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STUDIES OF PHOTOIONIZATION PROCESSES FROM
GROUND-STATE AND EXCITED-STATE ATOMS AND MOLECULES

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Abstract

Recent triply-differential photoelectron spectroscopy experiments designed for the study of correlation effects in atoms and molecules shall be described. Final-state symmetry of the $n=2$ state of helium has been determined. The non-Franck-Condon behavior of vibrational branching ratios and large variations of the angular asymmetry parameter has been observed for shape resonances and autoionizing resonances in CO and other molecules. Recent observations of the photoionization of excited sodium atoms will also be described.

I. Introduction

Studies of photoionization processes in atoms and molecules seek to understand the effects of the correlated motion of the electrons comprising the system. The central field approximation and molecular orbital calculations reached maturity with the age of the computer, but experimental evidence and the development of advanced techniques to handle the motion of many electrons have revealed some the subtleties of electronic interactions.

Correlation between electrons in atoms and molecules can be most effectively studied by exciting or ionizing atoms and molecules in the VUV and soft X-ray region extending over the photon energy range 5-250 eV. The measurement science involved, absorption spectroscopy, photoelectron spectroscopy, and spin polarized photoemission, is at the frontier of atomic and chemical physics. The source which stimulated much of this research and without which much of this research would be impossible is synchrotron radiation. The unique properties of the radiation namely its continuum nature, its polarization and its high intrinsic brightness, are qualities that cannot be found in other sources spanning the photon energy range of interest to atomic and molecular physicists. The information about partial and total cross sections, about angular distributions of photoelectrons and about spin polarized photoemission can provide new insights in such diverse areas as plasma physics, laser devices and astrophysics. The data are also of intrinsic interest and the experiments carried out provide important tests of the more sophisticated calculations, that include explicitly electron correlations such as the R-matrix theory, the Random Phase Approximation (RPA) and the many-body approximation.¹

This paper focusses on recent results obtained by photoelectron spectroscopy. Other techniques such as high resolution total absorption spectroscopy, with and without applied fields, spin polarized photoemission and polarized fluorescence spectroscopy will be covered by other authors.

Photoelectron spectroscopy permits the determination of each dipole accessible final state cross section as a function of photon energy. A measurement of the angular distribution and the energy distribution as a function of photon energy permits in addition to a measurement of the branching ratios and partial cross section of the dipole accessible channels, a measurement of the angular asymmetry parameter, β . The angular asymmetry parameter yields information about the relative phase of the dipole allowed continuum wavefunctions which complements information about the magnitude and energy dependence of the squared radial dipole matrix elements connecting the initial and final continuum states.

While most of the photoionization measurements utilizing synchrotron radiation as a source have been made with the system in the ground state, the availability of cw dye lasers have opened up the possibility of studying the photoionization of atoms and molecules from an initial state other than the ground state.² This new field has just barely been exploited but offers the opportunity to study for example, autoionizing resonances that decay to states of parity opposite to that of the ground state. Furthermore, with lasers one can prepare the atom in a very specific state and study the geometrical properties of the system in addition to the dynamical properties of the atom. This paper will include as an example some very recent photoionization data from laser excited atoms.

II. Method

When linearly polarized photons interact with randomly oriented atoms and ionize them, the angular distribution of the differential cross section obeys the following relationship:³

$$\frac{d\sigma_i}{d\Omega} = \frac{\sigma_i}{4\pi} [1 + \beta_i P_2(\cos \theta)], \quad (1)$$

where β_i and σ_i are the asymmetry parameter and the photoionization cross section of the i th channel. The angle θ is the angle between the electron ejection direction and the polarization vector. Formulae can be derived for unpolarized light and for elliptically polarized radiation. If the electron spectrometer is set at an angle θ equal to $54^\circ 44'$, the so-called magic angle, $P_2(\cos \theta) = 0$ and $\frac{d\sigma_i}{d\Omega} = \frac{\sigma_i}{4\pi}$. Thus the geometry of the electron spectrometer can be arranged so that the partial cross section can be measured directly.

