

# Assignment of impurity states in xenon-doped argon clusters. Perturbed atomic Rydberg states versus impurity Wannier excitons and the implications for doped rare gas solids

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## Abstract

Electronic excitations of  $\text{Xe}_M\text{Ar}_N$  clusters are studied using fluorescence excitation spectroscopy in the energy range of the electronic excitations of pure Xe. The composition of the clusters is changed between  $\text{XeAr}_N$  and pure  $\text{Xe}_M$  by varying the concentration of Xe gas in a coexpansion between 0.01% and 15%. The evolution of the absorption bands of  $\text{XeAr}_N$  clusters is investigated as a function of cluster size ( $N=10\text{--}5000$ ). The character of the excitations is discussed in view of two theoretical models, namely perturbed atomic states and Wannier impurity excitons. The experimental results clearly favour the model of perturbed atomic states which should also be a suitable description for excitations in Xe-doped solid Ar.

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## 1. Introduction

Electronic excitations of impurity atoms imbedded in a host material are of fundamental interest to the understanding of impurity centers in insulators [1]. A topic of current interest in this context is the character of the excited states and energy transfer processes which take place after the electronic excitation in micro-crystals and free clusters and the relation to their size. Furthermore, it has been shown that doping of clusters can substantially simplify the interpretation of the level structure [2,3] because the electronic excitation takes place at one well-defined atom and can not move through the cluster.

An important basis for the understanding of excitation and decay processes in clusters is the understanding of corresponding processes in the macroscopic solid. Solid rare gases doped with rare gas atoms can be regarded as model systems for deep im-

purity states [1] being complementary to the text book examples for shallow impurity states in semiconductors [4]. In the latter case, the binding energy of an impurity atom should only depend on the properties of the *host* material, namely the dielectric constant and the effective mass of the conduction band electrons. On the other hand, in the case of deep impurity states such as electronic excitations of rare gas atoms in rare gas solids the situation is not as simple because the size of the excited electronic orbital can vary between values smaller than the nearest neighbour distance and several times the nearest neighbour distance depending on the main quantum number of the excited state. This is a direct consequence of the small dielectric constant of rare gas solids. As a result, two limiting cases for the characterization of electronic excitations of atoms embedded in rare gas matrices can be thought.

(1) Tightly bound states with an orbital size small

compared to the nearest neighbour distance. These states can be regarded as atomic Rydberg states perturbed by the surrounding atoms of the matrix. In this case the excited electron belongs to the impurity and a 1:1 correspondence to the excitation in the free atom is expected although the excitation energy may be considerably shifted.

(2) Weakly bound states with extended orbitals being, to a certain extent, equivalent to the Wannier excitons of the host material. In this case, the bound electron-hole state is formed from the positively charged core of the impurity and an electron from the conduction band of the *host* material. Accordingly, the excitations are expected to form exciton series converging to the bottom of the conduction band of the host. The transition energies, in particular the spacing between the levels, is determined by the properties of the host material, namely the dielectric constant and the effective mass of the conduction band electrons.

Naturally, it can be expected that a transition takes place between the two limiting cases depending on the size of the orbital under discussion. Since the radius of an excited orbital increases with the main quantum number, both cases can in principle be observed in one material.

Pioneering work in this field was done by Baldini and Knox with a detailed experimental and theoretical study of electronic excitations of Xe-doped solid Ar [5]. These experimental data are analyzed in the spirit of the Wannier impurity exciton model outlined above. In the meantime many experimental and theoretical studies on electronic excitations in the doped solid [6,7]<sup>1</sup> and liquid [8–11] rare gases were performed. While the results in the dense gas and in the liquid are preferably interpreted in a description of perturbed atomic states, the interpretation in the solid is done in the impurity exciton model [6,7]. An extrapolation of the observed series of absorption bands in the solid using the Wannier impurity exciton model gives an energy of 10.6 eV for the bottom of the conduction band which is considerably smaller than the value of 10.97 eV from the photoconductivity measurements [12]. To solve this discrepancy a reinvestigation of the density dependence of the ab-

