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Electron-Impact Ionization of Alkali Metals

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Classical binary-encounter calculations using a Hartree–Fock velocity distribution for the bound electrons have been carried out for electron-impact ionization of alkali metals. The effect of inner-shell ionization, as well as the excitation of some autoionizing levels, has been included. A satisfactory agreement with recent experimental observations has been achieved.

I. INTRODUCTION

The electron-impact ionization of alkali metals (Li, Na, K, Rb, and Cs) has been extensively investigated by experimental[1–8] and theoretical approaches.[9–19] An elegant discussion on electron-impact ionization of the alkali metals has been given by McDowell.[20] The experimental observations[1,2,5–8] indicate that the removal of an electron from the inner shell, as well as excitation of an inner electron to autoionizing levels, contributes significantly to the cross section. These contributions are more important for the heavier atoms (K, Rb, and Cs) and lead to appearance of multiple maxima in the ionization curve. The theoretical calculations on alkali metals may be grouped into two main categories: (a) Born approximation computations[9-12] (these are limited to Li and Na) and (b) classical binary-encounter calculations[13-15] using Gryzinski[21] or Stabler[22] expressions and using hydrogenic or δ-function velocity distributions for the bound electrons.

The classical model used in the above computations did not take into account the indistinguishability of the incident and bound electron (unsymmetrical collision model) and is not reliable for low incident energies. These difficulties are removed in the symmetrical collision model introduced by Vriens.[23] Also, as shown by the computations with the Gryzinski model, the choice of velocity distribution[24,25] for the bound electron has very important effects on the calculated cross sections. In view of these, none of the above calculations can be regarded as providing the best classical estimate of the ionization cross sections. A few theoretical calculations[16,17] have been carried out for electron-impact ionization of alkali metals using Stabler's[22] expression and the Hartree–Fock velocity distribution for the bound electron. Apart from these, some empirical calculations have been done by Drawin[18] and Prasad.[19]

In the present work we have attempted to examine the structures in the total ionization curves of K, Rb, and Cs due to electron impact. We have used the symmetric model as well as the correct Hartree–Fock velocity distribution for the velocity of the bound electron to obtain single-ionization cross sections. The contribution of inner-shell ionization has been explicitly included as well as estimates of cross sections for excitation into several autoionizing levels.

II. THEORETICAL METHODS

Expressions for electron-impact ionization and excitation cross sections, including exchange and interference due to Vriens,[23] are given by

$$Q_i = \frac{\pi e^4}{E_1 + E_2 + U_i}\left[\left(\frac{1}{U_i} - \frac{1}{E_1}\right) + \frac{2E_2}{3}\left(\frac{1}{U_i^2} - \frac{1}{E_1^2}\right) - \frac{\phi'}{E_1 + U_i}\ln\frac{E_1}{U_i}\right], \qquad (1)$$

with

$$\phi' = \cos\left[\left(\frac{R}{E_1 + U_i}\right)^{1/2} \ln\frac{E_1}{U_i}\right],$$

and

$$Q_e = \frac{\pi e^4}{E_1 + E_2 + U_i}\left[\left(\frac{1}{U_n} - \frac{1}{U_{n+1}}\right) + \frac{2E_2}{3}\left(\frac{1}{U_n^2} - \frac{1}{U_{n+1}^2}\right) + \left(\frac{1}{E_1 + U_i - U_{n+1}} - \frac{1}{E_1 + U_i - U_n}\right)\right.$$
$$\left. + \frac{2E_2}{3}\left(\frac{1}{(E_1 + U_i - U_{n+1})^2} - \frac{1}{(E_1 + U_i - U_n)^2}\right) - \frac{\phi''}{E_1 + U_i}\ln\frac{U_{n+1}(E_1 + U_i - U_n)}{U_n(E_1 + U_i - U_{n+1})}\right], \qquad (2)$$

with

$$\phi'' = \cos\left[\left(\frac{R}{E_1 + U_n}\right)^{1/2} \ln\frac{E_1 + U_i - U_n}{U_n}\right],$$

where U_{n+1} is to be replaced by E_1 for $U_n \leq E_1 < U_{n+1}$. In the above expressions E_1 is the energy of the incident electron, E_2 is the kinetic energy of the bound electron, and R is the Rydberg constant. U_i is the ionization potential of the target atom, while U_n and U_{n+1} are the excitation energies of the level under consideration and the next higher level, respectively.

