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Multiple photoelectron processes and their relationship to electron energy spectra

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Some processes are discussed in which more than one electron is ejected by an atom which absorbs a photon. Illustrations are given from the measured photoionization cross-sections in the production of Xe^{2+}, Xe^{3+}, Cd^{2+}, and Zn^{2+} by monochromatic vacuum ultraviolet radiation of energy less than 85 eV. Of photons absorbed at 63 eV, 30% produce doubly charged ions in Xe and Cd, and 20% do so in Zn, all by direct emission. The role which double electron emission and single and multiple Auger electron emission may play in electron energy measurements is brought out, and the relationship with atomic theory is briefly discussed.

Introduction

It is the purpose of this communication to call attention to the role which multiple electron processes may play in photoelectron energy measurements and to illustrate the magnitude of such processes by discussion of recent measurements of photoionization cross-sections for the production of multiply charged ions in Xe, Cd and Zn. Measurements of the probabilities of the various multiple electron processes can make significant contributions to atomic physics.

The usual basis for atomic calculations is the Hartree–Fock model (Hartree 1928, 1957; Fock 1930) or one of its modifications by Slater (1951), Herman & Skillman (1963), and others (Lindgren 1966; Liberman 1968). In these models, each electron is pictured as moving in the average field, with exchange, of all the other atomic electrons and the nucleus. Typically, a single Slater determinant is used to describe the atom; each electron is in an orbital. The only correlation is through the electron spin. This approach has been very successful in the calculation of energy levels of complex atoms (Herman 1963; Siegbahn *et al.* 1967), but somewhat less successful in the prediction of photoionization cross-sections (Cooper 1962; Manson & Cooper 1968; Fano & Cooper 1968).

If a single Slater determinant is used, absorption or emission of a photon involves (in first order) only a single electron; the usual single electron jump selection rule is obeyed. It is only in the next order of approximation, in which removal of one electron disturbs the potential in which another electron moves, that multiple electron processes are allowed by the theory. The effect of this disturbance in potential has been used in calculations of 'shake off' in nuclear and X-ray cases (Levinger 1953) but it is not likely to be important in the cases of the outer electrons which will be discussed here.

If the Hartree–Fock picture based on a single Slater determinant (and thus well-defined orbitals) breaks down, if there is strong correlation between pairs of electrons, then removal of an electron should profoundly disturb one or more of the remaining electrons, and multiple electron transitions would be expected. Multiple electron transitions have been known in atomic spectroscopy since Russell & Saunders (1925) recognized multiplets arising from double electron transitions. Since that time, many observations of double electron transitions have been made,

most notably in absorption spectra by Garton and colleagues (Garton & Codling 1959; Garton, Parkinson & Reeves 1962*a*; Garton 1962*b*); Ditchburn & Hudson (1960), and Madden and associates (Madden & Codling 1965; Codling, Madden & Ederer 1967). In all of these cases, the lines observed were caused by excitation of two electrons to discrete bound states. These observations suggest the existence of continua associated with excitations in which one or more electrons are raised simultaneously to unbound states. In fact such continua have been observed. Ditchburn & Hudson (1960) clearly show an absorption continuum in Ca at the series limit of the several 3dmp series. These series arise from double electron transitions and terminate on the ^2D excited state of the Ca^+ ion. Comes (1965) has measured the photoionization cross-section for production of doubly ionized xenon from threshold to 44 eV and Carlson, Krause, and colleagues (Carlson 1967; Krause, Carlson & Dismukes 1968; Krause 1969) have reported electron energy spectra and mass spectra from multiple electron processes excited by X-rays. Theoretical discussion of double electron processes can be found in the review of Fano & Cooper (1968).

In the following sections, cases in which two electrons are excited simultaneously to unbound states will be demonstrated and discussed, then the implications of multiple ionization for photoelectron spectroscopy will be examined.

Results

The apparatus involved in the experiments reported here has been described in detail elsewhere (Cairns, Harrison & Schoen 1969; Harrison, Schoen, Schubert & Cairns 1969). Since the main interest here is in the implications for electron energy measurements, we omit apparatus description and proceed directly to the results of measurement.

The photoionization cross-sections for the production of various charge states of Xe are shown in figure 1. These results have been made absolute by comparison with Samson's (1966) measurements of the absorption cross-section.

Of particular interest are the cross-sections for double and triple ionization. At energies less than 67.5 eV, the double electron emission cannot be caused by an Auger effect; therefore a true deviation from the single electron picture has been observed. It is to be noted that for Xe, at a photon energy of 60 eV, the double ionization process occurs in about one photoabsorption of three. Deviations from a central field model are therefore strong. The double ionization observed is more than an order of magnitude greater than that calculated from a single ionization followed by shake off.

