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Experimental observation and theoretical calculations of triply excited $2s2p^2\,{}^2S^e$, $^{2,4}P^e$, $^2D^e$ and $2p^3\,{}^2P^o$, $^2D^o$ states of fluorine

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An alternative experimental technique for efficient population of triply excited states in atoms and ions is presented. The states are produced by triple electron capture in energetic ion-atom collisions. The method is used to study autoionizing $2s2p^2\,{}^2S$, ^2P, ^2D, ^4P and $2p^3\,{}^2P$, ^2D states of fluorine. Differential cross sections, resonance energies, and Auger decay branching ratios were determined from the experiment. Results are compared to different calculations based on the hyperspherical close coupling method.

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The study of triply excited states of atoms and ions presents opportunities to probe multiparticle excitations of a quantum system, thus providing tests for the most advanced atomic theories. For these states, interelectronic correlation plays a crucial role in determining their properties. As a result, theoretical descriptions based on the conventional independent particle model fail completely. Triply excited states, in general, are difficult to produce from the ground state by single-photon absorption or by electron impact excitation, since both processes rely on the weak electron-electron interaction to promote more than one electron in a single collision. Thus, only with the advent of intense light sources in the last decade have experimental studies of triply excited states in Li atoms been initiated. A number of these states have been investigated using photoion and photoelectron spectroscopy [1–6]. These experiments have stimulated an avalanche of theoretical calculations [7–11] that, in general, described fairly well specific experimental results.

While the employment of synchrotron radiation for such studies has yielded considerable information on triply excited states of Li atoms, the insufficient densities of ionic targets ruled out the possibility to investigate triply excited resonances in Li-like ions. Furthermore, the limited nature of the photoexcitation technique prohibited the population of quartet states. The absence of available experimental data for three electron ions has prevented theorists from pursuing a global understanding of triply excited states, such as new classification schemes, approximate quantum numbers, and possible approximate selection rules for the formation and the decay of these states.

In this paper, we demonstrate a different method, relying on the strong electron-projectile Coulomb interaction, to efficiently form triply excited states of ions and atoms. The states are produced via triple electron capture in energetic ion-atom collisions. By the proper selection of collision partners, any triply excited state of any ion can, in principle, be populated. The technique is demonstrated by studying the $2l2l'2l''$ intrashell states of fluorine, and experimental measurements are compared to theoretical calculations based on the hyperspherical close coupling method (HSCC). In particular, all $2s2p^2$ and $2p^3$ triply excited states of F^{6+} ions are populated in collisions of bare 16 MeV F^{9+} ions on Ar. Multiple transitions from these states into the continua of F^{7+} are identified from the ejected electron spectra in the direction of the ion beam and are used to determine transition energies, branching ratios, and absolute differential cross sections for the observed states. The experimental branching ratios are compared to available theoretical calculations.

Triply excited states have been previously observed in energetic ion-atom collisions [12], however, since the states were formed via the excitation process, only very few of them had been identified. Multiply excited states were also formed in low-energy ion-atom and ion-surface collisions, but the resolution in these experiments was not sufficient for the identification of individual states [13]. Recently, triply excited states of ions have been produced by resonant transfer and excitation (RTE) using metastable ion beams [14]. Although, the technique has been successfully applied to measurements of autoionization rates and branching ratios in Li-like ions, the selectivity of the RTE process leads to the population of mainly $2s2p^2\,{}^2D^e$ states. The triple electron capture, as illustrated in this paper, is a more robust method. In the present work only the $2l2l'2l''$ intrashell triply excited states are investigated, but the technique can be extended to the production of other hollow states by utilizing appropriate ion-atom collision systems.

The present measurements were carried out at the J. R. Macdonald Laboratory at Kansas State University, using the 7 MV EN tandem Van de Graaff accelerator. Magnetically selected F^{9+} beams were focused into a 5 cm long differentially pumped gas cell. The Auger electrons, resulting from the collision with argon, were emitted at energies corresponding to transitions of triply excited states to $1s2l$ final states of F^{7+} and detected with a zero-degree hemispherical spectrograph [15]. The unique feature of this spectrograph is the capacity to analyze electrons in an energy bandwidth of about 20%, which significantly facilitates experimental measurements of low intensity processes such as triple electron

capture. The ejected Auger electrons were decelerated to obtain the present optimal resolution of the system (0.25%). Double differential cross sections were measured with a total uncertainty of 30%, calculated by taking the quadrature sum of the statistical (20%) and absolute (25%) uncertainties. The latter incorporates mainly the electron detection efficiency of the spectrograph. Two potential sources of experimental uncertainties are represented by the possible contamination of F^{9+} beams with other charge states and the double collisions in the gas cell. The single collision regime was established by setting the Ar target pressure at 20 mTorr corresponding to the middle of the linear interval of the electron yield-target pressure curve. Also, the formation of F^{8+} or F^{7+} contamination beams, which could contribute to the electron emission from populated states, has been shown to be negligible [16]. Consequently, it was demonstrated that the observed triply excited states of F^{6+} are formed in a single collision of F^{9+} ions with Ar.

