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# Shakedown in core photoelectron spectra from aligned laser-excited Na atoms

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In an experiment combining a state-of-the-art visible laser system with the vacuum ultraviolet beamline I411 at the storage ring MAX II, shakedown satellite lines in the $2p$ photoelectron emission of excited Na atoms have been observed. A close investigation of these lines shows a strong dependency of the line intensities from the linear polarization angle of the laser light. The shakedown electrons are preferably emitted into the direction of the laser electric field vector.

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Synchrotron-based photoemission spectroscopy is a well-established technique to study the electronic structure of free atoms, which is fundamental for the understanding of the properties of molecules, clusters, and condensed materials. In most photoelectron studies the initial state is either the ground state or a thermically excited state. However, it was realized relatively early that it is also necessary to study photoemission from atoms in excited states [1]. This leads to possible effects due to polarization and the additional energy in the system.

Combined laser and synchrotron spectroscopy has been used to investigate laser polarized ground states of transition metals to compare the dichroic effect with the magnetic dichroism on solid states [2] and to examine laser tailored atoms [3]. The $2p$ photoemission of laser-excited atomic sodium has been examined by Cubaynes *et al.* [4] at a bending magnet beamline of the superACO storage ring. Recently, a much better resolution of these lines has been obtained by the same group at the third generation synchrotron radiation facility Advanced Light Source (ALS) [5]. These important results show the great potential for the detailed information this method can give about the electronic structure of atoms.

Beside the importance for understanding the structure of free atoms, laser-excited and aligned atoms can also serve as model systems for more complex systems such as molecules, clusters, and conjugated polymers, and for solid state and surface physics. A good example demonstrating the importance of atomic effects for understanding the findings of inner shell photoelectron spectroscopy in the solid state, are the striking similarities found in the angular dichroism structure of magnetized thin layers with laser oriented atoms for chromium [6], gadolinium, and europium [7].

Photoelectron spectroscopy is classically described in terms of the direct photoionization and shake-satellite [8,9] processes. In the shakeup processes, the single photoionization is accompanied by a change of the valence shell configuration. For excitation far from the threshold the so-called normal (monopole) shake process dominates. In this process the angular momentum of the photon is given to the leaving photoelectron. For near threshold excitation conjugate shakeup is also observed. Here the angular momentum of the photon is taken by the remaining ion.

In ground-state spectroscopy, only shakeup and shakeoff processes can be observed. In these processes the emitted electron has a reduced kinetic energy with respect to the direct photoemission. This energy is used to excite or ionize a valence electron. In photoionization from excited atoms the so-called conjugate shakedown (CSD) process becomes possible. In CSD the laser-excited valence electron undergoes a dipole transition to another orbital while the excess energy is transferred to a core electron, which is released in a monopole transition. Due to the laser energy, the resulting electrons are observed with a higher kinetic energy compared with the main photolines of nonlaser excited atoms that have the same final states. It is obvious that this process is not possible for atoms with an unexcited ground state. To get reasonable resolution and count rates, third generation synchrotron sources in combination with state-of-the-art laser systems are needed.

In this paper we present the observation of a shakedown process in the photoionization of atomic sodium in the $^2P_{3/2}$ state with an energy of 2.1 eV relative to the ground state. The beam of atomic sodium was produced by a resistively heated oven at a relatively low temperature of 230 °C to give a vapor pressure of $10^{-3}$ mbar [10] in the crucible. The atoms have been excited by linearly polarized yellow (588.995 nm, $h\nu$=2.1 eV) light of a single mode tunable liquid dye laser. The laser intensity of 450 mW focused to an approximately 1-mm focus has been about two orders of magnitude above saturation so that fluctuations of the laser intensity didn't lead to changes of the amount of excited

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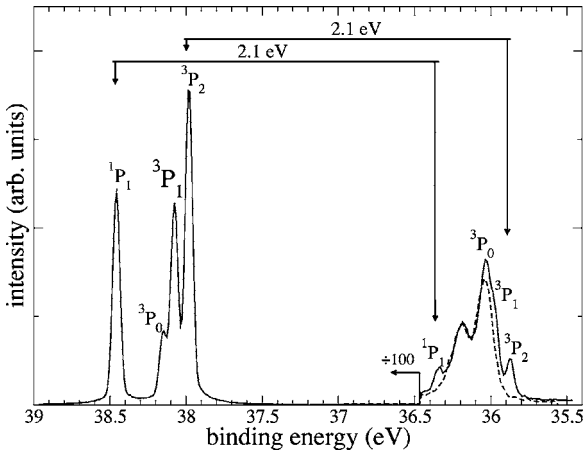


FIG. 1. Na $2p^{-1}$ photoemission with shakedown lines. The main lines are scaled down by a factor of 100. The shakedown spectrum gives the same final states as the direct emission shifted by the excitation energy of 2.1 eV. They are superimposed by a broadend cluster feature (dashed line).

atoms in the beam. The photoelectron spectra have been recorded with the equipment built in Oulu [11], containing a Scienta SES-100 electron spectrometer in the magic angle of 54.7° with respect to the electric field vector of the synchrotron radiation.