Photoelectron spectroscopy has been used with several types of spectrometers to measure σ and β for a large variety of atoms and molecules. Recently lasers have been used to prepare atoms and molecules in an excited state and another laser or synchrotron radiation has been used to photoionize the atom or molecule.² In this case Eq (1) is not valid in general and the differential cross section is given by a more general formula^{4,5} for an axially symmetric system (i.e., one in which the polarization vectors of the photon beams lie in the same plane) with randomly oriented atoms or molecules in the initial state.

$$\frac{d\sigma}{d\Omega} = A_0(t) + A_2(t) P_2(\cos \theta) + A_4(t) P_4(\cos \theta). \quad (2)$$

The quantity θ is the angle between the synchrotron radiation polarization direction and the electron emission direction. The functions $P_n(\cos \theta)$ are the Legendre polynomials of order n and the quantities $A_n(t)$ are coefficients which are products of appropriate photoexcitation cross sections, Clebsch-Gordan coefficients and a time dependent factor that accounts for the mixing and beating of the intermediate and/or final states. This in general, would be the formula which would govern the angular dependence of the VUV photoionization cross section of laser excited atoms. Under some experimental conditions, the alignment of the intermediate state may be reduced significantly at laser powers presently available. This reduction in alignment is caused by radiation trapping, which reduces the polarization of the trapped photons relative to that of the incident laser beam. In many circumstances, therefore, a set of operating conditions can be chosen so that the angular dependence of the cross section reduces to Eq (1).

III. Examples

III. A. Helium

The Coulomb field provides a unique opportunity to study different theoretical many-body formalisms because the Coulomb force governing the correlated motion of the atomic electron cloud is precisely known. Helium is the simplest system that exhibits correlation effects in the photoionization processes. Because of its general importance as a test case, the photoionization cross section has been studied in great detail over a broad energy range.⁶ Many sophisticated calculations have been performed.⁷

Angle resolved photoelectron spectroscopy has been used with synchrotron radiation to determine the ratio, R , of the 2p to 2s partial photoionization cross sections and the weighted angular asymmetry parameter β for these two states.⁸

The value of the experimentally determined asymmetry parameter, β , for photoelectrons leaving the ion in the $n=2$ state is shown as a function of photon energy in Fig. 1. The dash-dot curve is obtained from the calculated value of σ_{2p} and σ_{2s} , the many body calculation of β_{2p} in Ref. 9 and the fact that $\beta_{2s}=2$. The value of β is rather insensitive to the type of model used in the calculation, however the ratio R , shown in Fig. 2, gives a much clearer indication of the model best suited to describe the symmetry in the $n=2$ state of helium. The values of R suggest that final-state correlation has a dominating influence on R as is shown by calculations that include final-state and ground-state correlation. The close-coupling calculations of Jacobs and Burke¹⁰

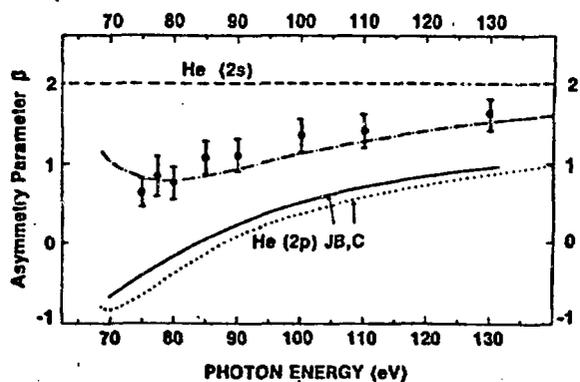


Fig. 1 The asymmetry parameter β vs. photon energy. Present measurements, circles. Calculation of β_{2s} from Ref. 10, solid curve. Calculation from Ref. 8 of β_{2p} , dotted curve. Asymmetry parameter $\beta_{2s}=2$, dashed line. Calculated value of β with $\beta_{2s}=2$, the present calculation of β_{2p} , and the calculated cross section from Ref. 9 for σ_{2s} and σ_{2p} , dot-dashed curve.

