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RESUME

L'utilisation combinée d'un laser à colorant continu et du rayonnement synchrotron émis par l'anneau de stockage à électrons ACO à LURE a permis les premières expériences de spectroscopie d'électrons sur des atomes portés dans un état excité et ionisés en couche externe et en couche interne. Les premiers éléments étudiés ont été le sodium et le baryum. Cette nouvelle méthode a permis de mesurer des forces d'oscillateur et des sections efficaces de photoionisation dans des atomes excités sur un domaine étendu d'énergies de photons. Récemment, des états atomiques très excités ont été préparés par l'action simultanée de deux lasers à colorant continus et du rayonnement synchrotron d'ACO, et leur autoionisation a été étudiée. Une revue de ces expériences est présentée. Leur extension possible grâce à la mise en service d'onduleurs montés sur des anneaux de stockage spécialement construits pour la production de rayonnement synchrotron, tel que Super ACO, est discutée.

ABSTRACT

By combining a cw laser beam with synchrotron radiation emitted by the ACO storage ring at LURE, in Orsay, we have demonstrated the feasibility of such photoionization experiments on excited atoms using electron spectrometry and we have obtained the first photoelectron spectra of laser-excited sodium and barium atoms. The oscillator strengths for transitions between core-electrons and optical orbitals in excited atoms have been determined and photoionization cross sections in excited atoms have been measured over a broad range of photon energies. More recently, two-electron highly excited autoionizing states have been produced and studied, using stepwise excitation with two cw dye laser beams to excite an outer electron and synchrotron radiation to excite an inner electron in sodium. A review of these experiments extending over a period of serveral years is given. The extension of these studies using undulator radiation and new storage rings is discussed.

I. INTRODUCTION

It is fair to say that the use of lasers has transformed many aspects of measurement science. This transformation is examplified by the many beautiful experiments that have been performed since the laser has been invented. For example, atoms can be laser-prepared with macroscopic dimensions and be used as ultra-sensitive detectors of infrared radiation.[1] Lasers have been used to slow atoms and cool them to millikelvin temperatures.[2] They have also been used to prepare atoms and molecules in a specific well characterized quantum state.[3] Experiments of this delicate nature would be difficult, if not impossible, to perform without the unique attributes of laser radiation. On the other hand, synchrotron radiation has also made a similar impact on the scientific community. Scientists have used the radiation for the development of small scale lithography (line pair resolution lower than one micrometer),[4] for softx-ray microscopy,[5] for determination of the structure of virus and proteins[6] and to study the electronic structure of a very broad range of gases and solids. There are now about 25 synchrotron facilities operational throughout the world. Yet, in spite of all the activity in both areas, the number of scientists that use synchrotron radiation and laser radiation as tools to do hybrid experiments has been very small up to now. However, the experiments that are possible have exciting scientific potential.

In this paper, we will give a brief outline of these laser-synchrotron radiation experiments in the field of atomic photoionization. The object of this paper is to stimulate the reader'sinterest to these new attractive applications of laser and synchrotron radiation to measurement science and not to produce an exhaustive critical survey of this research topic. In the first part, we will describe how these radiation sources were combined to observe the photoionization spectra of excited sodium and barium atoms, using electron spectrometry. Next, several examples of measurements of this type will be given. Finally, possible future developments will be described.

II. PHOTOIONIZATION OF ATOMS IN EXCITED STATES

The study of photoionization of atoms from excited states is not a new subject,[7] but new techniques make it a more tractable research endeavor than the heroic effort that was required a decade ago to obtain data on excited atoms.[8]

Why is the measurement of the subshell atomic and molecular photoionization cross sections important? By studying the photoionization process, the geometrical and dynamical properties of the electronic motion can be explored.[9] One of the important topics in atomic and molecular physics today is the development of theoretical models that adequately explain electron correlations.[10] Only a limited class of states can be probed, when the atom is in the ground state. Often, the ground state is an ensemble of nearly degenerate levels. While studies of ground state

photoionization is by no means complete,[11] the development of synchrotron radiation and associated instrumentation to utilize that source effectively over the wide spectral range that is available, and the development of laser sources of suitable intensity to maintain an adequate population of atoms in an excited state has provided an opportunity to extend cross section measurements to excited atoms and molecules.

For the study of atoms in the ground state, measurements of the angular distribution[12] and spin polarization of the ejected photoelectrons[13] have provided additional information about the characteristics of the wave function needed to describe the photoionization process.

Most of the measurements on excited atoms, up to now, have been obtained by single- or multi-photon absorption using lasers. With this mode of ionization, the energy range exploited is necessarily restricted to a few electron Volts above the first ionization threshold. By using a pulsed continuum source[14] or a laser-produced plasma,[15] absorption measurements from excited atoms have been extended over a broad energy range.

These measurements have stimulated theoreticians to calculate excited state cross sections. It is especially interesting to the atomic physics community if an atom is prepared in a specific well defined state. Photoionization of these atoms are among the most easily interpretable experiments that may be performed. In particular, the energy dependence of the $\ell \rightarrow (\ell-1)$ cross section for some excited atoms has been predicted[16] to have an unexpected minimum. This effect up to now has not been demonstrated. The excitation of an outer electron has been predicted to modify dramatically the effective potential experienced by inner-shell electrons with large quantum numbers.[17] Large changes in the oscillator strengths of some inner-shell transitions have been recently reported for excited atoms.[18] Finally, photoionization from an excited state allows one to produce autoionizing states with the same parity as the ground state; excited states like these have properties that make them candidates for soft X-ray lasers. Thus, there is a great deal of motivation to study photoionization of atoms in excited states.

III. EXPERIMENTAL ARRANGEMENT

The simplest measurement to determine photoionization cross sections is to detect the photoions produced by the interaction of the photons with the atoms being studied. For most of these experiments have probed the continuum only a few eV above the first ionization threshold, because tunable dye lasers are generally available only in the visible and the near UV. In that case, the electrons of only the outermost shell, specifically of alkali- and alkaline earth atoms, can be ejected into the continuum.

