the emission bands becomes feasible.

Table I lists the peak positions of the most prominent bands and their proposed assignment to specific particles Ag_n $(n=1,2,3)$ which is based on the following arguments:

(i) Absorption spectra of Ag atoms in noble gas matrices were measured by Gruen and Bates[10] and attributed to different transitions as listed in Table II. Their wavelengths compare fairly well with the chemiluminescence peaks of the present study compiled in the last column of this table which are therefore attributed to the decay of excited monomers Ag*. It should be noted that two sets of absorption bands with slightly different wavelengths were reported for a Ne matrix and were attributed to differences in the local geometry of the embedded metal atoms—an effect which has certainly also to be taken into consideration for a detailed discussion of the respective chemiluminescence data. Furthermore it is noteworthy that for an Ag-atom substitutionally isolated in the respective matrix a triplet is observed in absorption, whereas the fluorescence spectra only show a doublet, i.e., the local geometry of the electronically excited fragment is such that the degeneracy of the $P_{3/2}$-state is not lifted.

(ii) The band centered at 476 nm in Ar and showing vibrational splitting of 192 cm^{-1} in Ne with the most intense peak at 444 nm can unequivocally be identified with the $A \rightarrow X$ transition of the dimer Ag_2^*.[11] Figure 5(a) compared this band with the light emitted

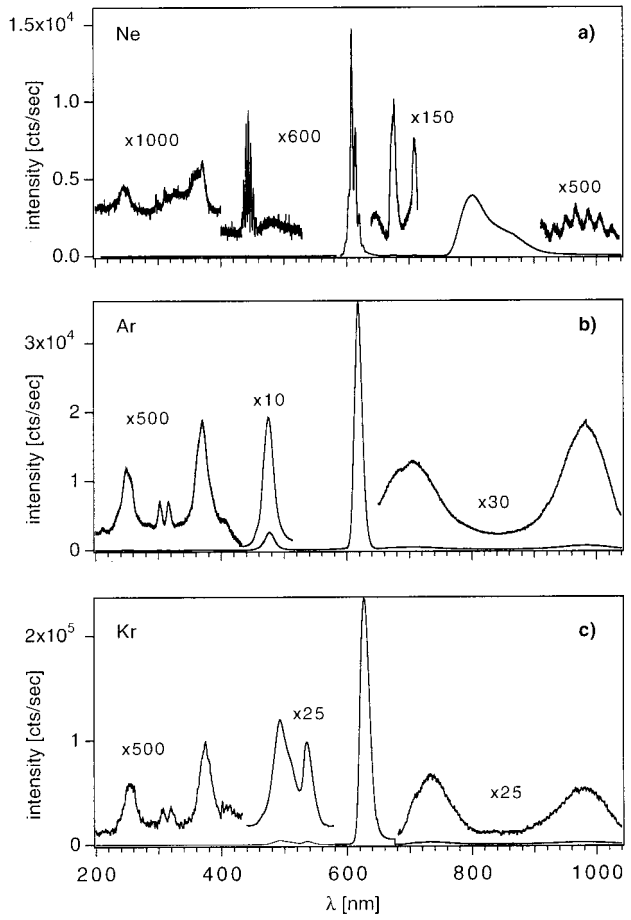

FIG. 4. Luminescence spectra during the condensation of silver atoms and dimers in Ne (~10 K), Ar (~30 K), and Kr (~40 K) matrices.

TABLE I. Summary of the observed emission lines during the cluster agglomeration process in Ne, Ar, and Kr matrices. Data marked by an asterisk indicate the dominant peak of the vibrationally resolved progression.

