RECENT DEVELOPMENTS IN PHOTOELECTRON DYNAMICS USING SYNCHROTRON RADIATION

T. A. Carlson and M. O. Krause
Oak Ridge National Laboratory
Oak Ridge, Tennessee 37830

J. W. Taylor, P. R. Keller and M. N. Piancastelli
University of Wisconsin
Madison, Wisconsin 53706

F. A. Grimm and T. A. Whitley
University of Tennessee
Knoxville, Tennessee 37916

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Summary

Through a collaborative effort of members of the Oak Ridge National Laboratory and Universities of Wisconsin and Tennessee, a comprehensive study of atoms and molecules using angle-resolved photoelectron spectroscopy and synchrotron radiation is underway at the Synchrotron Radiation Center, Stoughton, Wisconsin. Over 50 molecules and atoms have been investigated. These results, coupled with theory, aim at a better understanding of the dynamics of photoionization and of the wave functions that control these processes. In particular, attention is given to the following topics: metal atomic vapors, generalization of molecular orbital types, autoionization, shape resonances, core shell effects, satellite structure, and the Cooper minimum.

Introduction

In the 1960's and early 1970's, Turner[1] and others developed the field of molecular photoelectron spectroscopy, which is one of the more powerful experimental tools for studying the electronic structure of molecules. In this spectroscopy the use of a line source, usually the 21.22 eV HeI resonance line, plus the measurement of the kinetic energy of the ejected photoelectron provide the means of ascertaining the ionization potential for each of the valence orbital electrons. A photoelectron spectrum, however, gives more than a means of determining binding energies; it separates out the various ionization processes. The relative cross sections for the different photoionization events can be obtained from the relative intensities of the different photoelectron bands.

Some preliminary studies on cross sections were done with a few line sources;[2] but any comprehensive studies require a continuously variable, high intensity photon source, which covers a wide energy range. Such a source is synchrotron radiation. With the use of synchrotron radiation, photoelectron spectroscopy has entered a new phase. In the past, photoelectron spectroscopy measured ionization potentials. In the present, the interest lies in cross sections and angular distribution measurements. In addition, the dynamics of the photoelectron process is of paramount importance. For this reason it is useful to call the present phase, photoelectron dynamics.

The data to be described in this paper are derived from angle-resolved photoelectron spectroscopy measurements using synchrotron radiation from the Wisconsin Synchrotron Radiation Center (Tantalus I). In one experimental arrangement, a pair of spherical sector electron spectrometers are mounted on a rotatable platform perpendicular to the direction of the photon beam. Details regarding this apparatus are given elsewhere.[3] Three variables are examined: (1) kinetic energy of the ejected photoelectron by scanning the electron spectrometers, (2) photon energy by scanning the monochromator, and (3) the angle θ between the polarization vector of the photon source and the direction of the ejected photoelectron by rotating the platform. From these measurements the partial

cross sections or cross sections of the different photoelectron processes are obtained as a function of photon wave length. In addition, from intensities measured as a function of angle, θ, the angular distribution parameter β can be determined from

$$\frac{d\sigma}{d\Omega} = \frac{\sigma}{4\pi} \left[1 + \frac{\beta}{4} \ (3P \cos 2\theta + 1)\right]$$

where P is the degree of polarization of the synchrotron light.

In this review we shall confine discussion to work carried out by the collaborative efforts of researchers from Oak Ridge National Laboratory, the University of Wisconsin and the University of Tennessee. The program is characterized by the wide variety and number of atomic and molecular systems studied. In addition to studies on the rare gases, atomic data have been obtained on several metal vapors. The number of molecular systems studied has now reached 50. They range from simple diatomic molecules to complex heterocyclic organic compounds. The program also cuts across a wide range of phenomena.

A close relationship between theory and experiment has been maintained in most of our studies. In the case of molecules partial cross sections and β values have been calculated by Grimm and Whitley based on the multiple scattering method. Below we shall discuss results from various different areas of research taken over the past couple of years.

