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Observation of cluster-specific excitations in Xe_N clusters

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The absorption spectra of Xe_N clusters ($N=50-500$) exhibit extra absorption bands not seen in condensed Xe gas. They show up if the cluster radius is comparable to the radius of the electronic excitation. From the sharpness of the bands and from the energy-level positions it is concluded that these excitations have a character which combines features seen in molecular Rydberg states and excitons of the solid. This interpretation is supported by simple model calculations. For small clusters ($N \leq 150$) the number of extra absorption bands reflects the shell structure of the clusters.

The development of the electronic structure as single atoms put together to form a solid has been the subject of a great variety of research in the past decade.[1] There are fundamental questions to be answered about the appearance of energy bands in clusters and the influence of quantum size effects on the electronic structure of clusters. In the case of nonmetallic clusters, the evolution of electronically excited energy levels is particularly appealing because a gradual transition from molecular valence and Rydberg states to the exciton bands of the solid is expected. So far, most experimental investigations in this field have been restricted to either small clusters ($N=3-50$) in a free jet[2-4] or to large clusters ($N \geq 800$) embedded in a matrix.[5] Recently, experiments have been started[6-8] to investigate the evolution of electronically excited energy levels of rare-gas clusters over a very large mass range ($N=2-10^6$ atoms) by fluorescence excitation spectroscopy. It turns out that the transition to solid-state properties, namely, the appearance of excitonic absorption bands, takes place over a very large mass range, depending on the size of the electronic excitation.[7,8] So far, all electronic excitations detected in rare-gas clusters correspond either to molecular Rydberg states or to excitons of the solid.

In this paper we report on the observation of rather sharp "extra" absorption bands in medium size Xe_N ($N=50-500$) clusters previously not reported in condensed Xe gas. They show up if the cluster radius is comparable to the radius of the electronic excitation. From the energetic position it is concluded that these excited states are characterized by extended orbitals with a radius somewhat larger than the nearest-neighbor distance. Model calculations in the effective-mass approximation show that the radial probability function of the excited electron has two maxima—one inside and one outside the cluster. The narrowing of the absorption bands compared to the Wannier excitons of the solid indicates that these excitations are a new type of electronic excitations in nonmetallic material. Their character combines features seen in molecular Rydberg states and excitons of the solid. In analogy to "confined"[9] or "zero-dimensional"[10] excitons in microcrystallites and quantum wells they may be regarded as "cluster excitons" in which the atomic structure and the number of shells of the cluster play a crucial role.

The measurements were performed at the experimental station Clulu on the high-intensity Vacuum-UV beamline Superlumi[11] at the Hamburger Synchrotronstrahlungslabor HASYLAB (Hamburg). In summary, Xe_N clusters are generated in a nozzle expansion of pure gas or a gas mixture (15% Xe in Ar) using large conical nozzles (diameter 250 and 500 μm, respectively, opening cone angle $2\Phi=30°$) at a temperature between 150 and 300 K and a stagnation pressure between 0.1 and 1.5 bars. After passing a skimmer the cluster beam crosses the beam of monochromatized synchrotron radiation ($\Delta\lambda=0.05$ nm). The size distribution in the cluster beam was analyzed with a time-of-flight mass spectrometer in a different set of measurements.[12] Typically, the width ΔN [full width at half maximum (FWHM)] of the size distribution corresponds to the average number N atoms per cluster. The fluorescence light is detected undispersed with a closed channel-plate detector (CsTe photocathode, window cutoff—wavelength 112 nm).

Figure 1 shows a fluorescence excitation spectrum of Xe_N clusters containing approximately 150 atoms in an energy range from the lowest excitation up to 1.5 eV above the ionization limit. Below the ionization limit the fluorescence yield corresponds to the absorption coefficient because dark relaxation channels are of minor importance.[8,13] Apart from a few sharp extra bands marked with arrows, all bands have a 1:1 correspondence in the solid Xe. Usually, excitons in rare-gas solids form a hydrogenlike spin-orbit split exciton series.[13] The members are denoted by a main quantum number n. The radius of the exciton which is the separation between the electron and hole is proportional to n^2. Since the clusters are relative small only the $n=1$ and $n=1'$ (Frenkel-type) excitons contribute to the spectrum in accordance with previously reported findings.[8] The strong absorption bands of the $n=1$ and $n=1'$ states (the prime denotes the spin-orbit partner) have a substructure, which however is not well resolved in Xe_N clusters of this size:[8] The extra absorption bands indicated by arrows are energetically close to the $n=2$ and 3 (Wannier-type) excitons of solid Xe and might, therefore, in a superficial view be assigned to Wannier excitons. However, the evolution of these bands with cluster size clearly shows that they are,