Ag_n n	Neon (nm)	Argon (nm)	Krypton (nm)
	246	250	254
	⋯	285	⋯
1	298/301/304	303	307
1	311/314/317	316	321
	371	370	375
2	444* ($\omega_e=192$ cm^{-1})	476	493...515...536
3	609* ($\omega_e=160$ cm^{-1})	619	628
	676	683	709
	707	705	732
	798...809	⋯	⋯
	850	⋯	⋯
	978* ($\omega_e=172$ cm^{-1})	979	970

TABLE II. Summary of the absorption and emission lines of Ag atoms in noble gas matrices.

	Assignment		Absorption[a] (nm) I[c]	Absorption[a] (nm) II[c]	Emisson[b] (nm)
					310,60
	$S_{1/2} \rightarrow P_{1/2}$	:	324,5	319,5	313,90
					317,39
Neon	$S_{1/2} \rightarrow P_{3/2,1/2}$	:	310,5	305,5	297,79
					300,70
	$S_{1/2} \rightarrow P_{3/2,3/2}$	:	313,5	309,5	304,33
	$S_{1/2} \rightarrow P_{1/2}$	:	315,0	⋯	316
Argon	$S_{1/2} \rightarrow P_{3/2,1/2}$	:	298,6	⋯	
					303
	$S_{1/2} \rightarrow P_{3/2,3/2}$	:	303,8	⋯	
	$S_{1/2} \rightarrow P_{1/2}$	:	322,9	⋯	321
Krypton	$S_{1/2} \rightarrow P_{3/2,1/2}$	:	309,3	⋯	
					307
	$S_{1/2} \rightarrow P_{3/2,3/2}$	:	313,6	⋯	

[a]Reference 10.
[b]Chemiluminescence (own measurements).
[c]I, II, two different trapping sites.

from Ag_2 clusters in a Ne matrix upon excitation with monochromatised light ($\lambda = 425$ nm) from a xenon lamp. The practically identical peak positions and vibrational splitting are clear indications for the assignment of this chemiluminescence band to Ag_2^* species. With the latter the spectral features are even sharper than with the fluorescence spectrum since the latter comprises different transitions in the excitation process as well as complex relaxation processes, etc.

(iii) The band with maximum intensity at 609 nm in Ne (centered at 619 nm in Ar and at 628 nm in Kr) is attributed to the decay of the Ag_3^* species. In Fig. 5(b) it is compared with the corresponding fluorescence band which shows similar vibrational splitting ($\approx 160\ cm^{-1}$) and peak positions. Harbich *et al.*[12] reported about fluorescence spectra from mass selected clusters in Ar and Kr matrices and attributed emissions at 622 nm (Ar), respectively, 626 nm (Kr) to Ag_3 species for which the corresponding absorption bands were at 492 nm (Ar) and 514 nm (Kr).

According to Ref. 13 the chemiluminescence band at 370 nm might also be due to Ag_3, but here the assignment is uncertain such as is also the case with a series of further bands which most likely originate from larger clusters or transient fragments.

IV. DISCUSSION

The results presented support the previously proposed mechanism leading to light emission.[6] Any spurious effects leading to energy supply, such as interference with electrons or ions, chemical reaction with impurities or cavitation associated with the collapse of local bubbles, can be ruled out, so that we are left with the energy gain accompanying agglomeration of small clusters to larger ones as the source for excess energy leading to electronically excited states decaying with the emission of photons. Thereafter the recombination of two small clusters M_n and M_m leads to a particle M_{m+n}^*, where the excess energy from the bond formation is stored in electronic excitation. This latter species may eject a smaller fragment M_1^* which is still electronically excited and may subsequently decay by photon emission.

