Doppler-Free Resonant Raman Auger Spectroscopy of Ne$^+$ $2s2p^5 3p$ Excited States

K. Ueda,[1,*] M. Kitajima,[2] A. De Fanis,[3] Y. Tamenori,[3] H. Yamaoka,[4] H. Shindo,[2] T. Furuta,[2] T. Tanaka,[2] H. Tanaka,[2]
H. Yoshida,[5] R. Sankari,[6] S. Aksela,[6] S. Fritzsche,[7] and N. M. Kabachnik[8,†]

[1]*Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Sendai 980-8577, Japan*
[2]*Department of Physics, Sophia University, Tokyo 102-8554, Japan*
[3]*Japan Synchrotron Radiation Research Institute, Sayo-gun, Hyogo 679-5198, Japan*
[4]*Institute of Chemical and Physical Research, Sayo-gun, Hyogo 679-5198, Japan*
[5]*Department of Physical Science, Hiroshima University, Higashi-Hiroshima 739-8526, Japan*
[6]*Department of Physical Sciences, University of Oulu, FIN 90401 Oulu, Finland*
[7]*Fachbereich Physik, Universität Kassel, D-34132 Kassel, Germany*
[8]*Fakultät für Physik, Universität Bielefeld, D-33615 Bielefeld, Germany*
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Using very high resolution achieved by the Doppler-free resonant Raman Auger technique, we have resolved the lowest terms of the series of inner-valence excitations $2s2p^5(^{1,3}P)np$ ^2S, ^2P, and ^2D in Ne$^+$. The measured Auger anisotropic parameters and branching ratios help to establish the assignments of these levels. The measured lifetime widths are in reasonable agreements with *ab initio* calculations available in the literature.

Spectroscopic studies of excited states of atomic ions constitute an important part of atomic physics not only because they provide benchmarks for the critical evaluation of theoretical calculations but also because of the demands which arise from the other areas such as astrophysics and plasma physics. In the past decade, considerable attention has been attracted to the so-called inner-valence excited states in rare-gas atomic ions. These states have been observed in the satellite spectra of outer-shell photoionization [1] and their formation is generally interpreted as a result of ionization of a valence electron and simultaneous excitation of another one to an unoccupied Rydberg orbital. The photoexcited inner-valence ionic states are often subject to autoionization [2] which contributes significantly to the atomic photo-double-ionization [3]. Photoexcitation and autoionization of these states have been studied in a number of experimental and theoretical investigations [4–10].

The inner-valence excited states can also be reached by the resonant Auger transitions from the core-excited states. The use of resonant Auger decay has some advantages since in this way one can reach the states which are hardly accessible via the outer-shell photoionization because of their weak coupling to the direct ionization channel. The use of the resonant Auger decay has been limited by the broad photon bandwidths and 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 significantly. If the excitation photon bandwidth is smaller than the natural width of the core-excited resonance, the profile of the observed resonant Auger line is given by the convolution between the instrumental line shape function and the Lorentian profile with the width determined by the lifetime of the final ionic state. The instrumental function is in turn given by the convolution of the monochromator and analyzer line shape functions and Doppler broadening due to thermal motion of the sample gas [11–13] and generally well described by a Gaussian profile or a sum of Gaussian profiles. With the decrease of the monochromator and analyzer bandwidths, the instrumental function is eventually governed by the Doppler broadening, as long as the gaseous samples are in the gas cell at room temperature. Thus, if one can suppress the Doppler effects, one can in principle reach the ultimate resolution. The Doppler energy shifts can be described by the scalar product between the electron momentum and that of the emitter. Thus, the Doppler effect can be suppressed if one uses the molecular beam with a negligible transverse velocity component and if the emitted electrons are sampled perpendicular to the molecular beam. In this way, we have successfully achieved unprecedented resolving power, i.e., over 10 000, in energy analysis of Auger electrons. This resolution allows us to obtain the natural widths of the inner-valence excited states.