Atomic Systems

The branching ratios and β values have been measured[3] for the $5p_{1/2}$ and $5p_{3/2}$ subshells of Xe from 20 to 105 eV. Comparison between theory and experiment has allowed one to evaluate the relative importance of relativistic and many-body effects. The dependence of β on the photon energy is influenced predominantly by the many-electron interaction, while the difference between the β parameters of the spin orbit components reflects largely the relativistic effects.

Experiments were carried out on silver in the vapor phase from 15 to 125 eV.[4,5] Angular distribution parameters and partial cross sections for the 4d, 5s and shakeup satellite lines were determined. The atomic β data were found to agree remarkably well with the data on metallic Ag,[6] although the 4d electrons become part of the conduction band in the metal. As another result, the data were found to agree well with the relativistic random phase calculations carried out[7] for the closed shell atom Pd.

The 3d subshell of Mn metal vapor has been studied for cross section and β values from 25 to 100 eV[8] (see Fig. 1). Particular attention was paid to the behavior of β passing through a resonance at 50 eV, which is attributed to a 3p → 3d excitation. A sharp rise in β was noted about 0.5 to 1.0 eV below the resonance. These data represent a challenge to the theoretician because the many-electron and many-channel interactions are difficult to treat.
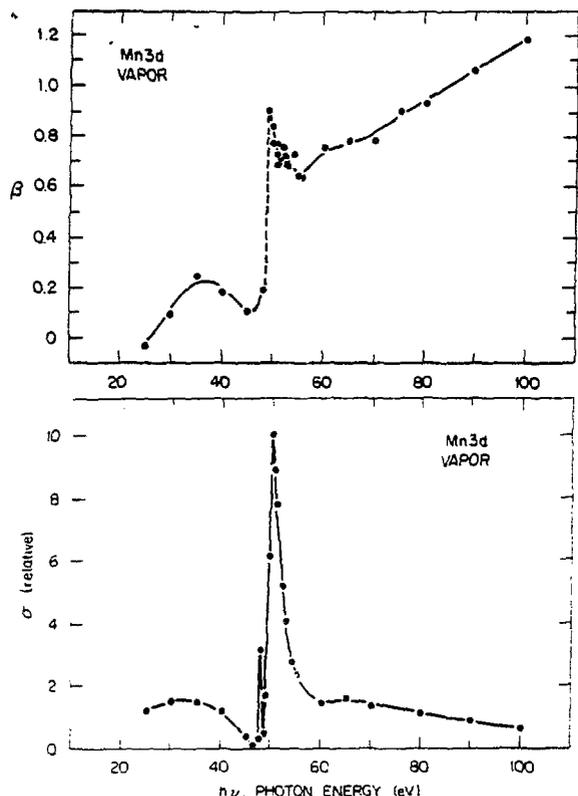
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Fig. 1. β values and partial cross sections for the 3d shell of Mn showing effect of the 3p → 3d resonance at 50 eV.
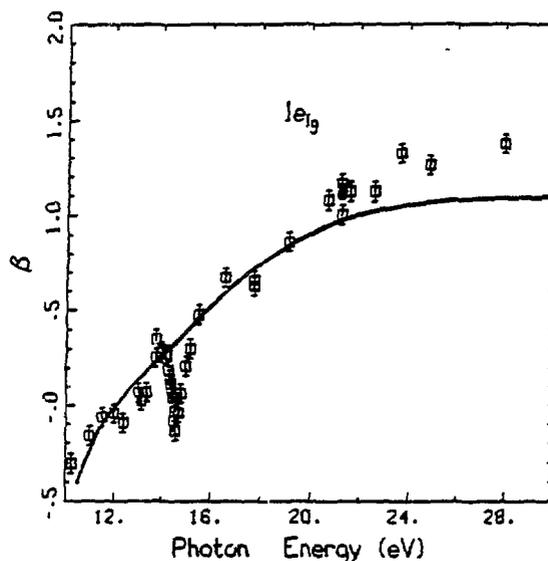

Fig. 2. The angular distribution parameter, β, is plotted as a function of photon energy for photoionization in the $1e_{1g}(\pi)$ orbital of benzene. The experimental data are given as open squares. The solid line represents calculations based on the MSXα method (ref. 13). The spectral feature at about 14.7 eV may be due to a short-lived auto-ionization state.