sorption bands of Xe in dense gaseous and liquid Ar was undertaken [13] and this pointed to an incorrect assignment of some absorption bands in the pioneering work [5]. For most of the bands observed in the liquid, and even in the solid, an interpretation based on perturbed atomic Rydberg states is proposed [13]. However, the assignment of one of the most prominent bands in Xe-doped Ar which seems to be essential for the understanding of the character of the excited states remains open [13]. As an elegant way of obtaining further information on this problem, the electronic excitations can be investigated by studying their evolution with size in Xe-doped Ar<sub>N</sub> clusters. So to speak, the study of doped clusters is not only interesting in its own right but it may also shine some light on the problem of the assignment of energy levels in the macroscopic solid and can contribute to our understanding of the bulk phase.

## 2. Experiment

The measurements were performed at the experimental apparatus Clulu at the high-intensity beamline Superlumi [14] at the Hamburger Synchrotronstrahlungslabor HASYLAB. A detailed description of the experimental set-up is given in Ref. [15]. For the purpose of excitation, the synchrotron radiation (SR) is monochromatized in the VUV spectral range (band pass 0.25 nm corresponding to 14 meV at 8 eV) and focused into the cluster beam. Xe<sub>M</sub>Ar<sub>N</sub> clusters are prepared in a nozzle expansion (nozzle diameter 0.2 and 0.5 mm respectively, opening angle of the diverging part of the conical nozzle  $2\theta=30^\circ$ ; stagnation pressure  $P_0$  up to 2 bar, temperature  $T_0$  between 120 and 300 K) of gas mixtures of 0.01%–15% Xe in Ar. The temperature of the XeAr<sub>N</sub> clusters is estimated to be close to the temperature of pure Ar<sub>N</sub> clusters which is about 25–35 K [16], at least for clusters with  $N>100$ . For smaller clusters, the temperature may be smaller because the degree of condensation is low and hence, the heat of condensation can be distributed more efficiently to the uncondensed part of the beam. Before entering the main experimental chamber the central part of the beam passes through a skimmer. The composition of the clusters and the size distribution is analyzed with a time-of-flight mass-spectrometer in a different set of measurements. For

<sup>1</sup> A collection of the work on doped rare gases is given in Ref. [1], chapter 3.3.

these measurements a smaller nozzle with 0.08 mm diameter was used in order to reduce the pressure in the main experimental chamber. The average size of the clusters is then calculated from these results using scaling laws [16]. Deviations of the size distribution determined this way from the 'true' size distribution of the neutral clusters in the beam are expected to be of minor importance for clusters with  $N$  larger than 50.

The fluorescence light is detected with a closed channel plate detector (CsTe photocathode, MgF<sub>2</sub> window). Fluorescence excitation spectra are recorded by measuring the fluorescence intensity as a function of the excitation energy by scanning the monochromator. Since non-radiative decay channels are expected to be of minor importance [15], the spectra recorded this way correspond to the absorption coefficient of the clusters.

### 3. Results

The dominant absorption bands of pure Xe gas are due to transitions from the highest unoccupied 5p state to empty  $ns$  and  $md$  states ( $n=6, 7, \dots; m=5, 6, \dots$ ). As a result of the spin-orbit splitting in the core, the observed lines are split into separate series which are denoted according to the  $j$ - $l$ -coupling [17]. Transition energies of atomic Xe are indicated at the top of Figs. 1 and 2. At least for the smallest mixed clusters, namely the XeAr dimer, this classification scheme of atomic Xe should be useful. Fluorescence excitation spectra of Xe<sub>*M*</sub>Ar<sub>*N*</sub> clusters prepared in expansions with different concentrations of Xe gas are presented in Fig. 1. In the case of the smallest concentration of 0.01% Xe, the dominant contribution should be due to Ar clusters doped with one Xe atom. This has been checked with mass spectrometric measurements. It should be noted that under these conditions only about 5%–10% of the clusters contain a Xe atom. The average size of the clusters increases with increasing Xe concentration. The average size changes from approximately 50 atoms (0.01% Xe concentration) to 150 atoms for 15% Xe. For concentrations larger than 3% only pure Xe<sub>*N*</sub> clusters are formed. The fluorescence excitation spectra recorded with these Xe rich mixtures are in good agreement with previously reported results for Xe<sub>*N*</sub> clusters pre-

