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The components of the photoionization cross section in the VUV and soft x-ray region

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ABSTRACT

The photoionization cross section is partitioned into its components by analyzing the emitted photoelectrons according to energy and intensity. The principle of the method is outlined and experimental results on neon, krypton, manganese and beryllium are discussed.

1. INTRODUCTION

We are all familiar with the distinctive sawtooth shape of the photoabsorption cross section presented in textbooks and in various compilations of data and calculations. We might have become so used to the sawtooth shape that we might associate it with every subshell of any element. However, at low photon energies below about 1 KeV, the photoabsorption cross section generally deviates from the sawtooth behavior which is characteristic of the interactions of energetic photons with deep atomic shells. The cross section may no longer display a jump at a threshold, and it may be drastically enhanced or suppressed in certain regions, showing broad as well as narrow features. This response of the atom to an electromagnetic perturbation is caused by the fact that the atomic potential in the outer regions of the atom where the interaction takes place is no longer Coulomb-like. Furthermore, it indicates the presence of strong interaction between the various bound electrons and between the various possible ionization channels.

The investigation of this regime requires special techniques. Theoretically,¹ a realistic potential must be chosen and many-electron interactions for both the initial and final states must be considered. For heavier atoms, relativistic effects can become important even in the outer atomic regions and at low energies. Experimentally,² special excitation sources, sample preparation and detection systems are needed, although some of the dramatic changes occurring in the cross section can hardly escape detection in even a simple experimental apparatus. However, a basic and quantitative understanding of the electronic structure and dynamics that underlie the photoionization process calls for detailed data which are obtained in rather sophisticated experiments involving many different targets. "Universal scaling" laws that have served us well for many years at the higher photon energies cannot be expected to be formulated. Hence, a few measurements of a few elements are not sufficient.

In the past 10 to 15 years, much progress has been made in our aim to delineate the photoeffect at low energies.^{1,2} Much of the progress has come from the availability of synchrotron radiation and its combination with photoelectron spectrometry. In addition, the use of atomic targets has proven most beneficial because of the possibility of creating conditions of single photon-atom collisions, and because of the fact that data from these targets can be directly compared with theoretical predictions which are by their intrinsic nature atomic. In the following, I shall briefly discuss some representative results of investigations of atomic photoionization by way of its most direct, primary consequence, the photoelectron. The emphasis will be on the experimental aspects of these studies.

2. SOME BASIC CONSIDERATIONS

The photoabsorption cross section, which can be determined from the attenuation of a photon beam by a target, is virtually identical with the photoionization cross section at energies below 1 to 2 KeV. The photoelectric effect is the dominant photon interaction. As a result, the ejected photoelectron can be used to probe the interaction between the photon and the target atom (which may be free or incorporated in a compound or solid). If both the number and the energy of the photoelectrons created are measured, two important pieces of information are obtained: the photoionization cross section from the number of electrons, and the specific photoionization process occurring at a specific site from the energy of the electron. As specific processes, we can recognize single photoionization and double photoionization or photoionization with excitation. By integrating over the entire spectrum of ejected photoelectrons the total photoionization cross section is obtained, and by distinguishing the spectral features, the components that make up the total cross section are identified and their strengths are determined. The number of

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components can be great and their strengths can vary considerably as seen in Fig. 1, in which the photoelectron spectrum of Pb is shown. In this case, 10 components can be distinguished at the very low photon energy of 18 eV. The spectrum gives evidence of photoionization taking place in the 6p and 6s subshells and reveals all the components as well as their strengths.

How is a spectrum such as the one presented in Fig. 1 measured and how is it analyzed? In principle, photons from a suitable source, such as an electron storage ring, an x-ray

Fig. 1. Photoionization of atomic Pb by 18.4 eV photons. Photoelectron spectrum indicates ionization of 6p and 6s electrons leaving the ion in various multiplet states.

or discharge tube, strike a target atom and photoelectrons emitted into a small cone are dispersed in an electron energy analyzer and counted by a high efficiency detector. For a given photon energy $h\nu$, the photoelectron energy is given by

$$E(e, \text{kin}) = h\nu - E(n\ell j) \quad (1)$$

where $E(n\ell j)$ is the energy of the electron in the orbital $n\ell j$. Hence, the observed electron is referenced to its origin. In cases in which the remaining ion core rearranges itself giving rise to multiplet and satellite structures, the energy $E(n\ell j)$ is preferably expressed as the energy difference between the final ionic state and the atomic ground state.