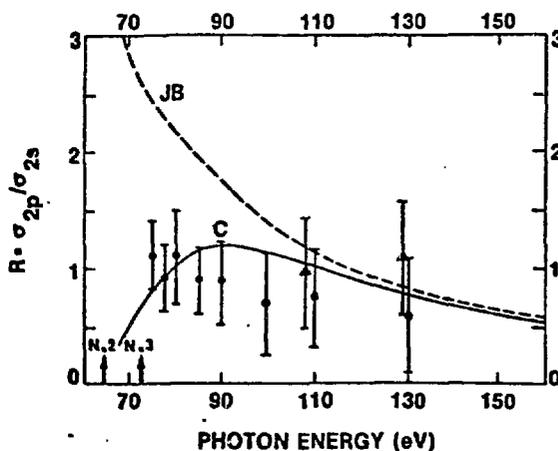


Fig. 2. The value of $R = \sigma_{2p} / \sigma_{2s} = (2 - \beta) / (\beta - \beta_{2p})$ vs. photon energy (circles). Earlier measurements are shown as triangles. Theoretical values of R are obtained from Ref. 8 (dashed curve) and from Ref. 9 (solid curve). The ionization plus excitation thresholds for the $n=2$ and $n=3$ final states of the helium ion are shown in the vertical arrows.

suggest the cross section near threshold is dominated by the photoionization process that leaves the ion predominantly in the 2p state. By contrast, the many-body calculation of Ref. 9 suggests that the cross section is dominated by the photoionization process that leaves the ion in the 2s state at threshold. At high photon energies the sudden approximation becomes more appropriate and R approaches zero as it becomes a measure of overlap between the hydrogenic 2s final state and the correlated initial state.

III. B. Carbon Monoxide

The carbon monoxide molecule is an interesting case that exhibits many of the phenomena that can be studied by photoelectron spectroscopy. It has been thoroughly studied using many different experimental techniques. The total cross section the dissociation ionization and double ionization cross sections have been measured,¹¹ the partial cross sections have been obtained for the outer valence orbitals¹² and the inner valence orbitals.¹³ Space does not permit an exhaustive review of the work¹⁴ on this molecule; only a few of the dynamical properties of the molecule will be described.

The partial cross section for the X $2\Sigma^+$ and the B $2\Sigma^+$ electronic states of CO⁺ exhibit a shape resonance. These resonances were observed by Plummer et al¹² and interpreted by Davenport.¹⁵ Later Dehmer et al¹⁶ predicted that the vibrational branching ratios and the β parameters for the vibrational levels would show a dramatic variation in the region of the shape resonance due to the coupling the electronic and the nuclear motion of the molecule. This effect was observed^{14,17} in the X $2\Sigma^+$