Figure 1 shows an overview over the spectrum showing the direct $2p$ photoemission at binding energies between 35.5 and 39 eV with an ionization energy of 61 eV. The experimental line width has been determined to be 60 meV. The binding energy scale has been calibrated with respect to optical data [12]. In this spectrum two structures are clearly visible. The structure between 37.8 and 38.6 eV is the direct sodium $2p^6\,3s\,^2S_{1/2}\rightarrow 2p^5\,3s\,^{1,3}P_J$ emission, i.e., ordinary photoemission from the ground state. The $2p$ hole couples to the $3s$ valence electron giving rise to one $^1P$ and three $^3P$ final states. The same final states can be reached by the $2p^6\,3p\,^2P_{3/2}\rightarrow 2p^5\,3s\,^{1,3}P_J$ conjugate shakedown transition in the initially laser-excited atoms. Having the same final states but a laser-excited initial state, this structure must obtain a kinetic energy that is higher than for photoemission to the same final states from the nonexcited ground state with an amount corresponding to the laser photon energy, i.e., 2.1 eV. The shakedown lines will thus be situated at 2.1 eV lower apparent binding energy than the main lines from nonlaser excited sodium, i.e., between 35.7 and 36.5 eV apparent binding energy. This energy range has been scaled up by as much as a factor of 100 to make it comparable to the main lines.

It is clearly visible from Fig. 1 that the shakedown feature contains an additional structure that is broader and does not fit into the final state scheme. This structure turned out to be independent of the laser excitation and to have a fixed intensity ratio compared with the direct sodium $2p$ emission. The dashed line in the figure shows this structure without laser excitation. The clear dependence of this structure from the sodium beam suggests that these lines originate from small sodium clusters. It is well known that sodium easily forms clusters during evaporation. To our knowledge no photoemission spectra from small sodium clusters have been reported.

To analyze the atomic line free from the cluster feature, the spectrum taken without laser excitation has been fitted by two Gaussian profiles with a width of 114 and 162 meV separated by 159 meV and a intensity ratio of 1.65. These parameters give a reasonable agreement with the spectrum and have been used to obtain the contribution of the atomic lines from the spectrum. A closer examination of the shakedown and cluster lines is given in Fig. 2(a). The triangles show datapoints taken with a laser electric field vector tilted 45° with respect to the horizontal electric field vector of the synchroton radiation and 9.7° with respect to the spectrometer. For this spectrum a least square fit to the data and the decomposition into the atomic shakedown part and the direct $2p$ emission from the clusters is shown. For fitting the lines the above-given structure of the cluster feature, as well as the energy splitting of the $^1P$ and $^3P$ finals states, has been fixed to reduce the amount of free parameters and thereby increase the accuracy of the fitted intensities.

In Fig. 2(b) the results of similar fittings to spectra taken at four different laser polarizations are shown. In order to compensate for different count times, sodium densities, and synchrotron radiation intensities, the spectra are scaled to the