The number of electrons $N(i)$, which are observed at an energy characteristic for the component i , are proportional to the differential cross section $d\sigma(i)/d\Omega$, namely

$$N(i) \propto d\sigma(i)/d\Omega = \sigma(i)/4\pi [1 + g(i)(1 + 3p\cos 2\phi)/4] \quad (2)$$

where $\sigma(i)$ is the partial photoionization cross section, $g(i)$ the so-called angular distribution parameter, p the polarization of the photon beam and ϕ the observation angle relative to the polarization direction. If an angle ϕ is chosen for a given p such that $1 + 3p\cos 2\phi = 0$, the number of electrons $N(i)$ will then be directly related to the partial cross section:

$$N(i) \propto \sigma(i) \quad (3)$$

Ordinarily, a proportionality factor for Eq. 3 cannot be established easily, and the partial cross sections $\sigma(i)$ are determined only on a relative basis as a function of photon energy. However, if the absolute total cross section is known and all possible photoionization pathways are delineated, absolute partial cross sections can be determined by partitioning $\sigma(\text{tot})$ in accordance with the measured ratios $N_1:N_2:N_3:\dots:N_i$. Specifically, $\sigma(\text{tot})$ is composed of the following components $\sigma(i)$:

$$\sigma(\text{tot}) = \sum_{n\ell} \sigma(n\ell) + \sum_{n\ell, n'\ell'} \sigma(n\ell, n'\ell') + \text{triple} + \dots \quad (4)$$

where the $\sigma(n\ell)$ refer to single electron emission from the energetically accessible subshells $n\ell$, which may be further subdivided into multiplet term components, and the $\sigma(n\ell, n'\ell')$ refer to two-electron processes in which an $n\ell$ electron is ionized and an $n'\ell'$ is concomitantly excited to an unoccupied bound or continuum state. Finally, events involving three electrons are indicated in Eq. 4. All the processes summarized in Eq. 4 are induced by a single photon.

3. PHOTOIONIZATION OF NEON

The total photoionization cross section of an element was partitioned into its components for the first time in the case of neon.⁴ The various processes were recognized with the aid of photoelectron spectra excited by characteristic lines from x-ray tubes. At photon energies exceeding the K threshold (0.9 KeV), the following events take place: (a) the photon ejects a single electron from either the K shell, the 2s or the 2p subshell, (b) the emission of a K electron is accompanied by the excitation of an L electron to the M, N... shell, for example 2p + 3p, (c) the emission of an L electron is accompanied by the excitation of a second L electron, and (d) two electrons from any combination of the filled shells are ionized. The relative $\sigma(i)$ were derived from the electron spectral distributions, except for the double ionization processes for which ion spectroscopic data were utilized. Normalization of the relative $\sigma(i)$ to the absolute $\sigma(\text{tot})$, which had been determined previously by traditional techniques, allowed us then to determine an absolute $\sigma(i)$ for each of the components. The results are displayed in Fig. 2; it is interesting to note that, at energies greater than 1 keV, $\sigma(i)$ for the multiple processes associated with the K shell ionization, designated as (ϵ, n) and (ϵ, ϵ) for ionization with excitation and double ionization respectively, are greater than those for single processes in the 2p and 2s subshells.

Fig. 2. The partition of Ne photoionization cross section into the components of single and double photoionization processes. (From Ref. 4.)

4. PHOTOIONIZATION OF KRYPTON

While for neon a complete partitioning of $\sigma(\text{tot})$ could be accomplished with the use of a few discrete line sources because of the smooth behavior of $\sigma(i)$, this procedure will not generally suffice. Instead, a continuously tunable source, such as synchrotron radiation, will be needed in the general case for mapping out the $\sigma(i)$ over a wide range of energies. For example, the $\sigma(i)$ for single ionization in the 3d, 4s, and 4p subshells of krypton were measured⁵ on a small mesh with the aid of synchrotron radiation, and the results are shown in Fig. 3. Although in this case two electron processes were not investigated, it becomes nevertheless clear that $\sigma(4p)$ is the dominant component below 60 eV and $\sigma(3d)$ above 120 eV. The normalization of the partial cross sections to the absolute total photoionization cross section was made at the very low energies where ionization takes place in the 4p subshell (squares and crosses in Fig. 3) and the 4s subshell (inverted triangles and daggers).

