

SINGLE-ELECTRON CAPTURE BY Cl^{2+} (^4S , ^2D , ^2P) FROM RARE-GAS TARGETS

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(Received 12 November 1987)

ABSTRACT

Translational-energy spectroscopy (TES) of Cl^{2+} and Cl^+ ions together with state-selected single-electron capture (SEC) reactions of 6 keV Cl^{2+} ions from rare-gas targets (except He) have been carried out using a novel translational-energy spectrometer. Experimentally observed transitions in the TES of both ions indicate that, in addition to the ^4S ground state, the Cl^{2+} incident ion beam contained the excited states ^2D and ^2P . No excited states were observed in the incident Cl^+ ions but, following collisions with He atoms, the ^1S excited state is populated. The use of TES to identify the excited states within the incident ion beam allows more reliable assignments of the observed reaction channels in the SEC spectra.

INTRODUCTION

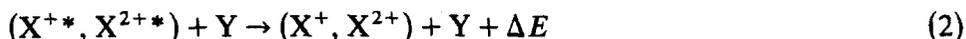
Charge-transfer reactions between doubly charged atomic ions and atomic targets have attracted considerable attention in recent years [1–5 and references cited therein]. In addition to its important role in the areas of astrophysical and high-temperature plasmas, this class of reaction is fundamentally important in providing experimental data needed to check the validity of some theoretical models. Single-electron capture by a doubly charged (X^{2+}) atomic ion from an atomic target (Y) can be written as



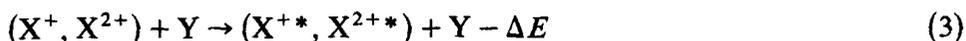
where ΔE is the endo/exothermicity of the reaction channel. One of the essential requirements for an accurate identification of the reaction channels in SEC spectra is a reliable calibration of the energy scale, ΔE , and knowledge of the excited states within the incident doubly charged ion

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beam. Energy calibration is needed to account for any contact potentials and field non-uniformity near the energy analysers. In the present investigation, the collision systems $\text{Ar}^{2+}\text{-He}$ and $\text{Ar}^{2+}\text{-Ne}$ have been used to calibrate ΔE . These two systems were chosen, because (a) the reaction channels for single-electron capture are well known [1,3] and (b) kinematically the two ions Ar^{2+} and Cl^{2+} are comparable. The above calibration, together with identification of the metastable excited states within the projectile ion beam, made the assignment of the reaction channels in the SEC spectra more reliable. In TES, the projectile ion beam experiences grazing collisions with a neutral target gas. The collision-induced transitions between the quantized energy levels of the ion or of the neutral target are experimentally observed as changes in the translational energy of the incident ion. Gain in the translational energy of the incident ion is caused by superelastic collisions where an initially excited ion (X^{+*} , X^{2+*}) is de-excited



whereas loss in the translational energy is caused by inelastic collisions [Eq. (3)] occurring when an incident ion in its ground state (X^+ , X^{2+}) is excited in the collision



We report here high-resolution TES of Cl^{2+} and Cl^+ together with single-electron capture by Cl^{2+} from rare gas targets (except He).

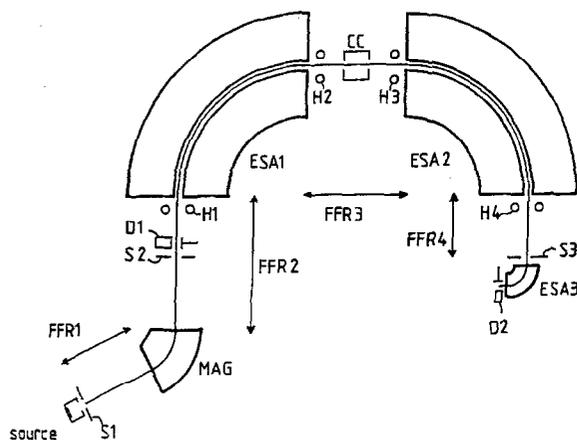


Fig. 1. Schematic diagram of the translational-energy spectrometer. S1, S2, and S3 are focal plane resolving slits; D1 and D2 are electron multiplier detectors; FFR is the field free region; H1-H4 are electric hexapole lenses; CC is the collision cell; MAG is the magnetic sector; and ESA is the electrostatic analyser.