Characterization of Molecular Orbitals

There have been attempts in the past to correlate β values obtained with HeI radiation with character-istics of molecular orbitals. In particular, it has been observed[9] that π orbitals for unsaturated hydro-carbons have relatively high β values. Because β values are a sensitive function of the photoelectron energy, generalizations based on a single photon energy are, at best tenuous. We have investigated a large number of organic molecules containing double and triple bonds.[10] It was found that the most salient feature characterizing the π orbitals with re-gard to the β values was a rapid rise in β between 2 and 10 volts above threshold, which was generally considerably larger than found for the corresponding σ orbitals. Calculations based on the Xα scattering method of β as a function of photon energy have been made for acetylene,[11] ethylene[12] and benzene[13] and were found to be in excellent agreement with experiment especially for the π orbitals (cf. Fig. 2). It is, therefore, hoped that more detailed examination of the theoretical calculations will give realistic limits and boundaries to our generalizations regarding mole-cular orbital types.

Besides advancing our knowledge regarding mole-cular orbital types, such systematic studies provide a means of identifying the different bands in a com-plex photoelectron spectrum. For example, a series of azabenzenes were studied,[14] in which it was determined that while the π orbitals showed a rapid rise in β value as a function of photon energy, the nitrogen non-bonding n orbital gave a rather flat response. Using this generalization, it was possible to assign the relative ordering of ionization in pyridine to be $n(7a_1)$, $\pi(1a_2)$, which, hitherto, has been a contro-versial question.

Autoionization

Autoionization offers an alternate route to direct photoionization. A two-step process can occur, whereby resonance absorption into an excited virtual state is followed by autoionization. The kinetic energy of the ejected electron can be identical for both direct photoionization and the two-step event, but the cross sections, the branching ratios of the vibrational bands and the β values can be entirely different for the different ionization routes. Sharp changes in cross sections and β values due to autoioni-zation as a function of photon energies are a common feature, particularly up to about 10 volts above the ioniz-tion threshold for a given orbital. We have recently examined such behavior in the first and second ionization bands of N_2O.[15] Extensive studies on autoionization have been also carried out else-where.[16]

In addition to sharp structure due to longer-lived autoionizing states, there is also evidence for short-lived autoionizing states that give rise to broader spectral features. Such a situation has been used to explain broad dips in both the cross section and β values for the 2π orbital of acetylene[11] at a photon energy of about 14 to 15 eV. A full explanation of these features in acetylene is still under discus-sion.[17] It is interesting to note, however, that similar depressions in β a few volts above the ioniza-tion threshold were also found for the π orbitals of ethylene[12] and benzene[13] and in fact for most of the π orbitals of unsaturated hydrocarbon that have been studied[10] (cf. Fig. 2). Thus, the question raised by the study of acetylene may be very general ones.

Shape Resonances

A shape resonance arises from an electron being excited into a quasibound electronic state supported by a potential barrier. In molecules this barrier can be a centrifugal molecular potential. Shape resonances

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can be predicted within the framework of a single electron model, such as the multiple scattering Xα method. Experimentally, shape resonances are seen as broad peaks when partial photoionization cross sections are plotted against photon energy. In addition, the angular distribution parameter is strongly affected by a shape resonance. The behavior of the vibrational structure is sensitive to the presence of shape resonances. This has been evident, for example, in nitrogen for both the branching ratios and variations in β values.[18,19] The effect on the vibrational structure arises from the fact that the shape resonance itself is strongly dependent on the internuclear distance. The effect on vibrational structure can be felt at a considerable distance in photon energy from the point where the resonance occurs.

