Site-Specific Excitation and Decay Processes in XeAr$_N$ Clusters

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Time- and energy-resolved fluorescence methods with synchrotron radiation excitation are used to investigate excitation and decay processes of electronically excited XeAr$_N$ clusters ($N = 20$–5000). For excitations related to the first resonance transition of Xe, pronounced size and site effects are reported. In particular, three distinct sites of atomic Xe are established. Selective excitation of Xe *on top* of the cluster surface results in an escape of the electronically excited atom, whereas Xe atoms initially located *in the interior* of the cluster remain after electronic excitation *in the interior* of the cluster.

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The progress in understanding the evolution of dynamic and chemical size effects in clusters is expected to provide a central contribution towards a merging of the microscopic and macroscopic points of view in the description of level structure and dynamics from small molecules to condensed phases [1]. The processes of energy acquisition, storage, and disposal in clusters are of particular interest for the elucidation of dynamic size effects in large finite systems [2]. So far, most of our knowledge of the excited-state dynamics of neutral clusters involving electronically excited states comes from theoretical work on neat and doped rare-gas clusters [2,3]. Classical molecular-dynamics (MD) calculations predict a gradual transition from reactive molecular-type relaxation (predissociation, fragmentation) in small clusters to nonreactive condensed-matter-type relaxation in large clusters [2]. In the case of Xe$_M$Ar$_N$ clusters, qualitative and quantitative differences between relaxation of electronically excited species initially located *in the interior* or *in the surface* of the cluster are predicted.

In this Letter the first detailed experimental investigation on excitation and decay processes of neutral clusters involving electronically excited species is reported. The system XeAr$_N$ ($20 \leq N \leq 5000$) has been chosen instead of neat rare-gas clusters, because doping considerably simplifies the interpretation of the data [4]. Time- and energy-resolved fluorescence spectroscopy using state-selective excitation with synchrotron radiation is used to investigate the character of the primary excited states and subsequent relaxation processes. Three different well-defined sites are identified: Xe atoms *on top* of the cluster surface, Xe atoms *inside the surface* of the cluster, and Xe atoms *in the interior* of the cluster. The energetic separation of the different absorption bands allows a detailed investigation of the relaxation process depending both on the location of the Xe atom and on the cluster size.

The measurements were performed at the experimental setup Clulu [5] behind the high-intensity Superlumi beam line [6] at HASYLAB. For excitation purposes, synchrotron radiation (SR) is monochromatized in the vacuum-ultraviolet (VUV) spectral range (resolution interval 0.25 nm) and focused into the cluster beam. XeAr$_N$ clusters are prepared in a nozzle expansion (nozzle diameter 200 μm, opening angle of the diverging part $2\Phi = 30°$, stagnation pressure p_0 up to 2 bars, temperature T_0 between 120 and 300 K) either of a gas mixture of 0.01% Xe in Ar or by a deposition technique [7]. In the latter case, a beam containing neat Ar$_N$ clusters is crossed by a jet of Xe atoms. The temperature of the clusters prepared in the conventional expansion is estimated to be close to the temperature of neat Ar$_N$ clusters, which is about 40 K [8]. The composition of the clusters and the size distribution in the beam is analyzed with a time-of-flight mass spectrometer in a different set of measurements. Distortions of the "true" size distribution of neutral clusters due to fragmentation upon ionization are expected to be of minor importance for N larger than 50. Typically, the width of the size distribution ΔN corresponds to the number N of atoms per cluster.

The fluorescence light is detected either undispersed with a closed channel-plate detector (CsTe photocathode, MgF$_2$ window) or it is analyzed with a homemade VUV monochromator. The monochromator is equipped with an open channel-plate detector (CsI coating) with a position-sensitive anode.

Fluorescence excitation spectra of XeAr$_N$ clusters ($N \approx 1000$) in the vicinity of the first resonance line ($5p \to 6s[3/2]_1$) of atomic Xe are presented in Fig. 1. Since dark relaxation channels are of minor importance, the total fluorescence yield corresponds to the absorption coefficient. The spectrum recorded on clusters prepared in a conventional expansion yields three distinct absorption bands labeled I, II, and III on the high-energy side of the resonance line. Band III is located at the same energy as the absorption line of Xe in solid Ar [9,10] and is therefore assigned to Xe atoms *in the interior* of the cluster. Bands I and II are assigned to an excitation of a Xe atom *on top* of the cluster surface and *inside* the cluster surface, respectively. The assignment of bands I and II is based on a comparison with a fluorescence excitation spectrum recorded on Ar$_N$ clusters containing approximately 4000 atoms covered with Xe atoms from a cross jet. In this case only two somewhat broader bands are observed, which are evidently related to excitations of Xe atoms close to the surface. Presumably, the broadening and the energetic shift relative to bands I and II result from an increased temperature of the cluster due to inelastic scattering with Xe atoms. Moreover, the above assignment of bands I and II becomes evident if the ener-