As a typical example, we consider here the Ne$^+$ $2s2p^5(^{1,3}P)nl$ states. Such states have been observed as satellites in the Ne $2s$ photoionization spectrum. The strongest satellites belong to the $2s2p^5(^{1,3}P)np$ ^2S series. The series $2s2p^5(^1P)np$ ^2S is rather broad, the lowest members of the series being the broadest. The measured width of the $2s2p^5(^1P)3p$ ^2S state is 410 meV [5]. The origin of such a large width was clarified by Armen and Larkins [4] and Sinanis *et al.* [7]. They showed that there are two types of the autoionization channels which contribute to the width. One is so-called inner-valence Auger transitions, which are similar to the usual Coster-Kronig transitions, such as $2s2p^5(^1P)3p$ $^2S \rightarrow 2s^22p^4$ ^{2S+1}L. Larger contributions to the width of the $2s2p^5(^1P)3p$ ^2S

state come from the so-called valence multiplet-changing (intermultiplet) transitions $2s2p^5(^1P)3p\,^2S \rightarrow 2s2p^5\,^3P$. These transitions become possible because of the strong singlet-triplet splitting of the $2s2p^5$ configuration and are characterized by a very small energy (≈ 0.3 eV) of the emitted Auger electron. In the $Ne^+\ 2s2p^5(^1P)3p\,^2S$ state, the valence intermultiplet transition is favored by large angular factors and radial integrals that lead to a very large width of the order of 0.5 eV [4]. Because three open subshells are involved, the inner-valence Auger transitions and especially the low-energy valence intermultiplet transitions are very sensitive to electron correlations [7]: this makes them especially interesting for further investigations. In early calculations [4] four other series of inner-valence excitations with an np outer electron, $2s2p^5(^{1,3}P)np\,^2P$ and $2s2p^5(^{1,3}P)np\,^2D$, have been predicted. Their calculated widths are in general an order of magnitude smaller than for the $2s2p^5(^1P)3p\,^2S$ state; the expected widths of these states are 20–60 meV [4]. These levels have never been seen in the photoionization spectra since they are weakly coupled to the direct photoionization channel.

In this Letter, we report the first spectroscopic observation of the $2s2p^5(^{1,3}P)3p\,^2P$ and $2s2p^5(^{1,3}P)3p\,^2D$, as well as $2s2p^5(^{1,3}P)3p\,^2S$, in Ne^+ and the measurements of their lifetime widths, using Doppler-free resonant Raman Auger spectroscopy. The population of the $2s2p^5(^{1,3}P)3p\,^2P$ and ^2D states is strongly enhanced by the resonant Auger decay. The resonant Auger transitions to these states have already been observed [14–16] as well as their decay to the doubly charged Ne^{2+} [16,17]. However, because of poor overall resolution of the early experiments, the multiplet structure of these states could not be resolved.

The present experiment has been carried out on the c-branch of beam line 27SU [18] at SPring-8, the 8-GeV synchrotron radiation facility in Japan. The radiation source of this beam line is a figure-8 undulator [19]. 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. Thus, one can perform the angle-resolved electron spectroscopy with an electron spectrometer fixed in the horizontal direction, switching the direction of the polarization vector by changing only the undulator gap. The monochromator installed on this beam line has a resolving power of over 14 000 at photon energy 867.12 eV corresponding to the Ne $1s \rightarrow 3p$ excitation.

The "Doppler-free" electron spectroscopy system consists of a hemispherical electron spectrometer of mean radius 200 mm (Gammadata-Scienta SES-2002) and a molecular beam source (MB Scientific MBS JD-01) [20]. Briefly, the beam device has an orifice of 1 mm × 8 mm, covered by a 1-mm thick microchannel plate with the channel diameter 10 μm. The direction of the molecular beam is vertical. The photon beam crosses the molecular beam at right angles and the length of the

interaction section is ~ 8 mm. The lens axis of the spectrometer is horizontal and thus perpendicular to the molecular beam. The entrance slit of the spectrometer is parallel to the interaction section. In this alignment, the Doppler effect can be suppressed, because the transverse velocity component of the molecular beam is negligible.