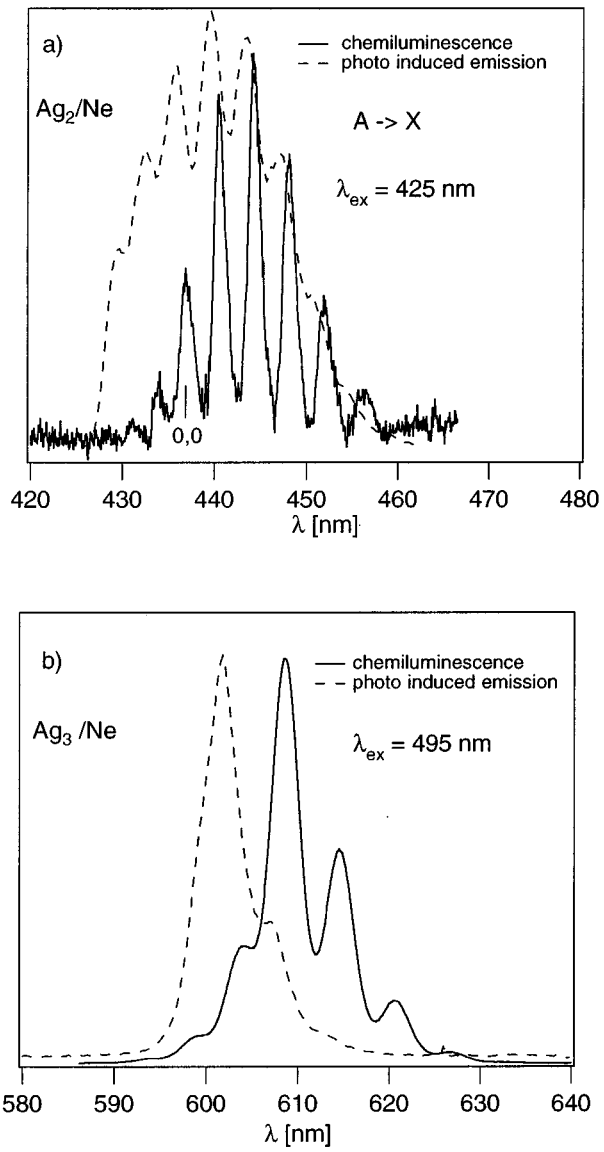

FIG. 5. Comparison of the photo induced fluorescence of Ag_2 (a) and Ag_3 (b) in Ne matrix with the emission which occurs during the agglomeration process. The excitation wavelength is 425 nm for the dimer and 495 nm for the trimer.

This model has to fulfill two requirements:

(i) The exothermicity $\Delta\epsilon_1$ of the reaction $M_m + M_n \rightarrow M_{m+n}$ has to exceed the excitation energy E^* for the process $M_{m+n} \rightarrow M_{m+n}^*$ plus the dissociation energy D for the step $M_{m+n}^* \rightarrow M_1^* + M_{m+n-1}$ viz.,

$$\Delta\epsilon_1 \geqslant E^* + D, \tag{1}$$

while on the other hand, the enthalpy $\Delta\epsilon_2$ of the over-

all reaction $M_m + M_n \rightarrow M_1 + M_{m+n-1}$ has to be at least equal to the energy $h\nu$ of the emitted photon,

$$\Delta\epsilon_2 \geqslant h\nu. \tag{2}$$

(ii) The lifetime of the electronically excited intermediate M^*_{m+n} has to be long enough to enable dissociation into $M_{1*} + M_{m+n-1}$.

The energetic boundary conditions rule out any recombination reactions between monomers and dimers. According to *ab initio* calculations, the binding energy of Ag_2 (i.e., the excess energy of the process $Ag + Ag \rightarrow Ag_2$) amounts only to 1.6 eV,[14] and hence an Ag_2^* species which subsequently decays into Ag_2 by emitting a photon with $h\nu = 2.6$ eV ($=476$ nm) is not feasible. Obviously the energy balance can only be fulfilled if a larger number of bonds is formed, that means if larger clusters are involved. There are unfortunately no numerical data available about the energies E^* and D involving electronically excited species, so that condition (1) cannot be checked. On the other hand there exists a series of data from *ab initio* calculations for ground-state properties of small Ag clusters,[15] from which the overall reaction enthalpy $\Delta\epsilon_2$ can be composed. Thereafter, for example, the reaction $Ag_6 + Ag_3 \rightarrow Ag_7 + Ag_1$ yields 2.7 eV, while the exothermicity of $Ag_5 + Ag_4 \rightarrow Ag_7 + Ag_2$ is 2.2 eV. These numbers are not yet completely fulfilling Eq. (2), whereafter $h\nu \approx 4$ eV for the formation of Ag_1 and $h\nu = 2.6$ eV for Ag_2, but it is felt that with somewhat larger clusters the energetic requirements may be fulfilled.