We now introduce new variables similar to those used by Catlow and McDowell[16] and define $s^2 = v_1^2/v_0^2$ and $t^2 = v_2^2/v_0^2$. $u = v_0^2$ is the ionization potential of the target atom in rydbergs. v_1 and v_2 are the velocities of the incident and bound electron, respectively, in atomic units. All the other energies involved have also been expressed in rydbergs. In terms of these variables, expressions (1) and (2) become

$$Q_i = \frac{4}{s^2 + t^2 + 1}\left[\frac{s^2 - 1}{s^2 u^2} + \frac{2t^2}{3}\left(\frac{s^4 - 1}{s^4 u^2}\right) - \frac{\phi'}{u^2(s^2 + 1)}\ln s^2\right] \pi a_0^2, \qquad (3)$$

with

$$\phi' = \cos\left[\left(\frac{1}{s^2 u + u}\right)^{1/2} \ln s^2\right],$$

and

$$Q_e = \frac{4}{(s^2+t^2+1)u}\left[\left(\frac{1}{u_n}-\frac{1}{u_{n+1}}\right)+\frac{2t^2u}{3}\left(\frac{1}{u_n^2}-\frac{1}{u_{n+1}^2}\right)+\left(\frac{1}{s^2u+u-u_{n+1}}-\frac{1}{s^2u+u-u_n}\right)\right.$$
$$\left.+\frac{2t^2u}{3}\left(\frac{1}{(s^2u+u-u_{n+1})^2}-\frac{1}{(s^2u+u-u_n)^2}\right)-\frac{\phi''}{s^2u+u}\ln\frac{u_{n+1}(s^2u+u-u_n)}{u_n(s^2u+u-u_{n+1})}\right]\pi a_0^2\,, \qquad (4)$$

with

$$\phi'' = \cos\left[\left(\frac{1}{s^2u+u_n}\right)^{1/2}\ln\frac{s^2u+u-u_n}{u_n}\right],$$

where u_{n+1} is to be replaced by s^2u for $u_n \leq s^2u < u_{n+1}$. The above expressions [(3) and (4)] have to be integrated over the continuous velocity distribution for the bound electron, and the final expressions for these cross sections become

$$Q_{\text{ion}} = n_e\int_0^\infty Q_i f(t)u^{1/2}dt\,(\pi a_0^2) \qquad (5)$$

and

$$Q_{\text{exc}} = n_e\int_0^\infty Q_e f(t)u^{1/2}dt\,(\pi a_0^2). \qquad (6)$$

n_e is the number of equivalent electrons in the atomic shell under consideration. The momentum distribution function $f(t)$ is defined as $f(t)=4\pi t^2u\,\rho_{nl}(u^{1/2}t)$, where

$$\rho_{nl} = \frac{1}{2l+1}\sum_{m=-l}^{+l}|\psi_{nlm}(\vec{x})|^2,$$

$$\psi_{nlm}(\vec{x}) = \frac{1}{(2\pi)^{3/2}}\int\psi_{nlm}(\vec{r})e^{i\vec{x}\cdot\vec{r}}d\vec{r}$$

is the Fourier transform of the one-electron orbital $\psi_{nlm}(\vec{r})=N_{nl}R_{nl}(r)Y_{lm}(\Omega)$, in which $R_{nl}(r)$ is the analytical Hartree-Fock radial function. Hartree-Fock radial wave functions for K have been taken from Synek and Rainis[26] and those for Rb and Cs from Clementi *et al.*[27]

III. RESULTS AND DISCUSSION

The calculated cross sections have been represented graphically in Figs. 1-3 along with the recent experimental results due to McFarland and Kinney[2(a)] and Zapesochnyi and Aleksakhin.[8] The experimental results are in good agreement with our calculations, lying always within a factor of 2. Zapesochnyi and Aleksakhin[8] have stated that there is a gradual shift towards lower energies of the first peaks as atomic number increases (this is not borne out by the figures given in their paper or the numerical values listed in their table). This is in agreement with our calculations. They have compared their results with the calculations using Gryzinski's method. These calculations are not able to reproduce the complex structure of the actual (experimental) ionization curves. The positions of the maxima in the calculated curves are also shifted towards higher energies by a factor of 2 as compared to the experimental values. Our calculations are able to explain more satisfactorily the complex structure and the positions of the maxima observed in the experimental curve.

