CONF 9103146--1

CONF-9103146--1

DE91 009917

ELECTRON CORRELATION EXPLORED THROUGH ELECTRON SPECTROMETRY USING SYNCHROTRON RADIATION

C. D. CALDWELL, S. B. WHITFIELD, AND M. G. FLEMMING
Department of Physics, University of Central Florida
Orlando, FL, 32816, USA

M. O. KRAUSE
Oak Ridge National Laboratory, Oak Ridge, TN, 37831, USA

ABSTRACT

The development of synchrotron radiation facilities as a research tool has made possible experiments which provide new insights into the role which correlation plays in electron dynamics and atomic and molecular structure. Features such as autoionizing resonances, normal and resonant Auger decay modes, and ionization threshold structure have become visible in a wealth of new detail. Some aspects of this information drawn from recent experiments on the alkaline earth metals and the rare gases are presented. The potential for increased flux and resolution inherent in insertion device-based facilities like the Advanced Light Source should advance this understanding even further, and some future directions are suggested.

1. Resonant Auger Decay

For photons which are energetic enough to allow two electrons to be removed from an atom, double ionization will ultimately occur. This double ionization can take place via a number of routes. The most common is the normal Auger effect, in which the first electron creates a hole in an inner shell, producing a highly excited ion which decays by emission of a second electron. Direct double ionization of two outer electrons can also occur, but this is generally low in intensity and therefore more difficult to observe. Of recent interest is the shake off[1] of electrons following excitation of an inner-shell electron to a Rydberg orbital which lies above the double-ionization threshold in energy and which can decay by emitting two electrons. These shake-off processes can be detected by looking at electrons which leave the excited atom with zero kinetic energy; a second electron carries all the additional energy of the photon.

Within the context of experiments which we have been conducting recently on the decay of inner shell excitations, we have begun an examination of the role of shake-off as a possible decay channel. We focus on shake-off as the limit of a shake-up process in which the final ionic state is the

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

"The submitted manuscript has been authored by a contractor of the U.S. Government under contract No. DE-AC05-84OR21400. Accordingly, the U.S. Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or allow others to do so, for U.S. Government purposes."

doubly charged ion, rather than a highly excited state of the singly charged ion. The technique we use is an extension of the Constant Ionic State (CIS) approach which has been very effective in determining the excitation paths which feed decay channels leading to specific final states of an ion. The normal single photoionization which occurs through an intermediate excited state may be represented according to:

$$A + h\nu \rightarrow A^* \rightarrow A^+(E_b) + e^-(\epsilon) \qquad (1)$$

The energy E_b is equal to the first ionization potential plus the energy of the excited state above the ground state. In the CIS technique both the photon energy $h\nu$ and the electron kinetic energy ϵ are scanned simultaneouly; thus, the electrons which are observed correspond to the production of an ion with energy E_b.

The functioning of the CIS scheme applied to shake-off studies is based on an extension of the above process to include the production of two electrons:

$$A + h\nu \rightarrow A^* \rightarrow A^{2+}(E_t) + e^-(\epsilon_1) + e^-(\epsilon_2) \qquad (2)$$

In this extended version, the energy E_t is the threshold for the production of a given final state of the ion. Once the final state is selected by a choice of E_t and ϵ_1 for the CIS scan, with $E_t+\epsilon_1=h\nu$, then the energy ϵ_2 must be zero (within the resolution of the electron detector). Thus, we are not only able to determine that an electron of zero kinetic energy has been observed; we are also able to specify the final state of the ion produced when that electron emerges. In a sense this experiment is a type of coincidence experiment in which only those electron pairs are detected in which one electron has zero kinetic energy. In principle and practice, this continuum method (CCIS) can of course be further extended to define an energy $\epsilon_2>0$ for one of the electrons.