One of the best example of experiments of this type was the determination of

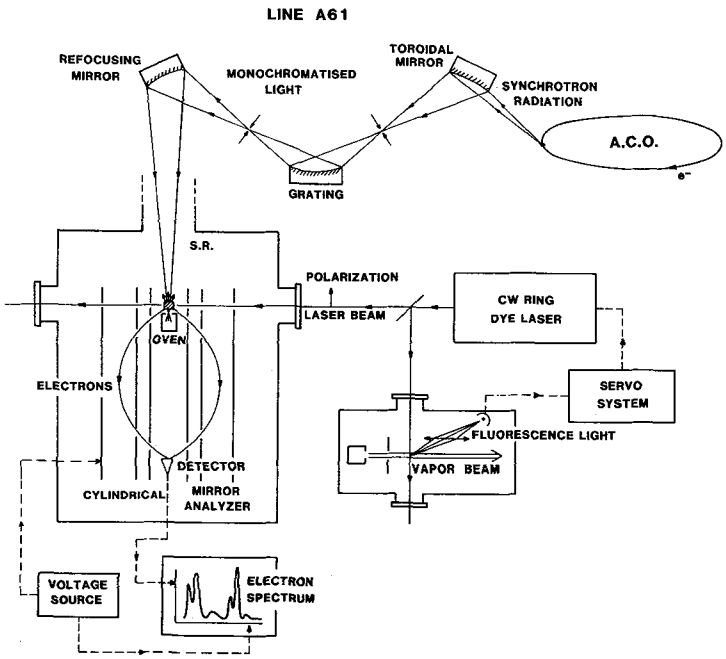

Fig.1 - Experimental set up for electron spectrometry studies of photoionization of excited atoms with synchrotron radiation. See detailed description in the text. (from Ref. 19).

the 3p photoionization cross section in laser-excited sodium atoms between the 3p ionization threshold (3.03 eV) and 4.3 eV, i.e. over a photon energy range of a little more than one electron volt. In one of the experiments associated with these measurements,[20] the $M_F = 3$ magnetic state is optically pumped by the circularly polarized laser radiation and another circularly polarized laser beam ionized the excited electron. This method allows the experimentalist to study continuum states that are degenerate. This is possible because the transitions obey dipole selection rules and circularly polarized radiation can only produce transitions with $\Delta M = \pm 1$. Thus, in one polarization, only continuum states with d-symmetry can be produced, and with the other polarization the final state will be a linear combination of s-and d-symmetry. Because of the lack of intensity, this type of ultimate experiment cannot yet be achieved using synchrotron radiation. The measurement of only the integrated photoionization cross section for Na was recently repeated in the same photon energy range, using synchrotron radiation and ionic detection.[21]

The only method available when electrons of several kinetic energies can be produced by monochromatic photons (e.g. for $h\nu > 5.14$ eV in the sodium case described above) is to use electron spectrometry . This technique permits one to select electrons associated with the ionization from each subshell of interest. One can thus

obtain the partial subshell photoionization cross sections over a wide range of photon energies. Photoelectron spectroscopy also eliminates spurious results that are possibly produced by radiation other than that occuring at the wavelength the monochromator is set at. This explains why photoelectron spectroscopy was the tool of choice to achieve the success of the first feasibility experiments combining the use of synchrotron and laser radiation .[22-25]

Equipment for such an experiment consists of a high throughput monochromator, a laser whose output is taylored for the particular experiment, and a chamber containing apparatus to detect the incoming photons and the ejected photoelectrons. Figure 1 is a representative example of a typical set up.[19] The synchrotron radiation of the ACO storage ring is monochromatized by a toroidal grating monochromator, delivering a flux of up to 10^{12} photons/sec in a 1% band pass for photon energies between 16 eV and 140 eV. The output of the monochromator is focussed by a second toroidal mirror onto the active region of the cylindrical mirror electron spectrometer (CMA). Inside the electron spectrometer, an oven, mounted on the common axis of the CMA and of the VUV beam, emits a weakly collimated beam of metal atoms (the ground state density is maintained at values lower than 10^{13} at/cm^3). The laser beam irradiates the atomic beam in a direction that is at right angles to the CMA axis. The beam waist of the laser radiation is adjusted to fit the size of the source volume of the CMA. The laser beam is produced by an argon-ion laser pumped ring dye laser which has an intensity of up to 10 watts/cm^2, and is linearly polarized in the orbital plane. The dye laser is stabilized to the transition between the ground state and the first excited state of the atoms under investigation by observing the fluorescence emitted from the excited atoms in an auxiliary atomic beam; the VUV beam is also partially polarized in the horizontal plane at right angles to the laser beam polarization, which is along the CMA axis.

A similar set up was used, later on, by the second group of scientists who have succeeded to combine synchrotron radiation and laser for experiments of this sort.[26]

IV. PHOTOELECTRON SPECTRA OF LASER-EXCITED SODIUM AND BARIUM ATOMS

During the first set of experiments on photoionization processes in laser-excited sodium[22-25]- and barium [25,27] atoms, in 1981-1982, the main features of interest have been observed. A typical photoelectron energy distribution in sodium is shown in Figure 2. The two photoelectron peaks in the upper frame of the figure, obtained with photons of 75 eV and without laser, are due to the ionization of one of the 2p electrons of sodium atoms in the ground state (peak near 38 eV binding energy) and the ionization of a 2p electron together with the excitation of the 3s electron to a 3p orbital (so-called satellite peaks near 42 eV binding energy). The excitation of this group of ionic levels is due to final-state electron correlations. The

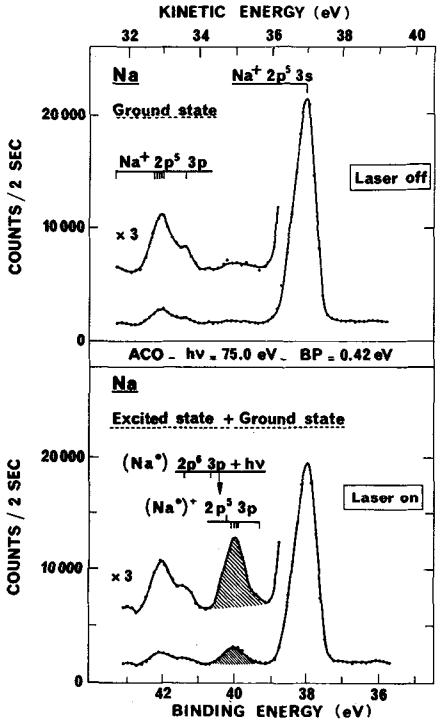

Fig. 2 - Photoelectron spectra of atomic sodium produced by 75 eV photons. Upper frame: the laser is off, all Na atoms are in the ground state; the large peak, near 38 eV binding energy, is due to photoionization of 2p electrons, with the ion left in its ground state; the smaller peaks are due to ionization of a 2p electron with simultaneous excitation of the 3s electron onto a 3p orbital. Lower frame: the laser is on, about 10% of the atoms are in the $2p^6 3p\ ^2P_{3/2}$ excited state; in addition to the photoelectron spectrum from atoms in the ground state, a new peak appears (hatched area), due to ionization of a 2p electron in the excited sodium atoms. (From Ref.22 and 23; note that, in reference 23, this figure has been mistakely interchanged by the editors with a figure similar to the figure 3 of the present paper, making the figure caption unintelligible).

