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## Angular Distributions from Resonant Two-Photon Ionization

Melissa M. Lambropoulos\* and R. Stephen Berry

*Department of Chemistry and the James Franck Institute, University of Chicago, Chicago, Illinois 60637*

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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 Goepfert-Mayer,<sup>1</sup> 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 photon 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,<sup>2</sup> 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,<sup>3</sup> Yang,<sup>4</sup> and Abragam and Pound<sup>5</sup>; Zernik<sup>6</sup> 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<sup>7</sup> 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<sup>8</sup> 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

ionization of alkalis,<sup>9,10</sup> and Hall<sup>11</sup> and Kishi and co-workers<sup>12-14</sup> showed that laser-induced photoionization of Cs and Na were best interpreted as two-photon processes of the type described by Bebb. The dependences of the two- and three-photon ionization cross sections on polarization have been studied experimentally by Fox, Kogan, and Robinson,<sup>15</sup> and interpreted theoretically by Lambropoulos.<sup>16</sup> These studies were all concerned primarily with transition probabilities and total ionization cross sections, and, at most, secondarily with angular distributions.

Further investigation of the angular distribution of photoelectrons appeared with the work of Cooper and Zare for atoms,<sup>17</sup> and of Buckingham, Orr, and Sichel<sup>18</sup> and of Tully, Berry, and Dalton<sup>19</sup> (TBD) for molecules. The work of TBD is particularly germane to the present work because TBD given an explicit derivation for the angular distribution of photoelectrons from *nonresonant* two-photon ionization, the sort described by Mayer. The TBD results were worked out in terms of the transition dipole matrix elements, under the conditions that the one-electron angular momentum quantum numbers of the active electron are good quantum numbers in the intermediate state.

In order to give a clear physical picture of the process of concern here, let us contrast two extreme situations of two-photon ionization. Suppose the target is an isotropic collection of gaseous atoms, and, for the sake of simplicity, assume that the photons all have the same linear polarization. Recall that in a one-photon ionization process, under these conditions the angular distribution of photoelectrons has the form

$$I_1(\theta) = \alpha + \beta P_2(\cos\theta), \quad (1)$$

where  $\theta$  is the angle between the polarization axis and the  $k$  vector of the photoelectron. In the nonresonant or Goeppert-Mayer limit of two-photon ionization, the angular distribution has the form

$$I_2(\theta) = \alpha' + \beta' P_2(\cos\theta) + \gamma' P_4(\cos\theta). \quad (2)$$

The reason for this result is simply that the intermediate states, generated by the action of vector interaction on a scalar distribution, correspond to an anisotropic spatial distribution. When the second photon is absorbed, the accessible continuum states are those that can be reached from that anisotropic intermediate-state distribution.

Now suppose that a relaxation process can occur in the intermediate state, and in particular, a relaxation process that can spoil the  $m_l$  quantum number of the active electron. If relaxation is complete, then the intermediate-state distribution becomes isotropic and the angular distribution of

photoelectrons must be given by (1), rather than (2). Clearly, for intermediate times, the coefficients  $\alpha'$ ,  $\beta'$ , and  $\gamma'$  of (2) must be functions of time and of the relaxation rate. It is our principal purpose here to show how  $\alpha' \rightarrow \alpha$ ,  $\beta' \rightarrow \beta$ ,  $\gamma' \rightarrow 0$ , and how one can infer relaxation times from measurements of these coefficients.

For collisional relaxation of atoms, the method gives essentially the same information as optical pumping, a relaxation time for  $m_l$ . For other processes, such as intramolecular energy conversion, one obtains new information.

## II. GENERAL THEORY

The basic problem is the determination of an intensity distribution

$$I(\theta) = \text{Tr}(\rho_f F) = \langle F \rangle, \quad (3)$$

where the trace is taken of the product of the final-state density matrix  $\rho_f$  and the detector operator  $F$ . The matrix  $\rho_f$  is conveniently evaluated as a succession of transformations of an initial-state density matrix  $\rho_i$ ; the initial state can be represented by the product of  $\rho_a$ , a matrix for the atomic system, and  $\rho_1$ , the matrix for the field associated with the first photon:

$$\rho_i = \rho_a \rho_1. \quad (4)$$

The transformations of the initial system are written in terms of the radiation interaction operator  $R_1$  for the first absorption process, the time evolution operator  $P$  for the interval between the first and second excitation processes, the density matrix  $\rho_2$  for the field associated with the second photon (and  $\rho_2$  may be the same as  $\rho_1$ ), and then the second radiation interaction operator  $R_2$ :

$$\begin{aligned} \rho_f &= \rho_e \rho_{\text{ion}} \\ &= R_2 P R_1 \rho_a \rho_1 R_1^\dagger P^\dagger \rho_2 R_2^\dagger. \end{aligned} \quad (5)$$

The final-state density matrix, like the initial-state density matrix, is expressed as a product; for the final state, the product is taken for the outgoing electron ( $\rho_e$ ) and the remaining ion ( $\rho_{\text{ion}}$ ).

Since our concern in the final state is only with the electron, we can specialize (3) to

$$I(\theta) = \text{Tr}(\rho_e \epsilon), \quad (6)$$

where we have replaced a general detector operator  $F$  with an electron detector efficiency operator  $\epsilon$ , and the total final-state density operator  $\rho_f$  with the part  $\rho_e$  referring only to the outgoing electron.

Insofar as the target absorber may have its own internal symmetry, there may be a natural set of axes in which to compute the transformations represented by (5). A linear molecule, for example,

has natural axes along and perpendicular to the internuclear axis. However, the final description of  $\rho_e$  should be in terms of laboratory axes, if it is to be useful for computing angular distributions. We may write the density matrix (and other operators, when appropriate) in terms of a representation in a series expansion in terms of irreducible tensors.<sup>20, 21</sup> Following the notation of Devons and Goldfarb,<sup>21</sup> we let  $a, b, \dots$  denote total angular momentum quantum numbers;  $\alpha, \beta, \dots$  denote the quantum numbers for the well-quantized components of angular momentum, and  $A, B, \dots$  indicate all other quantum numbers. Moreover the density matrix in its conventional angular momentum representation can be expanded in multipoles, or statistical (irreducible) tensors, thus:

$$\langle a\alpha A | \rho | a'\alpha' A \rangle = \sum (-1)^{a'-\alpha'} (a, \alpha; a', -\alpha' | aa'k_a \eta_a) \times \rho_{k_a \eta_a}(aA, a'A'). \quad (7)$$