We recorded sequentially and repeatedly the resonant Raman Auger spectra for transitions to the Ne^+ $2p^4(^1D)3p\ ^2P$, ^2D, and ^2F states and to the Ne^+ $2s2p^5(^{1,3}P)3p\ ^2S$, ^2P, and ^2D states via $1s \rightarrow 3p$ excitation. The final states $Ne^+\ 2p^4(^1D)3p\ ^2P$, ^2D, and ^2F do not decay further via electron emission. The energy separations between the doublet components are negligible according to the calculations described below. A separate measurement indeed confirms that a line profile of each of these Auger lines coincides with that of the Ne $2s$ and $2p$ photolines within the experimental uncertainties. Thus the summed-up spectrum for the transitions to the Ne^+ $2p^4(^1D)3p\ ^2P$, ^2D, and ^2F states was used for extracting the instrumental function. It turned out that the instrumental function can be well described by the sum of the two Gaussians with the widths (FWHM) of 63 and 101 meV; the ratio for the integrated areas of these two Gaussians is 1:0.45. To the first approximation the Gaussian with the width 63 meV corresponds to the convolution of the monochromator and analyzer line shape functions (i.e., pure Doppler-free component) while the Gaussian with the width 101 meV corresponds to a convolution of the Gaussian of 63-meV width and the Doppler profile with the width of 79 meV at room temperature.

The upper panel of Fig. 1 shows a portion of the electron spectra corresponding to the transitions to Ne^+ $2s2p^5(^1P)3p$ via the Ne $1s \rightarrow 3p$ excitation at photon energy 867.12 eV, whereas the lower panel shows a portion of the electron spectra corresponding to the transitions to $Ne^+\ 2s2p^5(^3P)3p$ via the Ne $1s \rightarrow 3p$ excitation. The relative intensity scale for the spectra recorded at two different polarizations is determined from the fact that the intensity of the spectrum integrated over the three components of $Ne^+\ 2p^2(^1D)3p\ ^2P$, ^2D, and ^2F is independent of the polarizations [13]. In the upper panel, two lines 1 and 2 are clearly resolved in the 90° spectrum. In the 0° spectrum, line 1 becomes weak and furthermore we notice one more broad line 3 at the foot of line 2. In the lower panel, lines 5 and 6 are resolved in the 90° spectrum, whereas line 5 is suppressed and a line 4 appears in the 0° spectrum. These transitions were observed previously with the instrumental width of ~ 1 eV [16]. At that resolution, none of the structures shown in Fig. 1 were separated. In order to extract the transition energies, branching ratios, the anisotropy parameters β, and the natural widths of these lines, we have carried out a fitting assuming that the line profile is described by a convolution of the Lorentzian function and the instrumental function with the two Gaussian components discussed above. In the fitting the unknown Lorentzian width of each line is constrained to be the same for
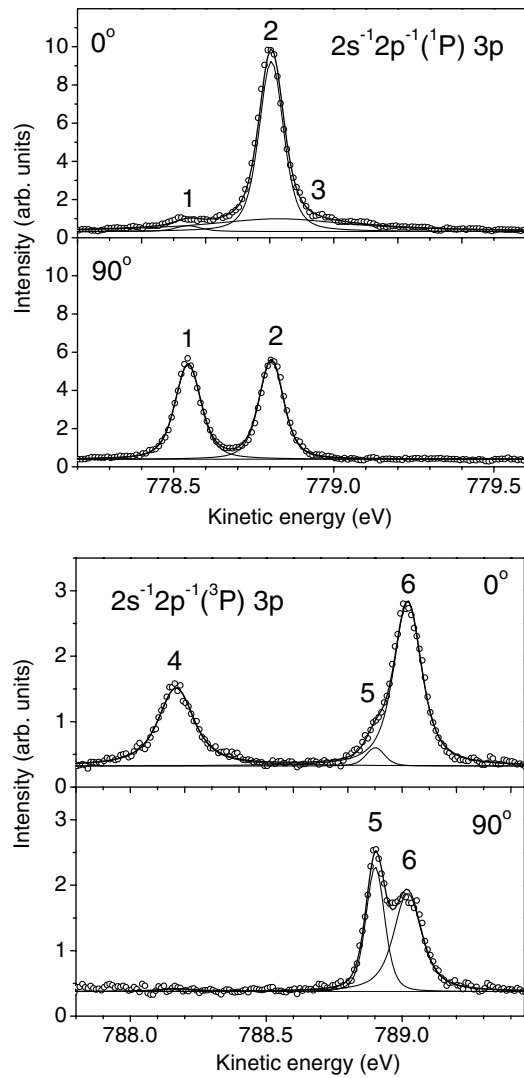
FIG. 1. A part of the electron spectra of the resonant Raman Auger transitions to the Ne^+ $2s2p^5(^1P)3p$ ^2P, ^2D, and ^2S states (line numbers 1, 2, and 3, respectively) and to the Ne^+ $2s2p^5(^3P)3p$ ^2S, ^2P, and ^2D states (line numbers 4, 5, and 6, respectively) via the Ne $1s^{-1}3p$ state at a photon energy of 867.12 eV with horizontal (upper) and vertical (lower) polarizations. The thick lines are the results of the fit, and the thin lines are the individual components.

