Photoelectron recapture as a tool for the spectroscopy of ionic Rydberg states

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We use recapture of near-threshold photoelectrons by postcollision interaction with Auger electrons as an effective method for population of the high-Rydberg states of subvalence ionized Ne ions. The subsequent intermultiplet Auger transitions are detected by high-resolution electron spectrometry. The series of transitions $2p^4(^1D)np\ ^2D, ^2F \rightarrow 2p^4\ ^3P$ up to $n=20$ are observed and identified with the help of multiconfiguration Dirac–Fock *ab initio* calculations.

Spectroscopic data on atomic ions are required for modeling of stellar atmospheres as well as for laboratory plasmas with their relevance for fusion reactors. Experimentally, the spectroscopic study of ions, in particular their electron spectroscopy, is a challenging task. In spite of big progress in this field (see, for example, a review by West [1]) there is still a need for the development of improved methods of spectroscopic investigation of atomic ions. The present methods currently existing for ion spectroscopy are always experimentally very challenging. In the past decade particular interest was attracted by a special class of autoionizing states of atomic ions, the so-called inner-valence excitations [2]. Consider, for example, a Ne$^+$ ion with a vacancy in the $2s$ subshell. A relaxation of this ion via "normal" Auger decay is energetically not allowed. However, if in the process of $2s$ ionization another electron is excited to a $3p$ or higher Rydberg orbital, such "two-hole one-particle" states may decay via the "participator" Auger transition [2,3]. Especially interesting are the transitions in which the two-hole configuration is not changed but only the core multiplets are different in the initial and final states. For example, in Ne$^+$, due to a significant singlet-triplet splitting, the $2s2p^5(^1P)3p$ states lie above the $2s2p^5\ ^3P$ level of Ne^{2+} and can decay to it. Such transitions, called valence multiplet changing or intermultiplet Auger transitions, are predominant in the low kinetic-energy part of the spectrum and determine the large width of the inner-valence-excited ionic states [4–9].

Spectroscopic information about these two-hole one-particle states so far was mainly obtained by studies of the satellite structure in the subvalence shell photoionization [10]. The state of the art of such ionization + excitation experiments has recently been demonstrated by Bolognesi *et al.*

[11]. They applied the technique of high-resolution threshold photoelectron spectroscopy to study the Ne$^+$ $2p^4n\ell$ satellite states and observed several Rydberg series, up to $n=26$ in some series. The energy positions and the quantum defects δ were determined. Although threshold photoelectron spectroscopy is indeed powerful, its application is limited to states which are coupled to the direct photoionization channel.

In principle, singly charged inner-valence-excited configurations can also be reached by resonant Auger decay of a neutral core-excited state, such as the $1s^{-1}3p$ photoexcited state in Ne. As an advantage, states can be populated by resonant Auger, which are hardly accessible via outer-shell photoionization. The exploitation of resonant Auger decay for spectroscopic purposes so far has been limited by the broad photon bandwidths and low resolution of energy analysis for high-energy Auger electrons. However, recent developments of high-resolution soft x-ray monochromators and of electron energy analyzers have improved this situation dramatically. Recent experiments employing a Doppler-free resonant Raman Auger technique [12] for studying Ne$^+2s2p^5np$ states have reached a resolution comparable with the natural lifetime width of the states considered [13,14]. In this experiment, the multiplet structure of the inner-valence states has been resolved. Some of these states lie above the double-ionization threshold and therefore can autoionize, emitting Auger electrons of comparatively low energy (10–30 eV). The spectroscopy of these second-step Auger electrons provides independent information about the inner-valence excitations competing in quality with the study of the first-step Auger decay [15]. The drawback of the resonant Raman Auger technique is that in this way it is not possible to excite higher members of the Rydberg series.

Highly excited ionic Rydberg states can be populated by a recapture process in near-threshold inner-shell photoionization. When the atom is photoionized just above the inner-shell threshold, the slow photoelectron is still near the ion at the moment when Auger decay occurs. Due to the postcollision interaction (PCI) the photoelectron is retarded and can

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be recaptured by the ion into one of its Rydberg orbitals [16,17]. If the final ionic state lies above the threshold for double ionization, the autoionization can occur through the inner-valence Auger decay. Excitation of Rydberg ionic states by photoelectron recapture was confirmed by the measurements of low-energy electron spectra in near-threshold photoionization of the Ar 2p shell [18,19].