Fig. 3. The partial photoionization cross sections of Kr (From Ref. 5.)

5. PHOTOIONIZATION OF MANGANESE

As pointed out in the introduction, the components of $\sigma(\text{tot})$ can be delineated best for free atoms. However, most elements must be specifically prepared for the atomic state and this is the reason why until now comprehensive measurements on atoms other than rare gas atoms have been scarce. The most detailed examination done so far pertains to Mn which can be produced with sufficient atomic vapor density at temperatures between 900 and 1000°C. The results are shown in Figs. 4 and 5 from 14 eV to 270 eV.^{6,7} Here, as in the case of neon, all components were identified (except for double ionization) and their strengths were normalized to the $\sigma(\text{tot})$, which was assessed in a different experiment. Because it is extremely difficult to measure an absolute cross section for an atomic vapor target, the absolute $\sigma(\text{tot})$ was taken from a study of the metal. The data corroborate the theoretical prediction that $\sigma(3d)$ is the strongest component throughout the low-energy range, although the 3p component which is split into a multiplet structure has a comparable strength above 200 eV.

Fig. 4. The component cross sections over the region of the 3p resonance region in Mn. (From Ref. 6.)

Fig. 5. Partial photoionization cross sections of atomic Mn at low photon energies. Only the major components are shown. (From Ref. 7.)

A striking feature appears in Fig. 4: at about 51 eV, all $\sigma(i)$ and hence $\sigma(\text{tot})$ undergo a strong resonance excursion. This resonance is due to the occurrence of another open channel at this energy, namely the excitation of a 3p electron to the half-filled 3d subshell. It is worthwhile to point out that this purely atomic effect retains its character in the solid state as measurements of $\sigma(\text{tot})$ for the metal have demonstrated.

6. PHOTOIONIZATION IN RESONANCE REGIONS

The irregular behavior of σ observed in Mn is a frequent event throughout the periodic table, and common in transition-series elements.³ It occurs whenever excitations from an inner shell to an outer partially filled shell interfere with the direct photoionization from the various accessible subshells. In fact, at the very low photon energies these resonances dominate the photoionization cross section. They may redistribute the strengths of the various components and they may shift strength from one spectral region into another. Quite frequently, the strengths coagulate within a resonance and virtually vanish outside. Figure 6 shows a simple illustrative case⁸ in which $\sigma(6s)$ of Hg is seen to be very strong at the positions of the $5d + np, nf$ excitations and very small in between.

Fig. 6. The 6s photoionization cross section through a resonance series in Hg.

7. PHOTOIONIZATION OF BERYLLIUM

Beryllium is one of the simplest atoms, yet the photoionization cross section in the neighborhood of the K threshold is complex⁹ even for the isolated atomic state as seen from Fig. 7. In addition to $\sigma(1s)$, which is of course the strongest component, the

Fig. 7. The relative photoionization cross section of atomic Be near the K threshold. Components of ionization and two-electron transitions are indicated. Ionization of a 2s electron is neglected. (From Ref. 9).

ionization-with-excitation components, especially $1s^2 2s^2 + 1s 2s 2p$, make considerable contributions. A very strong peak just above the 1s ionization threshold can be assigned to a $1s^2 2s^2 + 1s 2s 2p(^3P)3s$ resonance. Curiously, a similar structure has been reported for metallic Be and its origin has remained speculative. However, the atomic data which, by their nature, are free of secondary effects induced by close neighbors make it persuasive to regard this peak as real also in the metal and assign it to the same atomic process although the outer electrons are part of the conduction band.

8. CONCLUSIONS

It was shown that it has become possible to partition the photoionization cross section into its components and extract valuable information from this partition for both atomic theory and applications to solid state systems. Although fairly comprehensive data exist for a few elements, data are scarce or nonexistent for most others. Creation of a wider data base seems desirable because predictive powers are limited by the variety of behavior displayed at low photon energies.

9. ACKNOWLEDGEMENTS

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