The system we have examined is the production of the doubly ionized xenon ion following excitation of one of the 4d electrons to an np orbital.[2] For $n\geq 6$ this orbital lies above the $5s^25p^4(^3P_2)$ ground state of Xe^{++}, and shake-off becomes a possibility. Using the continuum CIS approach, we have measured the production of this state throughout the energy region beginning with n=6. The spectrum is given in Fig.1.[2] Appearance of electrons corresponding to ions at energy E_t is apparent at all the excitations which could be clearly resolved.

While it is tempting to regard the spectrum in Fig. 1 as arising solely from shake-off, the interpretation for the case of xenon is not as simple as that. The p^4 configuration in Xe^{++} gives rise to five terms, and there are Rydberg series ending on each of these terms. Thus, there is the possibility

of an overlap in energy between the ionization limit of one of the doubly charged ionic states and a Rydberg orbital corresponding to a series ending on a higher limit. This is illustrated in the energy level diagram in Fig. 2. If this occurs, then an electron would appear as a consequence of a shake-up process which would produce the singly charged ion in that excited state. This would subsequently autoionize into the corresponding continuum, producing a near zero-energy electron. It is impossible to distinguish between these two processes by using only one (ϵ_1, ϵ_2) pair through either the continuum CIS method or through the detection of zero-energy electrons.

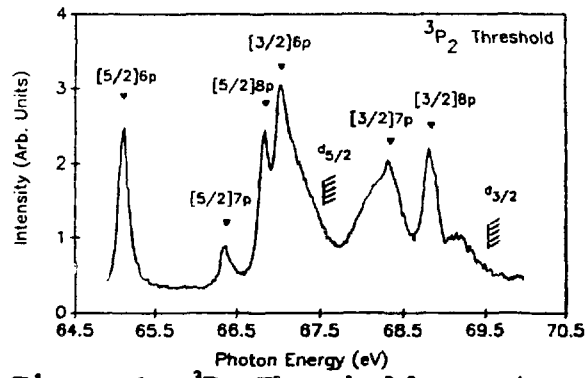

Figure 1: $^3P_2$ Threshold spectrum in Xe.

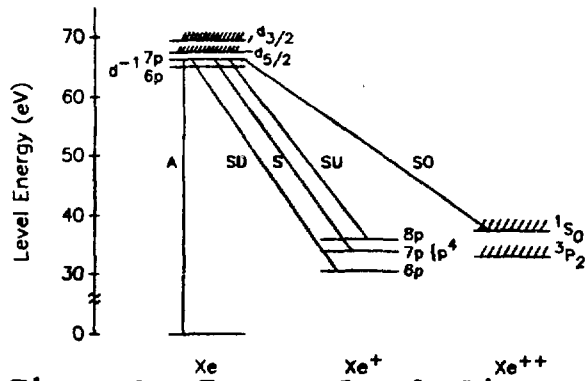

Figure 2: Energy Level Diagram for Xe

Although some measurements and calculations exist,[3] the locations of the higher-lying members of the Rydberg series ending on the Xe^{++} limits are not known. However, they can be calculated based on a quantum defect analysis. Even including possible inaccuracies in the calculated energy levels, there are numerous Rydberg levels which lie in close proximity to the Xe^{++} threshold which we are measuring. As we have observed in other experiments which will be discussed below, there is a strong probability for shake-up into these orbitals. Thus, we are inclined toward the interpretation that the structure shown in Fig. 1 is primarily due to shake-up, followed by autoionization, rather than to shake-off. This belief is supported by preliminary measurements which we have since conducted on the $^1S_0$ threshold, where essentially no structure is to be observed in the CCIS spectrum. (See Fig. 3.)

