

## Bound Delocalized Excited States in $I^-Xe_n$ Clusters

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By combining photoelectron spectra and photodetachment action spectra of  $I^-Xe_n$  clusters ( $n = 1-12$ ), we have identified bound extended excited electronic states. The critical size to the binding of such states is  $n > 4-5$ . The spatial confinement and the binding energy of the excited states increase monotonously with the cluster size. We discuss the analogy between these bound electronic states and the binding of excess electrons in the  $Xe_n^-$  clusters. This study introduces a new methodology for the investigation of empty bands in clusters, residing above or below the vacuum level, via the excitation of slightly perturbing impurity states. [S0031-9007(97)04337-8]

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Ground state noble gas atoms with their closed shell do not bind electrons. In the bulk, however, the collective polarizability of the rare gas atoms induces the energetic stabilization of excess quasifree electrons (the bottom of the conduction band of solid xenon lies  $\approx 0.58$  eV below the vacuum level [1]). Evidently, exceeding some size, xenon clusters bind excess electrons. These bound extended states are the precursors of the conduction band excess electrons in bulk xenon. As such, xenon clusters provide a classical model system in cluster science, where at some critical size the growing cluster acquires properties which are typical to the bulk and are not existent in smaller particles.

Two groups have performed theoretical calculations [2,3], predicting the minimal xenon cluster size to bind an electron to be 6-7 atoms; Martyna and Berne [2] have applied diffusion Monte Carlo simulations using a pair-polarization model, finding that an electron would attach to a cluster as small as  $Xe_6$ . Further calculations, taking into account the many-body polarization model, found the smallest cluster to bind an electron to be  $Xe_7$ . Stampfli and Bennemann [3] have proposed a dielectric continuum model to calculate the electron affinity of small rare gas clusters and determined the critical cluster size to be  $Xe_6-Xe_9$ . The experimental evidence for the existence of stable  $Xe_n^-$  was provided by Haberland and co-workers [4]. The existence of small  $Xe_n^-$  has been unambiguously demonstrated, yet the critical cluster size for electron binding in the ground state cluster was inconclusive ( $n = 6$  or smaller), due to the possible presence of electronically metastable  $Xe_n^-$ . In these experiments, the very low concentrations of clusters, resulting from their low electron binding energy, prevented further spectroscopic studies.

We have studied the evolution of bound excess electron states in the xenon clusters by using  $I^-Xe_n$  clusters. In its ground state the electron is localized on the anion, which is solvated by the xenon cluster. The bare iodine anion does not support any bound excited state, and the localized impurity electron can be only photoexcited to the

extended states in the xenon-iodine cluster. It is an analog process to the  $L$ -type excitations of  $F$  centers [5] into the conduction band, in alkali-halide crystals. We assume in this discussion that the excited states of the  $I^-Xe_n$  clusters highly resemble the ground state of  $Xe_n^-$  clusters. Such an approach has two distinct advantages. First, because of high electron affinity these clusters ( $>3$  eV) can be generated in large quantities. Second, both bound and unbound electron states in the xenon clusters are accessible via excitation from the deeply bound impurity state. We introduce here a new methodology for the investigation of empty band in clusters, via the excitation on slightly perturbing impurity states. This method is versatile and can be adapted to the investigation of states residing above or below the vacuum level, by using different detection schemes. We should note, however, some limitations in our approach. In such an experiment the conduction band of the xenon cluster would be perturbed, at least in small clusters, by the presence of the iodine core. Also, note that in the vertical photoexcitation process, we access nonrelaxed geometries of the xenon clusters.

Anion impurities embedded in rare gas clusters have been previously studied [6,7]. Those studies focused on the impurity ground state properties. Bowen [6] and co-workers have studied photoelectron spectroscopy (PES) of  $O^-Ar_n$  clusters, emphasizing the structural similarity between the mixed charged clusters and their pure rare-gas counterparts. Neumark and co-workers [7] have performed zero kinetic energy (ZEKE) spectroscopy and partially discriminated threshold photodetachment measurements on  $I^-Ar_n$  and  $Br^-Ar_n$  clusters from which electron affinities and potential curves were extracted. To the best of our knowledge, it is the first time that the anion serves as an impurity internal source of electrons for monitoring the delocalized states of the host cluster.