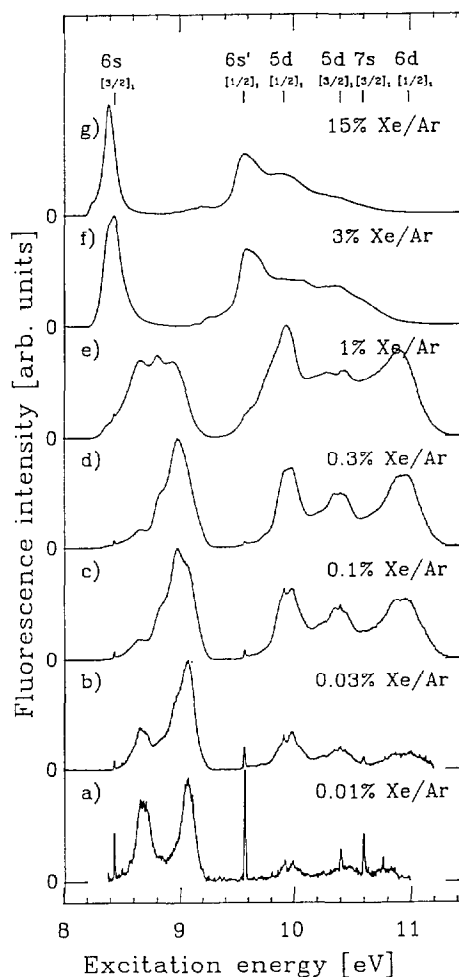


Fig. 1. Fluorescence excitation spectra of Xe<sub>*N*</sub>Ar<sub>*M*</sub> clusters as a function of the concentration of Xe gas in the mixture used for the coexpansion. For the lowest concentration (0.01% Xe in Ar) the clusters contain predominantly only one Xe atom. Transition energies of atomic Xe are indicated at the top of the figure. The average cluster size ranges between 30 and 200 atoms.

pared in an expansion of pure Xe gas [18]. A detailed analysis of the size distribution of beams prepared from mixtures of 0.03% to 1% Xe could not be contained from mass spectroscopic investigations as the large number of different combinations of Xe and Ar atoms leads to congested mass spectra. We will therefore give some estimates based on spectroscopic features. In the following discussion we focus on excitations in the energy range 8.3–9.2 eV which are related to the first dipole allowed transition of Xe into the 6s[3/2]<sub>1</sub> state. Depending on the cluster size this

