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PHOTOIONIZATION OF ATOMS AND MOLECULES USING SYNCHROTRON RADIATION

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The potential of synchrotron radiation as a probe of atomic and molecular structure and dynamics is outlined and described by examples taken primarily from photoelectron spectrometric data.

Photoionization is one of the more powerful probes of the electronic structure and dynamics of atoms and molecules. We may use hard photons and probe the inner regions of the atom, or we may use soft photons and probe the outer regions of atoms and molecules. In either case, we can observe the transmitted photons, the fluorescent photons (x rays), the photoelectrons, the Auger electrons, the ions, or the mass fragments. These products of photoionization can be further analyzed according to their energy, intensity, direction of emission (angular distribution), and polarization. Although as a rule only one of the products is observed in a given experiment because of the different instrumental requirements for measuring photons, electrons and ions, simultaneous observation of different species is possible and has, in fact, been done concurrently and in coincidence. Similarly, a full analysis according to all pertinent parameters is possible, but is seldom done because of the specialized arrangements needed to measure the angular distributions and spin polarizations effects in addition to the energies and intensities.

To delineate fully the electronic structure and dynamics, it is essential that the measurements of the various quantities be done as a function of photon energy. Ideally, the photon energy should be continuously variable. This is the point where the synchrotron radiation source enters which, with the aid of suitable monochromators, is continuously tunable over a wide range of photon energies, from far below 1 eV to some source-dependent cutoff energy in the 100 eV, 1 keV, or 10 keV region. Previously, photoionization studies had to rely largely on the discrete line energies provided by characteristic line emissions from x-ray anodes and discharge lamps. As a result, many energy ranges such as the threshold, autoionization, far-UV and soft x-ray regions could not be adequately investigated. However, these are the regions in which strong dynamic effects occur in both atoms and molecules, leading to rapid variations of cross sections,

Fig. 1. Photoabsorption spectra of nickel around and above the 3p threshold for the metal¹, the atomic vapor² and theoretical.³

angular distributions, and spin polarization over small energy ranges, and to the appearance of strong electron-correlation satellites.

In one of the early measurements that demonstrated the power of a synchrotron radiation source, the photoabsorption spectra of the 3d metals were recorded near and above the 3p thresholds. The absorption spectrum of nickel metal¹ is shown in Fig. 1 along with the spectrum of the vapor,² measured only recently, and the theoretical results of a many-electron calculation.³ This spectrum, like most spectra in the soft-photon range, shows the absence of the sawtooth shape, characteristic of the absorption cross section in the hard-photon range, where the hydrogenic model represents a good approximation. This is caused by the deviation of the atomic potential from the Coulomb potential,⁴ and, as in the case of Ni 3p, deviations from the single-particle central field model. The spectrum of Fig. 1 also shows a quite similar behavior between the absorption spectra of the metal and the free atom. This indicates that free-atom data, which can be directly compared with and interpreted by atomic theory, can be used as a valuable reference for the condensed matter, and for the purpose of estimating the relative importance of atomic and solid state effects.

Turning to the absorption spectrum of xenon displayed in Fig. 2, we find jumps in the cross section to be completely absent at the 5s, 4d, 4p and 4s levels, but a strong and broad delayed maximum following the 4d threshold. As the Hartree-Slater and especially the Hartree-Fock calculations (the latter broken down into its subshell constituents) indicate,⁴ the cross section between 70 and 700 eV is dominated by the 4d partial cross section, which goes through a Cooper minimum

Fig. 2. The photoabsorption spectrum of xenon. The theoretical HS-HF(V) results are partitioned into subshell components.

near 200 eV gives rise to a second, lower maximum between 300 and 400 eV. The "irregular" behavior of the partial cross sections makes their direct measurement highly desirable. This has, in fact, been done, first in krypton and neon and later in other rare gases including xenon, by way of photoelectron spectrometry using discrete sources and, most importantly, using synchrotron radiation sources.⁵ A typical setup which allows the measurement of partial photoionization cross sections and photoelectron angular distributions is sketched in Fig. 3; the sketch shows our arrangement, which is presently under construction.⁶ In Xe, the ESSR (electron spectrometry with synchrotron radiation) studies spanned the range $20 \lesssim h\nu \lesssim 200$ eV and included measurements of cross sections and angular distributions for 5p, 5s, and 4d, the $5p_{3/2}/5p_{1/2}$ and $4d_{5/2}/4d_{3/2}$ branching ratios, and correlation satellites. In addition, photoelectron spectra of the 4p, 4s, and M levels were recorded at $h\nu = 1.5$ keV.⁷ All data, but especially the ESSR data, show clearly that both many-electron and relativistic effects play an important role in Xe. Figure 4 displays the results⁸⁻¹⁰ for the asymmetry parameter β of the 5s electrons in Xe; and an excellent agreement is apparent between the experimental data and the relativistic random phase approximation (RRPA) calculation¹⁰ in which relativity and interchannel interactions are treated in an integral manner.

