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## Photoelectron spectroscopy of $\text{Xe}_n\text{I}^-$ clusters ( $n \leq 13$ )

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### Abstract

$\text{Xe}_n\text{I}^-$  clusters ( $n \leq 13$ ) have been studied by anion photoelectron (PE) spectroscopy at a photon energy of 4.661 eV and an electron energy resolution of 10 meV. Electron affinities (EA's) as a function of cluster size are extracted and compared to previous PE and tunable laser photodetachment spectra of these species. The EA's found in this study lie between those of the two earlier experiments. These discrepancies are attributed to calibration issues in the earlier PE spectra and the influence of charge-transfer-to-solvent states in the tunable laser experiments. © 2001 Elsevier Science B.V. All rights reserved.

### 1. Introduction

The study of size selected anion clusters by photodetachment has led to an improved understanding of the evolution of molecular properties with size [1,2]. Rare gas halide clusters are particularly well suited for studies of this type because their relative simplicity makes them accessible to detailed spectroscopic investigation [3,4]. Information about solvation effects, cluster structures, interatomic potentials, and charge transfer processes can be acquired through study of these clusters. In this work, we present photoelectron spectra of size selected  $\text{Xe}_n\text{I}^-$  clusters ( $n =$

1, 2, 4, 6–13). Examination of these clusters allows further insight into the energetics of these clusters, as well as an understanding of the discrepancies between previous experiments.

Several types of photodetachment spectroscopy have been applied to  $\text{Xe}_n\text{I}^-$  clusters in recent years, including total photodetachment cross-section (TPCS) measurements, [5,6] one- and two-photon photoelectron (PE) spectroscopy, [5,6] zero electron kinetic energy (ZEKE) and partially discriminated threshold photodetachment (PDTP) spectroscopy [7,8], and time-resolved measurements using femtosecond photoelectron spectroscopy [9,10]. These measurements have demonstrated considerably more complex spectroscopy and dynamics than might be expected for a cluster composed entirely of closed-shell atoms. Specifically, the total cross-section measurements by Becker et al. [5,6] showed sharp structure for clusters with  $n \geq 4$  that was attributed to cluster charge-transfer-to-solvent (CTTS) states, i.e. excited electronic states in which the excess electron

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on the iodine atom is ejected into the surrounding xenon atoms. Two CTTS states, separated by about 1 eV, were seen for each cluster; comparison of the TPCS and PE experiments indicated that the lower and upper CTTS states were just below the detachment thresholds for  $\text{Xe}_n\text{I}(^2\text{P}_{3/2})$  and  $\text{Xe}_n\text{I}(^2\text{P}_{1/2})$ , respectively. In the FPES experiments by Neumark and co-workers [9,10] the lower CTTS states near the electron detachment threshold showed no evidence for decay out to 250 ps, whereas the upper CTTS state decayed via spin-orbit induced autodetachment with a 0.5–1 ps time constant, depending on the size of the cluster.

Another striking feature of these sets of experiments are the significant discrepancies in the electron binding energies extracted from the PE spectra of Becker et al. [5,6] and the ZEKE/PDTP measurements of Lenzer et al. [7,8]. The PE spectra, in which the electron energy resolution was  $\sim 60$  meV, yielded vertical detachment energies (VDE's) that increased with cluster size and showed a distinct leveling off above  $n = 12$  suggesting a solvent shell closure at  $n = 12$ . (Note that the vertical detachment energy, VDE, in this paper is called the vertical binding energy, VBE, in the work by Becker.) The higher resolution (0.1–0.2 meV) ZEKE experiments showed that the vertical and adiabatic detachment energies for these clusters are similar, i.e. little geometry change occurs upon photodetachment, so that the adiabatic electron affinities (EA's) determined from these measurements should be directly comparable to the VDE's from the PE spectra. However, the apparent shell-closing observed in the PE experiments was not evident in the ZEKE/PDTP measurements. In addition, the ZEKE and PDTP experiments on  $n = 1$ –14 clusters yielded EA's significantly lower than the VDE's obtained by Becker et al., with discrepancies as large as 80 meV for the  $n = 12$  cluster.