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

2. Excited-State Population Enhancement in the Alkaline Earths

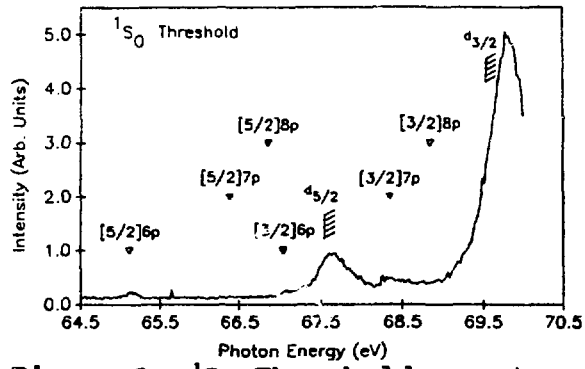

Figure 3: $^1S_0$ **Threshold spectrum in Xe**

Decay of Rydberg levels resulting from inner-shell excitations has been analyzed through the simple approach of shake theory.[4] Briefly summarized, within this description the decay is presumed to occur primarily through the break-up of an inner-shell orbital, and the electron which was originally excited has little role to play. This electron either remains in the orbital to which it was initially promoted, i.e. retains the same n value, and becomes a "spectator," or it is shaken up or down, i.e. the n value increases or decreases by one or more units, respectively, in response to the change in the effective Z value of the decaying core. The most obvious consequence of the correlation effects which this theory seeks to explain is the frequent appearance of enhancements in the population of excited states of the resulting ion over those created by the direct production as satellites in the case of non-resonant excitation. In many cases production of these excited states is not only enhanced, but becomes the predominant mode of decay. We note parenthetically that for higher n's, the ground state is rarely produced.

2.1 Beryllium

In an experiment which we completed some years ago[5] we observed a most startling result which occurred when the $1s2s^22p$ level of beryllium was observed to decay by electron emission: rather than produce the ground state of the ion, the decay proceeded in such a fashion as to create 95% of the ions in the $1s^22p$ excited state. Indeed, rather than form the ground state of the ion, the decay even preferred to shake up to create the $1s^23p$ state. A series of scans toward higher-lying $1s2s^23p$ and $1s2s^24p$ excitations demonstrated a general pattern of spectator and shake-up processes always predominating over ground state production and shake-down processes. An example of the PES spectrum following both the 3p and the 4p excitations[5] at low resolution which illustrates this behavior is given in Fig. 4. Notice that, while the 3p excitation produces the ion primarily in the 3p state, the 4p

excitation generates not only the 4p state but an equal number of ions in the 5p state.

2.2 *Magnesium*

In the work on beryllium information emerged which indicated that the results discovered for this species might be a general property of all beryllium-like ions.[6] An intriguing question then becomes, to what extent this behavior might be a property of the more complicated members of the alkaline earth series. To explore this question we recently conducted a series of measurements on the decay of excitations of one of the 2p electrons in magnesium.[7] While more complicated than beryllium, magnesium is still rather simple compared to the other alkaline earth elements. In particular, the energy region of the $Mg^{++}(1s^22s^22p^6)$ ground state is not overlapped by ionization limits of series of two-electron excitations as is the case for calcium and strontium. Decay of the 2p hole might also be expected to occur through a break-up of the $3s^2$ orbital in the same fashion as decay of the 1s hole in beryllium occurred through a break-up of the $2s^2$ orbital.