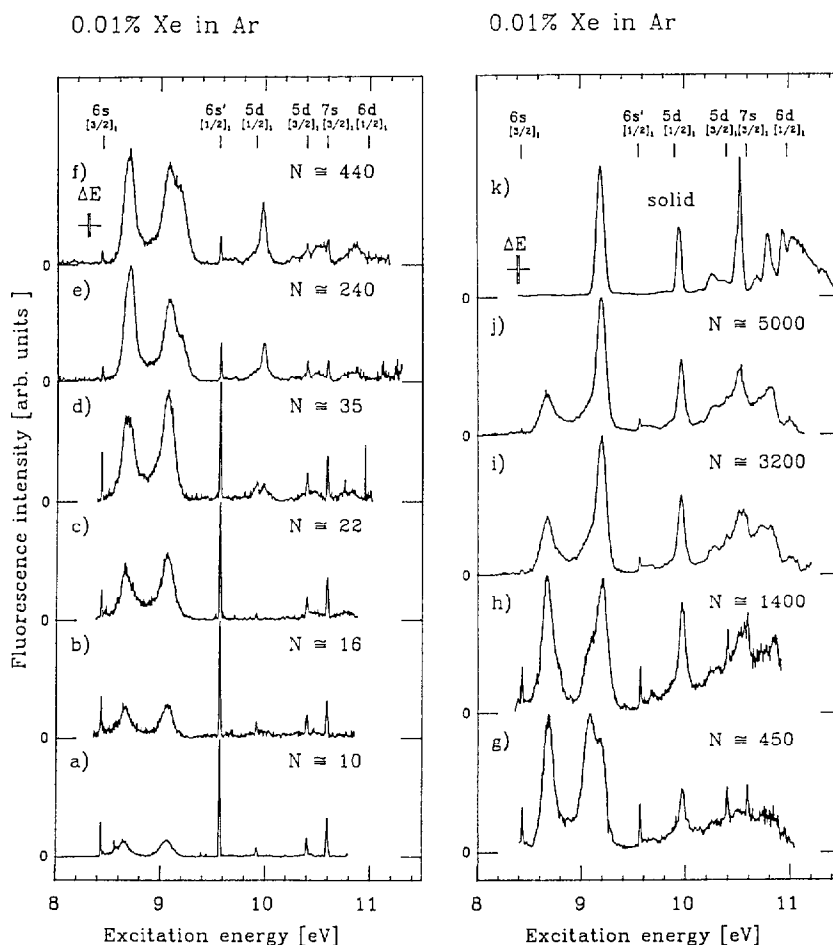


Fig. 2. Fluorescence excitation spectra of a coexpansion of 0.01% Xe in Ar. The dominant absorption lines are due to  $\text{XeAr}_N$  clusters. For comparison an absorption spectrum of Xe-doped Ar (1 ppm) from Ref. [19] is given in the uppermost panel (k).

band is split into three different bands. These bands are assigned to transitions of the Xe atom being located in different positions in the cluster or at the cluster surface [3]. At the lowest concentration of 0.01% Xe two bands are observed at 9.08 and 8.70 eV. Increasing the Xe concentration from 0.01% to 0.03% a shoulder emerges at the low energy side of the band at  $\approx 9.08$  eV and becomes prominent for 0.1%–0.3%. This band at 8.97 eV is assigned to  $\text{Xe}_2\text{Ar}_N$  clusters. If the concentration of Xe is further increased another rather sharp band is formed at 8.78 eV. Whether it is due to  $\text{Xe}_3\text{Ar}_N$  clusters or clusters containing even larger Xe complexes is an open question. We note in passing that strong changes of the

spectra by varying the concentration of Xe between 0.03% and 1% are only observed for the energetically lowest excitation into the 6s state.

We now turn over to the presentation of results for the lowest Xe concentration of 0.01% where, apart from the pure  $\text{Ar}_N$  clusters, predominantly  $\text{XeAr}_N$  clusters are formed. Fluorescence excitation spectra recorded under different expansion conditions ( $P_0$ ,  $T_0$ ) are displayed in Fig. 2. The average size of the clusters varies between 10 and 5000 atoms. For comparison an absorption spectrum of 0.001% Xe in solid Ar [19] is given in Fig. 2k. It should be noted that the sharp lines, being pronounced for small clusters, are due to free Xe atoms and probably small  $\text{XeAr}_N$

clusters which are always present in the beam. The average size of the cluster given in the figure refers to the size of pure  $\text{Ar}_N$  clusters. However, the size of the mixed clusters should not be very different because the concentration of Xe is low.