While the energy resolution of the PES experiments of Becker et al. was considerably lower than in the ZEKE experiments, this is not sufficient to explain the large discrepancy between the electron affinities obtained by the two sets of experiments. It is, however, important to realize that the two experiments are quite different. PE spectroscopy involves direct detachment to the neutral + elec-

tron continuum using photon energies well above the detachment threshold, whereas ZEKE spectroscopy is a tunable laser experiment which, in principle, can be sensitive to interference from anion excited states near the detachment threshold [11].

In an attempt to resolve these discrepancies, we report PE spectra of  $\text{Xe}_n\text{I}^-$  clusters ( $n = 1$ –13) taken at considerably higher resolution (8–10 meV) than the PE spectra reported by Becker et al. We indeed find strong evidence for a shell-closing at  $n = 12$ . Our electron affinities and vertical detachment energies are, in general, significantly lower than those reported by Becker, but somewhat higher than the EA's extracted from the ZEKE spectra. Simulated annealing calculations give excellent agreement with the new results.

## 2. Experimental

The negative ion time-of-flight photoelectron spectrometer used in this study has been described in detail previously [12–14] and only the relevant details will be discussed here.  $\text{Xe}_n\text{I}^-$  clusters are prepared by expanding a room temperature mixture of 2% hydrogen iodide and 20% xenon in argon through a pulsed valve operating at a backing pressure of 30 psig. The gas expansion is crossed in the continuum flow region by a 1 keV, 300  $\mu\text{A}$  electron beam. Negative ions are formed through dissociative attachment and are clustered and internally cooled as the supersonic expansion progresses. The ions are then accelerated to 3.25 keV and enter a linear reflectron TOF mass spectrometer ( $m/\Delta m \approx 2000$ ) where they separate in time and space according to their mass to charge ratios.

Photoelectrons are generated through detachment by a fixed frequency pulse (266 nm, 4.661 eV) from the fourth harmonic of a Nd:YAG laser. The laser firing time is varied by digital delay until the laser pulse temporally overlaps the mass selected ion packet of interest. Electron kinetic energies (eKE's) are determined by photoelectron time-of-flight (TOF) in a 1 m, field-free flight tube. All data are collected with the laser and pulsed valve operating at 20 Hz, with 40 000–400 000 shots

collected for each photoelectron spectrum. All photoelectron spectra presented are plotted as a function of electron binding energy (eBE), which is defined as

$$eBE = h\nu - eKE, \quad (1)$$

where  $h\nu$  denotes the photon energy of the detachment laser. The angle between laser polarization and electron collection is  $90^\circ$  for all presented spectra. The instrumental resolution is 8–10 meV at an electron kinetic energy (eKE) of 0.65 eV, and degrades as  $eKE^{3/2}$ . Chloride, bromide and iodide ions, for which the electron affinities and neutral spin orbit splittings are well known, are used as calibrants, yielding an eKE vs. electron TOF scale accurate to better than 2 meV in the electron binding energy range covered by the calibrants (3.059–4.002 eV).

### 3. Results

Photoelectron spectra of  $Xe_nI^-$  clusters ( $n = 1, 2, 4, 6–13$ ) taken at 4.661 eV are presented in Fig. 1. Only those bands corresponding to detachment to  $Xe_nI(^2P_{3/2})$  are shown; an additional band at about 1 eV higher eBE corresponding to detachment to  $Xe_nI(^2P_{1/2})$  is seen for clusters up to  $n = 7$ . As discussed previously [3], in clusters with rare gas atoms the degeneracy of the  $I(^2P_{3/2})$  state is split into the close-lying X and I states, and the bands shown in Fig. 1 represent partially resolved transitions to these two electronic states. The spectra show a stepwise shift to higher electron binding energy as xenon solvent atoms are added, with a decrease in shift at the  $n = 12–13$  transition. An abrupt decrease in peak width is also observed at the  $n = 12–13$  transition.

Fig. 2 compares four representative PE spectra ( $n = 4, 6, 8, 12$ ) from Fig. 1 and previously published ZEKE [8] and PE spectra [5,6], all for the (lower)  $Xe_nI(^2P_{3/2})$  band. The PE spectra of Becker et al. are represented by a convolution of their reported  $^2P_{3/2}$  state VDE with a Gaussian of 60 meV FWHM. Our PE spectra are clearly narrower than those obtained by Becker, as expected due to the higher resolution of our spectrometer. However, our spectra also peak at significantly lower