relative energy position of these $2p^5 3p$ excited levels is noted on the figure as vertical lines extending below the horizontal line identifying the configuration. The lower frame of Figure 2 corresponds to a photoelectron spectrum taken with some of the sodium atoms laser-excited to the 3p level. A new peak occurs, located at about 40 eV binding energy, shifted by 2.11 eV (the energy of the laser) from the $2p^5 3p$ electron satellite lines in the ground state. It is due to photoionization of a 2p electron in atoms with the outer electron in a 3p-orbital. By taking a spectrum similar to this one as a function of the photon energy, it is possible to map out the partial cross section to photoionize the 2p-electrons in the $2p^6 3p$ excited atom. The density of excited atoms must be determined if the cross section is to be obtained. This can be achieved by measuring the relative change in intensity of the peak at 38 eV binding energy in the spectra with the laser off and with the laser on. In this first series of experiments, relative populations of atoms in the 3p excited state were measured to be close to 10%.[22,23]

Figure 3 shows the second interesting feature observed in these first experiments on sodium.[22-25] The spectrum is taken at 31.40 eV photon energy and displays the effect of resonant photoemission of the excited outer 3p-electron, i.e. the formation of a core-excited autoionizing state in the $2p^6 3p$ excited atom, followed by a non-radiative decay of this state to the ground state of Na^+ ion. This photon energy corresponds to the excitation energy of the $2p^6 3p\ ^2P_{3/2}$ atoms to the $2p^5(^2P)3s3p(^3P)\ ^2D_{5/2}$ core-excited state via inner-shell excitation of a 2p electron

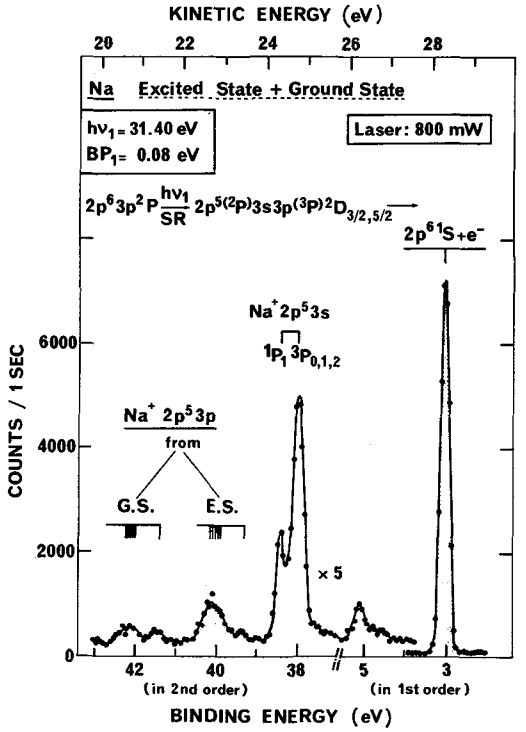

Fig.3 - Electron spectrum of Na obtained at a photon energy of 31.40 eV with the laser on. Photoelectrons due to ionization of a 2p electron by the radiation diffracted in second order by the monochromator (62.80 eV) appear between 38 eV and 43 eV binding energies, as in Fig.2. Photoelectrons from the direct ionization of a 3s electron appear at a kinetic energy of about 26.5 eV (binding energy of 5.14 eV). Note that this part of the spectrum has been magnified by a factor 5. Electrons emitted in the decay of the $2p^5 3s3p(^3P)\ ^2D5/2$ autoionizing state formed by excitation of a 2p electron by 31.40 eV photons in the excited sodium atoms produce the intense peak on the right part of the figure, at 3.03 eV binding energy on the first order scale: they correspond to resonant photoionization of the excited 3p electron. (From Ref.24).

to the first empty 3s orbital.[28] The whole frame of the figure shows the spectrum obtained at this photon energy with the laser on. In spite of the fact that the binding energy of the 2p electrons in sodium atoms in the ground state is about 38 eV and that the monochromator is set at a 31.40 eV photon energy, one observes electron lines due to photoionization of sodium atoms in the 2p-subshell. This occurs because the monochromator also transmits photons diffracted in second order by the grating (62.80 eV). Note that the band pass of the monochromator is high enough (0.08 eV) to allow for the observation of the doublet due to spin-orbit splitting in the $2p^5 3s$ ionic state configuration of Na^+ (^3P and ^1P final states). The small peak at about 26.5 eV kinetic energy is due to the direct photoionization of the 3s electron by 31.40 eV photons. Since the laser was tuned to the $2p^6 3s\ ^2S_{1/2} \longrightarrow 2p^6 3p\ ^2P_{3/2}$ transition, some of the atoms (about 30% in this case) are in the first excited 3p-state and one observes, at 40 eV binding energy, the photoelectron peak due to direct photoionization of the 2p-electrons in the excited atom. The intense feature near 28.5 eV kinetic energy arises from the decay of the $2p^5(^2P)3s3p(^3P)\ ^2D_{5/2}$ even-parity autoionizing state resonantly excited by stepwise laser (3p-excitation) plus VUV (2p-excitation) photon absorption. On the binding energy scale corresponding to first order photons, this feature is located at the binding energy of a 3p-electron in the excited atom (3.03 eV). When the synchrotron radiation is detuned from the resonance region, this feature disappears, because the direct, non-resonant pho-

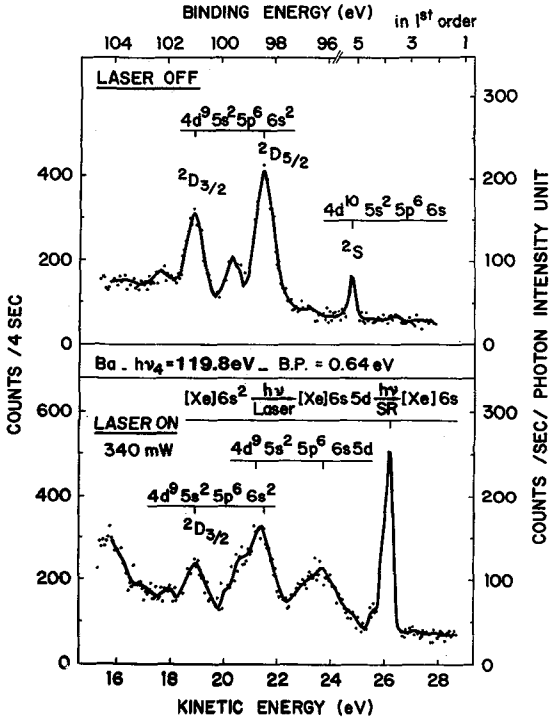

Fig.4 - Photoelectron spectrum of atomic barium ionized in the 4d-subshell by 120 eV photons diffracted in 4th order by the monochromator and in the 6s-outer shell by 30 eV photons diffracted in 1st order by the monochromator (upper part of the figure). In the lower part of the figure, with the laser on, the various photoelectron lines originate from ionization of atoms in the ground state and in the 6s5d excited states, as indicated. (From Ref.25).

toionization cross section of the 3p-electron is very small at this photon energy. The present day intensity of synchrotron radiation is too weak to allow its observation in photoemission studies.