As already mentioned, the evolution of the absorption bands in the energy range 8.4–9.3 eV which are related to the 6s state of Xe is discussed in a previously published article [3]. One main conclusion of this previous work was that the bands in the energy range 8.4–9.3 eV are due to excitations of Xe atoms located in different positions and sites in the clusters. The strong shift of the absorption lines in the cluster relative to the free atom is due to a spatial restriction of the excited orbital by the surrounding Ar atoms. In a crude approximation the energy shift reflects the number of nearest neighbours. Although molecular dynamics calculations of spectral lineshapes indicate that the assignment of the band must be modified slightly [20] the overall picture that Xe atoms at the surface as well as inside the cluster contribute to the observed spectra is supported by these calculations.

For the interpretation and assignment of absorption lines at higher energies two aspects must be considered.

(1) The oscillator strength of different bands depends mainly on the main quantum number of the excited state and decreases rapidly with increasing main quantum number.

(2) The evolution of the absorption bands with cluster size contains important information on the location of the Xe atom and the size of the orbital of the excited atom. Naturally, surface states are predominantly observed in small clusters. In this context, the ratio between the cluster radius and the radius of the excited orbital is of considerable importance [21,22]. If the radius of the cluster is much smaller than the radius of the excited orbital one can expect rather sharp absorption lines. This situation takes place for Rydberg states of the XeAr dimer. The other limit is given by the infinite solid where sharp absorption bands are also observed. In the size range in between, when the radius of the cluster is comparable to the radius of the excited orbital, impurity atoms located in different positions of the clusters give rise to a large number of bands forming rather broad continua.

For the 6s' state (the prime denotes excitation from

the  $^2\text{P}_{1/2}$  state) which is the spin-orbit partner of the first resonance line of atomic Xe, the evolution with cluster size differs slightly from that of the 6s state. Most notably, no distinct absorption bands with a spectral blue-shift of a few hundred meV relative to the atomic transition at 9.566 eV are observed up to a cluster size of  $N=15$ . This is rather surprising because the oscillator strength of transitions into the 6s and 6s' states are nearly identical [23]. On the other hand, the intensity of the sharp line at 9.566 eV, which is within the band pass of excitation identical with the transition energy of the 6s' state, is much larger in spectra 2a–2e than that of the line at 8.434 eV due to the 6s state. This indicates that small  $\text{XeAr}_N$  clusters contribute substantially to the line at 9.566 eV. On increasing the clusters size to a few hundred atoms, a weak band with a maximum at 9.65 eV and a more intense band at  $\approx 9.97$  eV emerges. The intensity ratio between the band at 9.97 eV and the band at 9.21 eV which is assigned to excitations of Xe atoms in the interior of the cluster or Xe atoms in substitutional sites in Ar matrices is nearly constant (see Figs. 2e–2k). We therefore conclude that the band at 9.97 eV is due to excitations of Xe atoms into the 6s' state in substitutional sites in the interior of  $\text{Ar}_N$  clusters or in solid Ar matrices. This assignment is in accordance with the recent measurement in dense gaseous and liquid Ar [13] but it is in contradiction to the assignment in the pioneering work [5,6]. In Refs. [5,6] this band is assigned in an impurity Wannier exciton model to the  $n=2$  exciton while the band at 10.53 eV is assigned to the  $n=1'$  exciton which should be equivalent to the 6s' state in an atomic description. In view of the intensity variation of the three bands at 9.21, 9.97 and 10.53 eV this assignment is rather unlikely because the two low energetic band show a similar evolution with cluster size while the band at 10.53 occurs only in rather large clusters.

Before we switch over to the discussion of the absorption bands in the energy range 10–11 eV we would like to come back to the observation of some differences in the evolution of absorption bands related to the 6s and 6s' states. As already mentioned there is no clear splitting of the bands related to the 6s' state into bulk and surface states as in the case of the 6s state. We therefore assume that the excited state potentials which are responsible for the spectral shifts are somewhat different. Measurements in the dense

gas indeed show that there are substantial differences in the potential curves of XeAr with 6s and 6s' dissociation limits. Finally, we would like to note that corresponding excitations in XeNe<sub>N</sub> clusters show a different behaviour: in the case of Xe-doped Ne<sub>N</sub> clusters the 6s and 6s' states split in a similar way into bulk and surface states [24].

