ELECTRONIC ENERGY DISSIPATION PROCESSES
IN DOPED RARE GAS CLUSTERS WITH A
SHELL-LIKE STRUCTURE

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Energy relaxation processes of photoexcited Ar$_M$ clusters ($M < 50$) covered with a shell of Kr atoms (up to 30 atoms) which are embedded in large Ne$_N$ clusters ($N = 3500$) are investigated with energy-resolved fluorescence spectroscopy. In the energy range of the Ne cluster absorption (16.5–18 eV) a strong energy transfer to the embedded Ar subcluster is observed, which results in desorption of electronically excited Ar$^*$ atoms. Ar$^*$ move through the Ne cluster, desorb and emit visible and near-infrared light in the vacuum ($4p \rightarrow 4s$). By coating the Ar clusters with Kr atoms, the Ar lines disappear and $5p \rightarrow 5s$ transitions of Kr become dominant. Additionally, new bands occur, which are assigned to transitions of perturbed atomic Ar $4p$ states inside Ne clusters. A simple kinematic model is suggested to describe the suppression of desorption of excited Ar atoms from Ne clusters.

1. Introduction

The electronic structure and dynamics of clusters has attracted considerable interest for many years since it gives new insight into the properties of condensed matter. Investigations on doped species offer the opportunity to get information about the host cluster and the impurity atoms or molecules, because the excitation is usually localized on the impurity.$^{1,2}$ Clusters can also serve as matrix for atoms, molecules and radicals. Because of their low chemical reactivity and the transparency within the vacuum-ultraviolet (VUV) spectral range, rare gases are especially well suited.$^3$ Supersonic free jets of rare gas clusters offer the possibility of isolating and characterizing molecules and complexes at very low temperatures, which are not accessible by other techniques.$^4$ As an example, recent studies on small (H$_2$O)$_6$ clusters embedded in large helium droplets demonstrated the preparation of the metastable cyclic water hexamer, which is only a local minimum on the associated potential energy surface.$^5$ The molecular rearrangement into the lowest energy configuration, a cage structure, is suppressed, because of the low He cluster temperature (0.38 K) and the rapid cooling mechanism.$^6$

The recent progress allows the investigation of chemical reactions inside large clusters by adding a third material.$^7$ The large cluster, which serves as a reaction medium, has many degrees of freedom, and can therefore be considered as a good thermostat as long as the reactants stay in contact with the cluster. The use of different host cluster materials allows the study of condensation and quenching reactions at different temperatures, ranging from $\sim 0.4$ K in He, $\sim 10$ K in Ne and $\sim 32$ K in Ar clusters, respectively.$^8,9$ Further advantages are of course, first, the possibility of controlled surface or bulk localization of a finite number of reactants and, second, the finite size of the reaction medium.

Desorption processes are the condensed matter analogs of unimolecular reactions and predissociation in gas phase molecules. It is well known that desorption of excited atoms and molecules play an important role in the relaxation cascade of light rare gas clusters (He, Ne) photoexcited in the VUV spectral range and which was also observed for small Ar clusters.$^{10,11}$ The aim of the present contribution is to provide experimental data on hindered desorption processes in Ar$_M$Kr$_K$Ne$_N$ clusters by modifying surface properties, which shed light on electronic energy dissipation processes in doped clusters and
in particular on the condensation of doped atoms in multishell structures.

The structure of the article is as follows. In Sec. 2 we describe the experimental setup for investigation of doped rare gas clusters with energy-resolved fluorescence spectroscopy. In Sec. 3 the experimental results are discussed and in the appendix we explain the method of size determination of embedded clusters.

2. Experiment

The measurements were performed at the experimental station CLULU at the synchrotron radiation laboratory HASYLAB in Hamburg. The molecular beam machine is described in detail elsewhere. Here, only a short summary of the major components is given, including the implemented experimental improvements.

Ne$_N$ clusters are prepared in a supersonic expansion through a conical nozzle (200 µm diameter, 4° opening cone angle). With a nozzle temperature of 30 K and a stagnation pressure of 200 mbar the average cluster size was determined to roughly $N = 3500$ using well-known scaling laws. The width (FWHM) $\Delta N$ of the size distribution is approximately $N$. In a first pickup process of argon atoms from a cross-jet (Q1) small Ar$_M$ clusters ($M < 50$) are formed inside the Ne cluster. In a second step the Ar$_M$Ne$_N$ system is doped by Kr atoms (Q2). The geometry of the interaction region and the main parameters are shown in the upper part of Fig. 1.