It is interesting to note that if one wants to study autoionization in ground or excited state alkali atoms, one must excite an inner-shell electron which has binding energy in the VUV. No tunable laser are available for this photon energy region. The continuum radiation emitted by a BRV source[28] or by a laser-produced plasma[15] (for photoabsorption experiments) or by an electron (positron) storage ring (for photoemission studies) must be used for these studies in the alkalis.

In barium, the laser was tuned to the $6s^2\ ^1S_0 \longrightarrow 6s6p\ ^1P_1$ resonance line at 2.24 eV. Under our experimental conditions, this excited state decays radiatively to the ground state and to the 6s5d $^{1,3}D_2$ metastable states in the source volume of the CMA. One of the first spectra that has been recorded is shown in Figure 4.[25] In the upper part of the figure, the photoelectron spectrum is obtained without the laser. The synchrotron radiation monochromator is set at a photon energy of about 30 eV in first order. The radiation diffracted in 4th order (near 120 eV) is able to photoionize 4d-subshell electrons of Ba atoms in the ground state (binding energies of 98.4 eV and 101.0 eV,[29] corresponding to the $4d^9 5s^2 5p^6 6s^2\ ^2D_{5/2,\ 3/2}$

final ionic states of Ba^+) One observes also, near 5 eV binding energy (on the first order binding energy scale), the photoelectron line due to ionization of the outer 6s electrons by photons of 30 eV energy. When the laser was turned on (lower part of the figure), the photoelectron spectrum was quite changed. First, the number of 4d-components is increased and the electron lines appear to be broaden, partly because of the overlapping between lines corresponding to different initial states of Ba atoms. The binding energy of these 4d-inner electrons in the 6s5d $^{1,3}D_2$ states is shifted by about 2.0 eV towards lower binding energies, compared to their values for ground state atoms.[29] In addition, the number of possible final ionic states is increased by multiplet splitting, because of the presence of three open-shells in the $4d^9 5s^2 5p^6 6s5d$ electronic configuration of the final ionic states. Second, an intense electron line appears at the binding energy of the 5d electrons,on the first order binding energy scale, in the excited atoms (3.8 eV), illustrating the enhancement of the outer-shell photoionization cross section at these photon energies. A similar splitting of the photoelectron lines was also observed very clearly for the ionization of the 5s and 5p electrons, in an energy range which was free of line overlapping arising from higher order diffracted photons. A typical example can be seen in Figure 5,[19,30] corresponding to a case where about 50% of the atoms had been laser-transfered to the metastable states. The shift of the binding energies occurs clearly to lower values in the 6s5d $^{1,3}D_2$ excited atoms, while it was to higher values in excited sodium atoms, compared to atoms in the ground state. This different behavior was explained by the calculations of the radial dependence of the electronic densities for each state.[31] The 5d orbitals in excited barium atoms are more penetrating than the 6s orbital. Consequently, the outer screening felt by the inner electrons is greater, which tends to decrease the attraction of the nucleus. For barium atoms excited in the 6s6p $^1P_1$ state, the difference with the ground state would be much smaller and of opposite sign. In another experiment[26], inner-shell photoionization in the $^1P_1$ state has been reported.

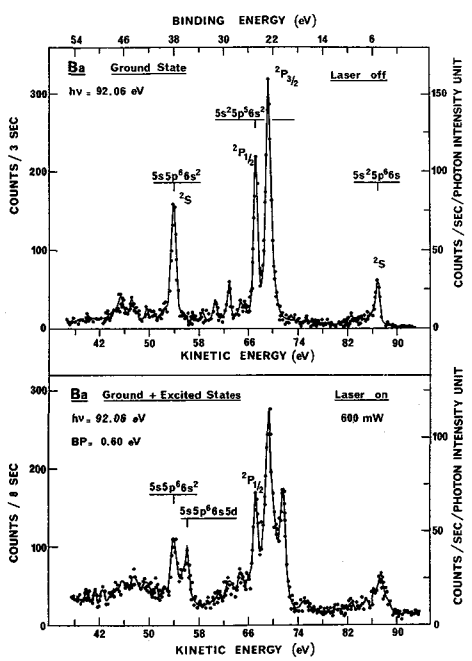

Fig.5 - Photoelectron spectra ejected from Ba atoms in the ground state (upper pannel) and in the 6s5d $^{1,3}D_2$ excited states (lower pannel) by 92 eV photons. The electronic configurations of the various final ionic states are marked on the figure. (From Ref. 19 and Ref. 30).

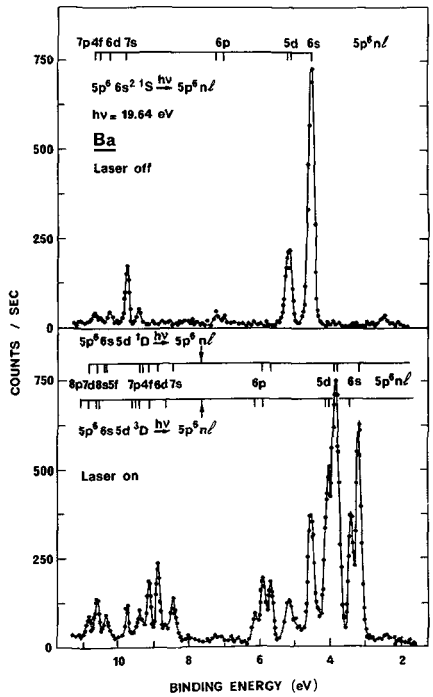

Fig.6 - Electron spectra of Ba taken at 19.64 eV photon energy. In the upper part of the figure is shown the spectrum of Ba atoms in the $6s^2\ ^1S_0$ ground state. In the lower part Ba atoms are in both ground state and $6s5d\ ^{1,3}D_2$ excited states. About 70% of the atoms have been laser-transfered in . of these excited states. The electronic configuration of the final ionic states arising from resonant ionization of the different barium atomic states present in the vapor are marked on the horizontal lines. (From Ref.32).