Absorption bands in the energy range 10–11 eV show a rather different behaviour than that in the lower energy range. In the energy range 10–12 eV the transitions into high Rydberg states such as 5d, 6d, 7s, 8s and the different spin-orbit components or  $n=2$  and  $n=3$  states in the Wannier impurity excitation model are expected to occur. For small clusters up to  $N=200$  only several sharp lines energetically close to the atomic resonance transitions are observed. These lines are sitting on top of a broad slightly modulated continuous background. The sharp lines are due to the absorption of free Xe atoms, the XeAr dimer and small mixed clusters. The continuous background signal is due to overlapping bands of excitations of larger clusters. We assume that both homogeneous (a large number of states as a result of the low symmetry of the clusters) and inhomogeneous (large width of the size distribution and large number of different isomers) broadening is responsible for the formation of an only slightly modulated background. With increasing cluster size the weak continuous background gains intensity at the expense of the sharp lines and becomes more structured. The spectrum of the largest clusters ( $N=5000$ ; see Fig. 2j) shows already striking similarities with the spectrum of Xe-doped solid Ar displayed in Fig. 2k. In order to get some information on a probable assignment it is helpful to look at the evolution (intensity, width) of the bands with size. In the energy range under discussion the band at  $\approx 10.53$  eV is the most prominent absorption band. Furthermore, this band starts first to grow when the cluster size is increased. In view of the large oscillator strength in the solid it cannot be assigned to an  $n=2$  exciton state in a Wannier impurity exciton description. A possible assignment could be a transition into the  $5d[3/2]_1$  state which also has a large oscillator strength in the free atom [25]. It should be noted that assuming this assignment there would be nearly no matrix shift for this transition. On the other hand, it is rather likely that there are two contributions to the measured

transition energy shift which may cancel, namely a shift of the ionization potential from the free atom to the solid and the shift due to the spatial restriction of the excited orbital. We therefore assume that the assignment of the band at  $\approx 10.53$  eV to the  $5d[3/2]_1$  state is convincing. We would like to point out that this assignment together with the assignment of the band at 9.97 eV to the 6s' state clearly favours the interpretation of the bands in a model of perturbed atomic states instead of the impurity Wannier excitation model. In the impurity Wannier exciton model one should expect that no d-symmetric states should be observed below the onset energy of photoconductivity at 10.97 eV [13] because d-symmetric exciton states in solid Ar are not observed energetically below the conduction band of the pure crystal [1]. Absorption bands of large clusters in comparison with a spectrum of Xe-doped Ar in an enlarged scale are displayed in Fig. 3. Even for large clusters containing approximately 5000 atoms there are remarkable differences with the spectrum of Xe-doped solid Ar in the energy range above 10 eV. Presumably the radius

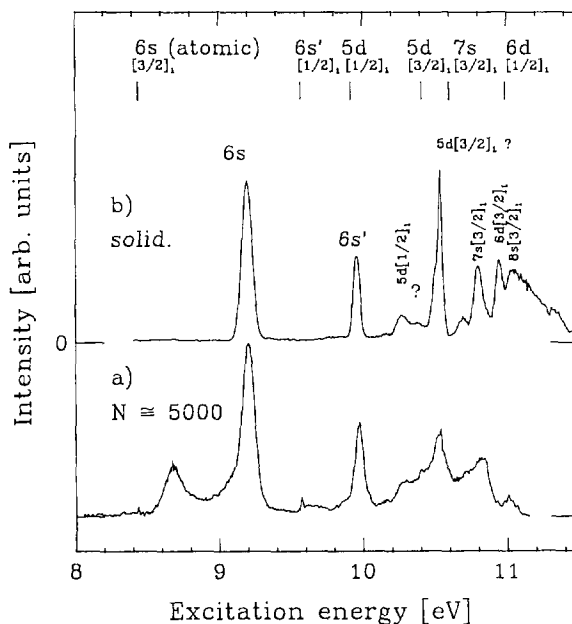


Fig. 3. Comparison between an absorption spectrum of Xe-doped Ar [19] and a fluorescence excitation spectrum of large XeAr<sub>N</sub> clusters. The assignment according to the interpretation as perturbed atomic states and the transition energies of free Xe atoms are given in the figure.