The size determination of embedded clusters bases on theoretical and experimental work done by Lewerenz et al. is explained in the appendix. According to theory, the number of picked-up atoms depends mainly on the Ne host cluster size and the average particle density, which is a function of the cross-jet pressure. In the middle part of Fig. 1 Ar and Kr particle density distributions $n(x, y_0)$ along the beam axis ($x, y_0$) are calculated for cross-jet pressures $p_Q$, temperatures $T_Q$ and capillary diameters $d_Q$ of 20 mbar, 300 K and 200 µm, respectively. The calculated average size of embedded clusters is shown in the lower part of Fig. 1. The linear dependency on the cross-jet pressure is used for the size determination in this contribution. We have to point out that all numbers are mean values for $M$; the width $\Delta M$ is approximately $M$.

After passing the interaction zone, monochromatic synchrotron radiation (11.5–22.5 eV) is focussed on the cluster beam 10 mm downstream from the nozzle ($\Delta \lambda = 0.25$ nm). The photoexcited doped clusters emit fluorescence light, which is detected spectrally undispersed by two photomultipliers [spectral sensitivity range: 160–930 and 28–550 (110–300) nm]. The total VUV luminescence yield is taken as a measure of the cluster absorption. For spectrally resolved measurements in the visible and near-infrared spectral range (VIS/IR) a Czerny–Turner type monochromator and a CCD camera was used ($\Delta \lambda = 6$ nm, respectively $\Delta \lambda = 0.6$ nm for high resolution).

3. Results and Discussion

In Fig. 2 the absorption spectrum of free Ne$_{3500}$ clusters is compared with the VIS/IR fluorescence
Excitation spectrum of Ar$_{50}$Ne$_{3500}$ clusters. The spectra are normalized to the maximum intensity. To assign the different bands the $n = 1$, 1' exciton absorption energies (spin–orbit split) of solid neon and the atomic Ne $^1S_0 ightarrow ^1P_1$ transition are indicated.$^{19}$ Similar to measurements on Ar$_N$, Kr$_N$ and Xe$_N$ clusters, the longitudinal exciton (1l') is very intense.$^{18,20,21}$

In optical normal-incidence transmission experiments, the longitudinal exciton normally does not couple to the incident transverse electromagnetic field. However, in reflection geometry and for rough surfaces, optical excitation of longitudinal modes becomes possible.$^{22}$ Considering that clusters have strongly curved surfaces, this might explain the occurrence of longitudinal excitons. The bulk and surface excitons are clearly separated. The surface state (1s') is located on the lower-energy side of the bulk exciton. The intensity of excitonic absorption bands depends sensitively on the cluster size and is directly related to the number of atoms in the interior and at the surface.$^{23}$

Since pure Ne clusters excited in the energy range of the first absorption bands do not emit visible or infrared light, the VIS/IR excitation spectrum is a fingerprint for a strong energy transfer to the embedded Ar cluster. From the relative bulk to surface intensities in the VIS/IR spectrum, we conclude that there are almost no Ar atoms sitting on the Ne cluster surface, because there is no energy transfer observed following surface excitation. There is no simple explanation for the different intensity ratios of longitudinal to transversal modes comparing the VUV and VIS/IR spectrum. Since in the relaxation process many different intermediate states are involved and not all of the corresponding rate constants are well known, a detailed analysis of the energy transfer rate is rather difficult.$^{24}$ More experimental data are necessary to distinguish between excited state specific and for example cluster size specific influences on the energy transfer rates.

In Fig. 3 the VUV fluorescence excitation spectrum of embedded Ar$_{40}$Ne$_{3500}$ clusters (a) is compared to an excitation spectra of free Ar$_{40}$ clusters (b). The excitonic transition energies of solid Ar are indicated. It is well known that in free small Ar clusters the most intense absorption bands are due to surface excitation.$^{25}$ In embedded clusters these bands disappeared completely, which gives strong evidence, as inferred above, that the Ar clusters are located inside the Ne clusters. The surface bands are shifted to higher energies and contribute to the absorption band located on the high-energy side of the 1l' exciton, because excited orbital of Ar surface atoms are perturbed by surrounding Ne cluster atoms. This particular band is related to the corresponding $^1S_0 ightarrow ^1P_1$ transition of single Ar atoms in Ne matrices, which is indicated in Fig. 3.$^{26}$