Resonant photoemission was also observed in barium, following inner-shell excitation of a 4d electron,[29] and of a 5p electron.[32,33] A resonant barium photoelectron spectrum is more complicated due to the many open photoionization channels. We show in Figure 6 a particularly interesting example, in the case of 5p-electron excitation. The upper panel is an electron spectrum obtained at a photon energy of 19.64 eV with the laser off. At this photon energy, the inner-shell 5p electron can be excited to orbitals that form autoionizing states. The spectrum illustrates the large number of ionic channels that are populated in this excitation process: photoexcitation plus autoionization. Of course, direct photoionization of the 6s electron is possible, but this channel has a very small cross section compared to the resonant autoionization process that is active here. Notice that the ion is left preferentially in the 6s and 7s states, suggesting a resonance of s final state symmetry.[33] The lower frame is a spectrum obtained at the same photon energy, but with the laser tuned to the $5p^6 6s^2\ ^1S_0 \longrightarrow 5p^6 6s6p\ ^1P_1$ transition. The $5d\ ^1D_2$ and $^3D_2$ metastable states become heavily populated even though the radiative transition rate to these states is 20 times smaller than to the ground state. The ground state population is reduced to a small fraction of the population with the laser off (less than 30% here, in some cases less than 10%), indicating very efficient pumping of the barium atoms into the excited states. The spectrum shows that, at this photon energy, resonant photoionization of both 6s and 5d electrons occurs with comparable intensities in atoms excited in the $^1D_2$ as well as in the $^3D_2$ intermediate states. One also observes a large number of intense satellite lines in the autoionization of the core-excited states. They correspond to $5p^6 6p$, $5p^6 7s$, $5p^6 6d$, $5p^6 7p$, $5p^6 8s$,

$5p^6 7d$ and even $5p^6 8p$ ionic configuration. At this photon energy, it seems that the whole satellite structure is resonating simultaneously, the intensity of all lines being enhanced in the autoionization process, in marked contrast with the ground state. This was the first observation of an almost pure satellite spectrum in the photoionization of atoms in excited states.

V. EXAMPLES OF RESULTS

After the success of these feasibility experiments, two main series of measurements were undertaken: a study of the variation of photoionization cross sections in excited barium atoms over a broad photon energy range and the determination of oscillator strengths for transitions of a core-electron in sodium or barium atoms , prepared in a specific excited state, to highly excited autoionizing final states. Concurrently, another group demonstrated its capability to achieve similar experiments.[26] More recently, we succeeded to produce and to study two-electron highly excited states, using stepwise excitation with two cw laser beams, to excite an outer electron, and synchrotron radiation to excite an inner electron in sodium. In the following paragraphs, we will illustrate the results obtained with several examples.

1. PHOTOIONIZATION CROSS SECTIONS IN EXCITED BARIUM ATOMS

From spectra such as the ones shown in figures 4 and 5, it was possible to follow the variation of a photoelectron line associated with the ionization of a particular subshell, and to determine, for the first time, the variation of photoionization cross sections of excited atoms over a broad range of photon energies including several ionization thresholds. As an example, we show in Figure 7 the energy dependence of the 5d photoionization cross section in excited barium atoms.[34] The absolute scale of the cross section was established by normalizing the experimental data for the 5p photoionization cross section for ground state barium atoms to the local density-based random phase approximation (LDRPA) calculations of Wendin.[35] The experimental results are compared to three different calculations. In the low photon energy range (10-40 eV), the one-electron theoretical results[35,36] reproduce the general non-resonant behavior of the cross section quite well, even better in fact than the LDRPA calculations that include correlation effects. However, if one takes into account the size of the error bars, such an excellent agreement should be considered as somewhat fortuitous. In particular, there is no a priori reason to choose one calculation over the other. The $5p \rightarrow 5d$ resonances, occuring below 20 eV photon energy, show up only in the LDRPA model, as expected. These results are consistent with the value of the 5d cross section previously measured near threshold, which was about 20 Mb between 4 eV and 5 eV photon energies.[48] In our experiment, as it will be explained later, it is not possible to determine the near-threshold behavior of the cross section.

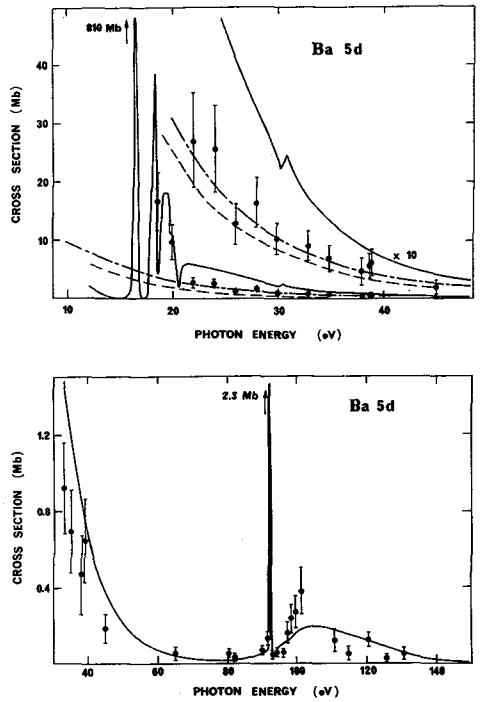

Fig. 7 - Variation of the 5d photoionization cross section in excited barium as a function of the photon energy, from 10 to 45 eV (upper part) and from 40 to 140 eV (lower part). One-electron theoretical results are from Hartree-Fock-Slater calculations (ref.36, —·—·—) and from LDA calculations (— — — — — —) Note that, in the original paper (ref.34), these two curves have been interchanged. Calculations taking into account electron correlations are obtained using LDRPA approximation (from Wendin, in ref.34, ————). (Fig. taken from ref. 34).

At higher photon energies, inner-shell interactions enhance the cross section when the 4d-ionization channels open at about 100 eV. A third one-electron calculation,[37] not shown, gives a slowly varying curve in this energy region. These resonance effects can be reproduced theoretically only when one takes into account inner-shell interactions between the 4d and the 5d electrons. [34] A resonant behavior due to interference between the direct photoionization process and inner-shell excitation to discrete final states with $4d^9 5s^2 5p^6 5dnl$ electronic configuration is also reproduced by the LDRPA calculations. A good agreement with experiment is obtained when the Auger lifetime of the 4d-hole is introduced into the calculations. This broadens the 4d → 4f resonance and strongly reduces its strength in the 5d-ionization channel.

Photoionization cross sections for inner-shell ionization of excited barium atoms have also been measured and are presented in another paper.[38] The main result of these measurements is that inner-shell ionization in 5s and 5p subshells of excited barium atoms is even more strongly enhanced, via inter-shell correlations with the 4d electrons, than for barium atoms in the ground state.