A clearly defined effect of shape resonance in molecules is experimentally exhibited by the fourth band in CO_2.[20] Experimentally determined β values together with calculations based on the multiple scattering Xα method are shown in Fig. 3. The calculations predict a deeper, more narrow β dependence curve. Part of this behavior has been shown[21] to arise from the effects of variation in internuclear distance caused by vibration.

Fig. 4. Effect on β above 2p core shell of silicon. Experimental data are for SiF_4 ● and $Si(CH_3)_4$ □. Lines show calculations for atomic silicon with lower values for more positively charged potential (ref. 25).
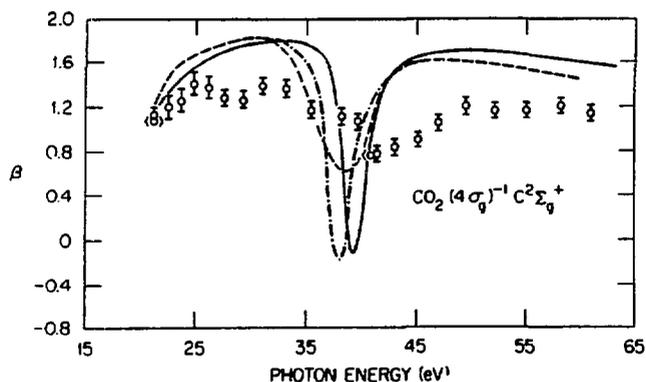

Fig. 3. The effect of a shape resonance on β is shown for the fourth band of CO_2. The experimental data are plotted as open circles (ref. 20); theoretical values are plotted as lines (refs. 20, 21). The dashed line includes the effect of changes in the internuclear distance.

Recently, calculations[22] in N_2O suggest a resonance in the σ continuum channel at a photon energy of about 30 eV, which strongly affect the cross section and β values of the 7σ and 6σ orbitals. These predictions have been confirmed experimentally,[22] although, quantitatively, substantial improvements in theory are obviously required.

Core Shell Effects

When photoionization occurs just above the ionization threshold for core shells, the photoelectron cross sections and angular distribution parameter can be sensitive to the molecular potential. Calculations suggest the region of sensitivity extends up to about 2 Rydbergs above the threshold.[23] The first published studies on β values measured above the core shell were carried out on the 3d shell of bromine[24] and the 2p shell of silicon.[25] For example, Fig. 4 contrasts the β value determined for the silicon 2p shell of SiF_4 and $Si(CH_3)_4$. The results coincide at higher energies, but below a kinetic energy of about 20 eV are quite discernably different. Atomic calculations can be used
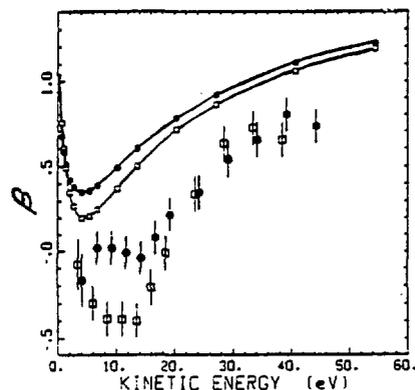
to predict the qualitative behavior by approximating the difference in the molecular potential in terms of net change.

Recent studies have been carried out on angle-resolved photoelectron spectroscopy of the K shells of molecules containing carbon, nitrogen, and oxygen.[26] Strong molecular effects were observed, including effects resulting from shape resonances. Core shell effects as revealed by photoelectron spectroscopy should prove to be a fruitful area of study in the future.

Satellite Structure in Molecule Spectra

A principal band in photoelectron spectra arises from the removal of an electron from an atomic or molecular orbital, the remaining electrons relaxing to the single hold configuration. In addition, processes also occur in which one or more of the remaining electrons are found in excited states. These other processes are identified in photoelectron spectra as satellite structure. The study of the satellite structure as a function of photon energy should help elucidate the nature of its origin.