Here,  $(a, \alpha; a', -\alpha' | aa'k_a \eta_a)$  is a Clebsch-Gordan coefficient, and  $k_a, \eta_a$  represent the quantum numbers, respectively, of the resultant of coupling  $a$  with  $a'$ , and its well-quantized component. (We use parentheses for Clebsch-Gordan coefficients and angular brackets for matrix elements.) Thus  $|a-a'| < k_a < a+a'$ . The multipoles or irreducible statistical tensors  $\rho_{k_a \eta_a}(aA, a'A')$  are independent of  $\alpha$  and  $\alpha'$ , and have only one quantum number  $\eta_a$  referring to a component. Similarly, the efficiency tensor  $\epsilon$  can be expressed in terms of its angular momentum representation  $\langle a'\alpha'A' | \epsilon | a\alpha A \rangle$  or its multipole or efficiency tensors  $\epsilon_{k_a \eta_a}(aA, a'A')$ , which are related as are the two forms of  $\rho$  by (7) and its inverse, which, for  $\epsilon$ , has the form

$$\epsilon_{k_a \eta_a}(aA, a'A') = \sum_{\alpha, \alpha'} (-1)^{a'-\alpha'} (a, \alpha; a', -\alpha' | k_a \eta_a) \times \langle a\alpha A | F | a'\alpha' A' \rangle. \quad (8)$$

A particular convenience of the irreducible-tensor representation is the form of the transformation from one set of axes to another, as in the transformation between laboratory or reference axes and molecule-fixed or natural axes:

$$\rho_{k_a \eta_a}(aA, a'A'; \text{lab}) = \sum_{\eta'_a} D_{\eta'_a \eta_a}^{k_a}(\text{nat} \rightarrow \text{lab}) \times \rho_{k_a \eta'_a}(aA, a'A'; \text{nat}). \quad (9)$$

We denote the sum over all components of a tensor of rank  $k_a$  by the tilde, e.g.,

$$\tilde{\rho}_{k_a}(aA, a'A') = \sum_{\eta_a} \rho_{k_a \eta_a}(aA, a'A'). \quad (10)$$

We also abbreviate with a caret, according to the

notation of Devons and Goldfarb,

$$\hat{l} = (2l+1)^{1/2},$$

where  $l$  may be any angular momentum quantum number.

#### General Expression

We derive the expression for the angular distribution  $W(\Omega)$  of photoelectrons by finding:

$\rho_{k_b \eta_b}(bB, bB)$ , the density matrix for the atomic excited intermediate state; the density matrix  $\rho_{k_f \eta_f}(fF, f'F')$  of the final state; and  $\epsilon_{k_e \eta_e}(e'E', eE)$ , the efficiency tensor for detection of the final electron. The dynamical relaxation during the intermediate state is introduced in a phenomenological way, as a set of random events, whose ensemble average is isotropic in space.

It is convenient to express the density matrices for the radiation field,  $\rho_{k_1 \eta_1}(L'_1, L_1)$  and  $\rho_{k_2 \eta_2}(L_2, L'_2)$ , in terms of the natural atomic or molecular coordinate system. Hence we introduce the appropriate rotation operators  $[D_{\eta_a \eta_1}^{k_1}(R)]^{-1}$  and  $[D_{\eta_b \eta_2}^{k_2}(R)]^{-1}$  explicitly into our expressions. The angular momentum coupling is expressed explicitly by the Clebsch-Gordan coefficients and the  $9-j$  symbols, in braces. The density matrix for the intermediate state is

$$\rho_{k_b \eta_b}(bB, bB) = \sum_{L_1, L'_1} \langle bB | R | aA, L'_1, b \rangle \langle aA, L_1, b | R^\dagger | bB \rangle \times \sum_{k_1 k_a} \hat{\delta}^2 \hat{k}_1 \hat{k}_a (k_b \eta_b | k_a \eta_a, k_1, \eta_1) \begin{Bmatrix} a & a & k_a \\ L'_1 & L_1 & k_1 \\ b & b & k_b \end{Bmatrix} \times \rho_{k_a \eta_a}(aA, a'A') [D_{\eta_a \eta_1}^{k_1}]^{-1} \rho_{k_1 \eta_1}(L'_1, L_1). \quad (11)$$

We obtain  $\tilde{\rho}_{k_b}$  by summing (11) over  $\eta_b$ .

Since we assume that the targets form an isotropic ensemble,  $\rho_{k_a \eta_a}$  vanishes unless  $k_a = \eta_a = 0$ ; that is, the isotropic distribution has only monopole terms. Moreover the density matrix  $\rho_a$  itself is diagonal, with equal elements, for the ensemble we postulate. (Experiments with oriented or suitably selected targets would require a different form of the density matrix, of course.) Thus, for our case,

$$\rho_a(a\alpha A, a'\alpha' A) = \hat{a}^{-2} \delta_{a\alpha} \delta_{\alpha\alpha'} \delta_{AA'}, \quad (12)$$

and, since  $\hat{a}(-1)^{a-\alpha}(a\alpha, a-\alpha | 00) = 1$ , and the Clebsch-Gordan coefficients form unitary matrices, we obtain the particularly simple form for the statistical tensors of the initial state,

$$\rho_{k_a \eta_a}(aA, a'A') = \hat{a}^{-2} \delta_{k_a 0} \delta_{\eta_a 0} \delta_{AA'}. \quad (13)$$

In other words, the statistical tensors are diago-

nal, vanish for all ranks greater than zero, and have diagonal elements  $(2a+1)^{-1}$  for states with  $a$  units of angular momentum. This allows us to reduce the  $9-j$  symbol to a  $6-j$  symbol,

$$\left\{ \begin{matrix} a & a & 0 \\ L'_1 & L_1 & k_1 \\ b & b & k_b \end{matrix} \right\} = \frac{(-1)^{L'_1+a+b+k_b}}{\hat{a}\hat{k}_b} \left\{ \begin{matrix} b & L'_1 & a \\ L_1 & b & k_b \end{matrix} \right\}, \quad (14)$$

so that the statistical tensor of the intermediate state becomes

$$\begin{aligned} \rho_{k_b, \eta_b}(bB, bB) &= \sum_{L_1, L'_1} \langle bB | R | aA, L'_1 b \rangle \langle aA, L_1 b | R^\dagger | bB \rangle \\ &\times \delta_{k_b, k_1} \delta_{k_a}(k_b, \eta_b | 00, k_1, \eta_1) \frac{(-1)^{L'_1+a+b+k_b}}{\hat{a}^2 \hat{k}_b} \\ &\times \left\{ \begin{matrix} b & b & k_b \\ L_1 & L'_1 & a \end{matrix} \right\} [D_{0, \eta_1}^{k_1}]^{-1} \rho_{k_1, \eta_1}(L_1, L'_1). \end{aligned} \quad (15)$$

Here, the statistical tensor of the radiation field  $\rho_{k_1, \eta_1}$  is in laboratory coordinates and the matrix elements of  $R$  and  $R^\dagger$  are calculated in natural molecular coordinates. Note that  $D_{0, \eta_1}^{k_1}$  is a multiple of an associated Legendre function.