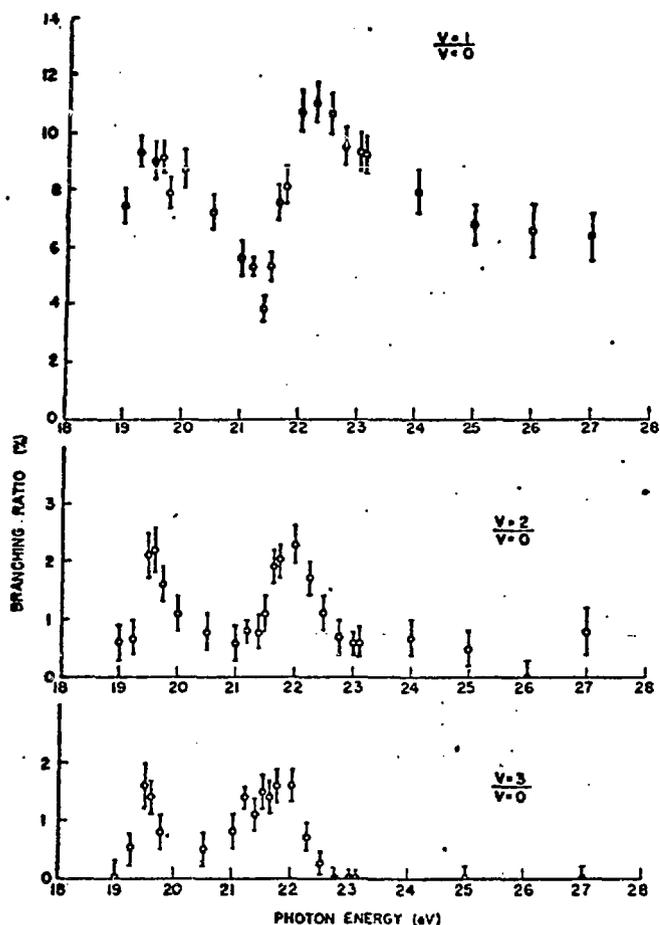


Fig. 3 Photoionization branching ratios for the $v=0-3$ levels of $\text{CO}^+ \times 2\Sigma^+$.

electronic state with an electron spectrometer capable of resolving the vibrational structure. The variation of the branching ratio as a function of photon energy is shown in Fig. 3 and the variation of the value of β for the different vibrational levels of the $\chi 2\Sigma^+$ electronic state is shown in Fig. 4. Below $h\nu \approx 21\text{eV}$ the main vibrational effects are caused by unresolved autoionization structure and threshold effects associated with the $B 2\Sigma^+$ state of CO^+ . Above 21eV the structure is caused mainly by the shape resonance centered at about 24eV . These v -dependent changes in β and the branching ratios have been observed in other molecules

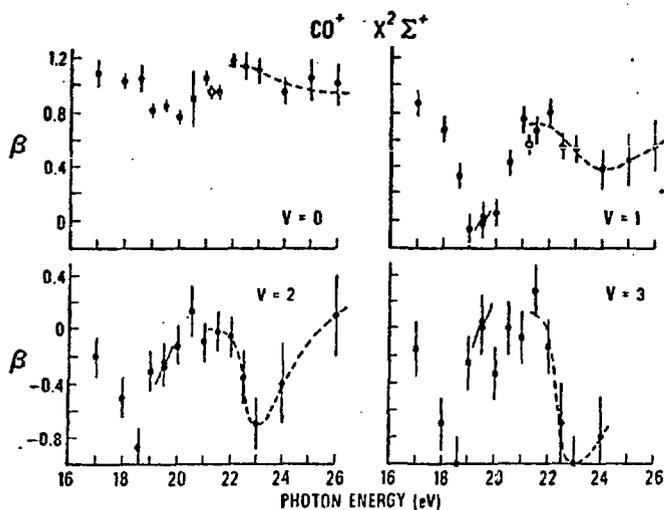


Fig. 4 Photoelectron asymmetry parameters for the $v=0-3$ vibrational levels of $\text{CO}^+ X^2\Sigma^+$ in the range $16 \text{ eV} < h\nu < 26 \text{ eV}$. The open circles are data by Hancock and Samson using He α resonances radiation. The dashed lines are hand drawn to illustrate the discussion in the text.

exhibiting shape resonances^{18,19} and show: that a broad pattern of deviation from the Franck-Condon vibrational intensity distribution can be expected in a shape resonance; that the pattern in CO qualitatively confirms a predicted pattern in N_2 and that the observed behavior reflects the v -dependent resonance profile which, in turn, depends on the relative position and shapes of the initial- and final-state potential energy curves.

A detailed high resolution study²⁰ which spans an autoionizing resonance in CO yields similar behavior, a large variation of β and a non-Franck-Condon behavior of the branching ratios in the resonance region.

III. C. Even-parity Autoionization Resonances in Laser Excited Sodium

It is possible² to produce by step wise excitation (laser plus VUV) even parity autoionizing resonances. These are detected by electron

spectroscopy. For example if one sets a VUV monochromator at 31.4eV the photon energy corresponds to the excitation $2^1 2p^5 2p^2 P \rightarrow 2p^5 (3s3p^1 P) 2^2 D_{5/2}$. The upper frame of Figure 5 shows a spectrum obtained at that energy without the laser. The small peak near 26.5eV kinetic energy is due to the direct ionization of 3s electrons. The feature between 24-25eV kinetic energy is due to ionization of 2p electrons by 61.8eV photons transmitted by the monochromator in second order. The lower frame of Figure 5 shows the photoelectron spectrum with the laser tuned to the $3s^2 S_{1/2} \rightarrow 3p^2 P_{3/2}$ transition. The intense feature near 28.5eV kinetic