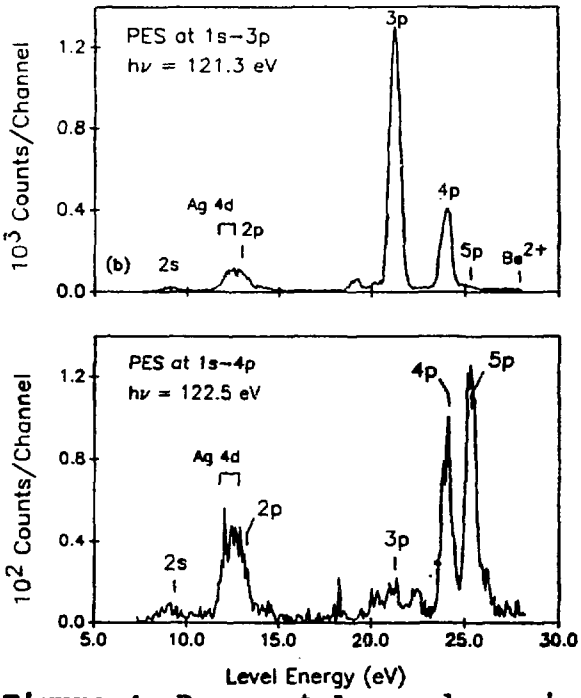

Figure 4: Resonant Auger decay in Be

Excitation from the 2p orbital in magnesium is very different in one regard from that of the 1s in beryllium in that there are two possible series, $2p^63s^2 \rightarrow 2p^53s^2ns$ and $2p^63s^2 \rightarrow 2p^53s^2nd$. Two examples of the results of the magnesium experiment are given in Fig. 5.[6] These particular spectra are chosen because they illustrate two important features of the behavior of the decay of these excited states. In panel (a) is shown the photoelectron spectrum resulting from the decay of the $2p_{3/2}6d$ and the $2p_{1/2}5d$ states. (These could not be resolved with the monochromator we used.) The appearance of the 5d and 6d spectators is clear, along with the 7d shake-up line. A spectrum of this type is rather typical for all the nd excitations we observed except for the 3d orbital and the $2p_{1/2}6d$ orbital. In the case of 3d excitation decay results

primarily in the production of the ground state, in complete discordance with the predictions of shake theory. The spectrum in panel (a) is also rather typical for excitations into all ns orbitals which we observed. The behavior which is most surprising is illustrated in panel (b) of the figure, the $2p_{1/2}6d$ excitation.

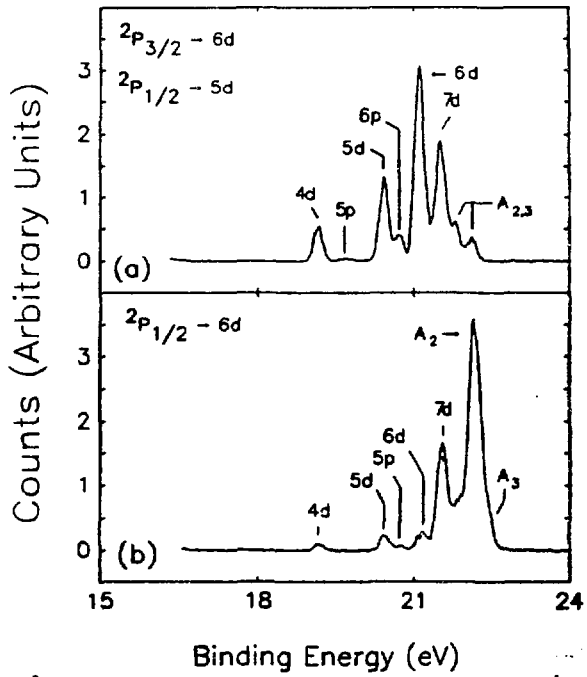

Figure 5: Resonant Auger Decay in Mg

In panel (a) two small features appear to the right of the spectrum. These are L_2-M_1M_1 and L_3-M_1M_1 Auger electrons which are produced by second order radiation from the diffraction grating. These are observed in all decay spectra which we measured and always appear with rather weak intensity, as expected from the small fraction of second order radiation which we expect. However, the same is not true for the excitation depicted in panel (b). Rather than appear as a simple weak feature due to second order radiation, the L_2-M_1M_1 Auger line appears as the dominant decay mode for this excitation. While this is certainly allowed energetically, it can only correspond to a shake-up transition in which the ion is left in the 11d final state. That this should occur is completely out of step with the general trend of the other decay modes. This normal pattern predicts that the 6d or 7d level of the ion should have appeared with the maximum intensity, not the 11d as observed. Also unclear is why only the L_2-M_1M_1 line should appear and not the L_3-M_1M_1 line. That this is true has been borne out by an independent series of measurements on the production of these two Auger lines following excitation to the resonances indicated above. While we are convinced that this is a real phenomenon, quantitative calculations are urgently needed if we are to understand this behavior.