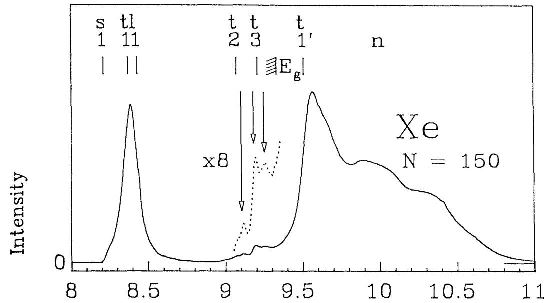

FIG. 1. Fluorescence excitation spectrum of small Xe_N clusters (average cluster size $N=150$ atoms per cluster). The extra absorption bands (cluster excitons) are indicated by arrows. The energetic positions of the excitons in solid Xe and the band-gap energy E_g are given in the figure (Ref. 13). Surface states are denoted by (s), and longitudinal and transverse branches of the bulk excitons are denoted by (l) and (t), respectively.

in fact, extra absorption bands. It should be noted that we have observed similar extra absorption bands also in small Ar_N and Kr_N clusters.

Here we concentrate on Xe_N clusters containing between 50 and 500 atoms that exhibit a very rich structure. Fluorescence excitation spectra that are equivalent to the absorption coefficient are displayed in an enlarged scale in Fig. 2. Three different size ranges can be distinguished: (i) very small clusters with $N \leq 20$; (ii) clusters with N in the range 50–500 which show cluster specific excitations; (iii) large clusters with N larger than 500. In the energy range under discussion (8.8–9.3 eV) clusters containing approximately 20 atoms or less are completely transparent. With increasing cluster size sharp absorption bands appear close to the energetic position of the $n=2$ exciton of solid Xe. Up to a certain size the number of absorption bands increases. In particular, the spectrum recorded in a beam containing on average 265 atoms/cluster yields seven absorption bands in this energy range. It should be noted that several bands appear at a certain cluster size and disappear for large clusters, while the energetic position is nearly unchanged. Clusters containing more than 800 atoms exhibit only two absorption bands. The strong band with a peak position at ~ 9.1 eV, depending on the cluster size, is assigned to the $n=2$ exciton. Additionally, in very large clusters a weak shoulder is observed at 9.3 eV and it is assigned to the $n=3$ exciton. The width of the $n=2$ exciton is nearly identical to the one in solid Xe.[14] It is obvious that the width of some of the extra absorption bands in small Xe_N clusters containing less than 500 atoms is significantly smaller. The weak band at 8.95 eV in clusters containing at the average 800 atoms is located on the low-energy side of the $n=2$ bulk exciton and vanishes in the solid-state limit. Therefore, it might be assigned to a $n=2$ surface exciton. The energetic position of this band and of the $n=2$ excitons in large clusters ($N \geq 500$) depends sensitively on the cluster size as it is observed for confined excitons in semiconductor quantum dots[15] and large Ar_N clusters.[16] Consequently, in large clusters these excitations are assigned to confined $n=2$ excitons.

Absorption profiles of beams containing Xe_N clusters with a size distribution centered around the closed-shell structures $N=55$ and 147, respectively, are presented in Fig. 3. Clusters containing roughly two shells around the central atom ($N=55$) yield two absorption bands denoted A_1 and A_2. Due to the width of the size distribution they are also visible as a small admixture in the spectrum of clusters containing approximately 165 atoms. The bands labeled C_1 and C_2 are due to larger clusters. The remaining bands denoted B_1, B_2, and B_3 are due to excitations of clusters with approximately three shells around the central atom ($N=147$). It should be pointed out that some of the bands, namely, A_1 and B_3 are rather sharp with a width (FWHM) of approximately 20–30 meV. This is two or three times smaller than the width of the $n=2$ exciton in solid Xe. Moreover, the energetic positions of the A and B bands which are given in Table I are nearly independent of the average size of the clusters in the beam, while the energetic position of confined excitons (C bands, see also Fig. 2) changes continuously and rapidly with the cluster size. Therefore, the A and B