In all cases (K, Rb, and Cs) our theoretical calculations show a second maximum arising due to the ionization of the np electrons ($n=3$, 4, and 5, respectively, for K, Rb, and Cs). Garcia[15] obtained double peaks in K, Rb, and Cs using Gryzinski's model with δ-function velocity distribution for the bound electron. McFarland[13] also obtained double peaks by the use of Gryzinski's expression with exponential velocity distribution. The work of McFarland has been criticized by Prasad,[19] who did not obtain these peaks in his empirical calculation. Tripathi *et al.*[17] considered the valence shell as well as inner-shell ionization of K but did not obtain the second maximum.

The position of the second maximum, in the case of Cs, obtained by us coincides very closely with the third maximum in the experimental curve,[8] but for K and Rb the calculated maxima are at considerably higher incident energies. To understand this we have to consider the effect of excitation to autoionizing levels. The existence of anomalous terms above the first-series limit has long been known in the spectra of heavy alkali metals. The doublet levels arising from these configurations have very small lifetimes and decay into the continuum of the singly ionized atom. According to the uncertainty principle these levels will involve considerable natural width. Encouraged by this situation, we surmised that the use of the classical method for calculation of excitation cross section may be more justified in such cases than in the other cases where lifetimes are of the order of 10^{-8} sec.

A. Cesium

It is clear from Fig. 1 that for incident energies up to 12 eV, experimental values are in very close agreement with our calculations, the experimental values being slightly higher but always within a factor of 1.2. For energies above 12 eV the calculated values are higher than experimental values but always within a factor of 2. The experimental single-ionization curve of the Cs atom as reported by Zapesochnyi and Aleksakhin[8] shows three prominent peaks at 9.5, 15, and 29 eV, respectively.

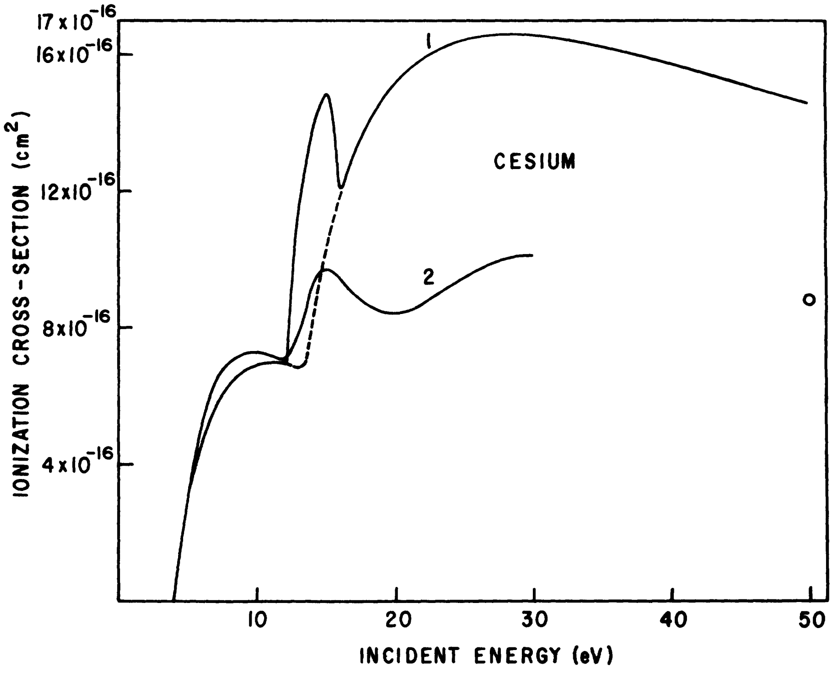

FIG. 1. Ionization cross section for cesium. Curve 1, present results including estimated values for autoionization; the dashed curve represents only the contribution of valence- and inner-shell ionization; Curve 2, Ref. 8. The circle denotes the measurement of McFarland and Kinney, Ref. 2(a).

The peak at 9.5 eV was discovered by them for the first time. The first peak is due to the ionization of the valence-shell electron, while the third broad peak has been explained as involving the ionization of an inner-shell (5*p*) electron. The second peak at 15 eV has been explained[5,8] as being due to excitation of autoionizing levels which decay into the continuum through a radiationless transition.

