Photoionization of Synchrotron-Radiation-Excited Atoms: Separating Partial Cross Sections by Full Polarization Control

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Resonant atomic excitation by synchrotron radiation and subsequent ionization by a tunable dye laser is used to study the photoionization of short-lived Rydberg states in Xe. By combining circular and linear polarization of the synchrotron as well as of the laser photons the partial photoionization cross sections were separated in the region of overlapping autoionizing resonances of different symmetry and the parameters of the resonances were extracted.

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Atomic photoionization is a fundamental quantum process of photon-matter interaction, which is of great importance in various domains of science. Many investigations have focused on photoionization from the atomic ground states benefiting more and more from advances in technology and experimental sophistication [1,2]. The final goal of these studies is to achieve detailed understanding of the photoionization dynamics and to provide the most solid basis for the comparison with theoretical models. Less attention has been given to photoionization of photoexcited states, although such states often possess an important feature: their electronic angular momentum is polarized due to a nonequal population of magnetic substates prior to photoionization. The importance of this initial polarization, which is determined by the excitation conditions, has been demonstrated and exploited in the studies of laser-excited states [3–6]. For example, by varying the polarization of the exciting laser and ionizing photon beams and by taking advantage of the dipole transition selection rules, it is possible to separate photoionization into different atomic continua when detecting simply the total ion yield [7–10]. Such data can be used, for example, to identify resonances in the photoionization cross section with respect to their angular momentum [10,11] and provide an important step towards the ''perfect'' experiment on photoionization [12] aiming at the complete quantum mechanical knowledge about the process.

In the present work, we accomplished a new approach with respect to the above laser experiments, applying synchrotron radiation (SR) with variable polarization to excite (''pump'') short-lived atomic states in the vacuum ultraviolet (VUV) regime and a tunable dye laser (''probe'') for the subsequent photoionization from this state. Today, SR is the unique easily tunable source offering circularly as well as linearly polarized VUV and soft x-ray photons. The use of the SR in the first step makes it possible to study, for atoms and molecules, the photoionization of highly excited and Rydberg states, which are of great interest in many respects [13]. It also opens the way for studying photoionization of core-excited states with the excitation energy of tens and hundreds of eV. In earlier experiments on SR-excited states, the main interest was given to probe resonances, which cannot be excited by a one-photon excitation due to the dipole selection rules [14] or to investigate photoionization into a flat continuum using only linear polarization [15]. Here we use an excitation scheme with variable linear and circular polarization for both photon beams thereby taking full advantage of the method. As first application we decomposed the photoionization cross sections of the SR-excited states $5p^5 5d$ and $5p^5 7s$ in the xenon atom into the individual components characterized by the total angular momentum J of the final (Xe ion + photoelectron) complex. In this way it was possible to resolve close-lying autoionizing Rydberg resonances with different total angular momentum, which are

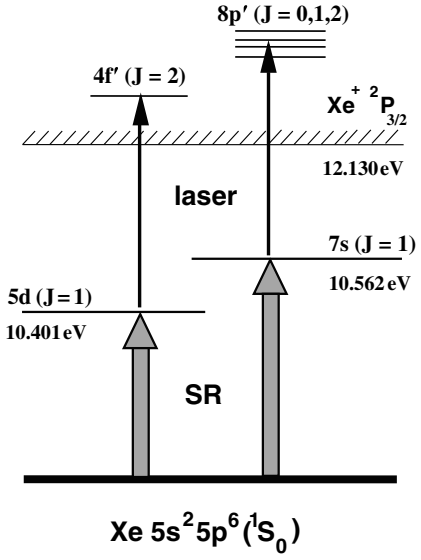

FIG. 1. Two-photon excitation scheme of Xe by SR + laser combination.

partially overlapping in the total cross section due to their natural lifetime broadening.