Negatively charged  $I^-Xe_n$  clusters were produced in the early stages of a supersonic expansion from a pulsed nozzle [8]. The expanding gas consisted of 3-4 bars mixture of 5% Xe in a 95% Ar, passed through a cooled ( $\approx -60$  °C) reservoir of methyl-iodide. The

expansion was intersected by a 100–200 eV electron beam, ending up in the formation of  $I^-Xe_n$  clusters. The newly formed clusters were mass separated by a Wiley-McLaren time of flight mass spectrometer [9] (TOFMS). Being extremely fragile, these clusters tend to dissociate spontaneously during their flight. Each mass peak contained the parent ion as well as its fragmented daughters. Therefore, we used a novel technique of mass gating that energy filters the selected mass peak to remove the spontaneous fragments from the mass spectrum [10]. The mass spectra of  $I^-Xe_n$  were characterized by “magic numbers” typical to noble gas clusters, if  $I^-$  was counted as well. Particularly intense was the peak of  $I^-Xe_{12}$ . We anticipate that this cluster is of the icosahedral structure with the  $I^-$  located in the center, symmetrically solvated by a shell of twelve Xe atoms.

PES at 4.66 eV photon energy of  $I^-Xe_n$   $n = 0-35$  were performed on mass-selected clusters in a “magnetic-bottle” type electron-spectrometer [11]. For  $n < 8$ , the clusters were decelerated before the photodetachment zone by a voltage impulse, down to a low kinetic energy ( $\approx 30$  eV) to reduce the Doppler-energy broadening of the photoelectron spectra. For  $n > 8$  this procedure was unnecessary, due to their lower velocity. Figure 1 displays the PES spectra (resolution  $\approx 60$  meV) of  $I^-$  together with the first twelve  $I^-Xe_n$  clusters. All of these spectra are characterized by two peaks (about 0.95 eV apart), corresponding to the two  $J$  states ( $J = \frac{1}{2}, \frac{3}{2}$ ) of the neutral iodine core in the final state. We have assigned the lower energy peaks of these spectra ( $J = \frac{3}{2}$ ) as the vertical binding energy (VBE) of the negatively charged clusters and listed them in Table I.

In order to study the excitation spectra of the impurity  $I^-$  into the xenon cluster, the mass-selected clusters were excited by an excimer-pumped tunable dye laser [12] over a spectral range of 3.0–3.71 eV below and above the VBE. We monitored the excitation cross section by recording the electron detachment from the cluster, or the fragmentation of the parent cluster [13] by using a tandem reflecting MS [14]. No laser-induced fragmentation was observed for any of the above species, and electron emission was the exclusive decay channel. Figure 2 presents the action spectra for these species. The arrows in Fig. 2 mark the energies of the VBEs as determined in our PES experiments. We have also crudely measured the relative cross section for absorption of the different clusters. Starting from  $n = 1$ , the peaks of the action spectra gradually increased by about an order of magnitude [15].

While electron detachment above the VBE may be a direct process, electron detachment below the VBE is connected with cluster rearrangement. Following the vertical photoexcitation, vibrational relaxation processes in the excited state, as well as internal vibrational energy contained in the cluster prior to the photoexcitation, may raise the electron above its adiabatic binding energy (ABE). Consequently, electron detachment occurs in a process which is