We note that the RRPA is also in excellent agreement with similar data in other noble gases. Most significantly, the RRPA predictions¹¹ are in excellent accord with spin polarization data¹² which have become available very recently. The spin-polarization determination adds another dimension to the photoionization probe of atomic dynamics, and it is gratifying to see that a single theoretical model is capable of giving correctly all dynamic parameters that are predicted by photoionization theory¹³ and are accessible to experimental scrutiny over a wide range of energies.

The variation of the spin polarization and cross section when going through autoionization features is shown in Fig. 5 for the case of Kr in the region between the $P_{3/2}$ and $P_{1/2}$ ionization thresholds. These data were obtained with circularly polarized synchrotron radiation,¹⁴ and the strong variation of the polarization, synchronous with the variation of the cross section, is evident in Fig. 5.

Up to now, the RRPA has not been applied to the calculation of the difficult problem of two-electron excitation or ionization. However, non-relativistic many-electron theory in the multibody perturbation theory model (MBPT) has been able to account^{15,16} for the double ionization cross sections of the outer shells of the lighter rare gases as measured¹⁷ by ion charge spectrometry in conjunction with synchrotron

Fig. 3. Schematic of ESSR setup for angular distribution and cross section measurements in free atoms and molecules.⁶ ES = energy analyzer, RP = rotatable platform, S = source, C = capillary, Sh = shield, Rd = rotary drive, O = oven, G = gas inlet.

Fig. 4. The asymmetry parameter of the Xe 5s photoelectron angular distribution (adapted from Ref. 5).

radiation. The cross section for simultaneous ionization and excitation of the prototype atom He has recently been measured from threshold to over 100 eV. The ESSR data¹⁸ for $\text{He} + h\nu \rightarrow \text{He}^+(n=2) + e$ were found to be in good agreement with the MBPT results, which include many channel interactions in initial and final states,¹⁹ and the fluorescence measurements²⁰ involving the same excited He^+ states clearly exhibited the autoionization structure toward the $\text{He}^+(n=3)$ level.

Photoionization processes and competing autoionization processes involving the promotion of two electrons are a manifestation of strong interactions between a number of alternate channels. In these events the resulting ion is left in an excited state. In perhaps the most famous case, that of Ba, identification of the processes was facilitated by the use of synchrotron radiation for measuring the absorption spectrum²¹ and photoelectron spectra, two of which are presented in Fig. 6.²² The spectra show the expected 6s photoline and correlation satellites indicative of the promotion of the second 6s electron to $ns(n \geq 7)$; $np(n \geq 6)$; and $nd(n \geq 5)$ states; however, at $h\nu = 19.94$ eV the 5d peak, and at $h\nu = 21.48$ eV the 6d peak acquire an unusual strength. What occurs is that, at these energies, two-electron excitation states are reached which being quasistationary rapidly decay into continuum channels via a radiationless transition. As in the classic autoionization process, this transition competes with the direct transition, but is evidently so strong that no interference structure (Fano profile) is observed.

Fig. 5. Cross section (a) and spin polarization of photoelectrons (b) in 4p autoionization region of Kr.¹⁴

Fig. 6. Photoelectron spectra of atomic Ba giving evidence of autoionization resonance enhancement of 5d and 6d peaks.²²

Instead, this two-electron resonance state enhances the nd peaks dramatically. The overall interaction can be represented by the following scheme:

where $5p \rightarrow 5d 6s$ has the character of a Coster-Kronig transition. Note in particular that each "step" involves simultaneous transitions of two electrons.

