Three-Step Excitation of Highly Excited Autoionizing States in Atomic Sodium by Use of Laser Beams and Synchrotron Radiation

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We have studied highly excited autoionizing states in atomic sodium, using two laser beams and synchrotron radiation. We have observed the electron spectra resulting from the decay of these $2p^5 3s 4p$, $2p^5 3s 4d$, and $2p^5 3s 5s$ states to the $2p^6\,{}^1S_0$ ground state of Na^+. The excitation energies and the relative oscillator strengths of inner-shell transitions in the excited atoms have been measured.

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In this Letter, we present the first experimental evidence that it is possible to produce and study highly excited atomic states, with use of stepwise excitation by several laser beams to excite one outer electron and synchrotron radiation to excite an inner electron. In our experiment, we used two dye lasers to promote the $3s$ electron of atomic Na to either the $4d$ or the $5s$ excited state via the resonant $3p$ state, and monochromatized synchrotron radiation to excite one of the $2p^6$ electrons to $2p^5 3s$ core-excited states. With the help of electron spectrometry, we have been able to observe electrons produced in the autoionization of several of these $2p^5 3snl$ $(n > 3)$ states and to measure the energies and the excitation functions of a number of them. Our results demonstrate a new capability of studying photoexcitation and photoionization processes in a widely increased number of excited atomic states over a broad range of photon energies. In particular, this new step may constitute an alternative approach to the current studies[1] of highly excited atomic states in which electron-electron correlations as well as screening are expected to produce large effects on the resulting autoionization spectrum.[2]

Two-electron excited atomic states, involving the simultaneous excitation of one inner- and one outer-shell electron, have been the subject of a large number of studies, since the earlier experiments in the rare gases.[3,4] However, these excited atomic states were produced exclusively via correlation effects in two-electron, one-photon transitions. The first experiment involving inner-shell excitation in an excited atom used a pulsed laser and a discharge lamp to measure, in photoabsorption, the energy of two-electron states in alkali metals.[5,6] During the last few years, the combination of a laser beam with a synchrotron radiation (SR) beam as the two sources of photons was successfully achieved[7-10] and used[11,12] to start studies of inner-shell photoionization processes in excited atoms over a wide range of photon energies. However, all these studies involved the excitation of the outer electron to only the first empty orbital. It was thus felt important to test if the broad spectral range accessible with SR could be efficiently combined with several lasers to study, at will, atoms in a widely extended number of highly excited states. Na was chosen for this feasibility experiment, because of the high intensity of SR available in the energy range of inner-shell excitation of a $2p$ electron. Also, Na is a good candidate to study the variation of electrostatic interaction of the excited electrons with the core, compared with correlations between them, while increasing progressively the principal quantum numbers n and n' of the $2p^5 nln'l'$ excited states.

In the work presented here, two laser beams combined with the synchrotron radiation from the Anneau de Collisions d'Orsay (ACO). The three beams are focused onto a weakly collimated sodium beam at the source volume of an electron cylindrical mirror analyzer (CMA). Electrons emitted at an angle of 54°44′ with respect to the CMA axis are energy analyzed. Na atoms are photoexcited to the $5\,{}^2S_{1/2}$ or $4\,{}^2D_{5/2}$ state in two steps by cw single-frequency dye lasers. A ring cavity, working with rhodamine 6G, is used to produce Na atoms excited into the $3\,{}^2P_{3/2}$ state with a typical output power of 600 mW. It is frequency stabilized by monitoring of the fluorescence of an auxiliary Na beam illuminated by a fraction of the laser beam. The second

step of the photoexcitation is achieved by a linear cavity dye laser of lower power (around 60 mW) working with either rhodamine 6G, at 6160 Å (Na $5^2S_{1/2}$) or rhodamine 110, at 5687 Å (Na $4^2D_{5/2}$). It is frequency stabilized with an external Fabry-Perot cavity. A small amount of the beam is also sent to the auxiliary Na beam after mixing with the first laser beam. Its frequency is tuned in order to optimize the intensity of the $4p \rightarrow 3s$ uv line, which is the second step of the radiative cascade occurring when the $5^2S_{1/2}$ or $4^2D_{5/2}$ states are photoexcited. The recording of this fluorescence allows for continuous monitoring of the efficiency of the two-step excitation during the data acquisition. Because of this radiative decay of the $5^2S_{1/2}$ and $4^2D_{5/2}$ states, atoms in the $4^2P_{3/2}$ state are also present in the vapor. The third step of the excitation is produced by the monochromatic SR: It is used, between 30 and 35 eV, to promote an inner $2p$ electron to the $3s$ empty orbital. As a consequence of this three-photon excitation, autoionizing states such as $2p^53s5s$ or $2p^53s4d$, and also $2p^53s4p$, may be produced in the vapor. The electrons emitted in the nonradiative decay of these states to the $2p^6\,{}^1S_0$ ground state of Na^+ are observed with the CMA. Since the density of Na (10^{12} to 10^{13} atoms/cm^3) is high, any laser-induced alignment of excited Na atoms would be destroyed, and the initial state can be considered as being isotropic.

