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Double electron capture by Xe^{4+} frorn He, Ne, Ar and Kr

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Abstract Single and double electron capture of Xe^{4+} colliding with He, Ne, Ar and Kr has been measured by Translational Energy Spectroscopy (TES) and the states of the ions involved analyzed. All the reactions presented here show a clear and systematic behaviour that the reaction window begins at approximately 2.3 Ånuclear separation and ends at a separation which clearly depends on the target ionization potential. The Xe^{4+} appearing potential ($Xe \rightarrow Xe^{4+}$) has been determined as *108.8* I *0.8* eV.

1. Introduction

Charge transfer collisions between slow ($v > 1a.u$), highly charged ions and neutral atoms have attracted an increasing amount of interest over the last decade. For example, a series of experiments[1,2,3] have amply demonstrated the utility of TES and how it can prove a tool to analyze state selective electron capture. Nevertheless, only very recently has double electron capture (DEC) by multicharged projectiles been investigatted by this technique (ref. 4,5,6,7,8 p.ex.).

In the present work, the energy defect (AE) of the DEC reaction (refer to equation 1), of *12* KeV Xe^{4+} on noble gases (GN) was determined by means of

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the translation energy gain (or loss) spectroscopic method. This allows the initial and final electronic states of reactants and products to be determined.

$$Xe^{4+} + GN \rightarrow Xe^{2+} + GN^{2+} \pm \Delta E \qquad (1)$$

2. Experiments and Results

The measurements presented here were performed on a novel, double focussing translational energy spectrorneter described in an earlier publication[9]. The Xe^{4+} was performned by electron impact (EI) ionization at an interna1 source pressure of ca. 5×10^{-4} torr. Ions were extracted through a 3 kV acceleration potential (ie corresponding to 12 keV translational energy). The 128 Dalton isotope of Xe^{4+} ($m/z = 32$) was selected by a magnetic mornentum analyzer and then passes through a cylindrical electrostatic energy analyzer in to a collision cell containing low pressure research grade noble gas target. The reaction products were energy analyzed by a further identical energy analyzer which was operated at ca. 3.0 eV (FWHM) energy resolution incident ion beam. The energy scale A E was calibrated performing the well known single-electron capture (SEC) reaction[10] at 6 keV of $Ar^{2+} + He$.

Single electron capture by Xe^{4+}

There are no spectroscopic data on the ionization energy of Xe^{4+} available in the literature. However using the Xe^{3+} ($5p^3\ ^2P_{3/2}$) appearing potential from More[11], the ionization energy of He and the energy loss (A E) of $I\delta X$ (this notation will be introduced later) observed in figure 1, it gives an Xe^{4+} appearing potential A.P. (Xe $\rightarrow$ Xe^{4+}) of (108.8 ± 0.8) eV. This value is in reasonable agreement with value presented by Kamber[12] of 110.9 eV.