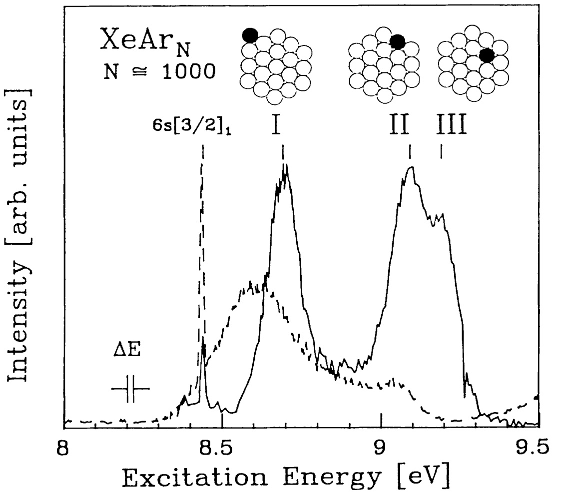

FIG. 1. Fluorescence excitation spectra of XeAr$_N$ clusters in the vicinity of the first atomic resonance line of Xe ($5p \rightarrow 6s[3/2]_1$). The full curve is recorded in a conventional expansion of a mixture of 0.01% Xe in Ar, whereas the dashed curve is recorded on pure Ar$_N$ clusters ($N \approx 4000$) covered with Xe atoms from an atomic cross jet. The different bands are assigned to excitations of Xe atoms *on top* of the cluster surface (I), *inside* the cluster surface (II), and *in the interior* of the cluster (III). For the different excitations the position of the Xe atom (solid circle) is schematically illustrated at the top.

getic shift relative to the atomic resonance line and the evolution with the cluster size is considered.

Fluorescence excitation spectra of XeAr$_N$ clusters containing on the average 20 to 5000 atoms are presented in Figs. 2(a)-2(d). For comparison an absorption spectrum [11] of solid Ar doped with 0.001% Xe is given in Fig. 2(e). Depending on the cluster size, up to four absorption bands, three of them already discussed in the previous paragraph, are observed instead of one band in Xe-doped solid Ar. The width of the bands I, II, and III is comparable to the width of the first absorption band of Xe-doped solid Ar. While the energetic position of the absorption bands changes only slightly with the cluster size, the intensity of the bands depends sensitively on the size. Clusters containing approximately twenty atoms exhibit two relatively sharp absorption bands (I and II) and additionally a broad continuum in between. With increasing cluster size, band III appears and becomes dominant in clusters containing more than 2000 atoms, whereas the intensity ratio between the other bands changes only slightly with the cluster size. The intensity ratio of the different bands directly reflects the surface-to-bulk ratio of the cluster [12] as observed for neat Kr$_N$ clusters [13]. This indicates that Xe atoms are located in different positions in Ar$_N$ clusters with nearly identical probability.

More detailed information on the actual position of Xe atoms *in* or *at* the cluster is obtained from the energetic position of the absorption bands. The blueshift relative to the atomic resonance line results from a repulsion of the excited electron by the neighboring Ar atoms. Therefore,