The region of the even-parity ionization continua in xenon between the two spin-orbit separated Xe II $5p^5$ ionization thresholds, $^2P_{3/2}$ and $^2P_{1/2}$, is dominated by overlapping Rydberg series of autoionizing resonances $np'[K]_J$ and $nf'[K]_J$ (for example [16–21], primes indicate a $^2P_{1/2}$ core), which decay to the Xe II $5p^5(^2P_{3/2})$ state (Fig. 1). We use the $j\ell$ coupling scheme, most appropriate for the excited states of the noble gas atoms, in which the orbital angular momentum ℓ of the excited electron $n\ell$ is strongly coupled to the total angular momentum j of the p^5 core, producing an intermediate angular momentum K, which sums up with the spin of the excited electron into the total angular momentum J. We concentrate on the ionization from the $5d[\frac{3}{2}]_1$ state ($h\nu_{\mathrm{SR}} = 10.401$ eV) in the region around the strong asymmetric $4f'[\frac{5}{2}]_2$ resonance [14] and on the region of the $8p'[K]_J$ multiplet excited from the $7s[\frac{3}{2}]_1$ state ($h\nu_{\mathrm{SR}} = 10.562$ eV). The former is an example of a simple test case, whereas the latter spectrum is complicated by unresolved autoionizing levels with different total angular momentum J and serves as showcase for the method.

The experiments were performed at the SU5 beamline of the SuperACO storage ring in Orsay, which was designed for measurements with variable polarization of the VUV radiation [22]. The degree of polarization took the values $P_c^{\mathrm{SR}} = 0.92$, $P_\ell^{\mathrm{SR}} = 0.06$ ($P_c^{\mathrm{SR}} = 0$, $P_\ell^{\mathrm{SR}} = 0.98$) in the circular (linear) polarization mode of the SR beam. The two counterpropagating photon beams were crossing an effusive gas jet in the acceptance volume of a time-of-flight analyzer. As a signature of the two-photon process we recorded the Xe^+ signal as a function of the laser wavelength, while the photon energy of the SR was tuned to the Xe $5p^55d$ and $5p^57s$ resonance, respectively (Fig. 1). The mass resolution of the analyzer was not high enough to separate the different Xe isotopes, but enabled us to distinguish between the formation of the singly charged atomic Xe ion and other photoionization events, like the production of Xe_2^+ dimers.

Because of the dipole selection rules, the SR-pumped state of Xe has a total angular momentum of unity and, hence, the atomic continua (channels) accessible by absorption of a laser photon have total angular momentum $J = 0, 1, 2$. The integral photoionization cross section from isotropic (unpolarized) excited state is described as $\sigma = \sigma_0 + \sigma_1 + \sigma_2$, where σ_J is the partial photoionization cross section into a channel with the total angular momentum J. To decompose the cross section σ into the partial cross sections σ_J is one of the main goals of the present study.

The photoionization cross section W for the collinear photon beams can be derived as [23,24]

$$W = \sigma[1 + \xi_1 P_c^{\mathrm{las}} P_c^{\mathrm{SR}} + \xi_2(1 + 3P_\ell^{\mathrm{las}} P_\ell^{\mathrm{SR}} \cos 2\varphi)] \quad (1)$$

where the degree of circular (linear) polarization of the ionizing laser radiation and SR is denoted by $P_c^{\mathrm{las}}(P_\ell^{\mathrm{las}})$ and $P_c^{\mathrm{SR}}(P_\ell^{\mathrm{SR}})$, respectively, $\varphi = \varphi_{\mathrm{las}} - \varphi_{\mathrm{SR}}$ is the angle between the principal axes of the polarization ellipses of the laser (φ_{las}) and SR (φ_{SR}) beams. We imply that in Eq. (1) P_c^{las} and P_c^{SR} are of the same (different) sign for photons of the parallel (antiparallel) spins. Information on the cross sections σ_J is contained in the two parameters

$$\xi_1 = \frac{3}{4\sigma}(2\sigma_0 + \sigma_1 - \sigma_2),$$
$$\xi_2 = \frac{1}{20\sigma}(10\sigma_0 - 5\sigma_1 + \sigma_2). \quad (2)$$

Equation (1) generalizes expressions used in analysis of the laser two-photon resonant ionization [9–11,25] to the case of arbitrary polarized photon beams. In our experiments only the laser light can be considered as completely polarized: $P_\ell^{\mathrm{las}} = 1$, $P_c^{\mathrm{las}} = 0$ ($P_\ell^{\mathrm{las}} = 0$, $P_c^{\mathrm{las}} = 1$) for linearly (circularly) polarized laser beam, respectively. To find the individual $\sigma_J (J = 0, 1, 2)$ three quantities can be measured as function of the laser wavelength with a subsequent solution of the corresponding set of equations: (i) the circular dichroism

$$\frac{W^{++} - W^{+-}}{W^{++} + W^{+-}} = \frac{\xi_1}{1 + \xi_2} P_c^{\mathrm{las}} P_c^{\mathrm{SR}}, \quad (3)$$