2.3 Strontium

In order to investigate the possible trends which exist

for the decay of excitations in the alkaline earth elements, we have recently made a series of measurements on the resonance enhancement of excited state ion production in strontium as well. Our data for this atom are still quite preliminary, but the type of behavior we are seeing can be illustrated by two simple spectra. In Fig. 6 are shown CIS scans focused on the 5s (dotted line) and 4d (solid line) states of the strontium ion. The very broad feature near 25 eV is the principal $4p \rightarrow 4d$ excitation. This feature appears in CIS scans fixed on both final states, albeit in quite different forms. This difference can be attributed to the number of different states which arise from the different couplings within the complex. Also visible at higher energies on the right are two weak features, one of which is only apparent in the 4d channel. Corresponding photoelectron spectra taken at these two features are given in Fig. 7. These spectra are not normalized to each other in absolute value; rather the contributions to the 4d production have been set arbitrarily equal to illustrate the observation regarding enhancement. In particular, one notices that there is virtually no ground state 5s production at feature 1. This is behavior which we have observed in other experiments as well, namely, that features which appear very weak in a normal absorption spectrum can be made readily visible through exploitation of the decay enhancement which they create. Although our analysis is still far from complete, we believe that the information which we acquire through these enhancement measurements can help us not only to identify excitations but to understand in more detail the dynamics of the decay process.

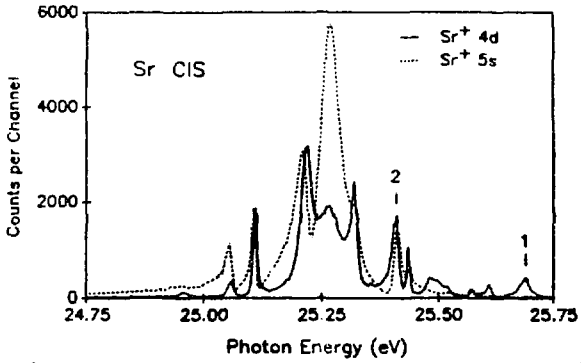

Figure 6: CIS spectrum for Sr

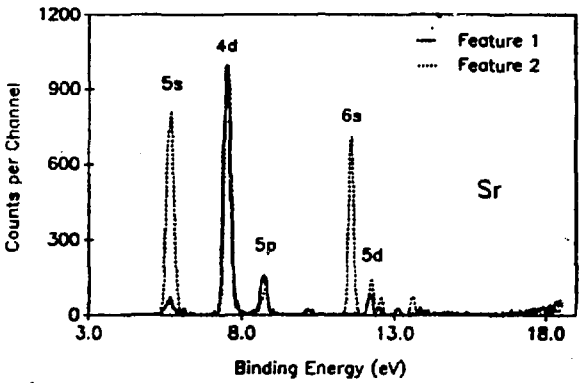

Figure 7: PES Spectrum for Sr

3. Gas-Phase Experiments at the Advanced Light Source

Although experiments on atoms and molecules using synchrotron radiation have helped create a revolution in our understanding of the details of electron dynamics and atomic and molecular structure, there are still limitations on the information we can acquire. These limitations are imposed by the levels of flux and resolution which are available in traditional radiation sources based on bending magnets. The next breakthroughs in the study of gas phase processes using synchrotron radiation are going to demand both higher flux and increased resolution, in other words, the third generation of synchrotron radiation sources. One such instrument is the Advanced Light Source (ALS) currently being constructed at the Lawrence Berkeley Laboratory in California. Based on insertion devices as radiation sources, this facility will have an extremely high brightness, contributing both to improved flux and improved resolution.