For example, our recent investigation of the fifth band of CS_2 showed that it does not arise from photoionization of the $4\sigma_u$ orbital.[27] In Fig. 5 we see that
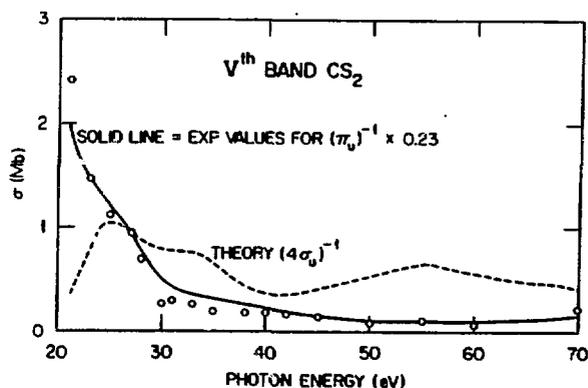

Fig. 5. Partial cross sections for fifth band of CS_2 showing best fit to assumption of multiple excitation (ref. 27).

if one assumes the partitioning of the excited and ground states following photoionization of the $2\pi_u$ orbital is independent of the photon energy and further uses the partition ratio derived from configuration interaction calculations,[28] then a good fit to the experimental cross section is obtained. In contrast, the calculated cross section, based on the assumption that the ionization band arises from photoionization of the $4\sigma_u$ orbital, is in poor agreement with experiment.

The satellite structure regions of the photoelectron spectrum of the valence band of N_2, from an ionization potential of about 23 to 43 eV, have been studied by Krummacher, et al.[29] We have recently extended these cross section measurements to the study of β values over the same spectral region.[30]

Cooper Minimum in Molecules

The Cooper minimum, which is a minimum in the photoelectron cross section as a function of photon energy, has been known for some time in atomic physics. An atomic orbital, which possesses a radial node, can show a Cooper minimum if in the calculation of the photoelectron cross section a radial matrix element describing a transition to one of the permissible continuum channels changes sign as a function of photoelectron energy. In addition to the cross section, the β values are also strongly affected and experimentally undergo changes near the Cooper minimum, which are often more susceptible to experimental measurement than the partial cross sections.

Reasoning that the Cooper minimum should also take place within molecular orbitals, we have made for the first time a systematic study of this phenomenon for the valence shell of molecules. Cooper minimum have been experimentally investigated for the following molecules: CS_2,[27] COS,[27] CCl_4,[31] Cl_2,[32] HCl, CCl_2CH_2, CH_3Br,[31] and HI. Parallel calculations using the multiple scattering $X\alpha$ method have been carried out on CS_2,[27] COS,[27] CCl_4,[31] Cl_2,[32] HCl, HBr and HI.

Typical results are to be seen in Fig. 6 for molecular chlorine. The lone pair orbitals (in the case of Cl_2: $2\pi_g$ and $2\pi_u$) behave closely like their atomic counterparts. (See, for example, the results[33] on the 3p orbital of Ar, which is isoelectronic with Cl^-.) This is to be expected. The non-bonding lone pair valence orbitals in a chlorine substituted molecule are anticipated to behave like an atomic chlorine 3p orbital. More surprising is the dip experienced by the bonding orbital, $5\sigma_g$, in the region of the Cooper minimum (ca. 32 eV).

Comparison between theory and experiment in Fig. 6 shows that the MSXα method does an excellent job in predicting the general properties of the Cooper minimum. Quantitatively, it predicts the Cooper minimum about 7 volts below experiment. However, this magnitude of error is also found in atomic calculations using the approximate Hartree-Slater potential. Good agreement between experiment and theory is also found[32] in the Cooper minimum for the cross section of the three chlorine orbitals.