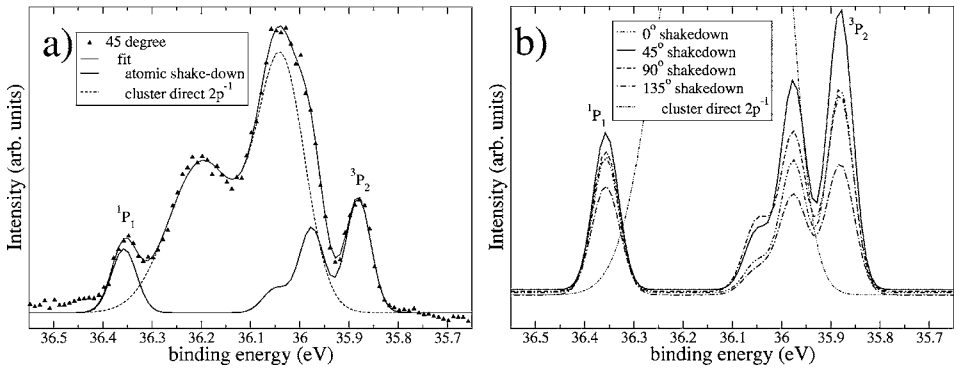


FIG. 2. Na $2p\,^6 3_p\,^2P_{3/2}\rightarrow 2p\,^5 3_s\,^{1,3}P_J$ shakedown lines superimposed by the direct $2p$ emission of sodium clusters. The left part (a) shows a recording of the spectra with the laser electric field in 45° with respect to the synchrotron radiation electric field vector. A decomposition has been done by performing a least-square fit of the cluster contribution and the four atomic lines with known binding energy. The right part (b) shows the results of the fits for four different angles of the laser polarization. A very marked dichroism is observed.

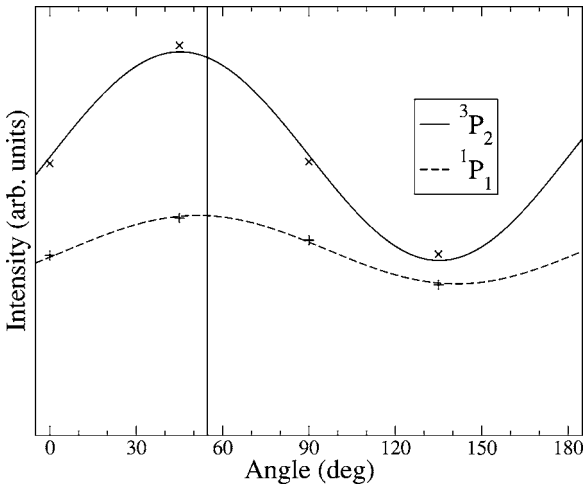


FIG. 3. Dependence of the Na $2p^6 3_p\ ^2P_{3/2} \rightarrow 2p^5\ 3_s\ ^1P_1$ and $^3P_2$ shakedown lines from the angle between the electric field vectors of synchrotron radiation and laser light. The vertical line at 54.7° marks the magic angle. For this angle the laser electric field vector is parallel to the direction of the detected electrons. The lines are least square fits of cosine functions to the data.

same intensity of the cluster signal. A clear dependency of the shakedown lines from the polarization of the laser light is observed. The electrons seem to be preferably emitted into the magic angle of 54.7° when the electric field of the laser light is tilted to 45°. For a laser electric field vector at 135° the shakedown lines are clearly reduced. These angular variations can be explained by linear dichroism, an effect that is well known in linearly aligned atoms [7]. Compared with earlier works on laser excited sodium [5], the spectra in this paper have been taken with considerably lower temperature (230 °C). This leads to a reduced vapor pressure and thereby provides reduction of radiation trapping effects that would destroy the alignment of the excited state. So a high grade of linear alignment of the excited sodium atoms can be expected in the present paper. Figure 3 shows the angle variations of the electron emission leading to the final states $^1P_1$ (+ symbol) and $^3P_2$ (× symbol).[1]

The angular distribution of the photoelectron emission can be described by the formulae given in the paper of Baier *et al.* [13]. In the notation of this paper, the angular-resolved photoemission cross section can be described by the equation [13,14]

$$\frac{d\sigma}{d\Omega} = \frac{\pi\alpha\omega}{3\sqrt{2J_0+1}} \sum_{k_0 k k_\gamma} \rho_{k_0} B_{k_0 k k_\gamma} F_{k_0 k k_\gamma} \equiv \sum_{k_0 k k_\gamma} \sigma_{k_0 k k_\gamma}, \quad (1)$$

where $\omega$ is the frequency of the ionizing radiation, $\alpha$ denotes the fine-structure constant and $J_0$ the total angular momentum of the initial state. The factors $\rho_{k_0}$ describe the initial state polarization, $F_{k_0 k k_\gamma}$ describe the geometry of the experiment and $B_{k_0 k k_\gamma}$ describe the process of photoionization. The $B$ parameters contain the two-electron matrix elements describing the shakedown process. To simplify the following discussion we call the addends in this equation $\sigma_{k_0 k k_\gamma}$.

In the presented case of the Na $2p^6\ 3p\ ^2P_{3/2} \rightarrow 2p^5\ 3s\ ^{1,3}P_J$ shakedown transition, the coefficients $k_0$ in Eq. (1) are limited to $k_0=0,2$ due to the total angular momentum $J_0=3/2$ of the initial state and the linear polarization of the laser light. For $k_0=0$ only the combinations $(k_0 k k_\gamma)=(000)$ and (022) are allowed. However, $F_{022}$ vanishes for the detection of photoelectrons in the magic angle so that only $\sigma_{000}$ describing the angle-integrated total cross section remains in the given experiment.