In this paper we suggest how the recapture process with the following autoionization can be systematically applied for spectroscopic study of the inner-valence Auger transitions in ions. Greatly improved intensity of the photon beam and the improved resolution of the spectrometer allow us to use this phenomenon as an effective spectroscopic tool. We demonstrate it on the example of valence intermultiplet Auger transitions in Ne$^+$ ions excited by photoelectron recapture in Ne 1s photoionization. In the decay of Ne(1s^{-1}) the strongest Auger line is the transition $1s^{-1} \rightarrow 2p^4$ ^1D. Thus, one can expect that the Rydberg states $2p^4(^1D)np$ will be most strongly populated in the recapture process. By observation of the $2p^4(^1D)np \rightarrow 2p^4$ ^3P intermultiplet "participator" Auger transitions, we have been able to observe recapture into these states up to $n = 20$ and to determine their spectroscopic properties.

The present experiment has been carried out on the c branch of the high-resolution photochemistry beamline 27SU [20–22] at SPring-8, the 8 GeV synchrotron radiation facility in Japan. The radiation source is a figure-8 undulator [23]. The direction of the linear polarization vector for the first-order harmonic light generated by this undulator is horizontal, whereas that of the 0.5th-order harmonic light is vertical. By changing the undulator gap, and monitoring the change of the photon flux, one can perform the angle-resolved electron spectroscopy with an electron spectrometer fixed in the horizontal direction. The high-resolution electron spectroscopy apparatus consists of a hemispherical analyzer (Gammadata Scienta SES-2002) coupled via an electrostatic lens to a gas cell and a differentially pumped chamber [24]. We have set the pass energy to 2 eV, with an analyzer slit width of 1.5 mm. We measured the electron spectrum in the kinetic-energy region 0.1–3.3 eV generated by photoionization of Ne atoms by photons of energy 100 meV above the 1s ionization threshold of 870.17 eV. The incident photon energy was calibrated by comparing the positions of the $1s^{-1}np$ resonances with known values [25]. The photon-energy bandwidth does not contribute to the observed electron energy width and was set to about 400 meV. The angle-resolved measurements have been done for two mutually perpendicular directions of linear polarization, so that the anisotropy of angular distribution of emitted electrons, as well as intensity, have been determined.

The measured low-energy electron spectrum contains several series of well-resolved transitions. In Fig. 1, we show two parts of the spectrum which correspond to the lowest members of the series for the transitions $2p^4(^1D)np \rightarrow 2p^4$ ^3P for $n = 5$ [Fig. 1(a)], $n = 6$ [Fig. 1(b)]. Black dots show the experimental results obtained for 0° emission with respect to the photon polarization direction. Open circles show the spectrum for the 90° emission. The lines represent the results of a least-square fit to the spectra with Gaussian
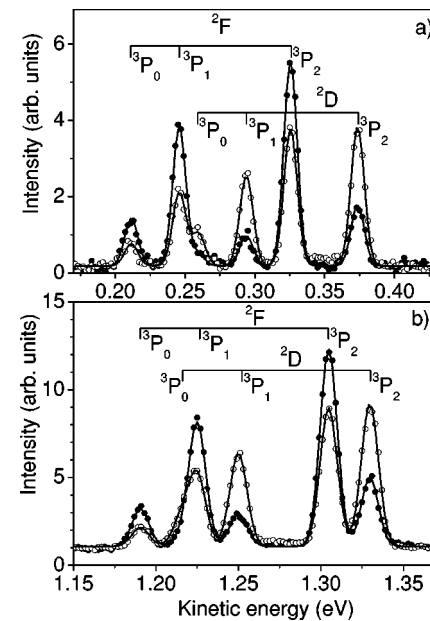

FIG. 1. Portions of the low-energy electron spectrum recorded at 0° (full circles) and 90° (open circles) relative to the polarization vector. The $2p^4(^1D)np$ $^2F, ^2D \rightarrow 2p^4$ ^3P autoionization decay of inner-valence-excited ionic Rydberg states of Ne, with $n = 5, 6$ are displayed in panels (a) and (b), respectively. The solid curves are the results of a least-squares fit described in the text.