2. *OSCILLATOR STRENGTHS OF INNER-SHELL EXCITATION TRANSITIONS IN EXCITED SODIUM ATOMS*

In the first of these new experiments,[39] we have measured oscillator strengths for transitions, in excited atomic sodium, involving even-parity autoionizing levels. The transitions between a laser-excited initial $2p^6 3p$ electronic configuration and autoionizing levels with $2p^5 3s3p$ configuration were systematically investigated.

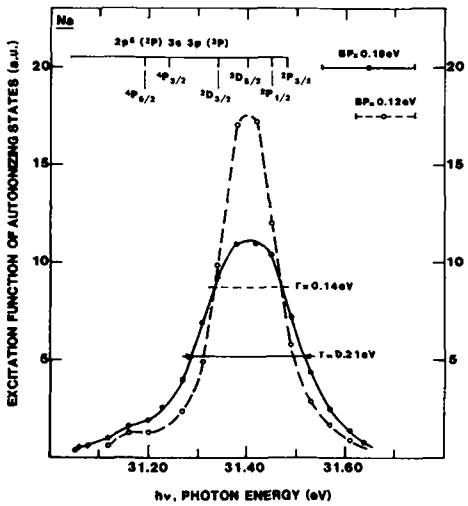

Fig.8 - Excitation function of $2p^5 3s3p$ autoionizing resonances in Na as a function of photon energy, around 31.40 eV, for two values of the monochromator band pass (BP = 0.12 eV and 0.19 eV). The scale of the ordinate has arbitrary units. The configuration and terms of the autoionizing resonances in the spectral range shown in the figure are taken from Sugar et al. (ref.28). (From Ref.19).

The general two- step excitation and autoionizing decay schemes are the following:

$$2p^6 3s\ ^2S_{1/2} + h\nu\ (\text{laser}) \rightarrow 2p^6 3p\ ^2P_{3/2}$$

$$2p^6 3p\ ^2P_{3/2} + h\nu\ (\text{SR}) \rightarrow 2p^5 3s3p\ ^2S_{1/2}, \text{ and } ^2D_{5/2,3/2}$$

$$2p^5 3s3p \rightarrow 2p^6\ Na^+ + e^-$$

When the 2p-electron is excited to the 3s orbital, the parent configuration 3s3p couples through the exchange interaction to form ^3P terms ($^2D_{5/2}$ and $^2D_{3/2}$ levels at 31.40 eV and 31.34 eV, $^2S_{1/2}$ level at 31.78 eV for the complete system) and ^1P terms ($^2D_{5/2}$ and $^2D_{3/2}$ levels at 32.69 eV and 32.85 eV, respectively).

A typical electron spectrum, obtained at 31.40 eV, has been shown in Fig.3. The group of resonances associated with $2p^5 3s3p$ configuration was scanned by step of 0.03 eV, between 31.00 eV and 33.00 eV . Figure 8 shows the excitation curve (convolution of the cross section and the monochromator band pass) measured around 31.40 eV for the terms having $2p^5(^2P)3s3p(^3P)$ coupling, with two different values of the monochromator band pass . The spectrum is not simple to interpret , because several resonances of significant intensities are simultaneously excited, even in the smallest band width of the monochromator. However, it is clear that most of the strength is in the $^2D_{5/2,3/2}$ levels, with some indication of the presence of the $^4P_{3/2}$ level. In strict L.S coupling, the ^4P levels should not autoionize. The small hump, around 31.20 eV, indicates that there is some mixing with the ^2D levels that do autoionize.

The value of the oscillator strength was determined for each group of inner-shell excitation transitions, using the excitation functions similar to the curve shown in figure 8. The data were normalized to the value of the direct 2p-photoionization cross section at 65 eV photon energy.[39] The sum of the oscillator strengths for all measured transitions was found to be 0.22(4), assuming that the radiative decay of the two-electron excited states is negligible. A comparison with the calculated values for the $2p^6 \rightarrow 2p^5 3s$ transition in the isoelectronic sequence of Ne-li-

ke ions (about 0.20) that LS coupling dominates and that the excited-3p electron acts chiefly as a spectator.

3. RESONANT PHOTOIONIZATION CROSS SECTIONS IN EXCITED-BARIUM ATOMS

We have already shown, in Fig.6, an example of photoelectron spectra that are measured in the energy range of the 5p-excitations. By continuously scanning the photon energy range from 16 eV to 22 eV, we have obtained partial cross sections for photoionization into the various continuum channels of Ba atoms in the ground state and in the $^{1,3}D_2$ excited states.[32,33] We present, in Figures 9, some selected examples of the results that have been obtained. In Fig.9a, the two curves are the photoionization cross sections for leaving Ba atoms, initially in their $6s^2\ ^1S_0$ ground state, in one of the $5p^6 6s\ ^2S_{1/2}$ (left part) and $5p^6 5d\ ^2D_{3/2,5/2}$ (right part) ionic states of Ba^+. The two curves in Fig.9b are the corresponding results for Ba atoms initially in the $5p^6 6s 5d\ ^1D_2$ excited state. Without going into details, the differences in the behavior of the ground state and of the excited state are striking. While, in both cases, one observes the influence of autoionizing resonances, involving core-excitation of 5p-electrons, whose effect is to strongly enhance the partial cross sections at some photon energies (for Ba atoms in the ground state, this effect has first been observed, using synchrotron radiation, by Rosenberg et al.[40]), it is clear that the number of resonances is increased for atoms in the 5d-excited state. Furthermore, the values of the cross sections at the maxima of the resonances is diminished for ionization of excited atoms. Promoting one of the 6s electrons into a 5d orbital has the effect of multiplying the possible couplings, since they are several open subshells in the intermediate $5p^5 n\ell n'\ell' n''\ell''$ resonant states. The oscillator strength for these transitions are spread over a larger number of resonances. From these data,