The manner of presenting the relaxation of the distribution of the intermediate state will be described below. We go on now to describe the density matrix of the final state in terms of its statistical tensors  $\rho_{k_f, \eta_f}(fF, f'F')$ . For ion plus electron,

$$\begin{aligned} \rho_{k_f, \eta_f}(fF, f'F') &= \sum_{bB, L_2, L'_2} \langle fF | R | bB, L_2, f \rangle \langle bB, L'_2, f' | R^\dagger | f'F' \rangle \\ &\times \sum_{k_b, \eta_b} \hat{f} \hat{f}' \hat{k}_b \hat{k}_2 \left\{ \begin{matrix} b & L_2 & f \\ b & L'_2 & f' \\ k_b & k_2 & k_f \end{matrix} \right\} (k_f, \eta_f | k_b, \eta_b, k_2, \eta_2) \\ &\times \rho_{k_b, \eta_b}(bB, bB) [D_{\eta_b, \eta_2}^{k_b}(R)]^{-1} \rho_{k_2, \eta_2}(L_2, L'_2). \end{aligned} \quad (16)$$

Again, the rotation operator  $D_{\eta_b, \eta_2}^{k_b}$  assures that the radiation field is described in natural molecular coordinates, or, as we have done here, the inverse transformation refers the molecular transition to the laboratory frame. Because the

density matrix  $\rho_{k_b, \eta_b}$  for the intermediate state is the result of an anisotropic excitation, we cannot, in general, make the same reductions of (16) that we made in deriving (15) from (11). If relaxation is complete in the intermediate state, that reduction is applicable, but we are interested in the more general situation here.

The "maximum-information" probability function is the angular correlation function for polarized ions and polarized electrons,

$$W(\Omega_i, \sigma_i, \Omega_e, \sigma_e) = \sum_{f, f', k_f} \tilde{\rho}_{k_f}(fF, f'F') \tilde{\epsilon}_{k_f}(fF, f'F'), \quad (17)$$

where  $F$  includes all quantum numbers for electrons and ions. The efficiency tensor components can be written in terms of the (presumed independent) electron and ion detectors whose efficiency tensors have components  $\epsilon_{k_e, \eta_e}$  and  $\epsilon_{k_i, \eta_i}$ :

$$\begin{aligned} \epsilon_{k_f, \eta_f}(fF, f'F') &= \sum_{k_e, \eta_e, k_i, \eta_i} \epsilon_{k_e, \eta_e}(eE, e'E') \epsilon_{k_i, \eta_i}(iI, i'I') \\ &\times (k_f, \eta_f | k_e, \eta_e, k_i, \eta_i) \hat{f} \hat{f}' \hat{k}_e \hat{k}_i \left\{ \begin{matrix} e & i & f \\ e' & i' & f' \\ k_e & k_i & k_f \end{matrix} \right\}. \end{aligned} \quad (18)$$

For the unobserved ion, the efficiency tensor

$$\epsilon_{k_i, \eta_i}(iI, i'I') = \hat{i} \delta_{k_i, 0} \delta_{\eta_i, 0} \delta_{i, i'}, \quad (19)$$

so that, like the reduction of (11),

$$\begin{aligned} \epsilon_{k_f, \eta_f}(fF, f'F') &= \hat{f} \hat{f}' (-1)^{e+i+f'+k_f} \\ &\times \left\{ \begin{matrix} f & f' & k_f \\ e' & e & i \end{matrix} \right\} \epsilon_{k_e, \eta_e}(eE, e'E'). \end{aligned} \quad (20)$$

Thus, we obtain the angular distribution function for the electrons

$$\begin{aligned} W(\Omega_e) &= \sum_{\substack{eE, e'E', \\ fF', k_f, \eta_f}} \rho_{k_f, \eta_f}(fF, f'F') (-1)^{e+i+f'-\eta_f} (\hat{f} \hat{f}' / \hat{k}_f) \\ &\times \left\{ \begin{matrix} f & f' & k_f \\ e' & e & i \end{matrix} \right\} \epsilon_{k_e, \eta_e}(eE, e'E'). \end{aligned} \quad (21)$$

If we use the electric dipole approximation, so that  $L_1 = L_2 = 1$ , and we take both photons in the same beam with the same polarization we find

$$\begin{aligned} W(\Omega_e) &= \sum_{a, e', E, E', f, f'} \langle f | R | b, 1; f \rangle \langle b, 1; f' | R^\dagger | f' \rangle \langle b | R | a, 1; b \rangle \langle b, 1; b | R^\dagger | b \rangle \\ &\times \sum_{k_f} \frac{\hat{f}^2 \hat{f}'^2}{\hat{k}_f} (-1)^{e'+i+f+k_f} \left\{ \begin{matrix} f' & f & k_f \\ e & e' & i \end{matrix} \right\} \sum_{k_b, \eta_b} \delta_{k_b, k_1} \xi(k_b) \hat{k}_b \hat{k}_2 \left\{ \begin{matrix} b & 1 & f \\ b & 1 & f' \\ k_b & k_2 & k_f \end{matrix} \right\} (-1)^{1+a+b+k_b} \frac{\hat{b}}{\hat{a}} \left\{ \begin{matrix} b & b & k_b \\ 1 & 1 & a \end{matrix} \right\} \\ &\times \sum_{\eta_f} (-1)^{k_f - \eta_f} \epsilon_{k_e, \eta_e}(e'E', eE) \sum_{\eta_1, \eta_2} (k_f, \eta_f | k_1, \eta_1, k_2, \eta_2) \rho_{k_1, \eta_1}(11) \rho_{k_2, \eta_2}(11). \end{aligned} \quad (22)$$

The function  $\xi(k_b)$  is the relaxation factor for the  $k_b$ -order statistical tensor for the intermediate state, which we shall discuss below.

#### Efficiency Tensor

We next construct the explicit efficiency tensor for the photoelectron, following Devons and Goldfarb. We assume that the detector does not measure spin, so that the spin contribution  $\langle \sigma | F | \sigma' \rangle$  or  $\langle \sigma | \epsilon | \sigma' \rangle$  is merely a  $\delta$  function  $\delta_{\sigma\sigma'}$ . If the axis of quantization for the angular momentum of the electron is along the propagation vector in the direction  $\Omega_e$ , the detector efficiency is

$$\langle L\Lambda | F | L'L'\Lambda' \rangle = \sum_{\sigma\sigma'} \langle L\Lambda | \Omega\sigma \rangle \langle \sigma | F | \sigma' \rangle \langle \Omega\sigma' | L'L'\Lambda' \rangle, \quad (23)$$

which gives efficiency tensors

$$\epsilon_{k_e \eta_e}(LL', L'L') = \sum_{\Lambda, \Lambda', \sigma} (-1)^{L'-\Lambda'} \langle L, \Lambda; L', \Lambda' | k_e \eta_e \rangle \times \langle L\Lambda | k_e \eta_e \rangle \langle L\Lambda | \Omega\sigma \rangle \langle \Omega\sigma | L'L'\Lambda' \rangle. \quad (24)$$

The frame most useful for us is the laboratory frame, in which the propagation vector of the electron is specified by the angle  $\Omega = \theta, \varphi$  and the  $z$  axis is the approximate symmetry axis of the radiation field. In such a system,

$$\epsilon_{k_e \eta_e}(LL', L'L') = \sum_{\eta'} C_{k_e \eta_e}(LL') D_{\eta_e \eta'}^k(\Omega) \quad (25)$$

and the coefficients

$$C_{k_e \eta_e}(LL') = \sum_{\sigma} (-1)^{L'-l'} \langle L, l; L', -l' | k_e \eta_e \rangle \times \langle L\Lambda | 0\sigma \rangle \langle 0\sigma | L'\Lambda' \rangle. \quad (26)$$