EXPERIMENTAL

Measurements were carried out in a novel double-focusing translational-energy spectrometer (Fig. 1). The experimental design of the instrument is based on a symmetrical arrangement of two identical electrostatic analysers [6]. The instrument and its performance are described elsewhere [7] and only a brief outline is given here. Cl^{2+} and Cl^+ were formed by electron-impact ionization of either HCl or CH_2Cl_2 maintained at a pressure of 10^{-6} torr within an ion source at a temperature of 450 K and using electrons of nominal energy 100 eV. The ions were extracted, accelerated through 3 kV, mass-selected by the magnet and passed into the collision cell within which gas was maintained at an indicated pressure of 1×10^{-6} torr.

The TES and SEC spectra were recorded by scanning the post-collision analysers ESA2 and ESA3 in tandem over the appropriate voltage range ($\sim 2V$ for SEC and $\sim V$ for TES), where V is the high voltage through which the ions are accelerated on leaving the ion source.

RESULTS

TES

The translational-energy spectra for Cl^{2+} and Cl^+ scattered off He are shown in Fig. 2(a) and (b), respectively. Two peaks due to superelastic and

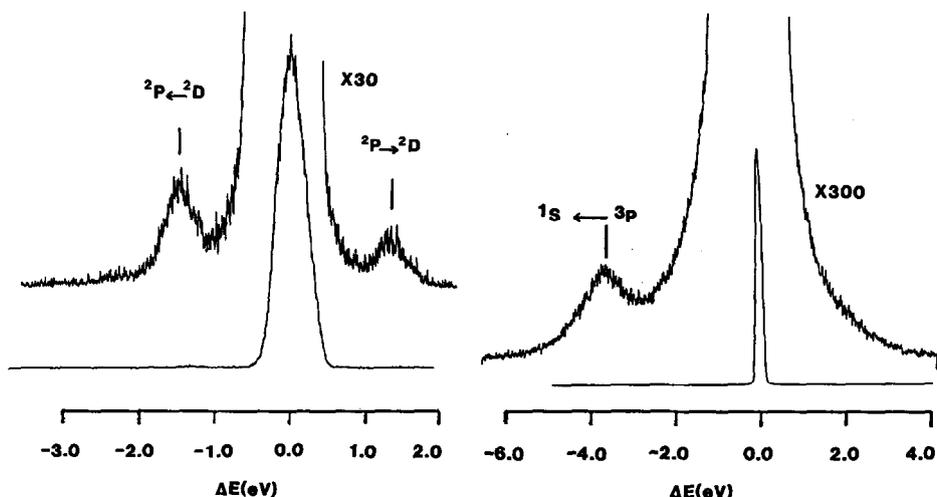


Fig. 2. Translational-energy spectra of (a) 6 keV Cl^{2+} ions scattered off He atoms and (b) 3 keV Cl^+ ions scattered off He atoms.

inelastic collisions are observed in Fig. 2(a). These peaks are attributed to electronic transitions between the two lowest electronic excited states $\text{Cl}^{2+}(^2D_{3/2}, ^2P_{1/2})$. The spectroscopically determined energy separation between these two states is 1.45 eV [8], which is in good agreement with the present value of 1.4 ± 0.2 eV. In the TES of Cl^+ [Fig. 2(b)] one inelastic peak is observed centered at an energy loss of 3.6 ± 0.2 eV. This peak is assigned to the transition $^3P_2 \rightarrow ^1S_0$. The spectroscopically determined energy separation between the two states involved is 3.46 eV. The absence of a superelastic peak at an energy gain of ~ 3.6 eV indicates that the $\text{Cl}^+(^1S_0)$ state is not populated in the ion source.