In order to maximize the population of $2l2l'2l''$ triply excited states in F^{9+} projectile ions, an appropriate atomic gas has to be chosen as a target. An ideal collision partner for F^{9+} ions is provided by atomic argon whose L shell energy (-9.45 a.u.) is located near the $n=2$ energy level of F^{8+} (-10.12 a.u.). For this collision system, the production of triply excited states of fluorine is realized primarily by the transfer of L shell electrons of Ar. Since triply excited states are identified from the energies of the corresponding Auger transitions, formation of other states, which have Auger energies close to the investigated ones, should be avoided. For bare fluorine ions, the major possible contamination will come from the decay of the $2l2l'3l''$ states. In the present collision system, however, these states are hardly populated since electron capture from the L shell of Ar to the $n=3$ shell of fluorine is very small, due to the difference in binding energies for these shells.

Figure 1 shows the measured Auger-electron spectra resulting from the collisions of 16 MeV F^{9+} ions with Ar. Auger electrons in the projectile rest frame energy range of 600—625 eV emitted from the $2s2p^2\,{}^2S$, ^2P, ^2D, ^4P and $2p^3\,{}^2P$, ^2D triply excited states were observed. The upper frame also shows Auger transitions from $2l2l'$ doubly excited states, formed by double electron capture. Auger energies of these well-known transitions were used for the precise energy calibration of the electron detector. Peak assignments and Auger transition energies are presented in Table I. For the $2l2l'2l''$ triply excited states, we can still use the conventional independent particle designations. Each state decays by Auger emission to $1s2l$ singly excited states of F^{7+}. These measured energies are compared to theoretical predictions where the energies of the triply excited states are calculated using the HSCC method. Clearly, there is a general good agreement between the calculated Auger energies and the experimental results. All the theoretical energies are within the experimental uncertainty of 0.25%. We note that the energies of $2l2l'2l''$ triply excited states of F^{6+} have also been calculated using the $1/Z$ expansion [9] and truncated diagonalization [11] methods, but these calculations show inferior agreement with the measurements.

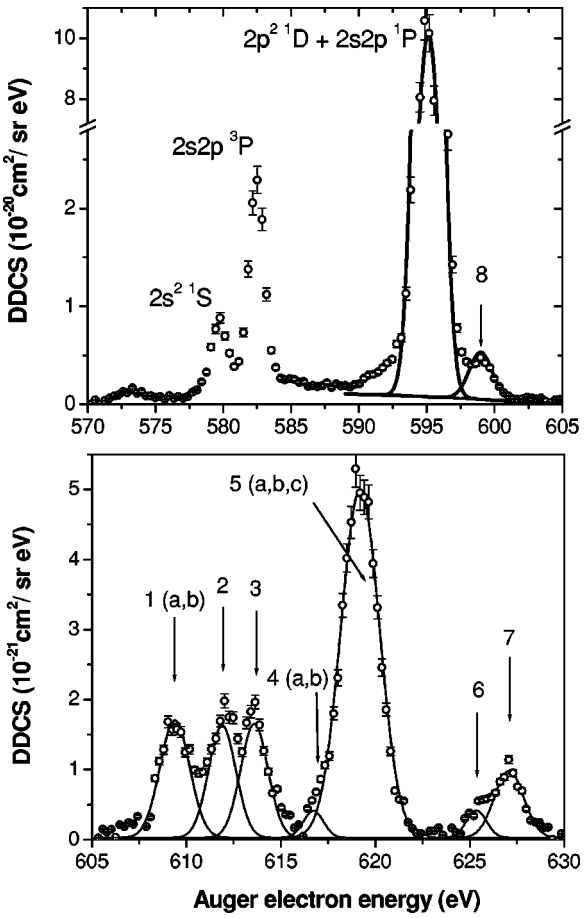

FIG. 1. Present experimental measurements of Auger decay channels from the triply excited states of Li-like fluorine into the continua of F^{7+} ions. The solid line represents the Gaussian fit to the experimental data.