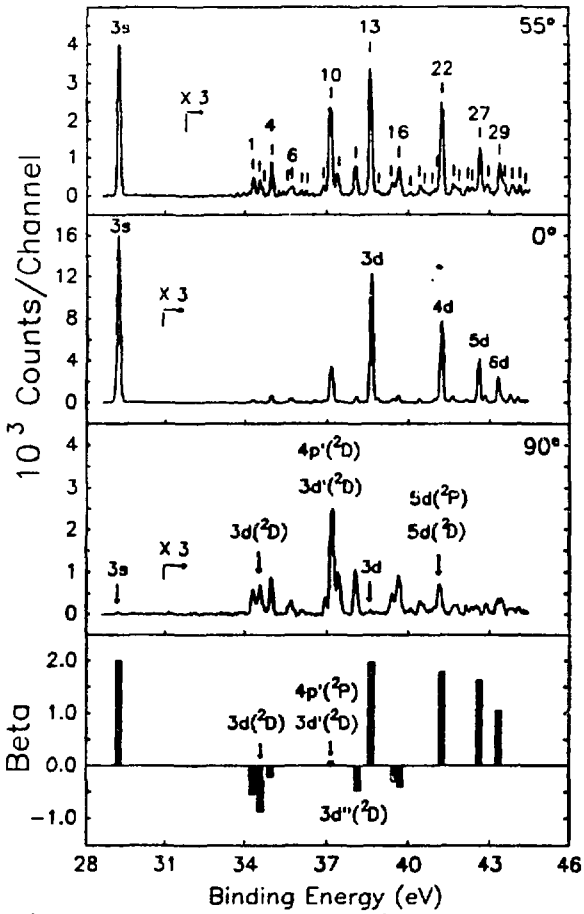

Figure 8: PES Satellite spectra of Ar

From a series of proposals which were submitted to the ALS Scientific Review Panel last year, two groups of scientists were selected as Principal Research Teams (PRTs) for cooperation with the ALS staff in determining the characteristics of the first two beamlines which the ALS will have in operation. One of the lines, called U-8 in consequence of its derivation from an 8-meter undulator source, will be devoted to gas phase processes in atoms and molecules. It will cover an energy range from 20-300 eV, with resolutions up to 10,000 over part of the spectrum. Although the list of experiments which are proposed for use on this line is quite long, a considerable portion of the activity

will be devoted to electron spectrometry. We anticipate that this new beamline will make measurements such as coincidence experiments, alignment determinations, spin determinations, and high resolution electron spectra routine.

As a last item in this presentation is shown in Fig. 8 an electron spectrum of the 3s state in argon,[8] together with the 3s,3p correlation satellites. This particular measurement was performed at the Synchrotron Radiation Center in Wisconsin on the undulator line which was in operation there for a time and provided a glimpse of what the future will bring. It is simply not possible to acquire the detail which is available in this spectrum through use of even the best bending magnet sources. The high degree of polarization of undulator radiation (P~100%) makes even the measurement of angular distributions for these features a much simpler task. Other measurements which we performed using this undulator source provide the same type of tantalizing results, leading us to expect that the marriage of electron spectrometry with synchrotron radiation will continue to create new insight into the details of electron correlation and dynamics.

4. Acknowledgements

This research was supported by the National Science Foundation under grant NSF-PHY-8907286. MOK acknowledges support by the Division of Chemical Sciences, U.S. Department of Energy under contract DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc.

5. References

1. P.A. Heimann, D.W. Lindle, T.A. Ferrett, S.H. Liu, L.J. Medhurst, M.N. Piancastelli, D.A. Shirley, U. Becker, H.G. Kerkhoff, B. Langer, D. Szostak, and R. Wehlitz, *J. Phys.* **B20** (1987) 5005.
2. C. D. Caldwell, (To appear in Nuclear Instruments and Methods, 1991).
3. J.E. Hansen and W. Persson, *Phys. Scrip.* **36** (1987) 602.
4. K.G. Dyall and F.P. Larkins, *J. Phys.* **B15** (1983) 3339.
5. C.D. Caldwell, M.G. Flemming, M.O. Krause, P. v.d. Meulen, C. Pan, and A.F. Starace, *Phys. Rev.* **A41** (1990) 542.
6. D. Petrini, *J. Phys.* **B14** (1981) 3839.
7. S.B. Whitfield, C.D. Caldwell, and M.O. Krause, (To appear in *Phys. Rev.* **A43**, March, 1991.)
8. M.O. Krause, S.B. Whitfield, J.-Z. Wu, C.D. Caldwell, P. v.d. Meulen, and R.W.C. Hansen, (To be published).