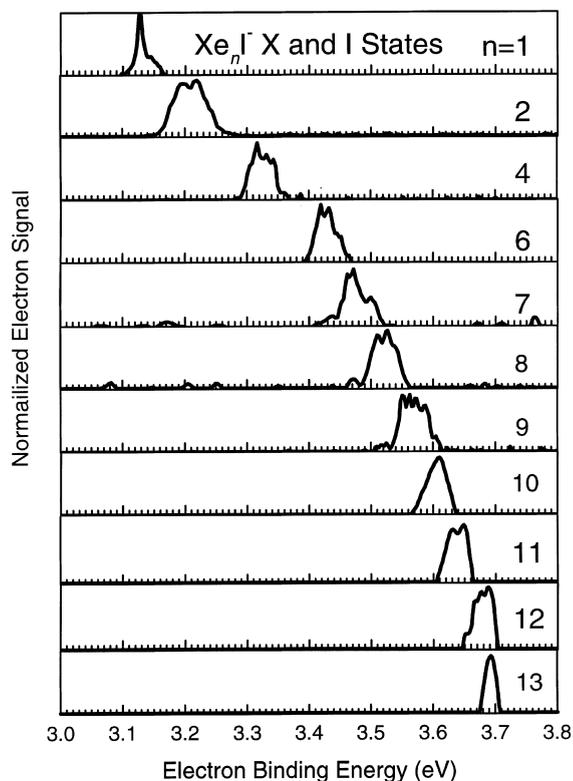


Fig. 1. The X and I state PE spectra for all  $Xe_nI^-$  clusters studied. ( $n = 1, 2, 7$ –40 000 laser shots,  $n = 4, 6, 10, 11$ –80 000 shots,  $n = 8, 9$ –120 000 shots,  $n = 13$ –320 000 shots, and  $n = 12$ –400 000 shots.)

eBE, the discrepancy increasing with cluster size to as high as 60 meV for  $n = 13$ . Comparison with the ZEKE spectra shows the opposite trend. Although our PE and ZEKE spectra agree for  $n < 4$ , the ZEKE spectra shift to increasingly lower eBE relative to the PE spectra as the number of xenon atoms increases, from 4 meV at  $n = 4$  to 27 meV for  $n = 12$ . The ZEKE spectra line up very well with the low energy edge of the lower CTTS bands as measured by Becker et al.

The bottom panel shows the new PE spectrum and earlier PDTP spectrum for photodetachment to  $Xe_6I(^2P_{1/2})$ , the II state of the neutral cluster, along with the upper CTTS band from the TPCS of  $Xe_6I^-$ . The difference between PDTP and ZEKE spectra is that the former are collected with zero delay between the laser pulse and electron extraction field, resulting in lower resolution but