The broad peak in the calculated ionization curve at 12 eV is clearly due to the ionization of the valence-shell electron and appears at a higher incident energy than the corresponding peak in the experimental curve (9.5 eV). The ionization of inner-shell (5*p*) electron begins at 13.15 eV (which is the ionization potential of the 5*p* electron) and rapidly increases to overshadow the contribution of the valence-shell ionization. The combined effect is to produce a flat peak in the (calculated) ionization curve at ~28 eV. The magnitudes of the calculated cross sections at the maxima, i.e., 12 and 28 eV are, respectively, $8.00\pi a_0^2$ and $18.82\pi a_0^2$ as compared to the experimental peak values of $8.37\pi a_0^2$ and $11.55\pi a_0^2$, respectively.

A very careful study of the autoionizing levels in Cs has been recently performed by Nygaard.[28] It has been shown that there is a multitude of autoionizing levels from 12.3 eV to nearly 20 eV above the ground state of Cs. The second peak at 15 eV has been attributed to excitation of the 5*p* electron to the autoionizing levels at 12.3, 13.5, 14.1, and 14.2 eV by Zapesochnyi and Aleksakhin.[8] We calculated the excitation cross section for the levels 12.3 and 14.1 eV taking 13.5- and 14.2-eV levels as the next higher levels. These cross sections for excitation were assumed to be the same as for ionization due to excitation of the autoionizing levels at 12.3 and 14.1 eV, respectively. Addition of these two cross sections to the sum of cross sections for ionization of valence- and inner-shell electrons increases the maximum cross section to $22.65\pi a_0^2$ but shifts the maximum to somewhat lower incident energy (26 eV). This large value of the cross section is a reminder of the essential limitation of the classical theory to estimate excitation cross sections.

As mentioned earlier, several autoionizing levels of Cs correspond to doublets and have lifetimes of the order of 10^{-15} sec. This would correspond to a natural level width of ~1 eV. It is known that the presence of quasibound states (otherwise referred to as resonances) leads to the appearance of sharp peaks[29] in the excitation cross-section curve. These resonances are characterized by very small lifetimes, and as the lifetimes of the autoionizing levels are several orders of magnitude lower than that of normal excited states, we surmised that the excitation cross-section curves for these states should also be similar in appearance. It is very difficult to introduce these features in classical theory, and so we made a simplifying assumption. We assumed that each autoionizing level contributes significantly to the cross section only for energies within 1 eV of the threshold energy. So we estimated the classical excitation cross section taking $|U_n - U_{n+1}| = 1$ eV and for each

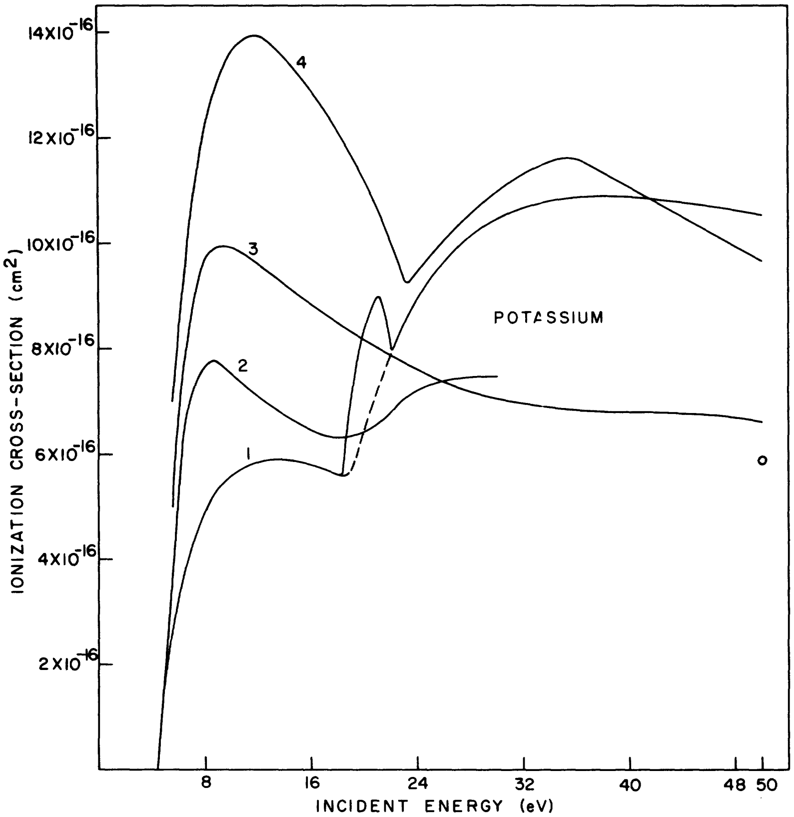

FIG. 2. Ionization cross section for potassium. Curve 1, present results including estimated values for autoionization; the dashed curve represents only the contribution of valence- and inner-shell ionization. Curve 2, Ref. 8. Curve 3, Ref. 17. Curve 4, Ref. 15. The circle denotes the measurement of McFarland and Kinney, Ref. 2(a).