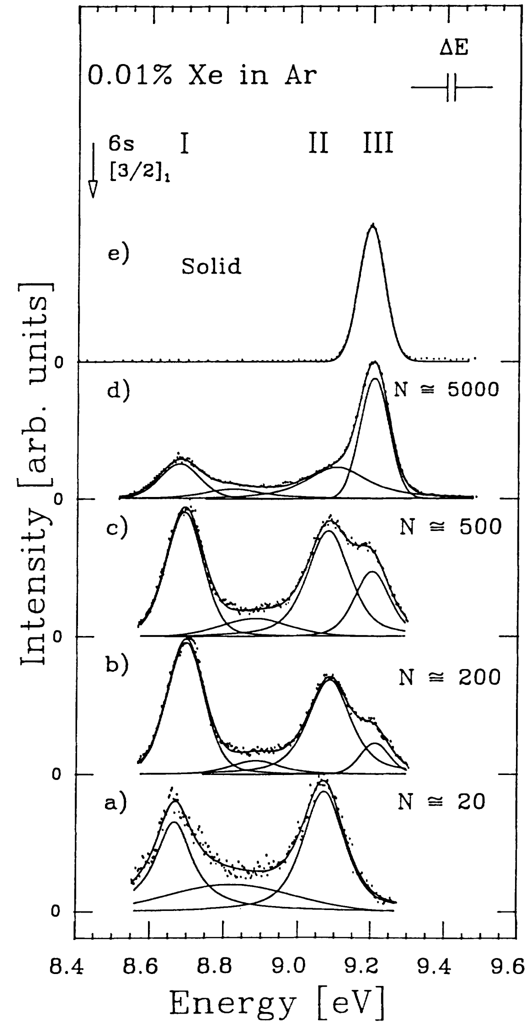

FIG. 2. Fluorescence excitation spectra (· · ·) and fitted contributions (——) of XeAr$_N$ clusters containing 20 to 5000 atoms in comparison with an absorption spectrum of solid Ar doped with 0.001% Xe (from Ref. [11]). For the assignment of the bands see Fig. 1. The energetic position of the first resonance line of atomic Xe is indicated by an arrow.

in a crude approximation one can expect [14] that the energetic shift ΔE is proportional to the number of nearest neighbors n,

$$\Delta E = \Delta E_0 n \, , \qquad (1)$$

where ΔE_0 is the energetic shift per nearest neighbor. Under the assumption that Xe atoms in the interior of the cluster (band III) are surrounded by twelve Ar atoms, the number of nearest neighbors for Xe atoms leading to band I and band II can be calculated from Eq. (1) and the measured energetic shift. In this way, four and ten nearest neighbors are obtained for bands I and II, respectively. An improved model which takes into account a nonlinear dependence on the number of nearest neighbors [12] gives a value of three, four to five, and nine nearest neighbors for band I, the weak continuum in between, and band II, respectively. These numbers are very reasonable for Xe *on top* of the cluster surface ($n=3$), Xe *inside* the surface of an icosahedra ($n=9$) or *inside* the surface (111) of a cuboctahedra ($n=9$), and Xe *at* surface imperfections or structures with an open shell ($n=4$-7). It should be pointed out that the small width of band I indicates that there seems to exist a unique surface site, being characterized by three nearest neighbors.

Selective excitation into one of these absorption bands allows a detailed investigation of the excited-state dynamics of Xe atoms located in different sites. Again, the energetic shift of the emission bands relative to the emission of the free atom can be used for the determination of the site of the Xe atom. Spectrally resolved fluorescence spectra of XeAr$_N$ clusters containing approximately 1400 atoms are displayed in Fig. 3. The sharp resonant emissions are assigned to scattered light. If Xe atoms *on top* of the cluster surface (band I) are selectively excited [see Fig. 3(a)], apart from scattered light only one very sharp emission line is observed. Within the error limits (4 meV) it fits with the resonance line $6s[3/2]_1 \rightarrow 5p$ of the free atom. This shows that the electronically excited Xe atom desorbs from the cluster surface.

On the contrary, excitation of Xe atoms *inside* the cluster surface (band II) leads to a very small redshift (~ 10 meV) of the emission line relative to the resonance line of the free atom [see Fig. 3(b)] and a small increase of the width. Therefore, it is concluded that the excited Xe atom decays while weakly bound somewhere *at* the cluster surface. Moreover, the change from a pronounced blueshift in absorption (0.63 eV) for band II to a small redshift in emission shows that the medium relaxes considerably around the excitation. We therefore conclude that the Xe atom is repelled out of the surface by a process which also leads to the desorption of electronically excited species in rare-gas solids [15]. Recently, very shallow minima at large internuclear distances were reported for several excited-state potential curves of heterogeneous rare-gas dimers [16]. They might be responsible for this weakly bound state. A weak band emitted at 8.62 eV exhibits a second relaxation channel which is only observed in clusters containing at least 1000 atoms. From the large blueshift (0.18 eV) relative to the resonance line of the free atom it is concluded that these atoms emit *inside* the cluster surface.

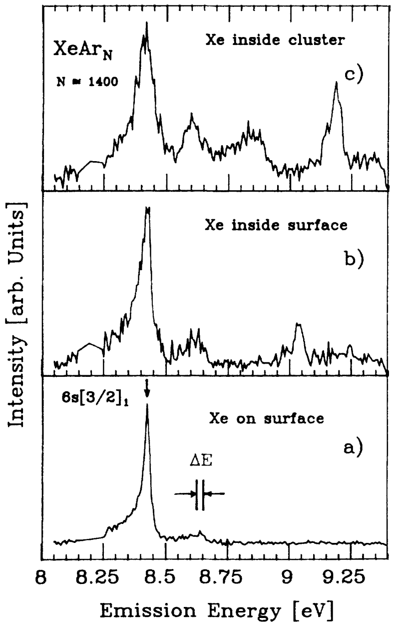

FIG. 3. Spectrally resolved fluorescence of XeAr$_N$ clusters recorded after primary excitation of (a) Xe atoms *on top* of the cluster surface (excitation energy $E=8.67$ eV), (b) Xe atoms *inside* the cluster surface ($E=9.05$ eV), and (c) Xe atoms *in the interior* of the cluster ($E=9.22$ eV). The energetic position of the first resonance line of atomic Xe is indicated at the top of (a). Resonant emissions are assigned to scattered light.