(ii) the linear dichroism

$$\frac{W(0°) - W(90°)}{W(0°) + W(90°)} = \frac{3\xi_2}{1 + \xi_2} P_\ell^{\mathrm{las}} P_\ell^{\mathrm{SR}}, \quad (4)$$

and (iii) the isotropic cross section

$$W(\varphi_0) = \mathrm{const} \times \sigma. \quad (5)$$

We denote by $W(\varphi)$ and W^{++} (W^{+-}) the photoion yield at an angle φ between the polarization directions of the photon beams and for the beams of photons with parallel (antiparallel) spins, respectively; φ_0 is the ''magic'' angle: $\cos 2\varphi_0 = -(3P_\ell^{\mathrm{las}} P_\ell^{\mathrm{SR}})^{-1}$. The extraction procedure for σ_J is independent of the intensity of the radiation, which is important for experiments with variously polarized SR.

As a result of possible atomic depolarization, the parameters of the SR beam, P_c^{SR} and P_ℓ^{SR}, no longer completely determine the polarization of the VUV-excited state. This effective polarization should therefore be found independently and Eq. (1) has to be modified accordingly. With respect to the present experimental conditions, there are mainly two depolarization effects that have to be taken into account [26]: collisions in the target gas jet and a precession of the angular momentum $\mathbf{J}$ of the electronic shell of the excited atom about the total angular momentum $\mathbf{F} = \mathbf{J} + \mathbf{I}$, where $\mathbf{I}$ is the nuclear spin. The latter depolarization due to hyperfine interactions occurs for the isotopes ^{129}Xe and ^{131}Xe with the nonzero nuclear spin $I = \frac{1}{2}$ and $I = \frac{3}{2}$, respectively. These two isotopes correspondingly represent 26% and 21% of the natural abundance of Xe; the other isotopes possess vanishing nuclear spin. Techniques for treating the depolarization

due to hyperfine interactions are well established [24,27]. Accounting for the depolarization in our case reduces to additional factors $G_k(k = 1, 2)$ at the parameters ξ_k in Eq. (1). Under conditions of incoherent excitation of the hyperfine levels by the SR beam, the depolarization factors G_k are expressed analytically in terms of the vector coupling coefficients. With particular values of the angular momenta and being weighted according to the abundances of the isotopes, they take the values $G_1 = 0.82$ and $G_2 = 0.67$. Furthermore, we describe depolarization due to the collisions by a single parameter $D(0 \le D \le 1)$ for both linearly and circularly polarized SR. As a result, Eq. (1) stays valid except substitution of $\xi_k \rightarrow DG_k\xi_k$.

Displayed in Fig. 2 are the extracted partial cross sections for ionization of the $5d[\frac{3}{2}]_1$ state, which have been obtained by applying Eqs. (3)–(5) for each individual energy point of the experimental data. A natural assumption that all three cross sections σ_J do not show similar resonances leads, at $D \approx 0.65$, to smooth (essentially vanishing) σ_0 and σ_1 with the strong $4f'[\frac{5}{2}]_2$ resonance in the $J = 2$ channel. This is in perfect agreement with the known dominance of the $J = 2$ ionization channel for the observed resonance structure [14]. The shape of the extracted $4f'[\frac{5}{2}]_2$ resonance in Fig. 2 (lower panel) is identical to the one obtained by direct measurements [14].