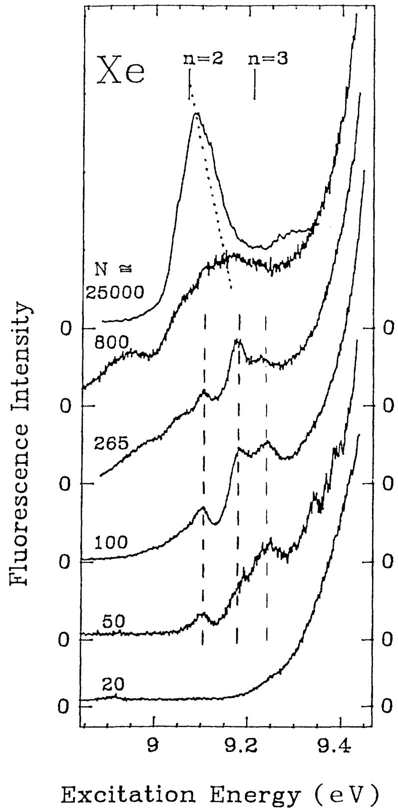

FIG. 2. Fluorescence excitation spectra of Xe_N clusters in the energy range of the $n=2$ and 3 excitons of solid Xe. The average cluster size N (atoms/cluster) and the energetic position of the $n=2$ and 3 excitons are indicated in the figure. Dotted and dashed lines are only for guiding the eye.

bands are fundamentally different from absorption bands due to confined excitons[5,16,17] and should be regarded as cluster excitons.

For the discussion of the observed spectral features it is instructive to compare the cluster radius R with the exciton radius r calculated in the Wannier approximation in the solid.[13] Closed-shell clusters[22] containing 55 or 147 atoms have a radius of 9.1 and 12.6 Å, respectively. Therefore, we can expect that the excited electron has a high probability to stay outside the cluster. For the interpretation of the A and B bands the shell structure of the clusters has to be considered. The similarity between the number of absorption bands and the number of closed shells around the central atom is striking, at least for the first three shells. In the following, a simple model is presented which illustrates the character of cluster excitons. One-electron orbitals were calculated by solving the radial part of the Schrödinger equation assuming that the hole will be fixed in the center of the cluster. This approach allows for one absorption band in the energy range of discussion in a nearly spherical cluster. Remaining absorption bands are assigned to excitations where the hole is located in one of the outer shells of the cluster.

TABLE I. Energetic positions of cluster-specific absorption bands in Xe_N clusters. For the assignment of the bands see text.

Absorption band	Energy (eV)
A_1	9.103
A_2	9.239
B_1	8.975
B_2	9.055
B_3	9.175

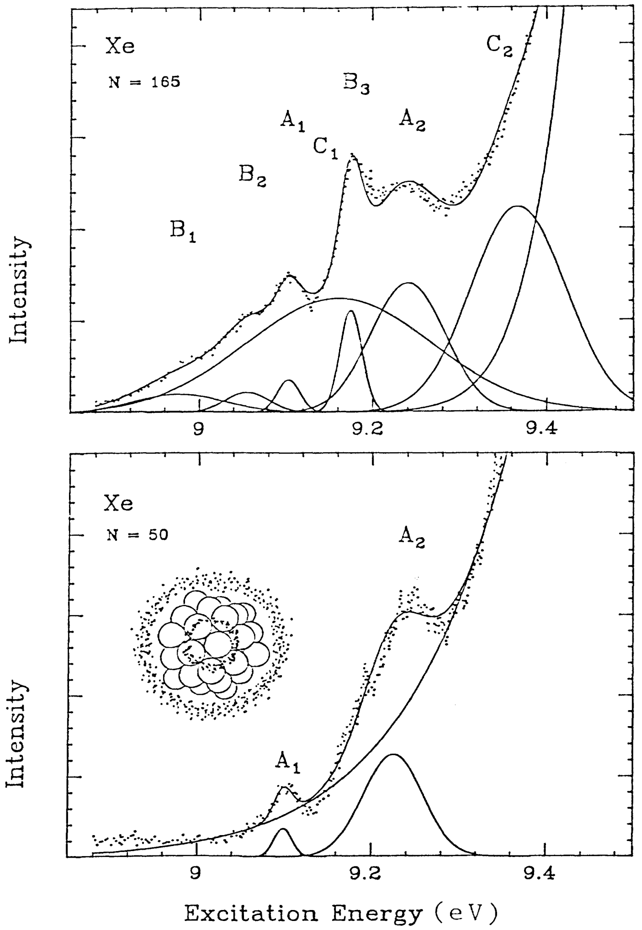

FIG. 3. Fluorescence excitation spectra (· · · ·) of Xe_N clusters containing approximately two and three shells around the central atoms, respectively. The different contributions and the fitted curves are given by solid lines. For the assignment of the different bands see text. The radial charge distribution of an excited electron in Xe_{55} according to Fig. 4 is shown in the lower part of the figure. Excitations of this type are responsible for the A bands.