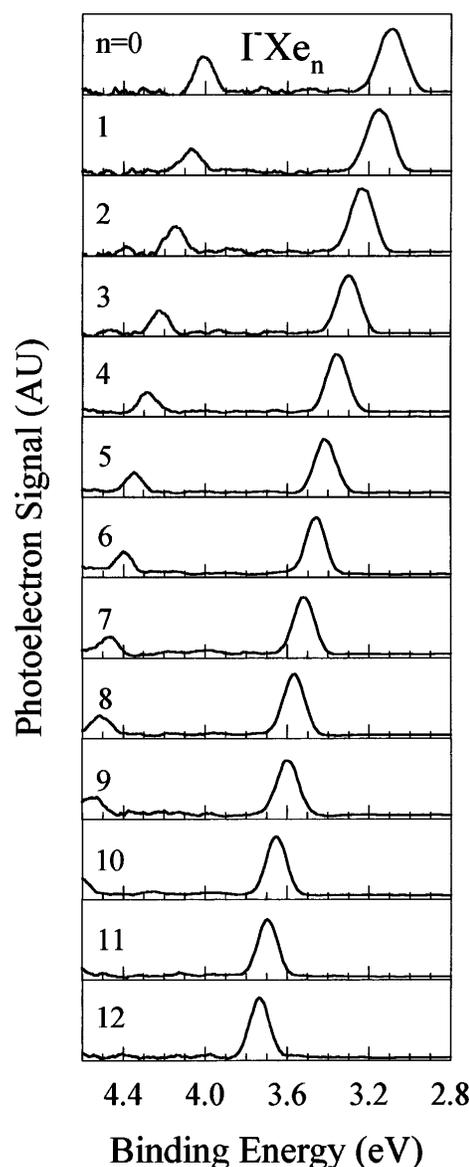


FIG. 1. Photoelectron spectra of the  $I^-Xe_n$  clusters,  $n = 0-12$ , taken using 4.66 eV photons.

analogous to thermionic emission. We believe that in the small energy range below the VBE the thermal detachment probability is uniform and close to unity. This assumption is supported by the recent measurements of Johnson and co-workers [16] on the charge transfer to solvent states in  $I^-(H_2O)_n$  clusters. In their measurements, the action photodetachment spectra to both  $J = \frac{1}{2}$  and  $\frac{3}{2}$  states of  $I$  were taken. These spectra were similar in shape and intensity for both final  $J$  states of iodine. Since the final state  $J = \frac{1}{2}$  state is always coupled to a detachment continuum, one can deduce that the electron detachment probability is high also in the vicinity of the  $J = \frac{3}{2}$  at energies lying below the vacuum level.

The action spectrum of the  $I^-Xe$  cluster is distinct, it rises slowly with energy, reaching a plateau at 3.5 eV.

TABLE I. Binding energies and excitation energies of iodide in  $I^-Xe_n$  clusters.

N	VBE <sup>a</sup> (eV) ( $\pm 20$ meV)	VDE <sup>b</sup> (eV) ( $\pm 3$ meV)	Binding energy of excited electron- $V_0$ (meV) ( $\pm 20$ meV)
0	3.06	...	...
1	3.13	...	...
2	3.22	3.255	-35
3	3.29	3.295	-5
4	3.35	3.339	11
5	3.41	3.391	19
6	3.46	3.440	20
7	3.51	3.486	24
8	3.56	3.532	28
9	3.60	3.569	31
10	3.65	3.608	42
11	3.69	3.641	49
12	3.73	3.675	55

<sup>a</sup>Vertical binding energy.

<sup>b</sup>Vertical delocalization energy.

This slow rise suggests the existence of resonance state in the detachment continuum, a precursor of what will be identified as the low lying bound states of larger  $I^-Xe_n$  clusters.

Starting with  $n = 2$ , the photodetachment spectra evolve with the cluster size in three aspects. First, the very broad detachment spectrum of  $I^-$ , characteristic of localized to continuum transitions, narrows gradually to bands ( $\sim 0.1$  eV for  $n = 12$ ). Second, the relative cross section of absorption over the scanned spectral range grows gradually with cluster size. Third, as the cluster grows, the peaks of the action spectra locate at an increasing energy spacing below the VBE.

Distinct spectral splittings of  $\approx 25$  meV show in the action spectra starting from  $I^-Xe_4$ . Their assignment is unclear to us. Action spectra of the selected  $I^-Xe_9$  cluster have been run at several nozzle expansion conditions to clarify their nature. At higher stagnation pressures, which we associate with lower cluster temperature, the high energy peak increased its relative intensity, while at higher nozzle temperature in the expansion, the low energy peak was higher. These experimental findings are consistent either with hot band peaks or with the existence of metastable isomers in the clusters. Recent ZEKE experiments on  $I^-Ar_n$  clusters performed by Neumark and co-workers [7] and calculation by Manolopoulos and co-workers [17] show similar splittings which were also attributed to hot bands [18].