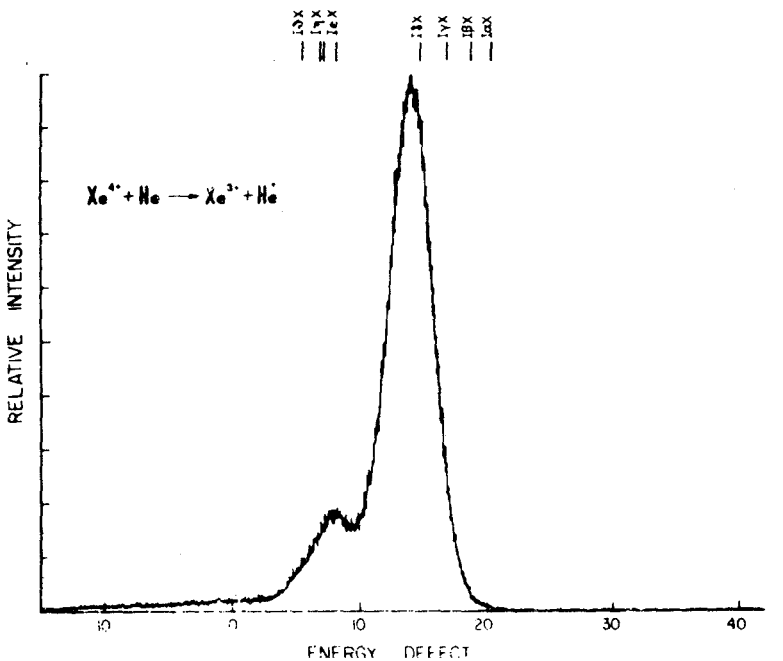

Fig. 1 - Translational energy spectrum of Xe^{3+} ions as obtained from a SEC reaction of 12 keV Xe^{4+} on He.

As the first excited state of He^+ lies 19.8 eV above the ground state target, excitation reaction channels were considered closed. Xe^{4+} was formed in the EI source at a nominal ionizing electron beam energy in the range 110 to 140 eV. The SEC spectra were found not to change as the electron impact was reduced to the threshold which shows that both broad peaks in figure 1 are associated with the primary beam ground state $5p^2\ ^3P$. Therefore, the only excitation channels open are the Xe^{3+} final states. The strongest peak corresponds to a capture from Xe^{4+} ground state into $5p^3\ ^2P_{3/2}\ (I\delta X)$ of the Xe^{3+} ion and the lowest peak, which is not resolved, is due to a series of contributions of $5p^3\ ^2P_j$ with $j = 1/2;\ 3/2;\ 5/2$.

The reaction channel identification was made using the spectroscopic tables of Moore[11] and from the recent publication by Kamber et *al.*[12]. A correction of the

tables present in ref. 12 has been made due to a new experimentally obtained value for the splitting between Xe^{4+} $5p^2\ ^1D$ and Xe^{4+} $5p^2\ ^3P$ which is now considered to be 1.3 eV[13]. The labelling was according to the nomenclature described by Kamber and colleagues[14] where the designation I, II and III stand respectively for the ground, first and second metastable states of Xe^{4+} ions; $\alpha, \beta, \gamma...$ indicate the ground and successive higher excited states of the projectile products and X, A, B represent the ground and higher excited states of the target; dots (...) indicate continuing channels.

In order to identify the "window region" it is worth-while to estimate the crossing radius. By neglecting the smallest contribution due to the poralizability, the crossing radius R, of the potencial curves between the initial and final states can be estimated through

$$R_c(\text{Å}) = 14.4\ f\ (4 - f)/\Delta E(\text{eV}) \qquad (2)$$

where f is the number of electrons transferred and A E is the energy defect.

Double electron capture by Xe^{4+}

The gas pressure inside the collision cell (10 mm in length) was kept at *ca.* 8×10^{-5} torr which ensured single-collision conditions. This was validated for all DEC spectra by checking that signal intensity increased linearly with the pressure up to the pressured used. In the DEC experiments, the fractional population of excited metastable states contained in the primary ions beam was unknown.

Figure 2a shows the translational energy spectra measured for the formation of Xe^{2+} ions from the collision of Xe^{4+} on He. The energy defect for this reaction lies between 5.5 and 28.1 eV (R, = 10.5 to 2.1 Å), which can only arise from excited states being present in the primary beam. This conclusion is reached as He^{2+} does not have excited states and the ground state to ground state channel $I\alpha X$ is endotermic by 3.33 eV. The beginning of the energy defect distribution observed is about 5.5 eV, which corresponds to the presence of $5p^2\ ^1S$ in the primary beam lying 5.8 eV above the ground state. That the distribution extends to 28.1 eV is evidence of the existence of other higher excited metastable states in the Xe^{4+}, which is 31.4 eV above the ground state.