profiles of full width at half maximum (FWHM) of 11 meV; this width is entirely due to the resolution of the electron spectrometer. Since the electron spectrometer is not rotated, measurements at 0° and 90° can be normalized in relative intensity simply by dividing the photon flux as measured by a photodiode. The spectra at the two angles are fitted simultaneously, so they have identical energy positions for each peak. The energy difference of transitions leading to the different components of the final $2p^4$ ^3P multiplet was kept fixed in the fitting to known values [26,27]. The kinetic-energy scale was calibrated from the positions of the transitions in the series $2p^4(^1D_2)np$ $^2F \rightarrow 2p^4$ $^3P_2$, whose limit is known to be 3.2 0385 eV [26,27]. The accuracy of the calibration of the energy scale is ±5 meV, and the accuracy of relative position of most observed peaks is ±1 meV. The transmission of the electron analyzer at different kinetic energy was investigated by comparing the peak height of the Ne 1s photoline with the value expected from its known cross sections, asymmetry parameters, and broadening and distortion due to the PCI effect; it resulted that in the energy regions covered by the spectra presented the intensity changes by no more than 15%.

Resolution of our experiment is sufficiently high to resolve not only the transitions to the different fine-structure levels of the final $^3P_{0,1,2}$ state, but also the multiplet structure of the excited Rydberg states. In order to identify the transitions, we have made *ab initio* multiconfiguration Dirac–Fock (MCDF) calculations of the energy positions, the relative intensities, and the anisotropy parameter β of the angular distribution for the considered transitions. Both initial and final ionic state configuration interactions were taken into account in a configuration space which included $1s^2 2s^2 2p^4 np$

TABLE I. Term values, intensity ratios, and angular anisotropy parameters β for the two lowest observed members of the series $2p^4(^1D)np\ ^2F \rightarrow 2p^4\ ^3P_{0,1,2}$ and $2p^4(^1D)np\ ^2D \rightarrow 2p^4\ ^3P_{0,1,2}$ $n=5,6$ of intermultiplet Auger transitions. Intensities have been normalized to the strongest transition for the respective n.

Initial state	Final state	T (eV)	Intensity ratio		β	
			Expt.	Theor.	Expt.	Theor.
$5p\ ^2F$	$^3P_0$	0.212	0.19(1)	0.18	0.55(11)	0.65
$5p\ ^2D$		0.260	0.16(1)	0.12	−0.56(10)	−0.70
$5p\ ^2F$	$^3P_1$	0.246	0.59(1)	0.58	0.45(6)	0.55
$5p\ ^2D$		0.294	0.44(1)	0.40	−0.57(6)	−0.60
$5p\ ^2F$	$^3P_2$	0.326	1.00(1)	1.00	0.28(5)	0.36
$5p\ ^2D$		0.374	0.71(1)	0.80	−0.46(5)	−0.34
$6p\ ^2F$	$^3P_0$	1.191	0.15(1)	0.18	0.55(10)	0.65
$6p\ ^2D$		1.216	0.13(1)	0.10	−0.64(10)	−0.70
$6p\ ^2F$	$^3P_1$	1.225	0.55(1)	0.58	0.40(6)	0.53
$6p\ ^2D$		1.250	0.46(1)	0.37	−0.55(5)	−0.57
$6p\ ^2F$	$^3P_2$	1.305	1.00(1)	1.00	0.24(5)	0.37
$6p\ ^2D$		1.330	0.75(1)	0.80	−0.42(5)	−0.35

nonrelativistic configurations ($n=3-7$) in the initial state and $1s^2 2s^2 2p^4$ configuration in the final state. Initial and final states were separately optimized using the atomic structure code GRASP92 [28]. The wave functions thus obtained were used for calculations of the Auger matrix elements exploiting the program package RATIP [29], and then the intensity and β parameter for each Auger line were evaluated assuming that the initial state population is statistical and the alignment transfer is not distorted by the PCI.