The clusters must, on the other hand, not be too large since otherwise condition (ii) will not be fulfilled, that means the lifetimes of electronic excitations become too short.

Atomic and molecular species are known to have radiative lifetimes of the order of 10^{-8} s which time is long enough for the nuclear motion accompanying bond rupture. This still holds for small Ag clusters. The lifetimes of Ag_2^* and Ag_3^* were determined to be around 0.5 and 1.3×10^{-8} s, respectively.[6,16] For bulk Ag, on the other hand, the lifetimes of ''hot'' electrons were determined to decrease from 6×10^{-13} s to 3×10^{-14} s when their energy is increased from 0.05 to 1 eV above the Fermi level.[17] This has to be attributed to very efficient scattering between quasifree electrons characterizing the metallic state.

The number of metal atoms in clusters characterizing the transition from the molecular to the metallic state has been the subject of long standing and extensive discussions, including numerous studies on the electronic properties of silver clusters.[18–22] A rather successful theoretical approach for modeling the electronic properties of clusters of Ia metals consisted in adopting the free-electron concept of bulk metals by solving the density functional equations for a jellium background,[23] leading to the picture of a delocalized electron gas confined to an ellipsoidal space. This ''shell'' model was considered to describe at least qualitatively well the ultraviolet photoelectron spectra of Ag_n clusters.[18,22] However, Taylor *et al.*[22] were led to the conclusion that for $n < 8$ the correspondence of the experimental data with the free electron shell model is poor. There exist, in addition, several studies on the optical absorption spectra of clusters in this size range which again indicate a breakdown of the delocalized electron model.[21,24] In particular, the spectrum for Au_{13} (Ref. 24) was found to be distinctly different from that calculated from the bulk optical properties, but to be in good agreement with the results of a molecular orbital calculation for an icosahedral configuration[25] whereafter the sp-band has not yet fully developed at this stage so that a description in terms of localized molecular orbitals appears to be more appropriate. Similar conclusions are reached in a study of the optical absorption spectra of Ag_7 and Ag_9 clusters.[21] According to the delocalized free electron model optical absorption spectra are dominated by a collective dipole excitation, the plasmon resonance,[19,20] which exhausts the oscillator strength to a large extent.[26] However, the measured spectra were found to be sharper and their intensities weaker than expected on the basis of this model from which it was concluded that for clusters as large as Ag_9 a description in molecular terms with distinct particle excitations is more appropriate.

These views are supported by observations made in the course of the present studies concerning the occurrence of absorption and fluorescence bands even in the near-infrared range which would not be compatible with the collective plasmon model.

On the other hand, the UPS study on Cu, Ag, and Au clusters by Smalley's group[22] comes to the conclusion that ''starting from a size of about twenty atoms the clusters can be regarded as small metallic pieces perturbed by their small size.'' As a consequence it has to be concluded that lifetime considerations restrict the size of Ag clusters whose agglomeration may give rise to the observed chemiluminescence effects to below about 10–20 atoms. It is just this size range which is present in our beams only with very small concentrations, and hence no light emission is observed in direct collision of two such beams. Instead the monomers and dimers embedded into the matrix become mobile and continuously coalesce until the critical sizes necessary for chemiluminescence upon further agglomeration is reached.

Of course, more detailed information about this question is only to be expected from experiments starting with size-selected clusters. Studies of this type are currently in preparation.

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