The projections of the form  $\langle 0\sigma | L\Lambda l \rangle$  are multiples of Clebsch-Gordan coefficients

$$\langle 0\sigma | L\Lambda l \rangle = (4\pi)^{-1/2} \hat{l} \langle l, 0, \sigma | L\Lambda \rangle, \quad (27)$$

for particles with total spin and orbital angular momenta  $l, s$  and well-quantized components  $0, \sigma$ . If polarization is not observed and we deal with electrons, for which  $s = \frac{1}{2}$ , the coefficients  $C_{k_e \eta_e}$  reduce to this form:

$$C_{k_e 0}(LL') = (8\pi)^{-1/2} \hat{L} \hat{L}' (-1)^{L+k-1/2} \times \langle L, \frac{1}{2}; L', -\frac{1}{2} | k_e 0 \rangle. \quad (28)$$

Table I contains values of the efficiency tensor for electrons, with angular momentum quantum numbers  $e, e'$  through  $\frac{9}{2}$ , corresponding to  $g$ -wave electrons.

#### Photon Statistical Tensor

The photon density matrix is most simply derived by the method given by Peshkin.<sup>22</sup> The pho-

ton is a spin-1 particle with a zero value of spin angular momentum along the propagation direction  $k$ . The photon wave function  $\Phi_\mu$  for arbitrary polarization  $\mu$  ( $\mu = +1$  for left- or right-circularly polarized light,  $\mu = x, y$  for linearly polarized light) is expanded in terms of  $2j$ -pole states for electric and magnetic multipoles  $|E_j, \pm 1\rangle$  and  $|M_j, \pm 1\rangle$ , with amplitudes given by coefficients  $c_{Mj\mu}$  and  $c_{Ej\mu}$ :

$$\Phi_\mu = \chi_{1\mu} e^{ikz} = \sum_{j=1}^{\infty} c_{Mj\mu} |Mj, \mu\rangle + c_{Ej\mu} |Ej, \mu\rangle. \quad (29)$$

For  $x$ - and  $y$ -linearly polarized light, we obtain

$$\Phi_x = -(2)^{-1/2} \sum_{j=1}^{\infty} |M, 1\rangle + |M, -1\rangle + |E, 1\rangle - |E, -1\rangle \quad (30)$$

and

$$\Phi_y = -i(2)^{-1/2} \sum_{j=1}^{\infty} |M, 1\rangle - |M, -1\rangle + |E, 1\rangle + |E, -1\rangle, \quad (31)$$

respectively. The density-matrix element specified by  $K, K'$  (which may be  $E$  or  $M$ ),  $j, j'$  and  $\mu, \mu'$ , for a pure state  $\Phi$ , is

$$\langle K', j'\mu' | \rho | Kj\mu \rangle = \langle K' j'\mu' | \Phi \rangle \langle \Phi | Kj\mu \rangle. \quad (32)$$

TABLE I. Values of expansion coefficients  $C_{k_e \eta_e}(LL')$  of the efficiency tensor.

$2e$	$2e'$	$k_f = 0$	$k_f = 2$	$k_f = 4$
1	1	1.414 21	0.0	0.0
1	3	0.0	2.000 00	0.0
1	5	0.0	2.449 48	0.0
1	7	0.0	0.0	2.828 42
1	9	0.0	0.0	3.162 27
3	1	0.0	-2.000 00	0.0
3	3	2.000 00	-2.000 00	0.0
3	5	0.0	1.309 30	-3.207 13
3	7	0.0	3.207 13	-2.390 45
3	9	0.0	0.0	1.906 92
5	1	0.0	2.449 48	0.0
5	3	0.0	-1.309 30	3.207 13
5	5	2.449 48	-2.618 61	2.267 78
5	7	0.0	1.069 04	-2.162 24
5	9	0.0	3.779 64	-3.057 88
7	1	0.0	0.0	-2.828 42
7	3	0.0	3.207 13	-2.390 45
7	5	0.0	-1.069 04	2.162 24
7	7	2.828 42	-3.086 06	2.900 96
7	9	0.0	0.930 48	-1.799 10
9	1	0.0	0.0	3.162 27
9	3	0.0	0.0	-1.906 92
9	5	0.0	3.779 64	-3.057 88
9	7	0.0	-0.930 48	1.799 10
9	9	3.162 27	-3.481 55	3.365 80

For an electric dipole process, we need only the  $|E1, 1\rangle$  and  $|E1, -1\rangle$  components. We have only

$$\rho_1(E, E) = \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix} \quad \text{for left circular,} \quad (33a)$$

$$\rho_1(E, E) = \begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix} \quad \text{for right circular,} \quad (33b)$$

$$\rho_x(E, E) = \begin{pmatrix} \frac{1}{2} & -\frac{1}{2} \\ -\frac{1}{2} & \frac{1}{2} \end{pmatrix} \quad \text{for } x \text{ polarized,} \quad (33c)$$

$$\rho_y(E, E) = \begin{pmatrix} \frac{1}{2} & \frac{1}{2} \\ \frac{1}{2} & \frac{1}{2} \end{pmatrix} \quad \text{for } y \text{ polarized,} \quad (33d)$$

$$\rho_u(E, E) = \begin{pmatrix} \frac{1}{2} & 0 \\ 0 & \frac{1}{2} \end{pmatrix} \quad \text{for unpolarized light.} \quad (33e)$$

The photon statistical tensor components are derived by the expansion we have already used:

$$\rho_{k_1 \eta_1}(1, 1) = \sum_{\mu, \mu'} (k_1 \eta_1 | 1\mu, 1\mu' \rangle (-1)^{1-\mu'} \times \langle E1, \mu | \rho | E1, \mu' \rangle. \quad (34)$$

These components take on the following values, if the reference ( $z$ ) axis is the propagation axis:

for  $x$  polarization ( $z$  reference):

$$\rho_{00} = 3^{-1/2}, \quad \rho_{20} = 6^{-1/2}, \quad \rho_{22} = \rho_{2-2} = -\frac{1}{2}; \quad (35)$$

for unpolarized light:

$$\rho_{00} = 3^{-1/2}, \quad \rho_{20} = 6^{-1/2}, \quad \rho_{22} = \rho_{2-2} = 0. \quad (36)$$

If the reference ( $z'$ ) axis for  $x$ -polarized light is taken along the polarization direction, then the tensor becomes diagonal, with

$$\rho_{00} = 3^{-1/2}, \quad \rho_{20} = -(2/3)^{-1/2}, \quad \rho_{22} = \rho_{2-2} = 0. \quad (37)$$

This is a particularly convenient choice because, if  $\rho$  is diagonal, the angular distribution  $W$  becomes a sum of Legendre polynomials.