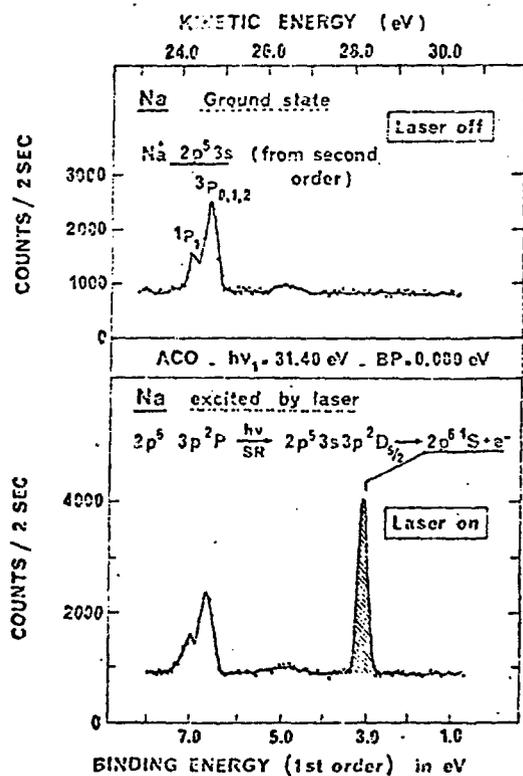


Fig. 5 Photoelectron spectra obtained at a photon energy of 31.4eV with the laser off (upper frame) and with the laser on (lower frame). Photoelectrons from the direct ionization of the 3s electron appear at a kinetic energy of 25.6eV. Photoelectron due to ionization of the 2p electron by second order radiation $h\nu=62.8\text{eV}$ appear with kinetic energy between 24-25eV. Electrons from the decay of the autoionizing $2p^5 3s3p^2 D_{5/2}$ resonances produce the hatched peak in the lower frame.

energy is due to the decay of the even-parity autoionizing resonances excited by step-wise laser plus VUV photon absorption. The area $^{22} N_{h\nu}$ of the photoelectron peak for 2p photoionization of the laser-excited atoms is proportional to the product of the excited state density and the photoionization cross section $\sigma(h\nu)$:

$$N_{hv} = KI_{hv} E_{hv} n_{3p} \sigma(hv) \Delta E, \quad (3)$$

where K is the spectrometer constant, I_{hv} is the photon flux at energy $h\nu$; E_{hv} is the kinetic energy of the photoelectron, n_{3p} is the density of laser-excited atoms and ΔE is the monochromator band pass. Similarly the integrated area N_R of the photoelectron peak for the autoionizing resonance given by:

$$N_R = KI_R E_R n_{3p} \int^{\Delta E_R} \frac{df_R}{d\epsilon} d\epsilon, \quad (4)$$

where I_R is the photon flux at the resonance excitation energy, E_R is the kinetic energy of the decay electron and ΔE_R is the monochromator bandpass. Since usually the monochromator bandpass is much larger than the width of the resonance, the integral over the oscillator strength density $\frac{df_R}{d\epsilon}$ in Eq (4) can be replaced by the oscillator strength of the resonance f_R . The ratio of Eq (4) to Eq (3) yields:

$$f_R = \frac{I_{hv} E_{hv}}{I_R E_R} [\sigma(hv) \Delta E] \frac{N_R}{N_{hv}} \quad (5)$$

All terms on the right hand side of Eq (5) can be determined experimentally. If we either measure $\sigma(h\nu)$ or assume that it equals the 2p photoionization cross section for ground state sodium we can obtain a numerical value for f_R .

IV. Conclusions

In this paper, a few examples have been given that demonstrate the versatility of photoelectron spectroscopy. In the future, the scientific community can look forward to detailed high resolution measurements of partial photoionization cross sections, angular distribution of photoelectrons, oscillator strength for autoionizing resonances, all as a function of

the state of specific valence excitation which include alignment or orientation of laser prepared intermediate states.

V. Acknowledgments

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