of the clusters is not sufficiently large compared with the radius of the excited orbitals. Under the assumption that the oscillator strength is only slightly modified it seems reasonable to assign the bands to 5d, 6d and 7s... states. For many of the bands the assignment is straightforward in view of the density dependence of absorption bands in the dense gas [13]. Only for the strong band at 10.53 eV the assignment based on the pressure dependence is unclear [13]. However, as already pointed out we propose to assign this band to the  $5d[3/2]_1$  level in view of the large oscillator strength. This band only becomes visible and sharp in clusters containing more than 1000 atoms. This indicates that more than the first coordination shell around the Xe atom must be filled. This is not unreasonable because the 5d orbital has a larger spatial extent than the 6s orbital [23].

#### 4. Conclusion

Electronic excitations of  $\text{Xe}_M\text{Ar}_N$  cluster are studied using fluorescence excitation spectroscopy with synchrotron radiation excitation in the energy range 8–11.2 eV in which the electronic excitations of pure Xe are located. By varying the concentration of Xe gas from 0.01% to 15% the composition of the clusters could be changed from  $\text{XeAr}_N$  to pure  $\text{Xe}_M$  clusters. For  $\text{XeAr}_N$  fluorescence excitation spectra which closely reflect the absorption profiles are investigated in the size range  $N=10$ –5000. The evolution of the different absorption bands depends sensitively on the size of the excited orbital. Furthermore, the location of the Xe atom in the clusters plays an important role: for the energetically lowest excitation related to the 6s state of atomic Xe a pronounced splitting into surface and interior cluster states is observed. For excitations with extended orbitals a broadening presumably due to the presence of different isomers is observed. There is a general trend that the bands become sharper with increasing cluster size.

For the description of the excited states, namely the impurity Wannier exciton and the perturbed atomic state description mentioned in Section 1 we can make the following conclusions.

(1) For the energetically lowest excitations in the energy range 8–10.5 eV the interpretation of the excited states as perturbed atomic states seems to be

appropriate. This is particularly true for the lowest excitation which splits into surface and interior states depending on the position of the Xe atom in the cluster. Furthermore, the occurrence of a d-symmetric state (5d, 6d) can only be explained in an atomic description because d-symmetric Wannier excitons are not observed in pure  $\text{Ar}_N$  clusters and solid Ar. Our results clearly show that the second strong absorption band of Xe-doped Ar at 9.97 eV must be assigned to the 6s' state in an interpretation of a perturbed atomic state instead of an  $n=2$  impurity Wannier exciton as suggested in Ref. [5].

(2) For highly excited states a conclusive statement cannot be made. Whether an excitation into the 7s state is regarded as a perturbed atomic excitation or the  $n=2$  exciton is to a certain extent a question of semantics. In order to give a definite answer further members of the exciton series must be analyzed in particular the energy spacing between the different states. However, it is obvious that the two descriptions should merge into each other for highly excited impurity states. Therefore, the question arises as to where the two models merge into each other. From our data we have the impression that only for states close to the impurity ionization limit does this take place. In other words the description of perturbed atomic states seems to be a suitable description for the excitations of Xe-doped  $\text{Ar}_N$  clusters.

In conclusion, the results for  $\text{XeAr}_N$  clusters show that in addition to information regarding the evolution of energy levels with size valuable information on the properties of the solid can be obtained.

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