Ar$_{30}$Ne$_{3500}$ clusters were doped in a second step with Kr atoms and investigated with energy-resolved spectroscopy [Figs. 4(a)–4(c)]. The excitation energy
Fig. 4. Fluorescence spectra of Ar$_{30}$Kr$_{K}$Ne$_{3500}$ clusters with $K = 0$ (a), $K = 12$ (b) and $K = 24$ (c) Kr atoms deposited on the Ar cluster surface. As an example some Ar 4p $\rightarrow$ 4s lines (dotted) and Kr 5p $\rightarrow$ 5s lines (dashed) are indicated. The excitation energy was 17.64 eV (Ne 1l exciton). A high-resolution spectrum of the charge-transfer transition Ar$^+$Kr $\rightarrow$ ArKr$^+$ is shown in the inset of Fig. 4(c).

was 17.64 eV (Ne 1l’ exciton). Without Kr doping the spectrum (a) consists of many sharp lines, due to free atomic Ar transitions (4p $\rightarrow$ 4s). The energy is transferred from the Ne cluster to the embedded Ar cluster and localized on excited atomic centres (Ar$^*$) near the Ar cluster surface. Due to the repulsive interaction with surrounding neutral Ar atoms, electronically excited Ar$^*$ moves through the Ne cluster and emits in the vacuum. This process is similar to exciton induced desorption in pure rare gas solids. In the so-called “cavity-ejection mechanism” the interaction (whether it is repulsive or attractive) is correlated to the sign of the $V_0$ value (electron affinity) of the respective solid. Detailed investigations show that the correlation holds not only for the undoped but also for doped materials. A repulsive interaction between the excited atom and the surrounding neutrals is expected for positive $V_0$. In solid Ar desorbed excited atoms with a kinetic energy of roughly 0.04 eV were observed. The results show that neon as a rather soft matrix is not able to suppress desorption and to cage the excited Ar atoms.

By coating the Ar clusters with up to approximately 24 Kr atoms [Figs. 4(b) and 4(c)], the Ar lines (dotted) disappear and 5p $\rightarrow$ 5s transitions of Kr (dashed) become dominant. Additionally, new bands occur, which we interpret as Ar transitions of perturbed atomic 4p states inside the Ne clusters. In this picture, the desorbed excited Ar atoms are prevented from reaching the Ne cluster surface due to inelastic collisions with the Kr shell atoms. In order to verify this assumption we introduced a matrix shift of 168 meV and a line broadening of 106 meV due to the Ne cluster atoms on the spectral distribution of the nonperturbed Ar emission [Fig. 4(a)]. The resulting spectrum (solid line) reproduces the shape of the underlying structure for emission energies less than 1.9 eV. To understand the origin of the mismatch for higher energies, we used high-resolution spectroscopy in this energy range. The result is shown in the inset of Fig. 4(c). The additional band is due to bound–bound charge-transfer transition of Ar$^+$Kr (Ar$^+$ 2P$_{1/2}$ + Kr $^1S_0$) $\rightarrow$ ArKr$^+$ (Ar $^1S_0$ + Kr$^+$ 2P$_{3/2}$) first measured in the gas phase by Tanaka et al. It is not surprising that ionic channels are involved in the relaxation cascade since the clusters were excited at 17.64 eV (Ne 1l’ exciton), which is higher than the excited ionic Ar 2P$_{1/2}$ state (15.937 eV).

In order to obtain additional information about the suppressed desorption process we have analyzed the fluorescence spectra in more detail. In Fig. 5 the fraction of excited Ar atoms reaching the Ne cluster surface and emitting in the vacuum is plotted as a function of Kr atoms coating the Ar cluster surface (solid circles). Therefore, we integrated the line intensities of the free Ar 4p $\rightarrow$ 4s emissions. The
results, depending on the number of deposited Kr atoms, are presented in Fig. 5. In a crude approximation the shielded Ar\textsubscript{30} cluster surface from which desorption is hindered is proportional to the number of coating Kr atoms K. The general trend of the experimental data fits with the linear function \( f(K) \). From the extrapolation of \( f(K) \), we derive the number of Kr atoms needed for a complete caging of excited Ar atoms, \( M_C = 30 \). It is well known that free small clusters condense in icosahedral structures and for instance the second closed shell around a cluster containing 13 atoms is already built of 42 atoms. The experimental results show that less atoms than a closed icosahedral shell are necessary to suppress the desorption process. If we assume in the case of Ar\textsubscript{13} that each Kr atom localize on the center of the 20 triangular faces on the surface of the Ar cluster (local minimum on the associated potential curve) we can explain the reduced number of coated Kr atoms needed to built a shell-like structure.