both 0° and 90° spectra. Values of transition energies, β, and branching ratios obtained from the fitting are summarized in Table I.

In order to assign the observed lines, we have compared the measured energies, the β values, and the branching ratios with the calculated ones. To this end, we have carried out a series of *ab initio* computations using the multiconfiguration Dirac-Fock (MCDF) approach. The Auger decay amplitudes are calculated by means of the computer program package RATIP [21] based on the MCDF atomic structure code GRASP92 [22]. Both the initial and the final ionic state configuration interaction are taken into account. In the initial state there are two strongly mixed resonant states with the total angular momentum $J = 1$ with dominant configuration $1s^{-1}3p$, which may be photoexcited from the ground state of the Ne atom. According to our calculations, however, the dipole excitation strength for one of them is 500 times larger than that for the other. Therefore, we ignored the second one and considered the decay of only one resonance to different channels. The resonant state wave function expansion consists of 422 configuration state functions (CSF) which include all possible single and double excitations within the configuration space of $1s, 2s, 2p-, 2p, 3s, 3p-, 3p, 3d-, 3d$ orbitals. For the description of the final ionic states ($J = 1/2, \ldots, 7/2$) with the dominant configuration $2s2p^53p$ we took into account 433 CSF which include all single and double excitations within the configuration space of $2p-, 2p, 3s, 3p-, 3p, 3d-, 3d, 4p-, 4p$ orbitals. The continuum wave functions for the Auger electron were calculated in the potential of the final ion, the exchange interaction being properly taken into account.

The results of calculations are shown in Table I. Comparing the measured values with the calculated ones averaged over the unresolved final J states for each multiplet, we attribute lines 1, 2, and 3 to the transitions to the $2s2p^5(^1P)3p$ ^2P, ^2D, and ^2S states, respectively, and the lines 4, 5, and 6 to the transition to the $2s2p^5(^3P)3p$ ^2S, ^2P, and ^2D states. The measurements are in reasonable agreement with the calculations for both the β values and the branching ratios.

TABLE I. Measured and calculated transition energies, anisotropy parameters β, and branching ratios (for each parent state) for the resonant Auger decay to the $2s2p^5(^1P, ^3P)3p$ ^2S, ^2P, and ^2D states of Ne^+. The uncertainties of the measured transition energies are ~0.02 eV in relative scale and ~0.1 eV in absolute scale.