The potential that is used to calculate the electron orbitals is given as the sum of a Coulomb part V_C and a polarization term V_p.[18,19] Outside the cluster the unscreened Coulomb potential is used, whereas inside the cluster the screening is taken into account. Close to the surface, polarization effects and the work function give rise to a small barrier.[18,19] A relevant part of the potential for Xe_{55} is presented in Fig. 4. Additionally, the radial probability of the electron in the second excited state ($n=2$) is included which is obtained by solving the Schrödinger equation with the free-electron mass outside the cluster and an effective electron mass of 0.37 free-electron masses inside the cluster.[20]

The radial probability for the second excited state ($n=2$) for Xe_{55} calculated in this way yields two maxima (see Fig. 4). The first maximum is located inside the cluster, whereas the second maximum is located outside. Inside the cluster the radial probability resembles an exciton envelope function similar to that calculated with the

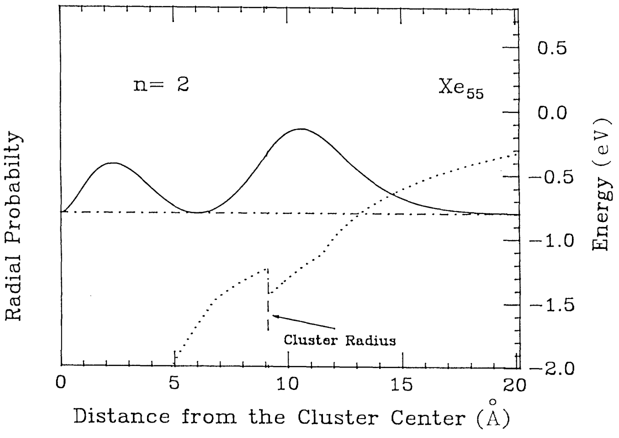

FIG. 4. Potential energy (· · · ·) for an electron in Xe_{55} assuming that the hole is fixed at the cluster center and the calculated radial probability (——) of an s-symmetric state with a main quantum number $n=2$. Parameter: cluster radius $R=9.1$ Å, dielectric constant $\varepsilon=2.22$; reduced exciton mass $\mu=0.37$ free-electron masses; band gap energy of the solid 9.33 eV, thickness of the surface layer 4.3 Å; work function $V_0=0.6$ eV (liquid Xe) (Ref. 13).

effective-mass approximation for the solid.[21] Outside the cluster the electron behaves like a weakly bound Rydberg electron of an atom or molecule. The charge distribution of the electron is illustrated in the lower part of Fig. 3. The large probability of the excited electron to be outside the cluster might explain the sharpness of some bands. This is because scattering processes with the remaining atoms that generally lead to a broadening of the absorption lines only take place inside the cluster. The transition energy of 9.38 eV calculated this way is somewhat larger than the experimental values of the bands A_1 (9.103 eV) and A_2 (9.239 eV). However, a good quantitative description cannot be expected because the assumption of effective masses of the solid is inappropriate for clusters of this size. Further theoretical work is needed for a precise assignment of the A bands, in particular, the localization of the hole inside the cluster. If the finite mass of the hole ($m_h = 2.1$ free-electron masses[13]) is considered we assume that excitations with the hole in the first and second shell around the central atom correspond to A_1 and A_2, respectively.

The simple model presented above gives some insight into the character of cluster excitons. Due to the shell structure the "radius" of the cluster increases stepwise. This might explain that no continuous variation of the energetic position of cluster excitons with the cluster size is observed (with increasing average cluster size in the beam additional absorption bands appear while other bands disappear, see Fig. 2). If it is further assumed that the hole is located in different shells of the cluster, that means, it only moves within well-defined shells, the number of absorption bands directly reflects the number of closed shells.

In conclusion, the appearance of cluster excitons is a direct consequence of the limited size and the shell structure of the clusters. The spherical charge distribution of the excited electron shown in Fig. 3 with two maxima, one inside and one outside the cluster, nicely illustrates the character of this new type of electronic excitation. So far, a quantitative description is only given for s-symmetric states where the hole is located in the center of the cluster. Quantum chemical calculations of excitations with the hole in outer shells of the cluster would be highly desirable to check our qualitative interpretation.

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