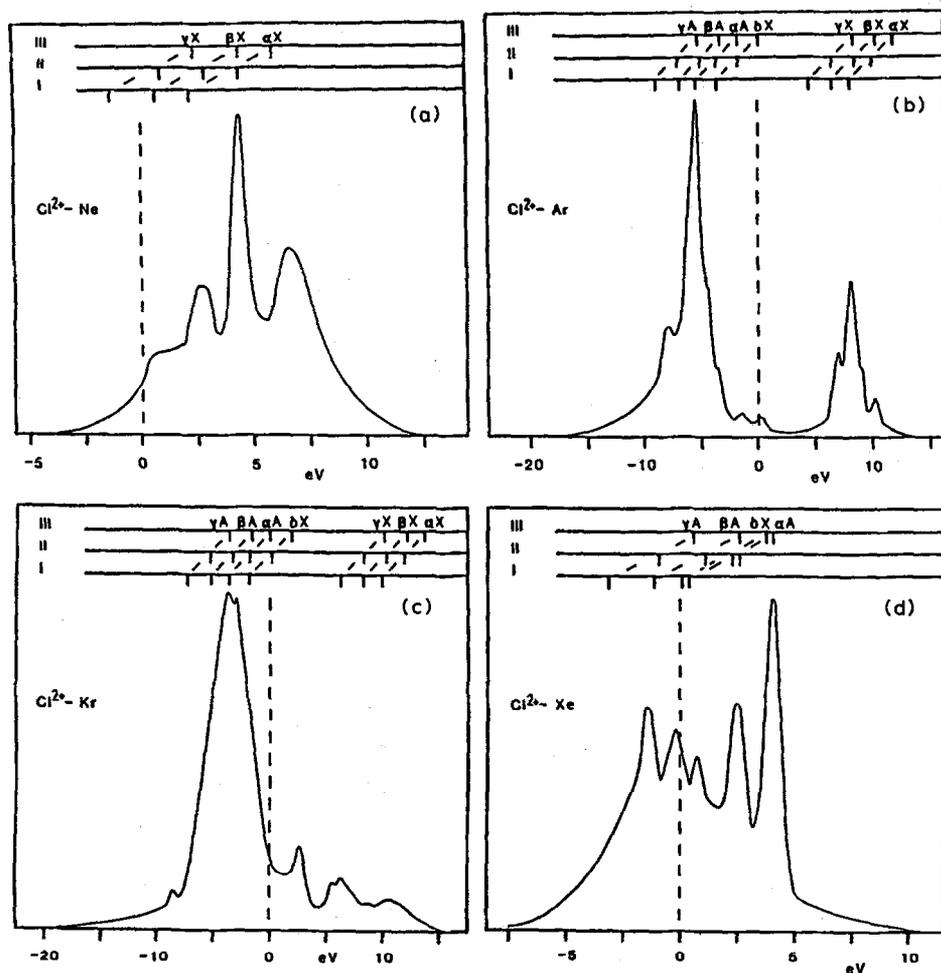


Fig. 3. Energy-change spectra for single-electron capture by 6 keV Cl^{2+} ions in (a) Ne, (b) Ar, (c) Kr; and (d) Xe.

TABLE 1

Energy levels for relevant chlorine and rare gas states with respect to the ground-state neutral

Ion	Designation	Level (eV)	Hasted's notation	Ion	Designation	Level (eV)	Hasted's notation
Cl ²⁺	³ P ³ ⁴ S _{3/2}	36.81	I	He ⁺	¹ S	24.6	X
Cl ²⁺	³ P ³ ² D _{3/2}	39.05	II	He ⁺	² S	65.4	A
Cl ²⁺	³ P ³ ² P _{1/2}	40.51	III	Ne ⁺	² P ⁵ ² P _{3/2}	21.6	X
Cl ²⁺	³ P ⁴ ⁴ P _{5/2}	49.01	IV	Ne ⁺	² P ⁶ ² S _{1/2}	48.5	A
Cl ⁺	³ P ⁴ ³ P ₂	13.01	α	Ar ⁺	³ P ⁵ ² P _{3/2}	15.8	X
Cl ⁺	³ P ⁴ ¹ D ₂	14.45	β	Ar ⁺	³ P ⁶ ² S _{1/2}	29.2	A
Cl ⁺	³ P ⁴ ¹ S ₀	16.46	γ	Kr ⁺	⁴ P ⁵ ² P _{3/2}	14.0	X
Cl ⁺	³ P ⁵ ³ P ₂	24.58	δ	Kr ⁺	⁴ P ⁶ ² S _{1/2}	27.5	A
				Xe ⁺	⁵ P ⁵ ² P _{3/2}	12.1	X
				Xe ⁺	⁵ P ⁶ ² S _{1/2}	23.4	A