#### Relaxation in the Intermediate State

We follow the method of Dillenberg and Maris<sup>23-26</sup> to derive a phenomenological description that parametrizes the relaxation of our intermediate state  $|bB\rangle$ . We assume that the intermediate state is a well-quantized pure state when it is first formed, and not a superposition of the sort set up in quantum beat experiments. The reference axis for this quantization is the natural axis for the incident light, either the polarization axis for linearly polarized light, or the propagation axis for circularly polarized or unpolarized light. The perturbation causing relaxation is assumed to be incoherent, so that it introduces no special phase relations among the states. Then we may write the relaxation equation for the diagonal elements of  $\rho$  as

$$\frac{d}{dt} \langle m | \rho | m \rangle = \sum_{m'} \Lambda_{mm'} \langle m | \rho | m' \rangle, \quad (38)$$

in terms of a transition matrix  $\Lambda$ . Conservation requires sums on rows or columns of  $\Lambda$  to be zero.

The perturbation process of a set of kinds of events  $K$ , associated with transition potentials (or  $T$ -matrix elements, more accurately)  $U_K$ , over whose effects we must sum or integrate gives

$$\Lambda_{mm'} = \sum P(K) [ |\langle Jm | U_K | Jm' \rangle|^2 - \delta_{mm'} ], \quad (39)$$

where  $P(K)$  is the relative probability of the  $K$ th-type of event. If the events differ according to class, as to their reference to spatial orientation, which we may denote by  $\omega$ , then

$$\Lambda_{mm'} = (8\pi^2)^{-1} \sum_{\text{classes } n} d\omega P_n(\omega) \times [ |\langle Jm | U_n(\omega) | Jm' \rangle|^2 - \delta_{mm'} ]. \quad (40)$$

Note that  $J$  represents the conserved quantum numbers, which, in our present context, will include the total orbital momentum of the active electron.

Now we make the physical assumption that  $P_n(\omega)$  is independent of  $\omega$ , and rotate our reference frame to evaluate the elements of  $U_n(\omega)$ :

$$\langle Jm | U_n(\omega) | Jm' \rangle = \sum_{\mu, \mu'} \langle Jm | D_{m\mu}(\omega)^{-1} | J\mu \rangle \times \langle J\mu | U_n(0) | J\mu' \rangle \langle J\mu | D_{m\mu'}(\omega) | Jm' \rangle. \quad (41)$$

Integration over angles reduces the transition matrix to the form

$$\Lambda_{mm'} = \sum_I S_{mI}^{-1} \lambda_I S_{Im}, \quad (42)$$

where

$$S_{Im} = (-1)^{J-m} \langle J, m; J, -m | I0 \rangle$$

and

$$\lambda_I = \sum_n P_n (-1)^{2J} J^{-2} \sum_{\nu, \nu'} \sum_{\mu, \mu'} [ \langle J\mu, J-\nu | I0 \rangle \times \langle J\mu', J-\nu | I0 \rangle \langle J\nu' | U_n | J\nu \rangle \times \langle J\mu | U_n^\dagger | J\mu' \rangle \delta_{\mu-\nu, \mu'-\nu-1} ]. \quad (43)$$

The matrix  $S_{Im}$  is the unitary matrix that diagonalizes  $\Lambda_{mm'}$  to provide the eigenvalues  $\lambda_I$ . These, in turn, define the time decay of the irreducible tensorial components of the density matrix, which describe the behavior of  $\langle m | \rho | m \rangle$ . The general solution to (38) is

$$\langle m | \rho(E) | m \rangle = \langle m | \rho_{\text{equil}} | m \rangle + \sum_{i=0}^{\infty} S_{mi} \zeta_i(0) e^{-\lambda_i t}, \quad (44)$$

where the initial conditions determine the  $\zeta_i(0)$ 's. The boundary conditions we apply are that the isotropic component  $\rho_{00}$  of the statistical tensor is

identically 1, and that all other  $\rho_{k_0}$ 's decay toward zero. (We can choose our axes so that  $\rho_{k_0}$  is identically zero for  $\eta \neq 0$ .) Writing the statistical tensor in terms of the density matrix, we have

$$\begin{aligned}\rho_{k_0}^{(t)} &= \sum_m (k_0 | J, m; J, -m) (-1)^{J-m} \langle m | \rho(t) | m \rangle \\ &= \sum_{i=0}^{\infty} R_{ki} e^{-\lambda_i t}.\end{aligned}\quad (45)$$

We now identify

$$\begin{aligned}R_{ki} &= \zeta_i(0) \sum_m (-1)^{J-m} S_{mi}(J, m; J, -m | k_0) \\ &= \zeta_i(0) \sum_m (-1)^{J-m} (-1)^{J-m} \\ &\quad \times (J, m; J, -m | i 0) (J, m; J, -m | k_0) \\ &= \zeta_i(0) \delta_{ik},\end{aligned}\quad (46)$$

so that the  $\zeta_k(0)$ 's are indeed the initial conditions of  $\rho_k(t)$ :

$$\rho_{k_0}(t) = \rho_{k_0}(0) e^{-\lambda_k t}.\quad (47)$$

Finally, we need only integrate over time, with the weighting factor  $e^{-t/\tau_b}$  for the intermediate state whose natural lifetime from spontaneous, stimulated, and reactive causes is  $\tau_b$ :

$$\begin{aligned}W(\Omega, t \rightarrow \infty) &= \int_0^{\infty} e^{-t/\tau_b} W(\Omega, t) dt \int_0^{\infty} e^{-t/\tau_b} dt \\ &= \frac{1}{\tau_b} \int e^{-t/\tau_b} \sum W_{k_b}(\Omega, 0) e^{-\lambda_{k_b} t} dt \\ &= \sum_{k_b} W_{k_b}(\Omega, 0) (1 + \lambda_{k_b} \tau_b)^{-1}.\end{aligned}\quad (48)$$

$$\begin{aligned}\Xi(a, b, i, e, f, e', f') &= \hat{f}^2 \hat{f}'^2 \hat{b} \hat{a}^{-1} (-1)^{e'+i+f} \sum_{k_f} \hat{k}_f^{-1} \begin{Bmatrix} f & f' & k_f \\ e & e' & i \end{Bmatrix} D_{00}^{k_f}(R)^{-1} C_{k_f 0}(e'e) \sum_{k_b} \delta_{k_b k_1} (1 + \lambda_{k_b} \tau_b)^{-1} \hat{k}_b \begin{Bmatrix} b & 1 & f \\ b & 1 & f' \\ k_b & k_1 & k_f \end{Bmatrix} \\ &\quad \times (-1)^{1+a+b+k_b} \begin{Bmatrix} b & b & k_b \\ 1 & 1 & a \end{Bmatrix} \rho_{k_1 0}(1, 1) \sum_{k_2} \hat{k}_2 \rho_{k_2 0}(1, 1) (k_f 0 | k_1 0, k_2 0).\end{aligned}\quad (50)$$

Every factor and term of  $\Xi$  is calculable except the relaxation factors  $(1 + \lambda_{k_b} \tau_b)^{-1}$  of each  $k_b$ th tensorial rank. In general, with two electric dipole processes, there are only five nonvanishing terms in  $\Xi$ , corresponding to the following combination of ranks:  $k_f=0, k_b=0; k_f=0, k_b=2; k_f=2, k_b=0; k_f=2, k_b=2$ , and  $k_f=4, k_b=2$ . We can reduce (50) to a simple sum over terms, each consisting of numbers, relaxation factors, and Legendre polynomials  $D_{00}^{k_f-1} = P_{k_f}(\cos \theta)$ :

$$\begin{aligned}\Xi &= B_{00} + B_{02} (1 + \lambda_2 \tau_b)^{-1} \\ &\quad + [B_{20} + B_{22} (1 + \lambda_2 \tau_b)^{-1}] P_2(\cos \theta) \\ &\quad + B_{42} (1 + \lambda_2 \tau_b)^{-1} P_4(\cos \theta).\end{aligned}\quad (51)$$

Note that  $\tau_b$  may be field dependent in intense radiation fields.