autoionizing level added this excitation cross section to the total cross section for all the incident energies lying within 1 eV of the excitation threshold. Taking the excitation cross section for the levels 12.3, 13.5, and 14.1 eV as calculated by the classical method and adding these to the total cross sections for incident energies 13, 14, and 15 eV, respectively, we find a peak cross section of $16.89\pi a_0^2$ at 15 eV. Our calculated ionization curve of Cs (Fig. 1) shows only two peaks because we have not calculated cross sections at energies lying between 12 and 13 eV. The peak at 12 eV is masked by the dominant contribution of autoionization which we have considered from 13 eV. The contribution of the excitation to the autoionizing levels is of the order of $\sim 5\pi a_0^2$, which is in reasonably good agreement with the value $\sim 2\pi a_0^2$ suggested by Nygaard.[5]

B. Potassium

In the case of potassium (Fig. 2) for incident energies up to 18 eV, experimental values are higher than our calculated values but always within a factor of 2. Above 18 eV the experimental values are in very close agreement with our calculations, the calculated values being higher but always within a factor of 1.5. The valence-shell ionization cross section for K is calculated to reach a peak value of $6.73\pi a_0^2$ at 13 eV, while the inclusion of the ionization of the inner-shell electron leads to the appearance of a broad peak of value $12.39\pi a_0^2$ at 38 eV. The experimental results show only two peaks at 8.5 and 27 eV, respectively. The position of the first peak is thus reasonably well produced but the second peak is shifted towards higher incident energy. It has been suggested by Zapesochnyi and Aleksakhin[8] that the second peak at 27 eV is contributed mainly by the process of excitation to the autoionizing levels lying between 18.7 and 20 eV above the ground state of potassium. The spectral tabulations of Moore[30] suggest the existence of $2p$ state at 18.7 eV above the ground state of K, excitation to which may lead to autoionization. If we calculate the excitation cross section in the usual manner and add it to the total ionization (valence plus inner-shell) cross section, the second peak attains a value $12.41\pi a_0^2$. If, on the other hand, we assume the resonance-type behavior, a third peak of value $10.22\pi a_0^2$ appears at ~ 21 eV. This peak is not very pronounced as in Cs, the excess contribution due to autoionization being only about $2\pi a_0^2$. No such peak is observed experimentally. Two explanations might be put forward: First, other, more prominent autoionizing levels may be

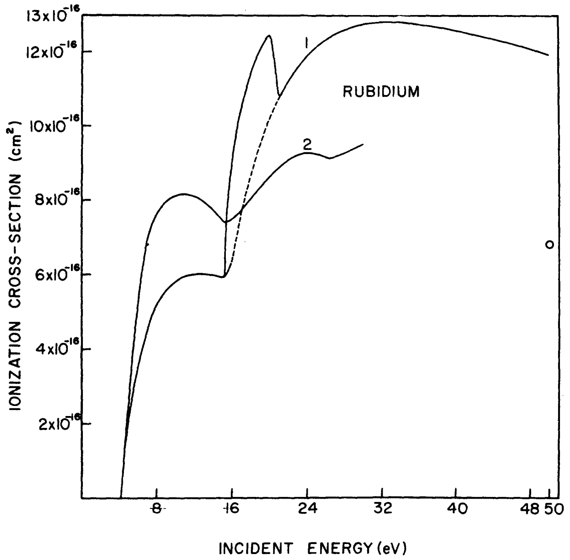

FIG. 3. Ionization cross section for rubidium. Curve 1, present results including estimated values for autoionization; the dashed curve represents only the contribution of valence- and inner-shell ionization. Curve 2, Ref. 8. The circle denotes the measurement of McFarland and Kinney, Ref. 2(a).

present above 20 eV. Second, the lifetime of this 18.7-eV level is not of the order of 10^{-15} sec but is larger, in which case the excitation cross section curve would be more broad. It may be possible to find the peak due to inner-shell ionization near 38 eV experimentally, by more careful investigation.