We could verify that we are able to prepare well-different shells, by changing the order of doping illustrated in Fig. 1. This means that in a first pickup process we prepared a K\textsubscript{F30}Ne\textsubscript{3500} and in a second step we deposit Ar atoms on the Kr surface. The doped clusters were then investigated with the same experimental techniques. In this configuration the Ar atoms hinder the excited Kr atoms from reaching the Ne cluster surface and emitting in the vacuum. The Kr lines (5p \( \rightarrow \) 5s) disappear and instead 4p \( \rightarrow \) 4s transitions of Ar become dominant. Again, new bands occur, which are interpreted as Kr transitions of perturbed atomic 5p states inside the Ne clusters. We have included the measured fraction of Kr atoms (open circles) that emits in the vacuum and the linear function \( f(K) \) (dotted line) for this geometry in Fig. 5. Since Ar atoms are smaller and lighter compared to Kr atoms, more Ar atoms are needed to cover the surface completely. Therefore the slope of the experimental data and of the \( f(K) \) function is smaller. The number of Ar atoms deposited on the embedded Kr cluster surface for a complete cage is extrapolated to \( M_C = 42 \). This value is larger because Ar atoms are smaller and lighter than Kr atoms and the suppression is therefore less effective.

It should be mentioned that with this stepwise pickup technique we succeeded in building a Kr shell around an Ar cluster which is not possible by other techniques, for instance coexpansion of a dilute ArKr gas mixture or coating a free Ar cluster with Kr atoms. During the coexpansion the Kr atoms penetrate inside Ar clusters or serve as a condensation nucleus for Ar clusters or coagulate into pure Kr clusters but they do not form a shell around small Ar clusters.\(^1\) This is indeed the stabilization effect due to the surrounding Ne cluster atoms.

4. Conclusion

The formation processes and electronical properties and the relaxation dynamics of Ar clusters embedded inside Ne clusters are investigated. In a second step multishell structures are prepared by coating the embedded Ar cluster with Kr atoms. Using energy-resolved fluorescence spectroscopy energy relaxation processes and in particular the movement of electronically excited atoms in Ar\textsubscript{M}Kr\textsubscript{K}Ne\textsubscript{N} clusters is investigated. Surface excitons of embedded Ar clusters disappear, while new absorption bands appear. They are assigned to excitons at the interface between the Ar subcluster and the Ne host cluster. Excitation of bulk Ne clusters leads to desorption of Ar\textsuperscript{*} atoms (resonant energy transfer). Kr shell atoms prevent the Ar\textsuperscript{*} from desorption. The fluorescence spectra exhibit transitions of perturbed atomic Ar 4p states inside the Ne cluster. The movement of excited atoms inside the cluster is described in a simple kinematic model. The interpretation of the experimental results is confirmed by changing the order of doping. By coating an embedded Ar cluster with single Kr atoms it was possible to prepare a well-defined multishell structure containing an Ar core and an inner shell of Kr atoms and an outer shell of Ne atoms.

Appendix

The probability \( P \) for a Ne cluster (capture cross section \( \sigma_{\text{cap}} \)) while moving through an interaction zone (length \( L \) and average particle density \( n_S \)) embedding \( k \) atoms is described by the Poisson statistics:\(^{16}\)

\[
P_k(L) = \frac{(\sigma_{\text{cap}} n_S L)^k}{k!} \cdot \exp(-\sigma_{\text{cap}} n_S T). \quad (1)
\]

The cross-jet particle density along the cluster beam axis \((x, y_0)\) is given by\(^{17}\)
\[ n(x, y_0) = C \cdot \cos^2 \left( \arctan \left( \frac{x}{y_0} \right) \right) \]
\[ \cdot \cos^2 \left( \frac{\pi}{2\Phi} \arctan \left( \frac{x}{y_0} \right) \right), \]
\[ C = \frac{Z_P g_Q^2 P_Q}{y_0^2 k_B T_Q}. \]

In this equation \( Z_P = 0.157 \) and \( \phi = 1.365 \) are numerical constants for rare gases.\(^{17}\) The average particle density \( n_S \) is simply
\[ n_S = \frac{1}{L} \cdot \int_0^L n(x, y_0) \, dx. \]

In a crude approximation, we assume that the sum of the Ne \( N \) cluster area and the atomic area is equal to the capture cross section:
\[ \sigma_{\text{cap}} = \pi \cdot (R + r)^2 = \pi \cdot \left( \frac{3}{4\pi \cdot \rho} \cdot N \right)^{1/3} + r \right)^2. \]

In this equation \( R \) is the cluster radius, \( r \) is the atomic radius and \( \rho \) is the particle density in Ne solids. Using Eqs. (1)–(4) we calculated the average size \( M \) of the embedded subcluster as a function of the cross-jet pressure \( P_Q \):
\[ M(P_Q) = \int_1^{\infty} k \cdot P_k(L) \, dk. \]

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References