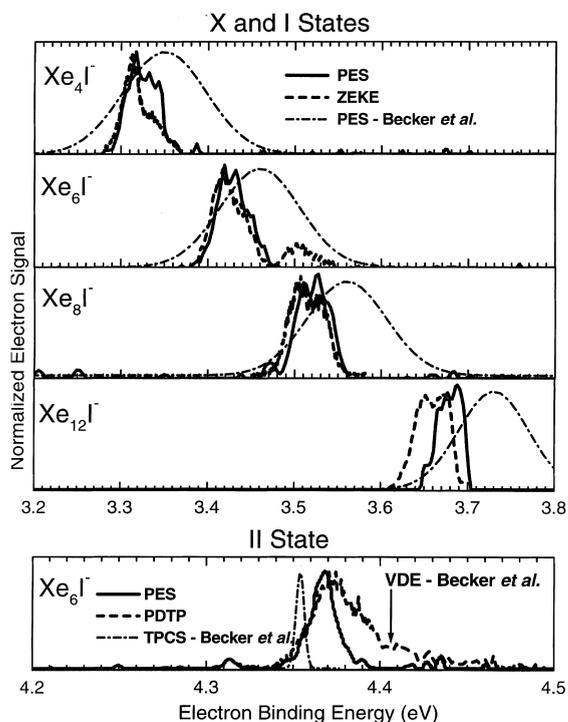


Fig. 2. Upper panel: Comparison of ZEKE (dashed) and PE (solid line) spectra for the X and I states of selected  $\text{Xe}_n\text{I}^-$  clusters, superimposed upon a representation of the PE spectra (dash-dot) of Becker et al. ZEKE spectra were taken from Ref. [8]. The PE spectra from Ref. [6] are represented by a convolution of the reported  $^2\text{P}_{3/2}$  state vertical detachment energy with a Gaussian of 60 meV FWHM. Lower panel: PE (solid) and PDTP (dash) spectra of the  $\text{Xe}_6\text{I}^-$  II state, along with the TPCS spectrum (dash-dot) of Becker et al. from Ref. [9] showing the upper CTTS peak. The PDTP spectrum is taken from Ref. [8]. The TPCS peak is represented by a convolution of their reported  $^2\text{P}_{1/2}$  state  $E(\text{CTTS})$  with a Gaussian of 6 meV FWHM. The vertical arrow indicates the  $^2\text{P}_{1/2}$  vertical detachment energy reported in Ref. [6].

substantially higher signal; the signal for the II state is too low to take a ZEKE spectrum. The major difference between the two spectra for clusters with unresolved vibrational structure is that the PDTP spectrum falls off less rapidly toward higher eBE [8]. In the panel, the arrow indicates the VDE from the PE spectrum of Becker, again at higher energy than our PES feature. The TPCS results of Becker et al. are represented by a convolution of the reported  $^2\text{P}_{1/2}$  state CTTS excitation energy  $E(\text{CTTS})$  with a Gaussian of 6

meV FWHM. In contrast to the lower energy  $^2\text{P}_{3/2}$  bands, the  $^2\text{P}_{1/2}$  PE and PDTP spectra are essentially identical, and both occur at a higher energy than the CTTS state.

#### 4. Analysis and discussion

Vertical detachment energies to the X and I states of neutral  $\text{Xe}_n\text{I}$  are obtained by fitting the observed PE bands in Fig. 1 to the sum of two Gaussian functions with variable position, amplitude and width. The peak separation of the two Gaussian functions was constrained by the X/I splittings reported in [8]. Although the observed spectra are clearly more complex than this form, the fitted profiles are essentially indistinguishable from the data. Our vibrationally-resolved ZEKE spectra of  $\text{XeI}^-$  and  $\text{Xe}_2\text{I}^-$  [7,8] showed that the X band maximum was equal to the adiabatic electron affinity for  $\text{XeI}$  and  $\text{Xe}_2\text{I}$ . We therefore assume that the X band maximum, i.e. the VDE to the X state, corresponds to the electron affinity for all clusters studied. The electron affinities and I state VDE's thus obtained are presented in Table 1.

Fig. 3 shows the electron affinities obtained in this work for  $n \geq 4$  along with those previously determined by Lenzer et al. [8] and the VDE's of

Table 1

Experimental adiabatic electron affinities, vertical detachment energies, and CTTS binding energies for the  $^2\text{P}_{3/2}$  states of  $\text{Xe}_n\text{I}^{\text{a}}$

No.	EA (eV)	I State VDE (eV)	$^2\text{P}_{3/2}$ CTTS $V_0$ (meV) <sup>b</sup>
1	3.127(0.005)	3.143(0.005)	
2	3.195(0.005)	3.218(0.008)	
4	3.320(0.006)	3.339(0.008)	1(7)
6	3.423(0.006)	3.446(0.008)	2(7)
7	3.468(0.006)	3.500(0.008)	3(7)
8	3.513(0.007)	3.536(0.008)	4(8)
9	3.554(0.008)	3.581(0.008)	8(9)
10	3.595(0.008)	3.616(0.008)	10(9)
11	3.635(0.008)	3.651(0.008)	12(9)
12	3.675(0.008)	3.692(0.008)	25(9)
13	3.688(0.010)	3.697(0.010)	24(10)

<sup>a</sup> Estimated uncertainties ( $\pm$ ) are given in parentheses. EA's and VDE's and their uncertainties are given in eV. CTTS binding energies and their uncertainties are given in meV.

<sup>b</sup>  $V_0 = \text{EA} - E(\text{CTTS})$ ;  $E(\text{CTTS})$  extracted from Ref. [6].