Fig. 7. Photoelectron spectrum of free Ag atoms, giving the relative photoionization cross sections of the 1^1D and 1^1S components.²³

So far, few open-shell atoms have been studied by photoelectron spectrometry and none by ESSR. However, as the experimental Ag^+ spectrum²³ (Fig. 7) and the theoretical calculations²⁴ of σ and β for Cl 3p (Fig 8) indicate, such studies offer the opportunity to examine the structure and dynamics at the term level. Doubtless, open-shell atoms will be investigated by ESSR in the coming years, and theoretical models which include both the relativistic and many-electron aspects will be developed in close interplay with experiment.

The availability of a continuously tunable radiation source is essential for the study of molecules because of their electronic-vibrational structure, the absence of a highly developed theory, the omnipresence of autoionization and shape resonance features, and the possibility of molecular fragmentation. Thus it is not surprising that a great effort has been and is being devoted to the measurement of partial cross sections, satellite structures and angular distributions. As an example, Fig. 9 makes a comparison between the recently measured β values of two of the four electronic states of CO_2 and the predictions of the Xa model.⁴⁵ A satisfactory agreement can be seen to exist between the data over the yet limited energy range and the rather simple, but obviously realistic theory. In other measurements^{26,27} the theoretical predictions of a shape resonance in $N_2(\sigma_g^2)$, which affects the vibrational levels dissimilarly, could be confirmed by and large, although the presence of autoionization structures necessitates more experimental and theoretical studies of greater detail to unequivocally identify the different features. The intensity variation of the photolines corresponding to different vibrational levels of the Π_u electronic state of acetylene is shown in Fig. 10 in the region of a shape resonance.²⁸ In general, the Xa multiple scattering model^{29,30} has been able to satisfactorily predict the major features of the ESSR data reported so far.^{25-27,31-33}

Synchrotron radiation in conjunction with the detection of zero-energy photoelectrons offers the unique opportunity to excite a molecule selectively — and deposit a well-defined amount of energy — and then determine the decay paths by detecting the fluorescence radiation, Auger electrons, or ion species (including charged fragments) in coincidence with the threshold electron.³⁴ Thus, a hitherto unknown specificity and flexibility in the study of molecular de-excitation has been placed at our disposal.

The time structure of synchrotron radiation has been put to good use in determining fluorescence lifetime measurements in atoms and molecules.³⁵ With a photon pulse width of less than 1 ns and periods up to nearly 1 μ s, decay times in the range of interest of outer shell radiative transitions are amenable to study.

In analogy with the spin polarization measurements of photoelectrons, the polarization of the fluorescence radiation of molecular ions and photodisintegration fragments has been investigated in recent experiments

Fig. 8. Theoretical partial cross sections and asymmetry parameters for photoionization of a 3p electron of Cl.²⁴

Fig. 9. Experimental and theoretical asymmetry parameters for two electronic states of CO_2 .²⁵

to gain additional dynamic information on molecules.^{36, 37} In particular, polarization measurements yield information on the alignment in space and degenerate channels, such as the $s + \epsilon p_{1/2}$ and $s + \epsilon p_{3/2}$ dipole allowed transitions.

In yet another application of synchrotron radiation to the study of the dynamics of the photon-atom-ion system, Auger electron spectra have been recorded under conditions of near threshold photoexcitation. If the photoelectron from an inner shell escapes at low velocity, it will interact with the "subsequently" emitted Auger electron, resulting in an acceleration of the Auger electron and an asymmetric broadening of the Auger line.⁵ Figure 11 shows an especially fine example of this so-called post-collision interaction in the case of XeN_5 excitation ($E_B = 67.55$ eV) and the $\text{N}_5 5p5p^1S_0$ Auger line.³⁸

As of now, synchrotron radiation is used in conjunction with electron, ion, and photon spectrometry primarily in the region from threshold to 150 eV, and occasionally to 280 eV. This is, of course, the least known yet the most important range to gain a better understanding of the structure and dynamics of atoms and molecules. However, the use of higher photon

Fig. 10. Experimental and theoretical relative intensities of the vibrational transitions in the ν_u band of acetylene.²⁸

Fig. 11. Shift of $\text{N}_5 5p5p^1S_0$ Auger line of Xe due to post-collision interaction during photoionization of N_5 electron.³⁸

energies, up to several keV, is of interest if we are to learn more about the processes in the vicinity of inner shell threshold and the behavior of relatively lightly bound electrons in very heavy atoms. Photons in the range $300 \lesssim h\nu \lesssim 1$ keV are difficult to monochromatize efficiently, but new developments in instrumentation are expected soon to routinely cover this region as well.

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