Examining the calculations more closely, it is found that while some lone pair orbitals (e.g., the $2\pi_g$ of CS_2[27] and the $2t_1$ of CCl_4[31]) behave nearly like atomic orbitals, others have characteristics not explicable by analogy. It should be remembered that for molecular orbitals the orbital angular momentum (ℓ) is not a good quantum number. Molecular orbitals can be expressed as a sum of partial waves both for the initial bound orbital and the continuum. In practice the main contribution to the photoelectron cross sections is made by only a few of these partial waves. It is interesting to note that in the case of the bonding orbitals, which like the 5σ of chlorine show a "partial Cooper minimum" (cf. Fig. 6) there occur
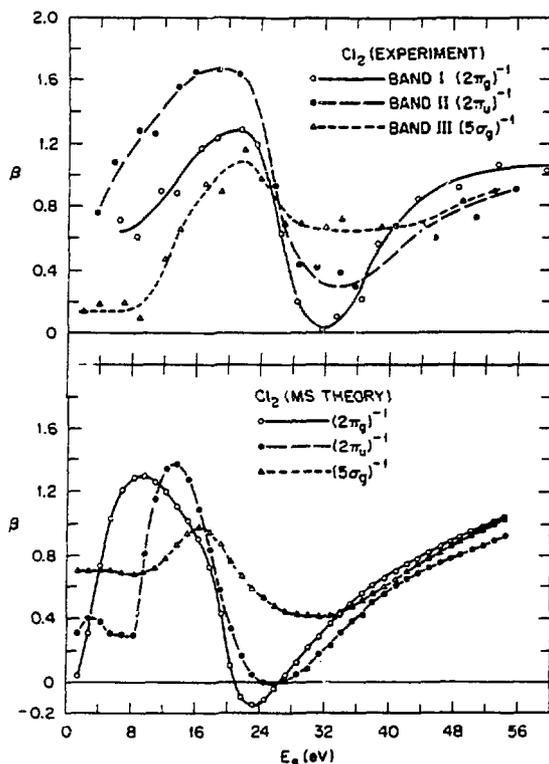

Fig. 6. The effects of the molecular Cooper minimum on the β values for Cl_2 (ref. 32).

contributions from matrix elements in the chlorine sphere corresponding to a $p \rightarrow d$ transition. It is hoped that further analysis of the calculation will allow one to separate out the different effects that make up the cross section.

Acknowledgements

References

1. D. W. Turner, A. D. Baker, C. Baker and C. R. Brundle, Molecular Photoelectron Spectroscopy: A Handbook of He 584Å Spectra (Interscience, London-New York, 1970).

2. W. C. Price, A. W. Potts and D. G. Streets, in Electron Spectroscopy, ed. D. A. Shirley (North-Holland, Amsterdam, 1972), p. 187; U. Gelius, in op. cit. p. 311.

3. M. O. Krause, T. A. Carlson and P. R. Woodruff, Phys. Rev. A 24, 1374 (1981).

4. M. O. Krause, P. R. Woodruff and T. A. Carlson, J. Phys. B 14, 2673 (1981).

5. M. O. Krause, T. A. Carlson, G. Leroi, D. E. Ederer and D. M. P. Holland (to be published).

6. R. F. Davis, S. D. Kevan, B. C. Lu, J. G. Tobin and D. A. Shirley, Chem. Phys. Lett. $\underline{71}$, 448 (1980).

7. V. Radojevic and W. Johnson (to be published).

8. M. O. Krause, T. A. Carlson and A. Fahlman (to be published).

9. R. M. White, T. A. Carlson and D. P. Spears, J. Electron Spectrosc. $\underline{3}$, 59 (1974); J. A. Sell and A. Kuppermann, Chem. Phys. $\underline{33}$, 367 (1978); T. Kobayashi, Phys. Lett. $\underline{70A}$, 292 (1979).

10. P. Keller, J. W. Taylor, F. A. Grimm and T. A. Carlson (to be published).

11. P. R. Keller, D. Mehaffy, J. W. Taylor, F. A. Grimm and T. A. Carlson, J. Electron Spectrosc. $\underline{27}$, 223 (1982).

12. D. Mehaffy, P. R. Keller, J. W. Taylor, T. A. Carlson, M. O. Krause, F. A. Grimm and J. D. Allen, Jr., J. Electron Spectrosc. $\underline{26}$, 213 (1982).