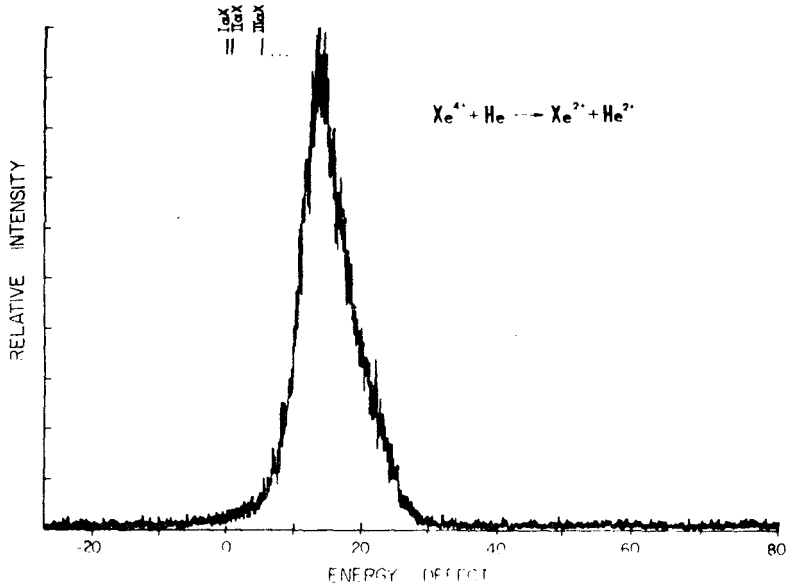

Fig. 2a

Figure 2b shows the translational energy change spectrum for Xe^{2+} DEC of Xe^{4+} on Ne. Again, this spectrum could not be resolved and corresponds to energy defects lying between 7.1 and 29.0 eV (R, = 8.1 to 2.0 Å). This reaction is dominated by capture into the $5s^2\ 5p^4$ configuration of Xe^{2+} giving the product states $Xe^{2+}(^1D)$+ Ne^{2+} (^3P) $I\beta X$; by target excitation of Ne^{2+} $(2p^4\ ^1D)$ through $I\alpha A$) and with a small contribution from $II\gamma X$. The spectrum shows probable contributions from the exoergic processes $I\alpha X$, $II\beta X$, $II\alpha X$ and reaction involving $Xe^{4+}(5p^2\ ^1S)$ $III\gamma X$, $III\beta X$ and $III\alpha X$. Features with energy defect higher than 21 eV can be assigned to high excited states present in Xe^{4+} beam which are 6 to 14 eV above the ground state. The results obtained in this experiment do not agree with the spectrum presented by ref. 12, where it shows a broad unresolved structure at zero energy defect extending to the endoergic region.

Figure 2c represents the DEC reaction of Xe^{4+} on Ar, which shows various peaks beginning to be resolved in a region between 8.7 and 22 eV exothermicity

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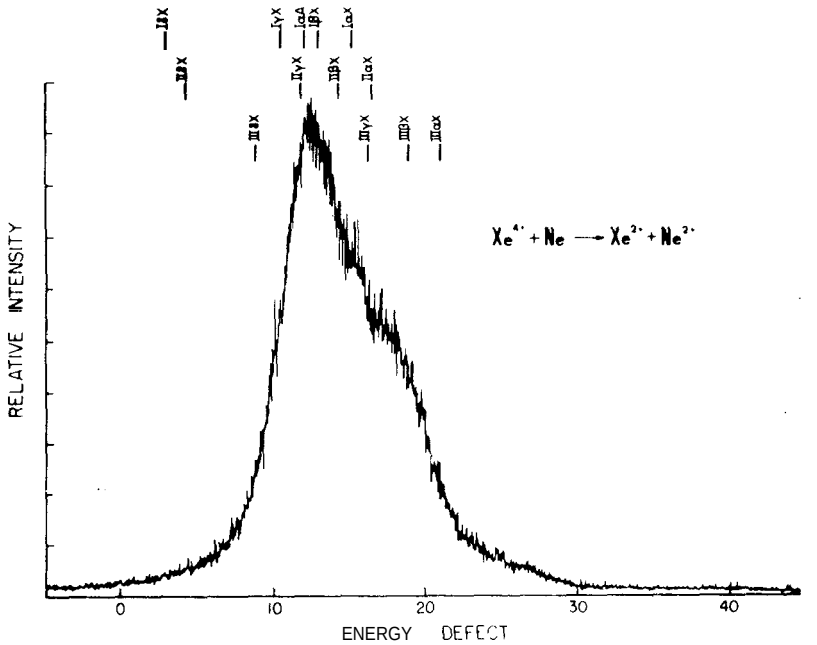