This expression incorporates all the relaxation information that we have included thus far in the analysis. However, it is still rather cumbersome in its present form.

#### Explicit Expressions

It is very useful for comparing predictions with experimental data, to express the angular probability function  $W(\Omega)$  in terms that allow all the angular parts to be calculated explicitly, once and for all, and to introduce the radial factors of the transition dipole matrix elements and relaxation factors as parameters or as numbers derived from microscopic theory. We choose the reference frame of the photon density tensor so that  $\eta_f=0$ . Then we may write

$$\begin{aligned}W(\Omega) &= \sum_{f, f'} \sum_{a, b} [\langle f | R | b, 1; f \rangle \langle b, 1; f' | R^\dagger | f' \rangle \\ &\quad \times \langle b | R | a, 1; b \rangle \langle a, 1; b | R^\dagger | b \rangle \\ &\quad \times \sum_{e, e', i} \Xi(a, b, i, e, f, e', f')].\end{aligned}\quad (49)$$

The factors  $\Xi$  contain the angular dependencies in terms of the irreducible tensors and the relaxation factors:

Naturally the coefficients  $B_{k_f k_b}$  contain all the dependence on the initial angular momentum  $a$ , the angular momentum  $b$  of the intermediate state, and the polarization of the radiation, as well as the angular momenta  $e, e'$  of the outgoing electron,  $i$  (of the final ion), and  $f, f'$ , the total angular momenta of the final channels.

We have derived a program and evaluated the five coefficients  $B_{k_f k_b}$  (actually,  $B_{k_f 0}$  and  $B_{k_f 0} + B_{k_f 2}$ ), to give the completely relaxed and completely unrelaxed distributions, respectively for all values of  $a, b, f, f'$ , and  $i$  from 0 through 5 and  $e, e'$  from  $\frac{1}{2}$  through  $\frac{5}{2}$ . The values are tabulated in Ref. 27 through  $a=2, b=3, f, f'=4, i=4$ , and  $e, e'=\frac{7}{2}$ .

TABLE II. Terms in the angular distribution of photoelectrons arising from ionization of sodium via the  $3p\ ^2P_{1/2}$  state and a 3371-Å (molecular  $N_2$  laser) photon. Note that the terms  $B_{22}$  and  $B_{42}$  are zero.  $\Xi = \Xi(a, b, i, e, f, e', f')$  is abbreviated as  $\Xi(b, f, f')$ , since  $a = \frac{1}{2}, i = 0, e = f$ , and  $e' = f'$ .

	$B_{00}$	$B_{20}$
$\Xi(\frac{1}{2}, \frac{3}{2}, \frac{3}{2})$	2.000	0.893
$\Xi(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$	1.000	0
$\Xi(\frac{1}{2}, \frac{3}{2}, \frac{1}{2})$	0	0.894
$\sum_{ff'} \Xi(\frac{1}{2}, f, f') (f R b)(b R^\dagger f')$	0.520	-0.32

$$W(\Omega) = 0.520P_0 - 0.032P_2$$

$$= 0.536 - 0.048 \cos^2\theta$$

#### Interferences

There is one point to bear in mind associated with the levels  $b$ ,  $f$ , and  $f'$ . Our present treatment is based on the assumption that the bandwidth of the excitation source is narrow enough to ensure that only one intermediate state  $|bB\rangle$  dominates the first excitation step. The results obtained by Hall<sup>11</sup> and by Kishi *et al.*<sup>12-14</sup> demonstrate that this is a realistic assumption for atoms. Moreover, the recent studies of Stevens, Swagel, Wallace, and Zare<sup>28</sup> demonstrate that this kind of preparation can be achieved for a molecule at least as complex as  $NO_2$ , in which the excited state is a single rovibronic level. It is unlikely that single intermediate states can be excited in

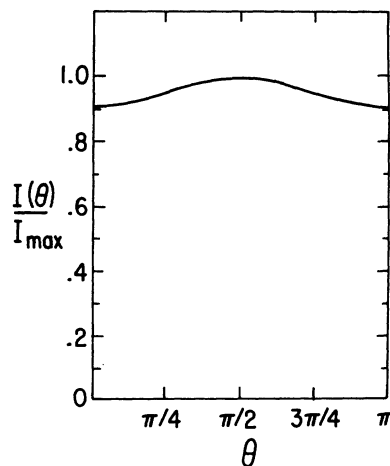


FIG. 1. Angular distribution of photoelectrons from ionization of Na ( $3p\ ^2P_{1/2}$ ) with 3371-Å light.

complex polyatomic molecules. For such systems, the description requires summation over all the closely spaced intermediate levels excited together by the absorption of the first photon. Moreover, the phase relations among these states are determined by the mode of excitation, so that the time dependence of the composite intermediate state must be taken into account explicitly, in addition to the time dependence associated with the relaxation processes we have described. The two-photon photoionization process then becomes a means to probe the composite intermediate state.

Even when the first photon excites only a single  $|bB\rangle$  intermediate state, the second photon generally excites two outgoing waves in which the departing electron has orbital angular momentum

TABLE III. Angular distribution terms in the ionization of sodium via the  $3p\ ^3P_{3/2}$  intermediate state and a 3371-Å photon. As in Table II, we abbreviate the indices to  $\Xi = \Xi(b, f, f')$ .