A typical set of electron spectra is presented in Fig. 1. In the upper panel is shown a spectrum with both lasers off and the SR monochromator set at a photon energy $h\nu$ equal to 33.06 eV, with a band pass of 0.2 eV. Photons of twice the first-order photon energy (66.12 eV) are also transmitted through the monochromator and photoionize the $2p$-shell electrons in ground-state Na atoms (peak labeled 2). With the first laser switched on (middle panel), photoelectron peak 1 appears. It is due to the photoionization of $2p$-shell electrons in $2p^63p\,{}^2P_{3/2}$ atoms. Since about 80% of Na atoms are still in the ground state, peak 2 is still present. When the second laser is also switched on (tuned here to the $3p \rightarrow 4d$ transition energy), new electron lines, denoted as 3 and 4, appear (lower panel). Peak 3 is due to autoionization from the discrete states resonantly excited by SR according to the scheme

$$2p^64p\,{}^2P_{3/2} + h\nu(\mathrm{SR}) \rightarrow 2p^53s4p\,{}^2D_{3/2,5/2}, {}^2S_{1/2}.$$

Similarly, peak 4 results from autoionization from the $2p^53s4d\,{}^2F_{5/2,7/2}$ excited states. Peaks 3 and 4 disappear when the SR monochromator is shifted off the resonance region, because the nonresonant $4p$ and $4d$ photoionization cross sections are small at these photon energies, or when laser II is detuned. In the present experiments, it was not possible to observe the low-intensity signal due to photoionization of $2p$ electrons in $2p^64p$ or $2p^64d$ atoms, because of the small population of atoms in these states, typically a few percent, and of the highly increased background when both lasers were tuned on resonance.

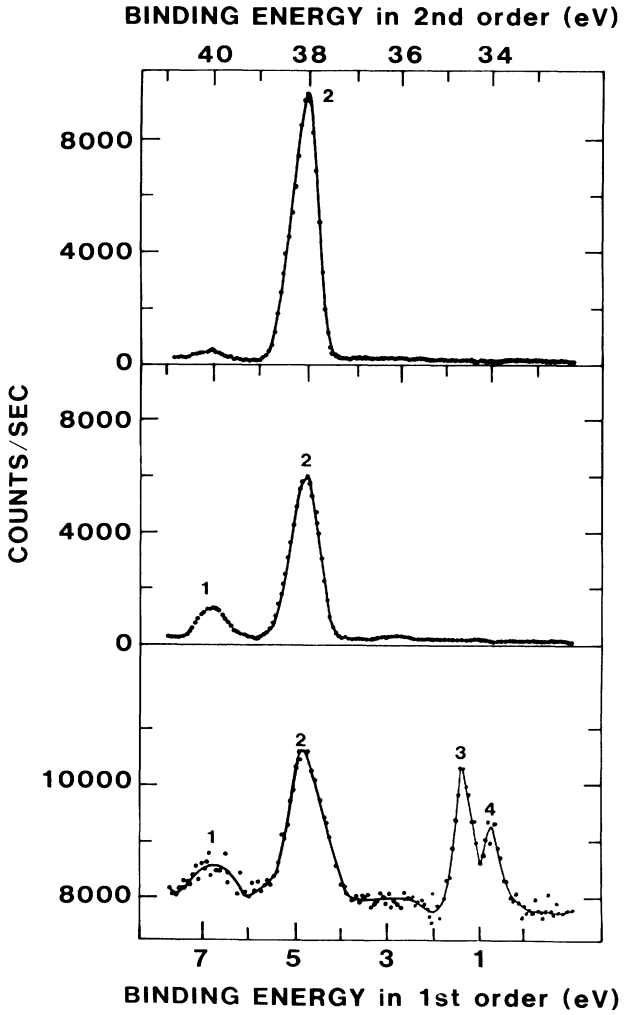

FIG. 1. Top: Photoelectron spectrum of Na taken at $h\nu = 33.06$ eV with both lasers turned off. Peak 2 is due to photoionization of the $2p$-shell electrons by photons of energy equal to twice $h\nu$ or 66.12 eV. Middle: Spectrum taken at the same $h\nu$ with laser I turned on; peak 1 is due to photoionization of the $2p$-shell electrons in $2p^63p$ atoms. Bottom: Spectrum taken at $h\nu$ with both lasers turned on; peaks 3 and 4 are due to autoionization of $2p^53s4p\,{}^2D$ and $2p^53s4d\,{}^2F$ states, respectively.