Based on these arguments, we attribute the high-energy band to the 0-0 transitions in the excitation spectra in the most stable cluster form. We relate these bands to transition from the localized electron on the iodide to excited states on the solvating xenon cluster. We consider them to be the vertical delocalization energy (VDE) of the impurity electron, and the precursors of impurity to

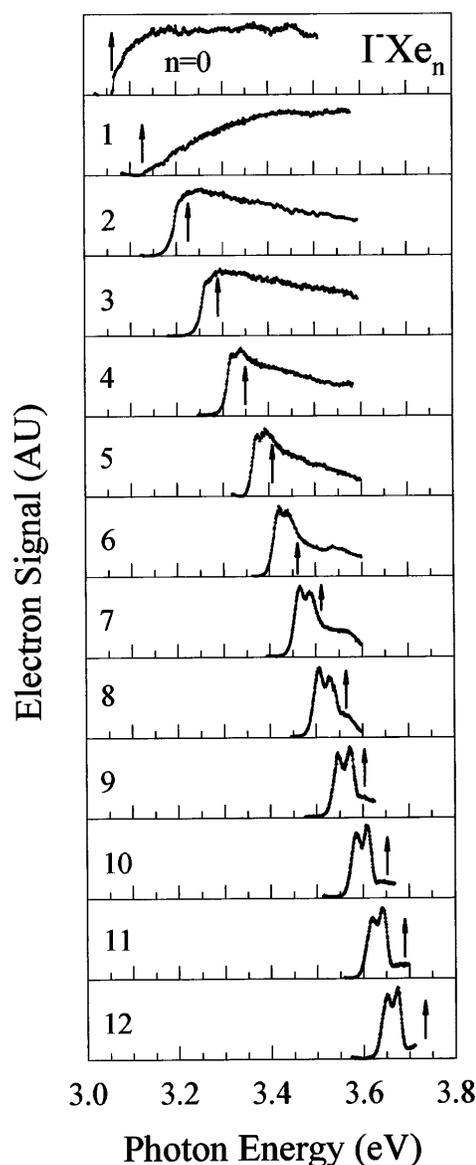


FIG. 2. Action spectra of the  $I^-Xe_n$  clusters, for  $n = 0-12$ . The arrows indicate the vertical binding energies (VBE) of iodide with final iodine state of  $^2P_{3/2}$ .

conduction band transitions in the bulk. The energy difference between the VBE and VDE may be positive or negative for bound and unbound delocalized states, respectively. These energies are the precursors of  $V_0$  in the bulk, namely the binding energy of the excess electron in the conduction band. In Table I we summarize the values of VDE and  $V_0$ . Note that  $V_0$  grows from negative values to zero at about  $n = 5$  and up to 55 meV at  $n = 12$ .

The picture, which unveiled from the above PES and action spectra, is the gradual evolution of bound excited states on the xenon solvent cluster. As the clusters grow, their binding energy increases. In parallel, the loosely bound excited states, which extend beyond the cluster size [2], shrink and gain oscillator strength. This is due to better electronic overlaps with the localized ground state,

at the expense of the transitions to the vacuum. Such behavior is typical to Rydberg states as well as to other loosely bound electronic states in clusters such as solvated excess electrons [19,20] and dipole bound states [16,21].

We would like to indicate the similarity of the bound electronic states in the excited  $I^-Xe_n$  clusters to the recently discovered excited bound states in  $I^-(H_2O)_n$  clusters by Johnson and co-workers [16]. In their experiments, they have discovered the existence of bound electronic states in the photodetachment action spectra of  $I^-(H_2O)_n$  clusters. Their spectra were assigned as the precursors of the charge transfer to solvent excitations in the spectra of the aqueous iodide. In both systems [ $I^-Xe_n$  and  $I^-(H_2O)_n$ ] the solvating media induce the appearance of extended and bound excited electronic states of iodide. The nature of the excited states, however, is distinct. Charge-permanent dipole interactions dominate the energies of  $I^-(H_2O)_n$ . The solvating water molecules rearrange in the ground-state cluster to form a localized potential well for the excited electron [22]. This phenomenon induces localization of the excited electronic state in the vicinity of the iodine core. In the  $I^-Xe_n$  system, the interactions are dominated by the polarizability of the xenon atoms, and the excited state need not be localized. On the limit of very large clusters would converge to excitation of the localized electron to the delocalized states in the conduction band of xenon. This method should be general for the investigation of excited states in any system with no permanent dipole moments.

In conclusion, we have identified bound delocalized electronic states in the  $I^-Xe_n$  cluster where the critical size to the binding of such states is  $n = 4-5$ . As the cluster grows, the excited state is more confined within the cluster boundaries and well stabilized with respect to the vacuum level. We intend to support this picture with further experiments.

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