	$B_{00}$	$B_{20}$	$B_{00}+B_{02}$	$B_{20}+B_{22}$	$B_{42}$
$\Xi(\frac{1}{2}, \frac{3}{2}, \frac{3}{2})$	0.707	0	1.414	0	0
$\Xi(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$	0	-0.200	0	-0.400	0
$\Xi(\frac{1}{2}, \frac{3}{2}, \frac{1}{2})$	0	-0.735	0	-1.47	0
$\Xi(\frac{3}{2}, \frac{3}{2}, \frac{3}{2})$	1.414	-0.505	0.283	0.128	0
$\Xi(\frac{3}{2}, \frac{1}{2}, \frac{3}{2})$	0	0.465	0	0.133	0.594
$\Xi(\frac{3}{2}, \frac{3}{2}, \frac{1}{2})$	2.121	0.759	2.55	1.30	7.727
$\Xi(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}) \times 0.226$	0.160	0	0.320	0	0
$\Xi(\frac{1}{2}, \frac{3}{2}, \frac{1}{2}) \times -0.066$	0	0.013	0	0.026	0
$\Xi(\frac{3}{2}, \frac{1}{2}, \frac{1}{2}) \times -0.480$	0	0.353	0	0.706	0
$\Xi(\frac{3}{2}, \frac{3}{2}, \frac{3}{2}) \times 0.005$	0.007	-0.003	0.0014	0.0006	0
$\Xi(\frac{3}{2}, \frac{1}{2}, \frac{3}{2}) \times 0.073$	0	0.034	0	0.0097	0.043
$\Xi(\frac{3}{2}, \frac{3}{2}, \frac{1}{2}) \times 0.256$	0.543	0.194	0.653	0.333	0.186
$\sum_{ff'} \Xi(\frac{1}{2}, f, f') (f R b)(b R^\dagger f')$	0.710	0.591	0.9744	1.0753	0.229

for  $\lambda_2\tau_b \gg 1, W(\Omega) = 0.710 + 0.591P_2 = 0.415 + 0.886 \cos^2\theta$

for  $\lambda_2\tau_b \ll 1, W(\Omega) = 0.974 + 1.075P_2 + 0.229P_4 = 0.522 + 0.754 \cos^2\theta + 1.002 \cos^4\theta$



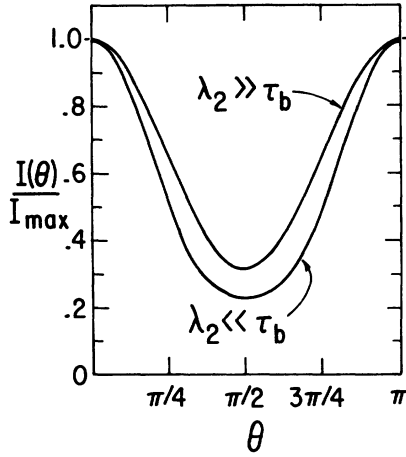


FIG. 2. Angular distributions for two-photon photoelectrons from Na, via the  $3p\ ^2P_{3/2}$  level and a 3371-Å photon. Upper curve: fast relaxation,  $\lambda_2\tau_b \gg 1$ ; lower curve, slow relaxation,  $\lambda_2 = 0$ .

one unit greater or smaller than in the intermediate state. Only if the intermediate state is an  $s$  level is the final state restricted to a single channel. Hence, in general, the sum over final states will contain pure terms associated with  $f$  and  $f'$  equal to  $b-1$ ,  $b$ , and  $b+1$  and, for each pair of exit channels, an interference term that depends both on  $f$  and  $f'$ . As in the angular distribution for single-photon ionization,<sup>17-19</sup> the coefficients appearing in  $W(\Omega)$  depend on the ratio of the  $b-f$  and  $b-f'$  dipole matrix elements.

### III. APPLICATION TO SODIUM

We present here the calculations for our atomic example. Photoionization of sodium illustrates how collisional relaxation can be determined by measurement of the angular distribution  $W(\Omega)$ ; in this case, the  $b-f$  and  $b-f'$  matrix elements can be estimated reliably enough to permit the full calculation of the five  $B_i$  coefficients to be done. The second example, that of two-photon ionization of the titanium atom, is the subject of experiments now in progress and the analysis will be presented with the experimental work. The titanium case offers a situation in which the angular distribution is a means to measure the ratio of channel amplitudes and the type of angular momentum coupling, which can be thought of as an intra-atomic relaxation process.

The resonant two-photon process with sodium can be studied with a first photon from a tuneable dye laser and a second photon from another fixed-frequency source such as a molecular nitrogen laser. The  $^3P_{1/2}$  and  $^3P_{3/2}$  levels are separated by  $17\text{ cm}^{-1}$ , with energies of  $16956$  and  $16973\text{ cm}^{-1}$ , respectively. Bandwidths of order  $0.1\text{--}1\text{ cm}^{-1}$  are achieved with tuneable dye lasers so each fine-structure component may be studied independently. The  $\text{N}_2$  laser (more specifically, the most important line for our own experiments, to be described elsewhere) has an energy of  $29661\text{ cm}^{-1}$ , and the ionization potential of sodium is  $41449\text{ cm}^{-1}$ .

TABLE IV. Transition amplitudes for all nonvanishing ( $l s j m | r | l' s' j' m'$ ) processes in the  $^2S_{1/2} \rightarrow ^2P_{1/2,3/2} \rightarrow ^2S_{1/2} \rightarrow ^2D_{3/2,5/2}$  two-photon process. (The redundant  $-m \rightarrow -m'$  amplitudes are omitted.)