With a complete set of spectra, it is possible to determine directly three quantities: (i) the absolute kinetic energy scale of the observed electrons, combining the photon energy with the binding energy of $2p$ electrons in ground-state sodium atoms; (ii) the absolute density of Na atoms in the ground state, from the intensity of peak 2, the measurement of the photon flux, the $2p$ photoionization cross section, and the transmission of the CMA; (iii) the density of atoms excited into the $3p$ state, typically 20% to 25% of the ground-state atom density.

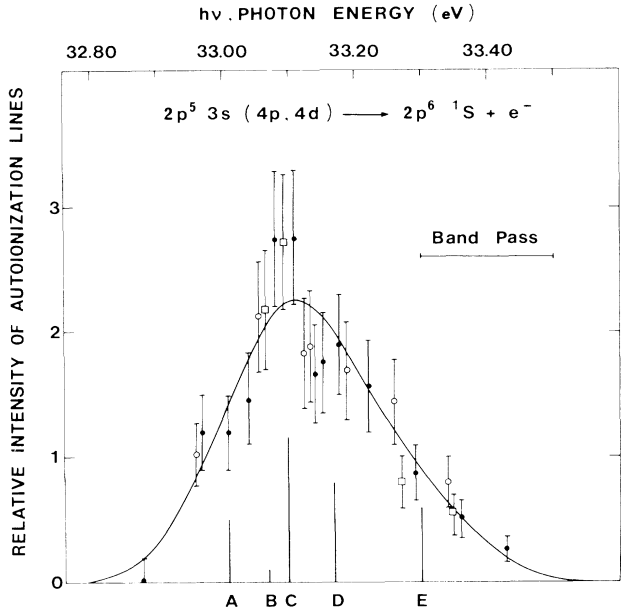

FIG. 2. Excitation function of autoionizing states as a function of photon energy for a SR monochromator band pass of 0.20 eV, in the case of $4d$ excitation. Three series of measurements, solid circles, open circles, and open squares are shown. The energies of autoionizing states A to E are the results of this experiment and are given in Table I, except for line B, taken from the A-B splitting measured in Ref. 6 (see text for details).

From the kinetic energy scale, it is possible to establish the binding energy (E_B) scales (see Fig. 1), in order to identify the observed structures.

In order to measure the energy and the excitation function of the autoionizing states, we scanned the photon energy range between 32.50 and 33.50 eV in both cases of laser excitation ($4^2D_{5/2}$ and $5^2S_{1/2}$). At each photon energy, we determined the kinetic energy and the normalized intensity of the autoionization lines. In the absence of a $2p$ photoelectron signal proportional to the density of atoms in the $2p^6nl$ states, we measured the ratio between the integrated area under lines 3–4 and under line 1.

Our results for the $4d$-excitation case are shown in Fig. 2. Three sets of data, each of them resulting from an independent series of measurements, are in excellent agreement with one another. Outside of the photon energy range marked in the figure, we observed autoionization lines arising only from the decay of $2p^53s3p$ states. In particular, we did not detect the existence of any autoionizing state produced by a dipole-forbidden transition. The solid line is the result of a computation established on the measured energies of the autoionizing states, lines marked A to E in the figure. Lines A and B correspond to transitions from the $2p^64p\,^2P_{3/2}$ to the $2p^53s(^1P)4p\,^2D_{5/2},^2S_{1/2}$ (A) and $^2D_{3/2}$ (B) states; lines C, D, and E correspond to the three dipole-allowed transitions $2p^64d\,^2D_{5/2}\rightarrow 2p^53s4d\,^2F_{5/2,7/2}$, and $^2P_{3/2}$, respectively. Since the natural width of the autoionizing states is negligible compared with the band pass of the monochromator, a Gaussian line profile was centered on each state energy; then, the relative intensity of each bar was adjusted to obtain the best fit to the experimental data. The resulting line is quite sensitive to small variation of the relative intensities. A simpler excitation curve was obtained for the case of $5s$ excitation: Only two unresolved states $2p^53s5s\,^2P_{1/2,3/2}$ were accessible by excitation from the $2p^65s\,^2S_{1/2}$ state, in addition to the $2p^53s4p$ states still present in the vapor.

We give, in Table I, our results for the energies and the assignments of the $2p^53snl$ autoionizing states. In contrast with the case of $2p^5(^2P)3s3p\,^{1,3}P$ states, the classification proposed in column 3 has been changed to $2p^53s(^{1,3}P)nl$, because the main exchange interaction is now between the $2p^5$ core and the $3s$ electron.[6] In the

TABLE I. Excitation energies $h\nu$ of autoionizing states in laser-excited atomic sodium: $2p^6nl\rightarrow 2p^53snl$.