13. D. Mehaffy, P. R. Keller, J. W. Taylor, T. A. Carlson and F. A. Grimm, J. Electron Spectrosc. (in press).

14. M. N. Piancastelli, P. R. Keller, J. W. Taylor, F. A. Grimm and T. A. Carlson (submitted for publication).

15. T. A. Carlson, P. R. Keller, J. W. Taylor, T. Whitley and F. A. Grimm (to be published).

16. A. Tabché-Fouhaile, I. Nenner, P-M. Guyon and J. Delwiche, J. Chem. Phys. $\underline{75}$, 1129 (1981); J. B. West, K. Codling, A. C. Parr, D. L. Ederer, B. E. Cole, R. S. Stockbauer and J. L. Dehmer, J. Phys. B $\underline{14}$, 1791 (1981); K. Codling, A. C. Parr, D. L. Ederer, R. Stockbauer, J. B. West, B. E. Cole and J. L. Dehmer, J. Phys. B $\underline{14}$, 657 (1981).

17. C. Unwin, I. Khan, N. V. Richardson, A. M. Bradshaw, L. S. Cederbaum and W. Domcke, Chem. Phys. Lett. $\underline{77}$, 242 (1981); A. C. Parr, D. L. Ederer, J. B. West, D. Holland and J. L. Dehmer, J. Chem. Phys. (in press).

18. J. B. West, A. C. Parr, B. E. Cole, D. L. Ederer, R. Stockbauer and J. L. Dehmer, J. Phys. B $\underline{13}$, L105 (1980).

19. T. A. Carlson, M. O. Krause, D. Mehaffy, J. W. Taylor, F. A. Grimm and J. D. Allen, Jr., J. Chem. Phys. $\underline{73}$, 6056 (1980).

20. T. A. Carlson, M. O. Krause, F. A. Grimm, J. D. Allen, D. Mehaffy, P. R. Keller and J. W. Taylor, Phys. Rev. A $\underline{23}$, 3316 (1981); F. A. Grimm, J. D. Allen, T. A. Carlson, M. O. Krause, D. Mehaffy, P. R. Keller and J. W. Taylor, Jr., J. Chem. Phys. $\underline{75}$, 92 (1981).

21. J. R. Swanson, D. Dill and J. L. Dehmer, J. Phys. B $\underline{14}$, 6207 (1981).

22. T. A. Carlson, P. R. Keller, J. W. Taylor, F. A. Grimm and T. Whitley (to be published).

23. F. A. Grimm, Chem. Phys. $\underline{53}$, 71 (1980).

24. T. A. Carlson, M. O. Krause, F. A. Grimm, P. R. Keller and J. W. Taylor, Chem. Phys. Lett. $\underline{87}$, 552 (1982).

25. P. R. Keller, J. W. Taylor, F. A. Grimm, P. Senn, T. A. Carlson and M. O. Krause, Chem. Phys. (in press).

26. D. A. Shirley, P. H. Kobrin, D. W. Lindle, C. M. Truesdale, U. Becker and H. G. Kerkhoff, Proceedings of International Conference on Inner Shell Ionization, Oregon.

27. T. A. Carlson, M. O. Krause and F. A. Grimm, J. Chem. Phys. $\underline{77}$, 1701 (1982).

28. J. Schirmer, W. Domcke, L. S. Cederbaum, W. van Niessen and L. Åsbrink, Chem. Phys. Lett. $\underline{61}$, 30 (1979).

29. S. Krummacher, V. Schmidt and F. Wuilluimier, J. Phys. B $\underline{13}$, 3993 (1980).

30. F. A. Grimm and T. A. Carlson (to be published).

31. T. A. Carlson, M. O. Krause, F. A. Grimm, P. R. Keller and J. W. Taylor, J. Chem. Phys. (in press).

32. T. A. Carlson, M. O. Krause, F. A. Grimm and T. A. Whitley, J. Chem. Phys. (in press).

33. R. G. Houlgate, J. B. West, K. Codling and G. V. Marr, J. Electron Spectrosc. $\underline{9}$, 205 (1976).