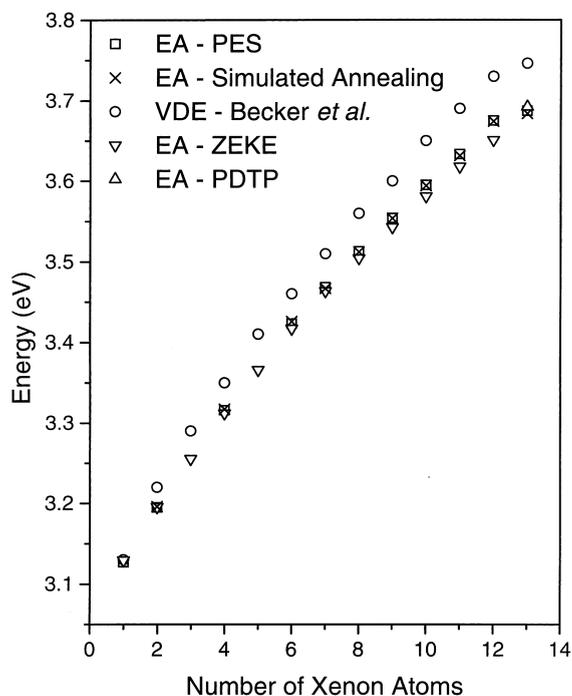


Fig. 3. Comparison of experimental and calculated EA's and VDE's for  $\text{Xe}_n\text{I}^-$ .

Becker et al. [6]. Our PE spectra (squares in Fig. 3) show that the cluster electron affinity increases steadily until the  $n = 12$ – $13$  transition, where the rate of increase abruptly levels off. This trend in electron affinity mirrors that previously observed in the PES experiments of Becker et al. (circles in Fig. 3). The evolution of EA as a function of cluster size suggests solvent shell closure at  $n = 12$ , as was indicated by the PE and two-photon PE results of Becker et al. A decrease in electron affinity is often indicative of a decrease in the binding energy of an additional solvent atom due to the weaker interaction of the solute ion with a solvent species outside the first solvent shell [15,16]. Our EA's are significantly lower than those of Becker et al., particularly for the larger clusters. It is clear from the direct comparison of the PE spectra in Fig. 2 that this discrepancy does not arise from differences in resolution or fitting procedures. Most likely it results from systematic calibration error in the PE spectra of Becker et al.

The assignment of a shell closing at  $n = 12$  is reinforced by the significant decrease in the peak width in our PE spectrum at the  $n = 12$ – $13$  transition. Similar effects were seen in the photoelectron spectra of  $\text{Ar}_n\text{O}^-$  [17]. This peak narrowing is a manifestation of the low cluster internal energy required for a weakly bound solvent atom outside the first solvent shell not to evaporate before the detection of the cluster. One therefore expects less contribution of vibrational hot bands just after a shell closing, with a consequent reduction in peak width.

We can use our EA's in conjunction with the CTTS excitation energies  $E(\text{CTTS})$  from the TPCS measurements of Becker et al. [5,6] to derive binding energies  $V_0$  for the lower CTTS excited states relative to the detachment continuum; these are given by  $V_0 = \text{EA} - E(\text{CTTS})$  and are listed in Table 1. For all clusters in which CTTS states are seen ( $n \geq 4$ ), the lower CTTS state is bound, with  $V_0$  increasing with cluster size. The values in Table 1 are lower than those previously reported by Becker et al. because our EA's are lower than the VDE's used in that determination. While these differences are small, they do bring the binding energies into better agreement with the calculated electron binding energies of comparably-sized  $\text{Xe}_n^-$  clusters [18–20]; as pointed out by Becker et al., the ground state of these clusters, in which the electron is bound by its interaction with the highly polarizable Xe atoms, should resemble the excited CTTS state in  $\text{Xe}_n\text{I}^-$  clusters.

Fig. 3 also shows that for clusters with  $n \geq 4$  the EA's from the new PE spectra are larger than those determined from the ZEKE/PDTP spectra of Lenzer et al. [8], and that the difference increases with cluster size. It is significant that the disagreement between the two measurements begins at the smallest cluster size ( $n = 4$ ) that supports a CTTS state, according to the TPCS measurements of Becker et al. Moreover, the ZEKE spectra of the X/I band are superimposable on the lower CTTS band in the TPCS spectra. It therefore appears that the ZEKE spectra reflect the position of the CTTS band rather than the detachment threshold. This raises the question of how excitation of an electronic state below the detachment threshold can lead electron signal that would be

detected in the ZEKE spectrometer. One possibility is that the electron signal is due to field-induced detachment caused by the pulsed electric field used to extract the electrons, an effect analogous to pulsed-field ionization of Rydberg states in ZEKE spectroscopy of neutral species [21]. Alternatively, if the clusters had a small amount of vibrational energy prior to electronic excitation, they could decay by thermionic emission [22], producing very slow electrons that would be indistinguishable from true ZEKE electrons produced by direct detachment just above threshold.