Initial state nl	Line[a]	Classification	$h\nu$[b] (eV)	$h\nu$[c] (eV)	State energy[d] (eV)	Relative intensity (arbitrary units)[e]
$4p\,^2P_{3/2}$	A	$2p^53s(^1P)4p\,^2D_{5/2},^2S_{1/2}$	33.01(3)	33.02	36.76(3)	100
	B	$2p^53s(^1P)4p\,^2D_{3/2}$	(33.07)	33.08	36.82(5)	20
$4d\,^2D_{5/2}$	C	$2p^53s(^1P)4d\,^2F_{7/2}$	33.10(3)		37.38(3)	170
	D	$2p^53s(^1P)4d\,^2F_{5/2}$	$^2F_{5/2}$	33.17(4)	37.45(4)	110
	E	$2p^53s(^1P)4d\,^2P_{3/2}$	$^2P_{3/2}$	33.30(5)	37.58(5)	80
$5s\,^2S_{1/2}$	F	$2p^53s(^1P)5s\,^2P$	$^2P_{3/2}$	33.15(3)	37.38(3)	400
∞		$2p^53s$	33.32[f]		38.46	

[a]As marked in Fig. 2 (except F).
[b]Photon energy, present measurements, except for line B deduced from Ref. 6.
[c]From Sugar *et al.*, Ref. 6.
[d]Referred to the $2p^63s\,^1S$ ground state of Na.
[e]These intensities have been tentatively normalized to the same $4p$ population (see text).
[f]From Moore, Ref. 13. normalized to the same $4p$ population (see text).

TABLE II. Binding energies of $2p$ electrons (in $2p^6nl$) and $3s$ (in $2p^53snl$ configurations) electrons in Na. The $2p$ and $3s$ binding energies in the $2p^63s$ ground state of Na are 38.0 and 5.14 eV, respectively (Ref. 13).

nl	$2p$ E_B[a] (eV)	$3s$ E_B (eV)
$3s$		7.1[b]
$3p$	40.1[c]	8.0[c]
$4d$	44.7	11.5[d]
$5s$	44.9	11.7[d]
∞	47.3	13.9[a]

[a]From Moore, Ref. 13.
[b]With the data of Wolf *et al.*, Ref. 16.
[c]Also measured by Bizau *et al.*, Refs. 7 and 11.
[d]Deduced from the present measurements.

case of the $2p^53s(^1P)4p\ ^2D_{5/2}$ state, our measurement is in excellent agreement with the value previously measured.[6] Our energy values are also in accord with the results of a recent configuration-average calculation with the code RCN/RCG calculation which gives 36.43 and 37.18 eV for $2p^53s4p$ and $2p^53s4d$ states, respectively.[14] The relative intensities given in column 7 result from the fitting procedure to the experimental data, after correction for the different relative populations of the $2p^64p$ state in the case of $4d$ ($4d$:$4p$ = 140:100) or $5s$ ($5s$:$4p$ = 190:100) excitations, as calculated from a steady-state radiative model based on the Einstein coefficients.[15] With the assumption that the radiative decay of the $2p^53snl$ states is negligible, these intensities are proportional to the oscillator strengths of the corresponding inner-shell excitation transitions.

It is remarkable that the excitation energy of a $2p$ electron to the $3s$ orbital remains practically constant, independent of the orbital in which the outer electron has been excited. This shows that the variation of the screening due to this outer electron is about the same for the $2p$ and $3s$ subshells. It is interesting to note also that the sum of the relative oscillator strengths for transitions from $2p^64d$ to $2p^53s4d$ states (360 in arbitrary units) and from $2p^65s$ to $2p^53s5s$ states ($\simeq$400) is about the same. A similar conclusion was already established for transitions $2p^63p \rightarrow 2p^53s3p$ compared with $2p^6 \rightarrow 2p^53s$. The difference for the case of the transition $2p^64p \rightarrow 2p^53s4p$ is yet unexplained, though various origins can be suggested (e.g., radiation trapping due to the high sodium density, differences in the radiative decay rates, etc.).

From our results, it is also possible to extract the variation of the E_B of a $3s$ electron in the $2p^53snl$ configurations. In contrast to the transition energies, the absolute variation of the E_B is quite dramatic, as can be seen in Table II, where we also indicate the E_B of a $2p$ electron. The creation of a $2p$ core hole first increases this E_B by about 40% (5.14 to 7.1 eV). Then, one sees a continued increase of this E_B with increasing values of the nl quantum numbers of the excited electron: This change in the E_B reflects the high sensitivity of this atomic parameter to shielding and correlations between the excited and the core electrons.

We have successfully demonstrated the feasibility of experiments combining several laser beams and synchrotron radiation to create and to study highly excited atomic autoionizing states. Large improvements could be expected from the availability of new storage rings, designed for the production of undulator radiation that should allow the extension of these experiments to the study of excited atomic states in which the two electrons would be simultaneously excited to high n orbitals.

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