Applying a similar method as for the photoionization from the $5d[\frac{3}{2}]_1$ state, we extracted the partial cross sections for photoionization from the $7s[\frac{3}{2}]_1$ state in the region of the $8p'[K]_J$ autoionizing Rydberg resonances (Fig. 3). Resonances with a fixed J value show up only in the cross sections with the same angular momentum, allowing in this way the separation and identification of the resonances. Note that the line at $E = 102\,830$ cm^{-1} in the total photoionization cross section (Fig. 3, top panel) consists of two components with different angular momentum, the strong $8p'[\frac{3}{2}]_2$ and the weak $8p'[\frac{1}{2}]_1$ resonances, which are clearly separated in the data for the partial cross sections. In addition, the method allows to extract the cross sections for photoionization into the nonresonant continua, showing that $\sigma_2 > \sigma_1 > \sigma_0$ and that the ratio is in qualitative agreement with the statistical weight of the channels, 5:3:1.

Table I summarizes the parameters of the observed $8p'[K]_J$ resonances. The shape of the resonances were fitted by the Fano formula [28]

$$\sigma = \sigma_b + \sigma_a(\varepsilon + q)^2/(\varepsilon^2 + 1) \quad (6)$$

convoluted with a Gaussian profile, which represents the experimental broadening due to the energy bandwidth of the laser $\Delta(h\nu_{\rm las}) = 1$ cm^{-1}. In Eq. (6), $\sigma_a(\sigma_b)$ represents the part of the continuum cross section that interacts (does not interact) with the discrete level; $\varepsilon = 2(E' - E)/\Gamma$ is the deviation of the excitation energy E' from the resonance position E in units of the resonance half width $\Gamma/2$; and the profile index q characterizes the asymmetry of the

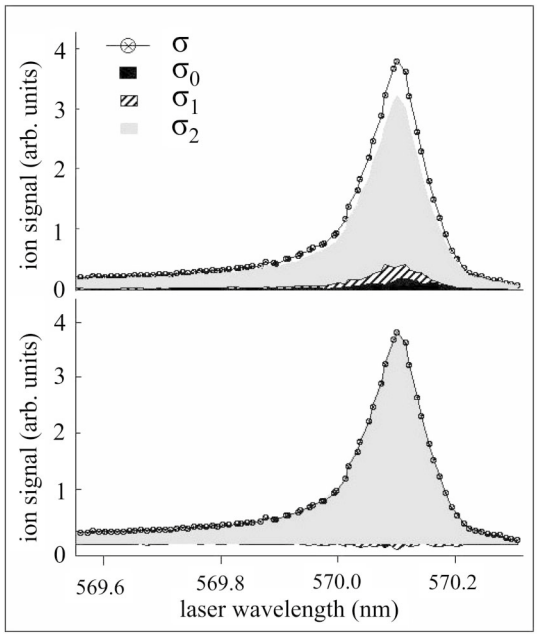

FIG. 2. Partial photoionization cross sections σ_0, σ_1, and σ_2 in the region of the Xe $4f'[\frac{5}{2}]_2$ resonance, assuming depolarization only due to the hyperfine interactions (upper panel) and including collisional depolarization (lower panel). For the factor D deviating from the value $D \approx 0.65$, the artifact resonances appear in the $J = 0$, 1 channels, like in the upper panel.

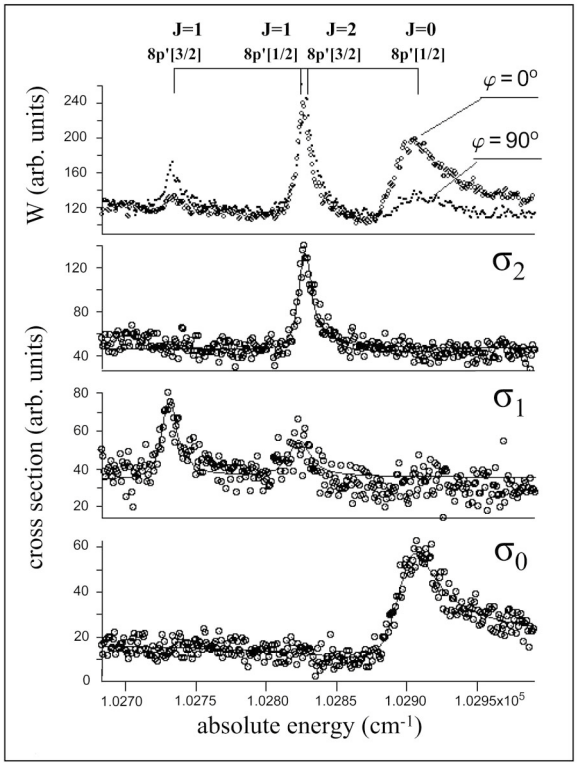

FIG. 3. Photoionization spectra in the region of the Xe $8p'$ resonances excited from the $7s[\frac{3}{2}]_1$ state using linearly polarized laser and SR radiation of parallel ($\varphi = 0°$) and perpendicular ($\varphi = 90°$) relative orientation of their electric field vector (upper panel). Partial photoionization cross sections σ_0, σ_1, and σ_2 in the same energy region (lower panels).