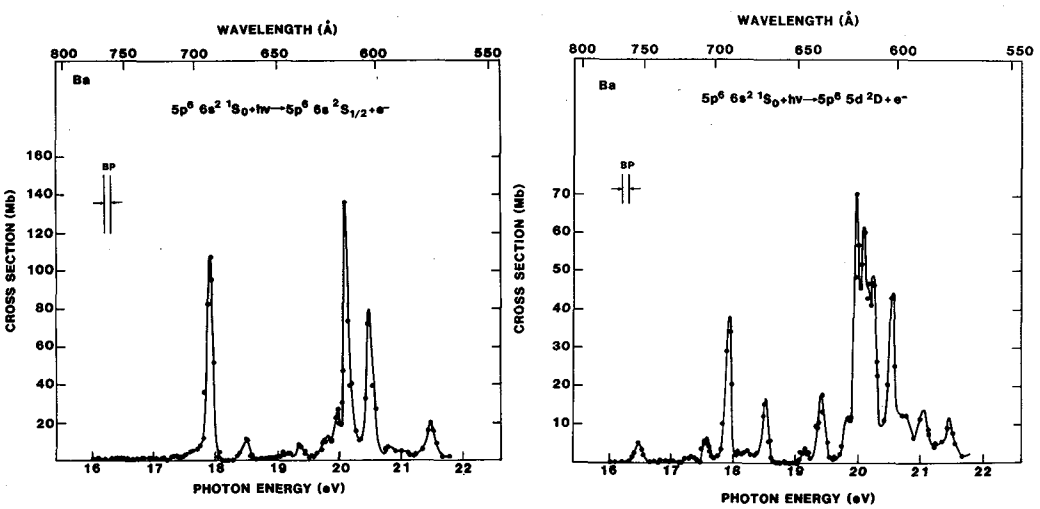

Fig.9a - Partial photoionization cross sections for leaving Ba atoms, initially in the ground state, in the $5p^6 6s$ (left part) or the $5p^6 5d$ (right part) ionic states(33).

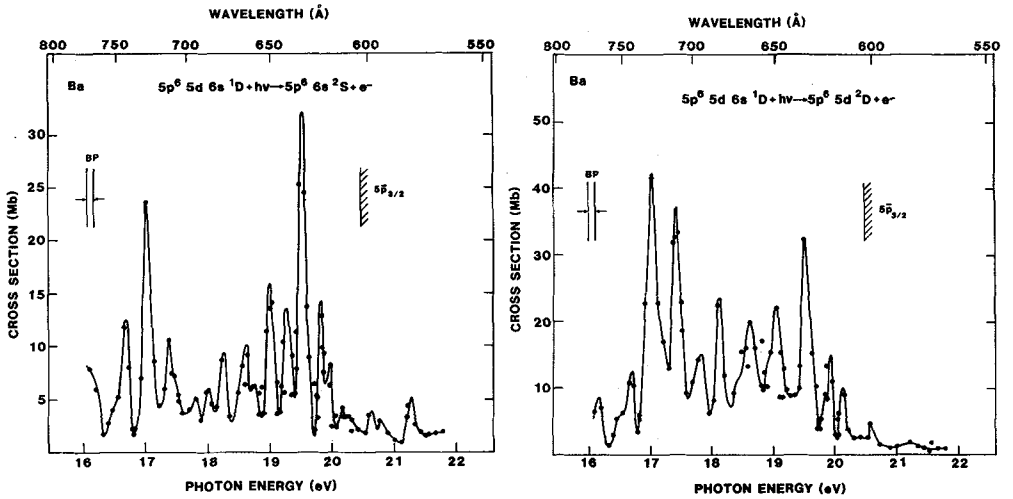

Fig.9b - Partial cross sections for photoionization of barium atoms in the $5p^6 6d5d\ ^1D_2$ excited state. As in Fig.9a, the two final ionic states are the $5p^6 6s\ ^2S$ (left part) and $5p^6 5d\ ^2D$ (right part) states. The values of the resonance maxima are strongly dependent on the monochromator band pass (0.11 eV here), but this effect does not affect the determination of the oscillator strengths. (From Ref. 32 and 33).

one can conclude[33] that all resonances present in the ground state can also be seen in the excited states, suggesting that at least part of the discrete intermediate states involving core-excitation of a 5p-electron in neutral barium are the same, i.e. they have to be represented by a strong mixing of configuration such as $6s^2$, 6s5d and $5d^2$.[41] Additional transitions are, of course, observed in the initially excited atom. It is worthwhile to note that the modest resolution (compared to the most recent photoabsorption data[42]) that had to be used here to get high enough photon flux enabled us to show clearly where the oscillator strength is mainly concentrated, especially for transitions from ground state atoms.

The highly complex spectrum of barium requires extensive computational effort for a detailed interpretation of the 5p-excitation spectrum. Even for the ground state, our data show[33] that the detailed interpretation of the photoabsorption spectrum[43] does not account for all experimental features observed in these photoemission experiments. The interpretation of the photoabsorption spectrum of excited barium[15] is far from being at end. The next generation of photoemission experiments must be carried out with a higher resolution, in ground state as well as in excited state atoms, to better understand these complex interactions. This can be achieved only with the high brightness expected from undulators mounted on new storage rings.

4. THREE-STEP EXCITATION OF HIGHLY -EXCITED AUTOIONIZING STATES IN SODIUM

The tunability range of cw lasers is rather limited, when one takes into ac-

count the power density that is needed in this photoemission experiments (several hundreds of milliwatts). Thus, it was important to test if several lasers could be efficiently combined with synchrotron radiation to study atoms promoted to an extended number of highly excited states. Na was chosen for this test experiment because of the intensity of synchrotron radiation available in the energy range of inner-shell excitation of a 2p-electron and of the tunability range of the lasers. Also, the experience gained in earlier studies of the first step of laser-excitation to the $2p^6 3p$ resonant levels was a prerequisite to the success of this more complex experiment.

Details on the experiment have been already published[44] or are given in another paper of this volume.[45] Basically, monochromatized synchrotron radiation and two cw laser beams are focussed into the source volume of the CMA already shown in Figure 1. The laser excitation is achieved in the following way: first, a ring cavity is used to prepare Na atoms excited in the $2p^6 3p\ ^2P_{3/2}$ state;then, the second step of the photoexcitation is produced by a stationnary wave dye laser which is tuned either to the $2p^6 3p\ ^2P_{3/2} \longrightarrow 2p^6 4d\ ^2D_{5/2}$ or to the $2p^6 3p\ ^2P_{3/2} \longrightarrow 2p^6 5s\ ^2S_{1/2}$ transitions. In the radiative decay of these states, atoms in the $2p^6 4p\ ^2P_{1/2,3/2}$ states are formed in the beam. The synchrotron radiation is used to promote a 2p-electron to the 3s-empty orbital. Fig.10 shows an example of electron spectra obtained during the first series of experiments, at a photon energy of 33.06 eV. The upper part and the middle part of the figure shows the 2p-photoelectron spectrum of Na atoms in the ground state (peak noted 2, lasers off) and in the first $2p^6 3p\ ^2P_{3/2}$ excited state (peak noted 1, Laser I)