Using the calculated values, we have identified the lines in the spectra shown in Fig. 1. The peaks correspond to the transitions $2p^4(^1D)np\ ^2F \rightarrow 2p^4\ ^3P_{0,1,2}$ and $2p^4(^1D)np\ ^2D \rightarrow 2p^4\ ^3P_{0,1,2}$ ($n=5,6$). The measured term values T and the measured and calculated relative intensities and β values are shown in Table I. Good agreement confirms our assignment.

It is interesting that the transitions $2p^4(^1D)np\ ^2P \rightarrow 2p^4\ ^3P_{0,1,2}$ are not seen in our experiment. A possible rea-

son for this is that the lifetime of the $2p^4(^1D)np\ ^2P$ states is much shorter than that of the ^2F and ^2D states, and due to their large width it might be impossible to separate them from the background. In our calculations the width of ^2P comes out two orders of magnitude larger than that of ^2F and ^2D, which is still not sufficient to explain the apparently complete absence of transitions originating from the ^2P state. However, as it was demonstrated earlier [7], accurate calculations of these widths should include electron correlations on a much larger basis than used in the present work. Thus, the reason for the absence of the $2p^4(^1D)np\ ^2P$ series is an open question.

Comparing the spectra in Figs. 1(a) and 1(b) one sees that the splitting of the ^2F and ^2D initial states diminishes with an increase in n, as expected. This tendency persists for $n=7-9$. At higher n, however, the multiplets are already not resolved. The spectrum for higher n is presented in Fig. 2. The strongest peaks are associated with the transitions $2p^4(^1D)np \rightarrow 2p^4\ ^3P_2$. However, rather often they overlap with the weaker lines corresponding to the transitions to other members of the ^3P multiplet. The series is clearly seen
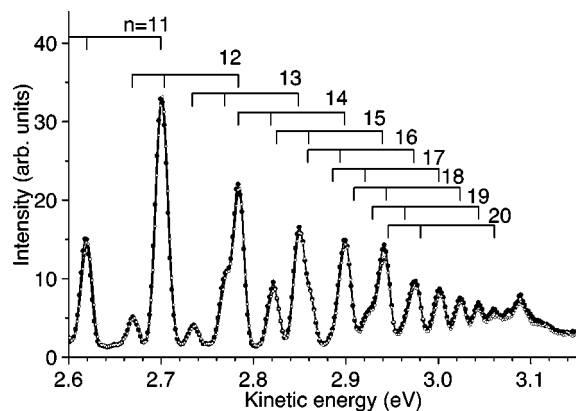

FIG. 2. Low-energy electron spectrum of the $2p^4(^1D)np\ ^2F, ^2D \rightarrow 2p^4\ ^3P$ autoionization decay of inner-valence-excited ionic Rydberg states of Ne, with $n \geq 11$, recorded at 0° (full circles) and 90° (open circles) relative to the polarization vector.

TABLE II. Term values T and quantum defects δ of the initial states for higher members of the series $2p^4(^1D)np \rightarrow 2p^4(^3P_2)$. The series limit is 3.2 0385 eV [26,27].

n	T (eV)	δ	n	T (eV)	δ
10	0.619	0.624(15)	16	0.230	0.60(16)
11	0.503	0.600(21)	17	0.202	0.60(08)
12	0.419	0.610(27)	18	0.180	0.60(10)
13	0.354	0.604(35)	19	0.160	0.58(11)
14	0.305	0.642(44)	20	0.143	0.49(14)
15	0.263	0.617(55)			

up to $n=20$. From the energy position of the lines the quantum defect δ is obtained and is presented in Table II together with the term values T. The obtained δ values are constant within the experimental errors and compare well with those derived from satellite state measurements [11].

In conclusion, the recapture process due to the PCI effect can be used as an effective means for populating the inner-valence Rydberg excitations of ions. In combination with high-resolution low-energy electron spectrometry it permits to study the series of intermultiplet Auger transitions. In a particular case of Ne^+ ions, we used this method to study the $2p^4(^1D)np\ ^2D,^2F \rightarrow 2p^4\ ^3P_{0,1,2}$ transition. We succeeded in resolving the multiplet structure of the initial states in the transition up to $n=9$. The series are observed up to $n=20$. The suggested spectroscopic method is expected to have a general applicability to light atoms and molecules containing first or second row atoms.

Note added in proof. Recently, the observation of some other ionic series based on the technique described here has been reported by Hentgens *et al.* [30].

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