TABLE I. Parameters of the Xe $8p'[K]_J$ resonances.

State	μ		$\Gamma_r(\mathrm{cm}^{-1})$		q
	this work	other	this work	other	this work
$8p'[\frac{3}{2}]_1$	3.589	3.590[a]	1080(190)	880(140)[c]	11.5(5.5)
				1150(50)[d]	
$8p'[\frac{1}{2}]_1$	3.555	3.555[a]	1560(460)	1570(60)[c]	20.6(8.5)
				2740(50)[d]	
$8p'[\frac{3}{2}]_2$	3.551	3.551(2)[b]	950(80)	1330(560)[e]	10.9(4.8)
$8p'[\frac{1}{2}]_0$	3.522		2900(200)	3910(560)[e]	2.3(0.2)

[a][18]; [b][19]; [c][17]; [d][16]; [e][19] for (9–12)p.

resonance and indicates mainly the ratio between the resonant and the direct transition amplitudes to the continuum. The parameters of a Rydberg state are defined in the standard way [29]: a state with energy E, width Γ, and principle quantum number n is characterized by the nearly n-independent quantum defect μ and the reduced width Γ_r according to

$$E_\infty - E = \mathrm{Ry}/(n-\mu)^2, \qquad \Gamma = \Gamma_r/(n-\mu)^3, \quad (7)$$

where $\mathrm{Ry} = 109\,736.86\ \mathrm{cm}^{-1}$ is the Rydberg constant for Xe and $E_\infty = 108\,371.4\ \mathrm{cm}^{-1}$ is the Xe $5p^5{}^2P_{1/2}$ ionization limit [30].

The $8p'[\frac{3}{2}]_1$ and $8p'[\frac{1}{2}]_1$ states have been observed before by means of laser spectroscopy from the $6s[\frac{3}{2}]_2$ and $6s'[\frac{1}{2}]_0$ metastable levels [16–18], while the $8p'[\frac{3}{2}]_2$ and $8p'[\frac{1}{2}]_0$ states were reached only by four-photon excitation from the ground Xe state [19]. The present measurements provide much more accurate widths of the $8p'[\frac{3}{2}]_2$ and $8p'[\frac{1}{2}]_0$ states and a so far undetermined experimental value for the quantum defect of the $8p'[\frac{1}{2}]_0$ state, which fits well to the weak linear dependence of μ for the Rydberg autoionizing states in Xe [19]. The reduced widths for the $8p'[\frac{1}{2}]_1$ state deviates from the one measured in [16]. This difference might be due to the low statistics of our data for this small resonance and need a more detailed discussion elsewhere.

In addition, the data allow us to determine the profile indices q for the $8p'$ resonances upon photoexcitation from the $7s[\frac{3}{2}]_1$ intermediate state (Table I), indicating the dominance of the resonant transition in the $J = 1$ and $J = 2$ partial cross sections. The data for the widths and profile indices give further challenges for *ab initio* theoretical calculations: the recent configuration interaction polarized-core semirelativistic calculations of reduced widths [31] deviate significantly from the measured values, while the profile indices, which need even more sophisticated calculations, are not available in the literature.

To summarize, we have carried out first photoionization experiments using variable circular and linear polarization of both the SR-pump and the ionizing cw dye laser in order to determine partial ionization cross sections from the VUV-excited atoms. This approach allows the decomposition of the total cross section into the contribution of each of the three participating channels with different total angular momentum. The large tunability of SR sources coupled to this technique opens up access to a wide range of new experiments. The potential of the method has been demonstrated by decomposition of the integrated photoionization cross section from the excited short-lived states of Xe and separating overlapping autoionizing resonances.

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