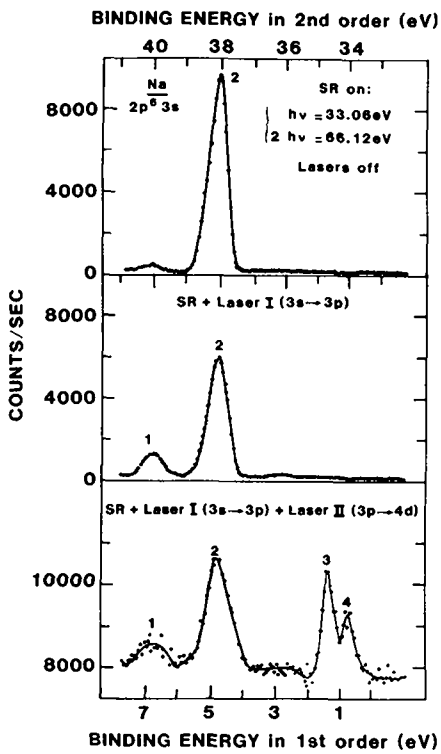

Fig.10 - Photoelectron spectra of Na atoms in various initial states taken at 33.06 eV photon energy. Top: peak 2 is due to photoionization of ground state atoms in the 2p-shell by photons of 66.12 eV. Middle: spectrum taken with laser I turned on: peak 1 is due to photoionization of the 2p-shell electrons in $2p^6 3p$ excited atoms. Bottom: spectrum with both lasers turned on: peaks 3 and 4 are due to autoionization of $2p^5 3s4p\ ^2D$ and $2p^5 3s4d\ ^2F$ states, respectively. (From Ref.44).

respectively. These spectra are basically the same as the ones presented in Figure 2 at a different photon energy (75 eV). When the second laser is also switched on (lower part of the figure), new electron lines, noted 3 and 4 , appear. Peak 3 is due to autoionization of the discrete states resonantly excited by the synchrotron radiation in the highly optically-excited sodium atoms, according to the scheme:

$$2p^6 4p\ ^2P_{3/2} + h\nu\,(SR) \longrightarrow 2p^5 3s4p\ ^2D_{3/2,5/2}$$

$$2p^5 3s4p\ ^2D_{3/2,5/2} \longrightarrow 2p^6\ ^1S_o\ (Na^+) + e^-$$

Similarly, peak 4 results from the autoionization of the $2p^5 3s4d\ ^2F_{5/2,7/2}$ excited states.

Peaks 3 and 4 disappear when the synchrotron radiation monochromator is shifted off the resonance region, because the non-resonant 4p- and 4d-photoionization cross sections are small at these photon energies, far above the ionization thresholds, or when laser II is detuned. By continuously scanning the photon energy range of interest, between 32.5 eV and 33.5 eV, it was possible to measure the energy of several of these newly observed autoionizing states and to determine the relative oscillator strengths of the inner-shell transitions having populated these excited states in the optically-excited atoms.

VI. FUTURE DEVELOPMENTS

The experiments described in the various sections of this paper are still difficult. Higher photon flux in a narrower band pass are essential if one wishes to go to a more quantitative analysis of photoionization processes in excited atoms and to measure processes with small cross sections. Large gains are expected from the undulators that are going to be installed on new storage rings especially built for the production of synchrotron radiation, such as Super ACO or the ALS. As brightness increases by several orders of magnitude, a large number of new experiments will become feasible such as:

1. Experiments with higher resolution, for the synchrotron radiation monochromator as well as for the electron spectrometer. The case of barium described previously is a particularly good example of a study for which such improvements are essential.

2. Experiments at lower atomic densities. This will make possible the study of metals with lower vapor pressures such as most of the transition metals and the rare earths. Furthermore, a significant decrease of the atomic densities in the interaction volume would considerably reduce the rate of low-energy electrons produced in collisional ionization of excited atoms. Figure 11 is an illustration of the present experimental problem, in the case of laser-excited barium atoms.[46] At low-kinetic energies, huge peaks, produced by Penning ionization of excited atoms followed by superelastic collisions, make it impossible to study the photoioniza-

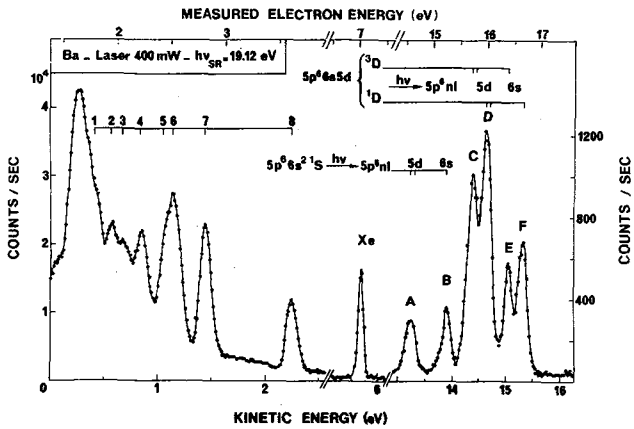

Fig.11 - Electron energy spectra produced by photoionization of excited barium atoms (right part, see also Figure 6) and in collisional processes (left part below 3eV kinetic energy). Note that the intensity of these low-energy electrons is about 30 times higher than the intensity of the photoelectrons. (From Ref.46)

tion processes in the particularly interesting energy range just above each ionization threshold. In addition, with lower atomic densities, studies of alignment effects, in connection with the polarization of the laser, may become one of the major activities in this new field (the feasibility of such an experiment has just been recently demonstrated on laser-excited lithium atoms [47]).

3. Experiments with lower laser powers, extending the usable tunability range of the cw dye lasers to atoms having higher excitation energies to the first resonant state.

4. Experiments in which two-electron high-lying core-excited states could be produced with synchrotron radiation; for example, in sodium, transitions such as $2p^6 n'\ell' \rightarrow 2p^5 n\ell\, n'\ell'$, with $n\ell > 3s$ have not yet been observed. Excitations from deeper electrons could also become feasible: in this type of studies, the higher brightness of synchrotron radiation emitted by undulators would compensate the decrease of the overlapping between the filled inner-shell orbitals and the empty optical orbitals. Ultimately, the study of planetary atoms might become possible in some cases.

5. Experiments in which the symmetry of the final states of the ion could be probed by measuring the angular distribution of the emitted electrons, as it is routinely done for atoms in the ground state.

6. Experiments in which the beam of an undulator would be used to excite atoms or ions; in that case, the further step of excitation or ionization would be provided by laser beams or by another beam of synchrotron radiation emitted by a second undulator.

7. Ultimately, experiments in which the dynamics of excited states could be studied, if it becomes possible to match the use of a pulsed laser to the pulsed emission of synchrotron radiation.

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