The situation for the II state (lower panel of Fig. 2) is rather different. The onsets and peak positions of our PE and PDTP spectra line up, and both lie noticeably above the upper CTTS band for the  $n = 6$  cluster. We expect that the ZEKE spectrum would line up with the PE spectrum in a similar fashion (the signal for the II state is too low to obtain a ZEKE spectrum). It therefore appears that the ZEKE/PDTP spectra are unaffected by the presence of the CTTS state. The likely reason for this is that the lifetime of the upper CTTS state is less than 1 ps [9,10]; it decays to  $\text{Xe}_n\text{I}(^2\text{P}_{3/2}) + e^-$  via spin-orbit autodetachment, a channel unavailable to the ground state. This process will produce high energy electrons that will not be detected in either the ZEKE or PDTP mode of electron detection.

In order to characterize the anion and neutral potential energy surfaces consistent with the new EA's, simulated annealing molecular dynamics calculations were performed. The methodology of these calculations, which include pair potentials and several types of many-body effects, has been described in detail previously [4,8]. The simulations yield minimum energy structures for the anion and neutral clusters, along with electron affinities and neutral state splittings. In our previous work on the ZEKE/PDTP spectroscopy of  $\text{Xe}_n\text{I}^-$  clusters, two sets of potential functions were used in the simulations. Referred to as 'Set I' and 'Set II' in [8], the potentials chiefly differ in the equilibrium bond distance of the X state of  $\text{XeI}$ . 'Set I' is based on a neutral Xe-I X state bond length of 4.049 Å, determined by emission studies of Tellinghuisen and co-workers [23]. 'Set II' employs a bond distance of 4.30 Å as obtained in

crossed molecular beam studies by Casavecchia et al. [24].

In our previous work, Set II was preferred because it predicted closed shell structures for all clusters  $n = 12$ –14, consistent with the absence of a change in slope of the apparent electron affinity vs.  $n$  at this cluster size; in contrast, Set I always yielded a clear shell closing at  $n = 12$  (icosahedral structure) with additional xenon atoms going into the second solvent shell. This trend occurs because a smaller assumed  $\text{XeI}$  bond length results in a smaller best fit  $\text{XeI}^-$  bond length. Thus, using Set I, the first shell of xenon atoms are more tightly packed around the iodide and the energetic penalty incurred upon inclusion of a 13th xenon atom in the first solvent shell is too large. In light of our new PE spectra, it appears that a smaller  $\text{XeI}$  bond length is in fact more appropriate, so new simulations were performed using the Set I pair potentials. The best results, shown in Fig. 3, were obtained with these pair potentials with the additional adjustment of the quadrupole exchange parameter to  $\beta = 0.7143 \text{ \AA}^{-1}$  from the  $\beta = 0.765 \text{ \AA}^{-1}$  used previously [8]. Note, however, that potential sets with  $R_m(\text{X})$  up to 4.25 Å will also reproduce the decrease in EA above  $n = 12$  equally well. The change of the potentials relative to our originally favored Set II is therefore indeed rather small. Moreover, our findings about the relative importance of the individual many-body-effects remain unchanged [8].

## 5. Conclusions

The PE spectra of  $\text{Xe}_n\text{I}^-$  clusters presented here and their analysis have resolved several issues and refined our understanding of these species. We observe the same trends in the electron affinities as was observed in the lower resolution PE spectra of Becker et al. [5,6], in particular strong evidence for a shell closing at  $n = 12$ . However, our spectra consistently occur at lower electron binding energies, a result we attribute to minor calibration problems in the earlier study. We also find that the EA's determined from the new PE spectra are higher than those obtained from the ZEKE and PDTP spectra of Lenzer et al. [8]. This discrepancy

is likely due to the influence of long-lived CTTS excited states of  $\text{Xe}_n\text{I}^-$  clusters just below the detachment threshold; these states apparently result in the production of electrons, either by field-induced detachment or thermionic emission, that are detected as ZEKE electrons. Interestingly, the latter discrepancy does not occur for detachment to the II state of the neutral cluster, an effect we attribute to the short lifetime of the corresponding CTTS state with respect to spin-orbit autodetachment, and the high kinetic energy of the autodetached electron.

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