One of the main goals for studying triply excited states is to find approximate quantum numbers such that they can be ordered into classification schemes [17–19]. In the past decade, the investigation of triply excited states using hyperspherical coordinates resulted in the successful classification of both the $2l2l'2l''$ and $3l3l'3l''$ manifolds [17,18]. By analyzing the correlated motion of the three electrons, intrashell triply excited states of atoms have been classified akin to the different bending vibrational normal modes of an XY_3 molecule, with X being the nucleus and Y being an electron. The classification, which was based on a model of three electrons on the surface of a sphere, has not yet been fully tested, largely, due to the lack of information on the energies of triply excited states, either from accurate calculations or from experiments. As a result, the HSCC method for three-electron systems has been developed in order to obtain a larger set of accurate theoretical data for analysis. In the HSCC method, which has been extensively employed for the two-electron systems [20], the total wave function is expanded in analogy to the Born-Oppenheimer approximation but with the hyperradius as the adiabatic parameter [17]. Figure 2 shows an example of the hyperspherical potential curves for the $^2P^o$ states of F^{6+} in the region where

TABLE I. Summary of present experimental results and theoretical calculations for the observed triply excited states of F^{6+}. Single differential cross sections (SDCS) are given in units of 10^{-21} cm^2/sr. Auger energies are calculated relative to the ground state of Li-like fluorine ($E=2242.2$ eV [9]).

Peak	Peak Assignment		Auger Energy (eV)				Branching ratios		
No.	Initial state	Final state	Expt.	HSCC calc.	$SDCS_{expt.}$	$SDCS_{calc.}$	Expt.	Theory [9]	Theory [25]
1*a*	$2s2p^2\,^2D$	$1s2s\,^1S$	609.4±0.5	609.35	3.3±0.6	6.05	0.41	0.44	0.52
1*b*	$2s2p^2\,^2D$	$1s2p\,^3P$		609.74					
2	$2s2p^2\,^2P$	$1s2p\,^1P$	611.9±0.6	611.73	2.9±0.7	3.19	0.45	0.39	0.44
3	$2p^3\,^2D$	$1s2p\,^1P$	613.6±0.6	613.60	2.9±0.8	1.02	0.32	0.25	0.24
4*a*	$2s2p^2\,^2S$	$1s2s\,^1S$	616.7±0.5	617.08	0.5±0.2	0.99	0.50	0.50	0.52
4*b*	$2s2p^2\,^2S$	$1s2p\,^3P$		617.47					
5*a*	$2s2p^2\,^2P$	$1s2p\,^3P$		618.11			0.55	0.60	0.56
5*b*	$2s2p^2\,^2D$	$1s2s\,^3S$	619.1±0.8	618.39	12.7±2.9	15.90	0.59	0.56	0.48
5*c*	$2p^3\,^2D$	$1s2p\,^3P$		619.04			0.68	0.74	0.75
6	$2s2p^2\,^2S$	$1s2p\,^3S$	625.4±0.5	625.73	0.5±0.2	1.35	0.50	0.37	0.47
7	$2p^3\,^2P$	$1s2p\,^3P$	627.1±0.5	627.12	1.8±0.4	1.86		0.78	0.60
8	$2s2p^2\,^4P$	$1s2p\,^3P$	599.0±0.7	599.29	9.5±1.9	13.10	1	1	1
				SDCS (sum)	34.4±7.7	43.84			

$2l2l'nl''$ triply excited states are located. In the HSCC method, the couplings among the potential curves are included and the solution of the coupled hyperradial equations allows one to obtain accurate energies and widths of the resonances. In particular, the coupling with the family of curves with sharp descent is responsible for the Auger transitions to the singly excited states of F^{7+}. Specifically, we used the *R*-matrix propagation method together with the slow variable discretization procedure [21,22] to solve the coupled equations. We obtained energy derivatives of the sum of the eigenphases directly from the *R* matrix at the fixed end point of the hyperradius $R\sim10$ a.u., and fitted to a Lorentzian function to evaluate energies and widths. This technique allows us to evaluate approximate energy positions and total widths without applying boundary conditions at $R\rightarrow\infty$ [23].