Excitation of Xe atoms initially located *in the interior* of the cluster [Fig. 3(c)] leads to the emission of three distinct bands at 8.429, 8.62, and 8.85 eV indicating that three different relaxation processes take place. The band at 8.85 eV which is strongly blueshifted relative to the $6s[3/2]_1$ state corresponds to an emission in Xe-doped solid Ar which is assigned to the emission of Xe atoms in the $6s[3/2]_1$ state in substitutional sites [10,17] (twelve nearest neighbors). This band is rather weak for small clusters but becomes dominant in very large clusters with $N \geq 5000$ [12]. The interpretation of the emission bands at 8.62 and 8.429 eV is a more complex problem. It should be pointed out very clearly that the emission at 8.429 eV differs significantly (energetic shift ~ 10 meV, larger width) from that of the free atom and from a similar emission in Fig. 3(b). Time-resolved measurements following primary excitation of Xe atoms *inside* the cluster show that the dominant decay channel has a time constant of the order of 100 ns. This is much larger than the decay time of the $6s[3/2]_1$ resonance state. We therefore conclude that at least the strong band at 8.429 eV is emitted from the metastable $6s[3/2]_2$ level. A corresponding band is observed in Xe-doped Ar [10,17] and assigned to the decay of the $6s[3/2]_2$ state located in a four-vacancy complex [17]. We therefore assume that Xe atoms in the $6s[3/2]_2$ state emit in a similar way at a vacancy or a microcavity inside the cluster. The emission band at 8.62 eV is assigned accordingly to the decay of Xe atoms in another vacancy complex where the Xe atom has a larger number of nearest neighbors. In summary, it should be pointed out clearly that after primary excitation of Xe atoms *in the interior* of the cluster the excited Xe atoms do not leave the cluster, at least in clusters containing more than 100 atoms.

In the following, we compare our experimental results with the findings of the theoretical work [2] mentioned in the introduction. The relaxation process is mainly affected by three quantities: (I) the repulsion energy which is, in a first approximation, proportional to the number of nearest neighbors; (II) the capability to transfer the excess energy to the Ar atoms; and (III) the distance of the Xe atom from the cluster surface. In the case of $XeAr_{12}$, which is the first closed-shell structure, primary excitation of Xe in the central position leads to the ejection of the electronically excited atom. On the contrary, electronically excited Xe atoms in surface sites remain weakly bound at the surface.

In case of $XeAr_{54}$, which is the second closed-shell structure, a direct comparison with our measurements is feasible. After excitation of the Xe atom *in the central* or *in the surface* position of $XeAr_{54}$ the excited Xe atom remains *in the interior* or *at the surface* of the cluster in either case. The escape of electronically excited Xe does not occur, because the large excess energy of Xe *in the interior* is very efficiently distributed over the large number of degrees of freedon. The latter result is exactly what we observe for clusters containing more than fifty atoms if Xe atoms initially located *in the interior* or *in the surface* are excited. Furthermore, there is strong experimental evidence (formation of microcavities or vacancies) for relaxation of the medium around the excited atom as is exhibited in the MD calculation [2].

In conclusion, time- and energy-resolved fluorescence methods are used for a detailed investigation of the excited-state dynamics of $XeAr_N$ clusters. Pronounced site and size effects in the excitation and decay processes of electronically excited clusters are reported for the first time. Compared to neat Ar_N clusters [18], the interpretation of the experimental data is considerably simplified, because the electronic excitation is located at the initially excited atom. Reactive (predissociation, fragmentation) and nonreactive decay processes are observed depending on the position or the site of the chromophore (in our case atomic Xe). Xe atoms are coordinated by three Ar atoms (*on top of the surface*), nine Ar atoms (*inside the surface*), or by twelve Ar atoms (*in the interior* of the cluster). The overall picture predicted by MD calculations [2] that the relaxation process is strongly affected by the location of the Xe atom in the cluster is well established by the experimental findings.

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