SEC

Results from state-selective single-electron capture for 6 keV Cl²⁺-rare gas systems (except Cl²⁺-He) are displayed in Fig. 3 as plots of product Cl⁺ ion intensity as a function of endo/exothermicity ΔE (eV); the locations of individual reaction channels are indicated and designated using Hasted

TABLE 2

Energy defects (eV) for Cl²⁺-rare gas single electron capture

Channel ^a	Target species				
	He	Ne	Ar	Kr	Xe
IαX	-0.8	2.2	8.0	9.8	
IβX ^c	-2.3	0.7	6.5	8.3	
IγX ^c	-4.3	-1.3	4.5 ^b	6.3	8.2
(IδX		-9.4	-3.6	-1.8	0.1)
IIαX	1.4	4.4 ^b			
IIβX	-0.1	2.9	8.7		
IIγX	-2.1	0.9	6.7	8.5	
(IIδX		-7.2	-1.4	0.4	2.3)
IIIαX	2.9	5.9 ^b			
IIIβX	1.4	4.4 ^b			
IIIγX	-0.6	2.4	8.2		
(IIIδX	-8.7	-5.7	0.1	1.9	3.8)
IαA	-41.6	-24.7	-5.4	-3.7	0.4

^a Channels occurring at $|\Delta E| > 10$ eV are omitted.

^b Channels with ΔE within the calculated reaction window.

^c Spin-forbidden transitions.

co-workers' notation [9]. The energy levels of the relevant chlorine and rare-gas states, obtained from ref. 8, are given in Table 1.

In order to aid the discussion, the energy defects, ΔE , for probable reaction channels are given in Table 2. For the Cl^{2+} -He collision system, the Cl^+ product-ion current was too weak ($\sim 10^{-17}$ A) to allow reasonable identification of the reaction channels.

DISCUSSION

Studies of electron capture by doubly charged atomic ions from atomic targets have shown that the transfer of charge occurs most readily in moderately exoergic reactions through avoided crossings of adiabatic potential energy curves describing the initial and final pseudo-molecular systems over internuclear separations, R , in a range between 3 and 10 Å. This has given rise to the concept of a reaction window [10].

In this investigation, a simplified expression for the coupling element describing the initial and final molecular wavefunctions [11] has been used to calculate the relative charge transfer cross-section as a function of the exothermicity, ΔE , for Cl^{2+} -rare gas collision systems. The resulting so-called "reaction window" is given in Table 3.

The Cl^{2+} -Ne energy-change spectrum [Fig. 3(a)] is dominated by the $\text{II}\alpha\text{X}$ reaction channel leading to ground-state Cl^+ ions which has a pseudo-crossing at $R = 6.2$ u. The two channels, designated $\text{III}\alpha\text{X}$ and $\text{II}\gamma\text{X}$, are exothermic by 5.9 and 0.9 eV, respectively, and involve the two excited states $\text{Cl}^{2+} (^2P_{1/2})$ and $\text{Cl}^{2+} (^2D_{3/2})$ observed in the TES spectrum [Fig. 2(a)] and the $\text{Cl}^+ (^1S_0)$ excited state observed in the TES spectrum of Fig. 2(b). The reaction channel $\text{I}\alpha\text{X}$ involving the ground states of Cl^+ and Cl^{2+} is exothermic by 2.2 eV, well outside the reaction window (5.6–6.9 eV, Table 3). This observation might explain the weakness of this channel compared with the $\text{II}\alpha\text{X}$ and $\text{III}\alpha\text{X}$ channels which have exothermicities within the