At energies greater than 67.55 eV, removal of a 4d electron from Xe causes an increase in the double electron cross-section through the Auger effect. In this spectral region, triple ionization is also observed. This is not caused by an Auger cascade in which single electrons falling cause the ejection of single electrons. Instead, the energetics of the situation force the conclusion that the fall of a single electron into the 4d shell causes the simultaneous ejection of two electrons.

The photoionization cross-section for production of Cd^{2+} is shown in figure 2. This has been put on an absolute scale by normalization with the single photoionization cross-sections of Marr & Austin (1969). In contrast to the case of 4d electron removal in Cd and Xe, there is no well defined rise in cross-sections caused by removal of a 4p electron in Cd, which occurs at roughly 72 eV. At an energy of about 63 eV, at which no Auger emission is possible, almost 30 % of the photons absorbed produce double rather than single ionization.

Figure 3 shows the double ionization cross-section of zinc, between 30 and 65 eV. The data of Marr & Austin (1969) have been used for normalization. No Auger processes can take place in this spectral region, but the double ionization nevertheless occurs in more than 20 % of the photoabsorptions at 63 eV.

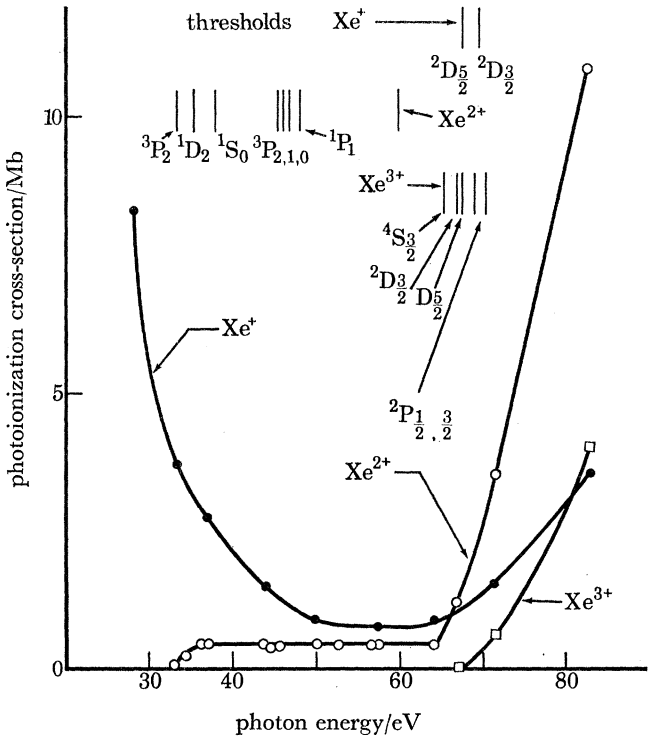

FIGURE 1. The cross-sections for the production of Xe^{+}, Xe^{2+} and Xe^{+} by photoionization.

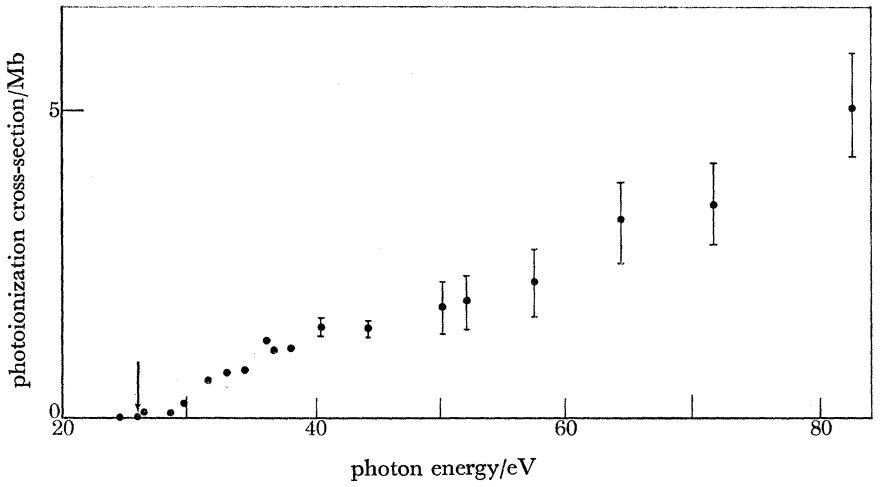

FIGURE 2. The cross-section for the production of Cd^{2+} by photoionization. The arrow indicates the threshold for double ionization.