Fig. 2b

(R_c = 6.6 to 2.6 Å). Two further peaks of very low intensity observed at $E = 32.0$ eV are assigned to the $I\beta X$ reaction channel $Xe^{2+}(5p^4\ ^1S) + Ar^{2+}(3p^4\ ^3P)$. This process might be expected because it involves the Xe^{4+} ground state. The neighbouring peak at 29.6 eV is associated with $I\gamma X$ reaction $Xe^{2+}(5p^4\ ^1D) + Ar^{2+}(3p^4\ ^3P)$. In the earlier investigation[11] the processes were not resolved.

The large structure lying between 12 and 22 eV is formed for five peaks at the resolution limit of the equipment. These are associated in a exoergicity order with $II\delta X$ and $I\delta X$; $I\epsilon X$, $I\xi X$, $I\eta X$ and $I\theta X$; $I\iota X$, $I\kappa X$, $I\lambda X$, $I\mu X$, $I\nu X$. The highest signal is due to reactions where Xe^{2+} is left in a highly excited state with a $5s^2\ 5p^3\ (4S^\circ)\ 6p$ configuration. However, it can be seen that a non-resolved shoulder appears at an exoergicity of around 13 eV where the density of states becomes too high to identify the individual reaction channel involved. This current data of Xe^{4+} on Ar presents a significant improvement compared with that of Kamber *et al*[12]. In addition to the improved energy resolution their spectrum

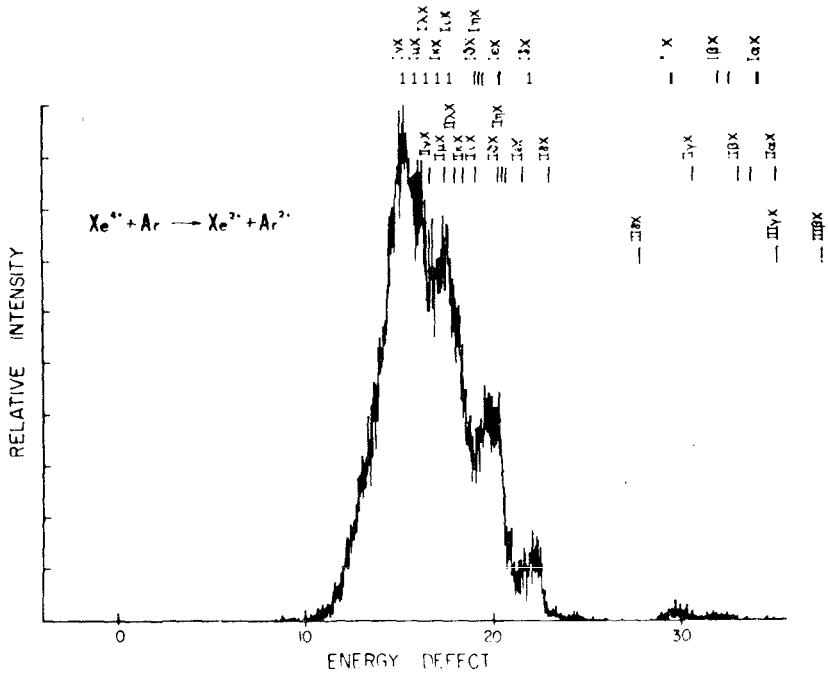

Fig. 2c

seems to be shifted by **3.8 eV** to the high energy defect region!

DEC reaction of Xe^{4+} on Kr is present in figure 2d. One can see a window reaction between **7.5** and **24 eV** exoergicity (R, = 2.4 to 7.8 Å) with some structure. The favourable capture region occurs in a range where the reaction exit channels of Xe^{2+} is very dense in number of states (above $5p^5\ ^1P\ (I\xi X)$), the metastable states are separated by less than 1 eV and, however, it was not possible to resolve them by our instrument.