In Fig. 2 classical calculations of Garcia[15] and Tripathi *et al.*[17] have also been shown for comparison. Garcia's cross-section values are much larger than our calculated values and the experimental results[8] for incident energies less than 18 eV. Two peaks are observed at ~12 and ~35.5 eV in his calculated cross-section curve. The calculated values of Tripathi *et al.* are in somewhat better agreement with the experimental results.[8]

C. Rubidium

The situation in the case of rubidium (Fig. 3) is intermediate between potassium and cesium. At incident energies up to 15 eV, experimental values are higher than our calculated values but always within a factor of 1.5. Above 15 eV, experimental values are in very close agreement with our calculations, the calculated values being higher but always within a factor of 1.5. The experimental single-ionization curve of the Rb atom shows the first peak at 10.5 eV. The valence-shell ionization cross section for Rb is calculated to reach a peak value of $6.85\pi a_0^2$ at 13 eV. Thus, the first observed peak is reproduced fairly well by our calculation. The experimental curve shows a second peak at 24 eV, whereas the peak due to inner-shell ionization is calculated to be of value $14.56\pi a_0^2$ at 33 eV. When the excitation cross sections to the autoionizing levels at 15.3 and 17.2 eV above the ground state of Rb are added, the second peak of value $16.26\pi a_0^2$ shifts to 31 eV. Assumption of sharp excitation peaks and inclusion of a third autoionizing level at 18.8 eV[30] would lead to a third peak at ~30 eV. The contribution to the cross section due to autoionizing levels in the case of Rb is ~$3\pi a_0^2$. If some unknown autoionizing level is present above 18.8 eV, the agreement with the observed peak at 24 eV would be better. The experimental curve due to Zapesochnyi and Aleksakhin[8] shows a clear indication of a third peak which might be at slightly higher energy than 30 eV. This may be correlated with the inner-shell ionization, the second peak being solely due to autoionization. More extensive search of autoionizing levels is needed for the clarification.

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Angular Distributions from Resonant Two-Photon Ionization

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A general theory is developed to treat two-photon ionization through a single intermediate state in which an arbitrary degree of relaxation may occur. The method is set up to probe the parameters governing the relaxation, by determination of the angular distribution of photoelectrons. The method is applied to the ionization of Na atoms, through the $3p\,^2P_{1/2}$ and $3p\,^2P_{3/2}$ intermediate states.

I. INTRODUCTION

This work deals with the photoionization of atoms by a two-step or resonant two-photon process. In contrast to the situation described by Goeppert-Mayer,[1] in which a virtual intermediate state of the absorber is represented as a superposition of many stationary states, we treat the case in which the energy of one proton matches closely an interval connecting a normally occupied state with some electric-dipole-allowed excited state of the absorber. This excited state then dominates the intermediate state of the two-photon absorption process. Our particular concern is to show how the angular distribution of photoelectrons produced in such a process provides data about the intermediate excited state. We develop a general theory for atoms, and apply it to the specific example of the ionization of Na atoms via the initial $3s \rightarrow 3p$ transition.

The kinds of information provided by the angular distribution of photoelectrons are of several varieties, as we shall see. One can obtain the ratio of transition amplitudes for photoionization in the two allowed channels that can be reached from the intermediate state. More important, one can obtain information about the relaxation processes that occur in the intermediate state. It was primarily for this purpose that we undertook the investigation of resonant two-photon ionization, and it will be in this area, we feel, that the method will be most useful. In the case of atoms, to which this piece is devoted, the major relaxation processes are collisional. However, in electronically excited molecules, even in complete isolation, relaxation processes may occur which influence the angular distribution of photoelectrons; future discussions will deal with such processes.

The analysis of angular distributions of photoelectrons has a venerable history in atomic physics,[2] although the subject, particularly in connection with multiphoton processes, has been much more developed in the context of nuclear and particle physics. General considerations governing the angular distributions for two-photon processes were given by Goerzel,[3] Yang,[4] and Abragam and Pound[5]; Zernik[6] provided explicit expressions for the angular distribution of photoelectrons produced by a nonresonant two-photon process from hydrogen atoms, particularly from the metastable $2s$ state. Yatsiv, Wagner, Picus, and McClung[7] carried out experiments on a resonant two-photon absorption process in potassium atoms, but the upper state in their study lay below the ionization limit. Bebb[8] determined theoretical transition rates for two-photon ionization of alkali-metal atoms, and pointed out that cesium could be studied as a near-resonant case if it were excited with the second harmonic of the ruby laser. Then Rizzo and Klewe demonstrated the multiphoton