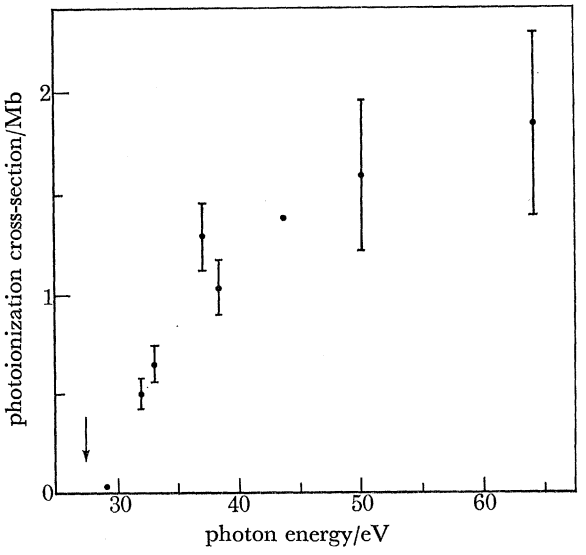

FIGURE 3. The cross-section for the production of Zn^{2+} by photoionization. The arrow indicates the threshold for double ionization.

IMPLICATIONS FOR ELECTRON ENERGY MEASUREMENTS

We first direct our attention to production of singly charged ions. The fact that double ionization was observed in Xe, Cd and Zn makes it appear likely that there are undiscovered processes in which one electron is excited to the continuum and, simultaneously another to a discrete state. Thresholds for these processes have not been detected in absorption cross section measurements or ionization measurements of the kind reported here, but similar thresholds have been found in the alkaline earths (Ditchburn & Hudson 1960). Electron-energy measurements appear to be the best way to detect these processes and to measure the relative probabilities for excitation to various states of the ion produced. By measuring the relative excitation probabilities, quantitative information about the distribution of oscillator strength in the double electron processes may be obtained. No thresholds of ionization-excitation processes have been observed in the cross-section for single ionization of Xe, Cd and Zn. Therefore, we conclude that no one of these processes contributes more to the total cross-section near its threshold than 15 % in Xe, 25 % in Cd, and 30 % in Zn. In the alkaline earths, however, the results of Ditchburn & Hudson (1960) indicate that contributions to the single ionization continuum from double electron processes may be as much as 50 % in some spectral regions. Carlson (1967) has been able to make some measurements in the X-ray region and has been able to compare his results in He with theory to show agreement within the rather large experimental error.

In cases of double ionization, electron energy measurements can also give definitive information, not available from other methods. Siegbahn *et al.* (1967) have clearly demonstrated the power of the method in studying simple Auger processes which lead to line spectra, but it should also be realized that the continuum generated by direct double electron removal can be separated from the simple Auger line spectrum in cases such as that shown for Xe double ionization at energies above 67.5 eV. In some cases, it may also be possible to separate the various continua available in double electron removal, such as those in Xe which may occur on the removal of two 5s, a 5s and 5p or two 5p electrons. Furthermore, study of the directly removed electrons and those produced by the Auger transitions should give the relative contributions of the $d_{\frac{3}{2}}$ and the $d_{\frac{5}{2}}$ to single and multiple ionization caused by d electron removal.

The triple ionization observed in Xe is also a manifestation of deviations from a simple single configuration Hartree–Fock picture, in that after photoemission from the 4d orbital two electrons are emitted simultaneously with the fall of a single electron from the 5p to the 4d state. This process should give rise to lines from the removal of the $d_{\frac{3}{2}}$ and $d_{\frac{5}{2}}$ electrons and a continuum from the Auger process. Electron energy measurements should confirm this. Furthermore it is entirely possible that the relative probabilities of fluorescence and simple Auger effect are different when the $d_{\frac{3}{2}}$ hole is filled from what they are when the $d_{\frac{5}{2}}$ hole is filled. To obtain the individual values one can measure the cross-sections for electron removal of $d_{\frac{3}{2}}$ and $d_{\frac{5}{2}}$ with electron energy analysis, then measure the relative intensities at the key fluorescence wavelengths. This is just a particular case of the more general situation in which electron energy analysis can be combined with fluorescence measurement to obtain individual cross-sections for various channels of the decay of excitation.

It has been common practice to dismiss electrons which appear to have a continuous energy distribution as scattered electrons. This may be justified when the excitation energy is low, but the examples given above indicate that it may not be justified when multiple ionization processes are possible.

In general, quantitative measurements of the number of electrons produced in each energy interval by the photoionization of atoms can make substantial contributions of our understanding of atomic physics and should be particularly helpful in problems of deviations from the single configuration Hartree–Fock picture of the atom.

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