	$l$	$s$	$j$	$m$	$r$ component	$l'$	$s'$	$j'$	$m'$	Amplitude
$^2S_{1/2} - ^2P_{1/2}$	(0	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	$z$	1	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	$3^{-1/2}\gamma_{01}$
	(0	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	$x - iy$	1	$\frac{1}{2}$	$\frac{1}{2}$	$-\frac{1}{2}$	$3^{-1/2}\gamma_{01}$
$^2S_{1/2} - ^2P_{3/2}$	(0	$\frac{1}{2}$	$\frac{3}{2}$	$\frac{1}{2}$	$x + iy$	1	$\frac{1}{2}$	$\frac{3}{2}$	$\frac{3}{2}$	$-2^{-1/2}\gamma_{01}$
	(0	$\frac{1}{2}$	$\frac{3}{2}$	$\frac{1}{2}$	$z$	1	$\frac{1}{2}$	$\frac{3}{2}$	$\frac{1}{2}$	$(\frac{2}{3})^{1/2}\gamma_{01}$
	(0	$\frac{1}{2}$	$\frac{3}{2}$	$\frac{1}{2}$	$x - iy$	1	$\frac{1}{2}$	$\frac{3}{2}$	$-\frac{1}{2}$	$6^{-1/2}\gamma_{01}$
	(0	$\frac{1}{2}$	$\frac{3}{2}$	$\frac{1}{2}$	$x - iy$	1	$\frac{1}{2}$	$\frac{3}{2}$	$-\frac{1}{2}$	$6^{-1/2}\gamma_{01}$
$^2P_{1/2} - ^2D_{3/2}$	(1	$\frac{1}{2}$	$\frac{3}{2}$	$\frac{1}{2}$	$x + iy$	2	$\frac{1}{2}$	$\frac{3}{2}$	$\frac{3}{2}$	$-(\frac{6}{5})^{1/2}\gamma_{12}$
	(1	$\frac{1}{2}$	$\frac{3}{2}$	$\frac{1}{2}$	$z$	2	$\frac{1}{2}$	$\frac{3}{2}$	$\frac{1}{2}$	$(\frac{10}{3})^{1/2}\gamma_{12}$
	(1	$\frac{1}{2}$	$\frac{3}{2}$	$\frac{1}{2}$	$x - iy$	2	$\frac{1}{2}$	$\frac{3}{2}$	$-\frac{1}{2}$	$(\frac{5}{3})^{1/2}\gamma_{12}$
$^2P_{3/2} - ^2D_{3/2}$	(1	$\frac{1}{2}$	$\frac{3}{2}$	$\frac{3}{2}$	$z$	2	$\frac{1}{2}$	$\frac{3}{2}$	$\frac{3}{2}$	$(\frac{3}{5})^{1/2}\gamma_{12}$
	(1	$\frac{1}{2}$	$\frac{3}{2}$	$\frac{3}{2}$	$x + iy$	2	$\frac{1}{2}$	$\frac{3}{2}$	$\frac{3}{2}$	$5^{-1/2}\gamma_{12}$
	(1	$\frac{1}{2}$	$\frac{3}{2}$	$\frac{3}{2}$	$x - iy$	2	$\frac{1}{2}$	$\frac{3}{2}$	$\frac{3}{2}$	$5^{-1/2}\gamma_{12}$
	(1	$\frac{1}{2}$	$\frac{3}{2}$	$\frac{3}{2}$	$z$	2	$\frac{1}{2}$	$\frac{3}{2}$	$\frac{1}{2}$	$15^{-1/2}\gamma_{12}$
	(1	$\frac{1}{2}$	$\frac{3}{2}$	$\frac{3}{2}$	$x - iy$	2	$\frac{1}{2}$	$\frac{3}{2}$	$-\frac{1}{2}$	$2(15)^{-1/2}\gamma_{12}$
$^2P_{3/2} - ^2D_{5/2}$	(1	$\frac{1}{2}$	$\frac{5}{2}$	$\frac{3}{2}$	$x + iy$	2	$\frac{1}{2}$	$\frac{5}{2}$	$\frac{5}{2}$	$-3^{1/2}\gamma_{12}$
	(1	$\frac{1}{2}$	$\frac{5}{2}$	$\frac{3}{2}$	$z$	2	$\frac{1}{2}$	$\frac{5}{2}$	$\frac{3}{2}$	$2(\frac{3}{5})^{1/2}\gamma_{12}$
	(1	$\frac{1}{2}$	$\frac{5}{2}$	$\frac{3}{2}$	$x + iy$	2	$\frac{1}{2}$	$\frac{5}{2}$	$\frac{3}{2}$	$-3(5)^{-1/2}\gamma_{12}$
	(1	$\frac{1}{2}$	$\frac{5}{2}$	$\frac{3}{2}$	$x - iy$	2	$\frac{1}{2}$	$\frac{5}{2}$	$\frac{3}{2}$	$3(10)^{-1/2}\gamma_{12}$
	(1	$\frac{1}{2}$	$\frac{5}{2}$	$\frac{3}{2}$	$z$	2	$\frac{1}{2}$	$\frac{5}{2}$	$\frac{1}{2}$	$3(\frac{2}{5})^{1/2}\gamma_{12}$
	(1	$\frac{1}{2}$	$\frac{5}{2}$	$\frac{3}{2}$	$x - iy$	2	$\frac{1}{2}$	$\frac{5}{2}$	$-\frac{1}{2}$	$3(10)^{-1/2}\gamma_{12}$

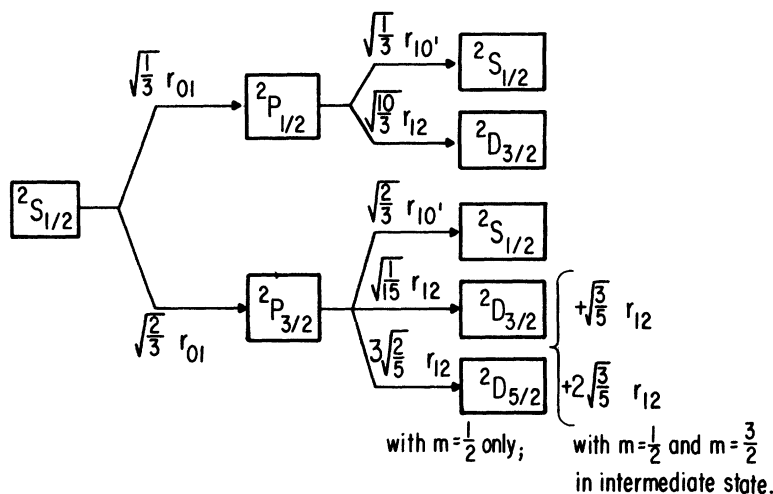


FIG. 3. Schematic diagram of the two-photon processes for ionization of Na through  $^2P_{1/2}$ ,  $^2P_{3/2}$  intermediate states. All amplitudes are for the  $z$  component, along the polarization axis.

Hence the kinetic energy of the outgoing electron, resulting from resonant excitation of the  $^2P_{1/2}$  or  $^2P_{3/2}$  level of Na, followed by absorption of a photon from the  $N_2$  laser, would be 5168 or 5185  $\text{cm}^{-1}$ , respectively.

From the quantum-defect method (QDM),<sup>29</sup> we obtain the radial factors for the two transition amplitudes

$$\text{Na}(3p - \epsilon's) = -0.475$$

and

$$\text{Na}(3p - \epsilon'd) = 0.575$$

(where we have given relative values only, and dropped the common constants superfluous for this calculation). The  $d$  wave consists of two components, coming from the channels  $^2D_{3/2}$  and  $^2D_{5/2}$ .

The process via  $^2P_{1/2}$  gives rise to a distribution involving only  $B_{00}$  and  $B_{20}$ , and independent of the relaxation. This is because a state with angular momentum  $j < 1$  has no tensorial components beyond  $k_b = 0$ . The angular distribution for two-photon ionization through the  $^2P_{1/2}$  state is described in Table II, and is illustrated in Fig. 1.

The ionization of Na via the  $3p^2P_{3/2}$  state is richer and affords a clear example of how the relaxation process could operate to change  $W(\Omega)$ .

The  $B_{ij}$  coefficients and angular distributions for this case are given in Table III, and the two extreme cases of  $\lambda_2\tau_b \ll 1$  and  $\lambda_2\tau_b \gg 1$  are shown in Fig. 2.

The sodium example is sufficiently simple that it can also be carried through in explicit terms, without the powerful irreducible tensorial techniques. By evaluating each transition amplitude ( $l'sjm|r|l's'j'm'$ ), one obtains the components explicitly that are contained in (49). These are given in Table IV, with the phase convention of Condon and Shortley.<sup>30</sup> For the case in which both photons have the same plane polarization, we obtain the amplitudes indicated in the diagram of Fig. 3. Note that if the two photons had bandwidths great enough to span the  $^2P_{1/2} - ^2P_{3/2}$  interval, the intermediate-state distribution would correspond to the superposition of these two states, and the expression for the angular distribution of photoelectrons would include interference terms between the two states. However, we expect most experiments on this system to be done with only one intermediate state,  $^2P_{1/2}$  or  $^2P_{3/2}$ , excited at a time.

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\*Present address: Joint Institute for Laboratory Astrophysics, University of Colorado, Boulder, Colo.

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