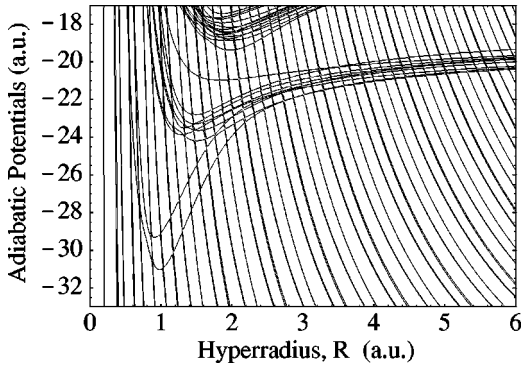

FIG. 2. Adiabatic hyperspherical potential curves for $^2P^o$ states of F^{6+} in the energy region of $2l2l'nl''$ triply excited states. The two lowest attractive potential wells support the two intrashell states $2s^22p$ and $2p^3$ of this symmetry. The family of curves with fast descent represent continuum states of F^{7+} which are coupled to triply excited states resulting in autoionization.

As explained earlier, triple electron capture is an efficient method for populating triply excited states without relying on the weak electron-electron interaction. To demonstrate the validity of this argument, we calculated the triple electron capture cross sections within the independent electron approximation. In the first step, the probability of transferring an *L* electron of Ar to the $2s$ or $2p$ states of F^{8+} is calculated using the standard two-center atomic orbital expansion method [24]. We can then calculate the probability of triple electron capture, within the independent electron model, which follows a simple binomial distribution. By integrating over the impact parameter plane, the triple electron capture cross section for each triply excited state is then calculated assuming statistical populations. In Table I, the theoretical differential cross sections for the zero degree Auger-electron emission from the observed states are compared to experimental results. The agreement is quite acceptable in view of the complexity of the process. This confirms that triply excited states are formed mostly without relying on the weak electron-electron correlation. However, electron correlation does play a major role in the calculated energies and the decay widths of triply excited states.

Table I displays Auger decay branching ratios obtained from present measurements along with a selection of theoretical predictions for triply excited F^{6+} ions [9] and Li atoms [25]. The determination of branching ratios in the present experimental technique is independent of the electron spectrometer constant and target pressure. This significantly reduces the experimental uncertainty, providing accurate information on the decay dynamics from populated states. An overall reasonable agreement between theoretical predictions and present experimental results was observed for all investigated Auger decay channels. In the analysis of peak 5, which represents a mixture of three decay channels from

$2s2p^2\,^2P$, ^2D and $2p^3\,^2D$ triply excited states, we relied on the knowledge of the branching ratios for the $2s2p^2\,^2D$ state measured in a previous experiment [14], where the ^2D resonance was selectively populated by RTE in metastable ion-atom collisions. Since in this work the $2s2p^2\,^2D$ to $^1S+^3P$ decay channel is measured separately (peak 1), the contribution of the other decay branch from this state (^2D to ^3S) into peak 5 has been evaluated. In order to extract the individual contributions of the remaining two Auger decay channels in peak 5, namely, $2s2p^2\,^2P$ to $1s2p^3P$ and $2p^3\,^2D$ to $1s2p^3P$, calculations within an independent electron approximation were performed and the results were normalized to the other decay branches (peaks 2, 3) from $2s2p^2\,^2P$ and $2p^3\,^2D$ states observed in the spectra.

The good agreement between experimental and theoretical branching ratios indicates a correct representation of the investigated triply excited states through a chosen configuration complex, as was stressed in the recent work of Chung [25]. Also, the agreement of the branching ratios calculated for Li atom with the experimentally measured ones for F^{6+} signifies that Auger decay branching ratios are insensitive to the nuclear charge along the isoelectronic sequence.

In summary, we demonstrate an alternative experimental method where triply excited states of atoms and ions can be efficiently populated via triple electron capture. Unlike photoabsorption or electron impact excitation from the ground state of an atom, which rely on the weak electron-electron correlation to populate triply excited states, the present method benefits from the stronger electron-projectile Coulomb interaction, resulting in the copious production of hollow states in ions and atoms. The technique was demonstrated by investigating autoionizing $2s2p^2\,^2S$, ^2P, ^2D, ^4P and $2p^3\,^2P$, ^2D states of fluorine produced in energetic collisions of 16 MeV F^{9+} ions with Ar atoms. The energies of these triply excited states are compared to different calculations based on the hyperspherical close coupling method. Differential cross sections for triple electron capture are calculated in the independent electron approximation and are shown to be in good overall agreement with the experimental data. In addition, the Auger decay branching ratios have been extracted from the electron spectra and compared to the limited calculations available in the literature. By proper selection of collision partners, we expect that triple electron capture can offer an efficient method for the study of triply excited states in different ions.

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