Final state	E_k (eV)		β		Br. ratio	
	Expt.	Theor.	Expt.	Theor.	Expt.	Theor.
$(^1P)3p$ ^2P	778.55	776.40	-0.94 ± 0.06	-0.996	0.35 ± 0.02	0.340
$(^1P)3p$ ^2D	778.81	776.66	0.15 ± 0.06	0.200	0.54 ± 0.02	0.561
$(^1P)3p$ ^2S	778.83	776.43	$2.0^{+0.0}_{-0.2}$	2.000	0.12 ± 0.02	0.099
$(^3P)3p$ ^2S	788.17	786.51	1.8 ± 0.2	1.998	0.15 ± 0.02	0.153
$(^3P)3p$ ^2P	788.90	787.52	-0.8 ± 0.1	-0.928	0.28 ± 0.02	0.324
$(^3P)3p$ ^2D	789.02	787.64	0.15 ± 0.05	0.156	0.57 ± 0.02	0.523

TABLE II. Measured and calculated widths in meV for the $2s2p^5(^1P, ^3P)3p \,^2S$, ^2P, and ^2D states of Ne$^+$.

Final state	Experiment		Theory	
	This work	Ref. [5]	Ref. [4]	Ref. [7]
$(^1P)3p\,^2P$	42 ± 5		20.7	
$(^1P)3p\,^2D$	34 ± 5		40.2	
$(^1P)3p\,^2S$	530 ± 50	410 ± 50	687	510
$(^3P)3p\,^2S$	120 ± 10	110 ± 40	18.8	122
$(^3P)3p\,^2P$	19 ± 5		10.3	
$(^3P)3p\,^2D$	80 ± 10		62.3	

The natural width has also been determined from the above described fitting procedure. The results are presented in Table II together with the existing theoretical calculations and previous measurements. In order to cross-check the results we have also measured the second-step Auger spectrum which results from the decay of the $2s2p^5(^{1,3}P)3p\,^{2S+1}L$ states. The energies of the second-step Auger lines are much lower than those of the first-step resonant Auger lines and thus the Doppler broadening is negligible even when we use the samples in the gas cell at room temperature. The width of the second-step Auger line depends on the electron analyzer bandwidth but is independent of the photon bandwidth. The observed width depends also on natural lifetimes of the initial and final states of the second-step Auger decay. In the present case, the lifetime broadening of the final state is negligible. We have carried out the fitting using a Voigt profile, with a known Gaussian width. The Lorentzian widths extracted from the fitting agree well with the ones obtained from the Doppler-free resonant Raman Auger spectra in most cases. The study of the second-step Auger decay will be described elsewhere.

Our results for the $2s2p^5(^{1,3}P)3p\,^2S$ lines agree reasonably well with those extracted from the early measurements for the satellite structure of Ne photoionization [5]. The measured widths of these states agree better with the elaborate theoretical calculations by Sinanis *et al.* [7] than the calculations by Armen and Larkins as obtained in a single-configuration Hartree-Fock approximation [4]: the single-configuration approach fails to reproduce the experimental width of the $2s2p^5(^3P)3p\,^2S$ state. Obviously, these transitions are very sensitive to electron correlations and can be well described only if the correlations are fully taken into account [7]. The widths of other multiplets ^2P and ^2D are much smaller than $2s2p^5(^1P)3p\,^2S$. The measured values are rather close to the predictions of Armen and Larkins [4]. An analysis of the contributions to the width of the $2s2p^5(^1P)3p$ states from the inner-valence participator Auger transitions and the inter-multiplet Auger transitions [4] shows that the former is dominant for the ^2P and ^2D lines while the latter determines the width of the ^2S line.

In conclusion, we have reported the observation of the lowest terms of the Ne$^+$ $2s2p^5(^{1,3}P)np\,^2P$ and ^2D series, using the Doppler-free resonant Raman Auger technique. The anisotropy parameters and the branching ratios of the Auger emission via the $1s^{-1}3p$ excitation to those states allow us to identify them unambiguously. The measured lifetime widths of these states are much lower than that of the known $2s2p^5(^1P)3p\,^2S$ state. This confirms the theoretical predictions that the inner-valence Auger transitions are mainly responsible for their decay.

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*Electronic address: ueda@tagen.tohoku.ac.jp
†On leave from Institute of Nuclear Physics, Moscow State University, Moscow 119899, Russia.

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