The observed peaks in figure 2d are superimposed over an envelope of several reactions where the Kr^{2+} ion is left at $4p^5\ ^3P$ state channels and are associated to $I\gamma C$; the strongest signal to $II\delta C$; and the shoulder at about 11 eV to a sum of channels $I\gamma C$, $II\varepsilon C$ and $I\delta C$.

3. Conclusions

In summary, translational energy spectra of double electron capture by Xe^{4+} colliding on atomic targets He, Ne, Ar and Kr, clearly show a "reaction window"

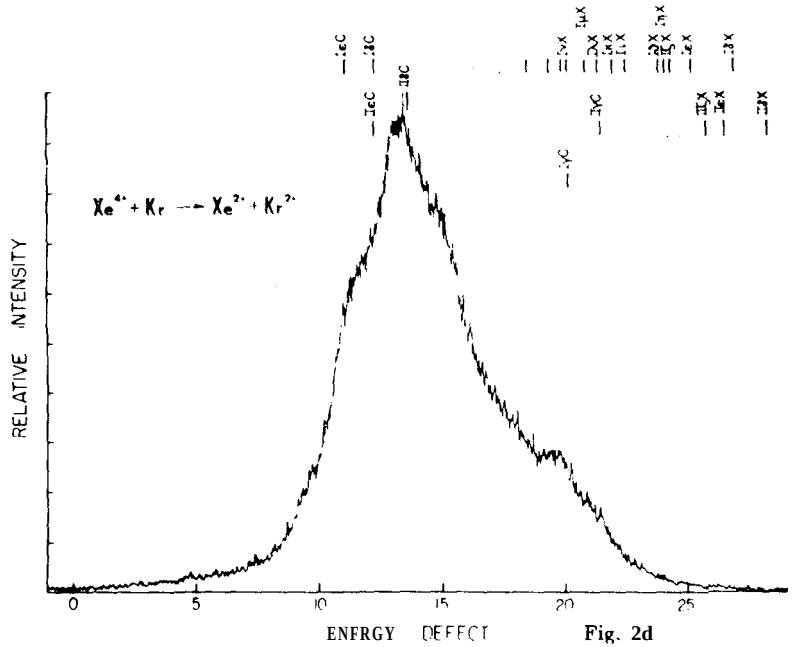

Fig. 2d

Fig. 2 - Translational energy spectrum of Xe^{2+} ions from the DEC reaction of 12 keV Xe^{4+} on (a) He, (b) Ne, (c) Ar and (d) Kr.

behaviour where the electron transfer is induced. The strongest signal for DEC is associated with a favourable internuclear separation R, over which pseudo-crossing of adiabatic potential energy curves describing the initial and final molecular systems take place.

For new systems studied, the window begins at approximately 2.3 Å. However, its end, in low energy defect region depends on the target atom employed ie 19.3, 15.3, 9.1 and 7.8 Åto He, Ne, Ar and Kr respectively. Qualitatively, the dependence was found but some theoretical effort is needed to understand the details of this effect. Unfortunately, while for SEC papers have been published (refs. 15, 16 and reference therein), for the processes involving double electron transfer the frame is still unfavorable with only few theoretical works present in the literature[17,18,19].

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Resumo

Foi medida a captura eletrônica dupla e simples não ressonante de Xe^{4+} colidindo em He, Ne, Ar e Kr pela espectroscopia da perda de energia (TES), com a interpretação dos estados dos íons envolvidos. Todas as reações presentes mostram um claro e sistemático comportamento onde a "reação janela" começa aproximadamente a uma separação internuclear de 2,3 Ae termina a uma separação que depende do potencial de ionização do átomo alvo. O potencial de aparição do íon Xe $\rightarrow$ Xe^{4+}) foi determinado como sendo $108,8 \pm 0,8$ eV.