The angular distribution of the photoelectrons due to the alignment of the initial state is described by the coefficients with $k_0=2$. For the given experimental conditions and $p$ symmetry of the outgoing photoelectron only $\sigma_{202}$, $\sigma_{220}$, and $\sigma_{222}$ distribute to the photoelectron cross section. The geometric factors of these addends can be taken from Table 1 of reference [13]

$$F_{202} = -\frac{\sqrt{5}}{2\sqrt{6}}[1 + 3\cos 2\varphi_a], \quad (2)$$

$$F_{220} = \frac{\sqrt{5}}{4\sqrt{3}}[1 + 3\cos 2(\varphi_a - \varphi_e)], \quad (3)$$

$$F_{222} = \frac{\sqrt{5}}{4\sqrt{21}}[-2 + 3\cos 2(\varphi_a - \varphi_e) + 3\cos 2\varphi_a]. \quad (4)$$

With $\varphi_a$ denoting the angle between the electric field vector of the laser and the synchrotron radiation, and $\varphi_e$ being the angle where the photoelectrons are detected, i.e., the magic angle of 54.7°.

Even without detailed knowledge of the photoemission process and the $B$ parameters some basic conclusions can be drawn out of this model. To emphasize this we briefly discuss the meanings of the three terms.

In $\sigma_{202}$, $k=0$ denotes evenly distributed photoelectrons; thus the detection angle does not appear in Eq. (2). $k_\gamma=2$ stands for a dipole distribution with respect to the relative angle between the photon polarizations. The resulting geometric factor gives a dipole distribution with an extremum for parallel electric field vectors of laser light and synchrotron radiation. This term vanishes for a magic angle between the electric field vectors.

In $\sigma_{220}$, on the other hand, $k_\gamma=0$ gives an independency of the relative polarizations. The contribution of this part to the total angular dependence is a dipole distribution around the laser polarization without any dependency from the synchrotron radiation polarization [Eq. (3)].

Finally $\sigma_{222}$ has a dipole character with respect to both the angle between the polarizations and between the emitted electron on the field vector of the laser light. For the given experiment, this term becomes extreme for an angle of the laser electric field vector exactly between the synchrotron radiation electric field vector and the emitted electrons, i.e., for an angle of about 27.35°.

[1]The emission leading to the $^3P_{0,1}$ states has not been considered for this comparison since these lines coincide in energy with electrons emerging from the sodium clusters, leading to errors in the estimation of the line intensities.

Due to the dipole character of the photionization process all these terms have the $\cos 2\varphi_a$ dependency in common. For this reason it is obvious that the angular dependency presented in Fig. 3 should follow a $\cos 2\varphi_a$ function. So a function of the form

$$I = I_0[1 + a \cos 2(\varphi_a - \varphi_0)] \quad (5)$$

has been fitted to both lines. The least-squares fit shown in the figure gives a relative modulation $a$ of 37.4% for the $^3P_2$ final state and 18.4% for the $^1P_1$ final state. The maximum angle evaluates to 45.2° for the $^3P_2$ state and 51.3° for the $^1P_1$ state. For the latter line, a reasonably good fit can also be reached with the assumption that the maximum is at the magic angle that is marked by the vertical line.

The fact that both dependencies show a maximum close to the magic angle leads to the conclusion that the term $\sigma_{220}$ plays the leading role in Eq. (1). The angle between the electric field vectors of the radiation has only a small influence on the photoemission and the photoelectrons are primarily emitted into the direction of the atomic alignment.

To further evaluate these findings a closer look into the underlying $2p^6\,3p\,^2P_{3/2} \rightarrow 2p^5\,3s\,^{1,3}P_J$ shakedown process is necessary. The initial and final state have the same parity. The process only complies with parity conservation if the emitted $2p$ photoelectron is excited into a $p$-symmetric continuum by a monopole transition. Simultaneously the $3p$ electron undergoes a dipole transition into the $3s$ orbital. To calculate the $B$ parameters in Eq. (1), the matrix elements of the underlying transitions have to be taken into account. A more detailed theoretical analysis of this will be made in a forthcoming paper.

In conclusion, we have observed the conjugate shakedown structures associated to Na $2p$ core photoionization of laser-excited Na atoms in a beam. The spectra show effects of dichroism and we find that the addend $\sigma_{220}$ plays the leading role for the description of the optical alignment effects.

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