TABLE 3

Reaction windows for Cl^{2+} -rare gas charge transfer

Target	Reaction window (eV)
He	6.1–7.5
Ne	5.6–6.9
Ar	4.7–5.7
Kr	4.3–5.2
Xe	4.0–4.8

reaction window. It is of interest to note that the energy-change spectrum of $\text{Cl}^{2+}\text{-Ne}$ closely resembles the energy-change spectrum of the well-known $\text{Ar}^{2+}\text{-He}$ [1] in which $\text{II}\alpha\text{X}$ (exothermicity 4.77 eV) is the dominant channel.

The energy-change spectrum for $\text{Cl}^{2+}\text{-Ar}$ [Fig. 3(b)] shows two groups of reaction channels, an exothermic group ($\Delta E > 0$) which is dominated by the $\text{I}\alpha\text{X}$ channel and an endothermic group ($\Delta E < 0$) dominated by the $\text{I}\alpha\text{A}$ channel resulting from a non-crossing endothermic channel involving excitation of the Ar target to Ar^+ ($3p^2S$). Other observed channels include $\text{III}\alpha\text{X}$, $\text{II}\gamma\text{X}$ and $\text{II}\gamma\text{A}$. The semi-classical approximations for this collision system predicts that only $\text{I}\gamma\text{X}$, involving spin-forbidden capture to Cl^+ (1S), appears within the reaction window. It is not surprising, therefore, that $\text{I}\gamma\text{X}$ makes only a minor contribution (if any at all) to Fig. 3(b). Consequently, non-crossing endothermic reactions assume greater significance.

The translational-energy distribution of Cl^+ ions formed from 6 keV $\text{Cl}^{2+}\text{-Kr}$ collisions [Fig. 3(c)] is comparable with the $\text{Cl}^{2+}\text{-Ar}$ spectrum, both having two groups of channels in evidence with the $\text{I}\alpha\text{A}$ endothermic channel dominating both spectra. In the case of $\text{Cl}^{2+}\text{-Xe}$, the available charge-transfer channels to low-lying Cl^+ states are so exoergic that none of these appears in the spectrum of Fig. 3(d). However, target excitation channels involving the $\text{Xe}(^2S)$ excited state occur within the reaction window with $\text{II}\alpha\text{A}$ having the maximum cross-section for charge transfer; other observed channels in the spectrum are easily identified.

CONCLUSIONS

Translational-energy gain/loss spectra of single-electron capture product ions following collisions of 6 keV Cl^{2+} with rare-gas targets (except He) have been measured in a novel translational-energy spectrometer. The energy defect scale was carefully calibrated; we believe the ΔE axis in Fig. 3 to be accurate to better than ± 0.2 eV. Our results show that the spectra of the collision systems $\text{Cl}^{2+}\text{-Ne}$ and $\text{Cl}^{2+}\text{-Xe}$ are dominated by the reaction channels $\text{II}\alpha\text{X}$ and $\text{III}\alpha\text{A}$, respectively. The dominance of both channels is in line with our semi-classical approximation, which shows that both channels are within their respective predicted reaction windows. The energy-change spectrum for $\text{Cl}^{2+}\text{-Ar}$ is dominated by the non-crossing endothermic channel $\text{I}\alpha\text{A}$. This is also in agreement with our semi-classical predictions which suggest that only the spin-forbidden exothermic $\text{I}\gamma\text{X}$ is within the reaction window and therefore non-crossing endothermic channels assume greater significance. The same conclusion is drawn regarding $\text{Cl}^{2+}\text{-Kr}$ since no exothermic channels fall within the calculated reaction window. The TES of Cl^{2+} and Cl^+ revealed that, in addition to the $^4S_{3/2}$ ground state, the Cl^{2+} incident ion beam contains the $^2D_{3/2}$ and $^2P_{1/2}$ excited states. No excited

states were observed in the Cl^+ incident ion beam but, in collision with He, the Cl^+ ($^1\text{S}_0$) state is strongly populated.

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