# Quantitative Theory of the Two-Photon Ionization of the Alkali Atoms*

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(Received 10 March 1966)

The theory of two-photon ionization of the alkali atoms is developed from the well-known perturbation formula for the second-order transition rate. Quantum defect Coulomb functions are used for both the negative and positive energy states. Spin-orbit splitting of the intermediate $p$ states is taken into account. The results are presented as dispersion curves of the transition rate for photon energies between the two-photon and one-photon thresholds. Cesium is of particular interest because the photon energy for the second harmonic of ruby laser light falls very near the $10p\,^2P_{3/2}$ level. For a photon energy of 3.57 eV, the transition rate (in cgs units) is found to be $2.6 \times 10^{-49} \times$ (photon flux)$^2$.

## 1. INTRODUCTION

THE low ionization potentials of the alkali atoms and the high intensities available from the second-harmonic ruby laser light combine to make possible the observation of two-photon ionization in systems simple enough to permit detailed calculations. Motivated by the possibility of being able to test *quantitatively* the application of perturbation theory to higher order processes involving intense light beams for the first time, the tedious task of carrying out accurate calculations for the two-photon ionization rates of the alkalies was undertaken.

To be sure, Goeppert-Mayer's theory[1] of the simultaneous absorption of two photons by an atomic system has had abundant experimental verification[2-8] since the advent of the laser. Also the recent work of Bebb and Gold[9] applying perturbation theory to make approximate predictions of the $N$-photon ionization rates of the rare gases has been experimentally verified for the seven (ruby) photon ionization of xenon.[10] Hall, Robinson, and Branscomb[11] performed careful measurements of the two-photon photodetachment of I⁻ obtaining an absorption cross section roughly three times that estimated by Geltman.[12] The discrepancy is somewhat larger than might have been anticipated for the rela-

tively simple atomic system I⁻ and is probably due to the use of plane-wave continuum states. The determination of better continuum functions is rather difficult.

Precise calculations have been carried out for the two-photon ionization of metastable $2S$-hydrogen by Zernik[13] and the $N$-photon ionization of hydrogen atoms by Bebb and Gold.[9] However, the experimental difficulties with these systems, while not insurmountable, are severe. Hence, the alkalies appear to present the first atomic systems readily accessible to more quantitative investigation both theoretically and experimentally. The theoretical results form the subject of this paper.

The dispersion in the two-photon ionization is rich in structure because of the presence of intermediate resonances. By using the second harmonic of presently available laser and Raman-shifted laser frequencies, the double-photon ionization cross sections can be investigated over a considerable range. In particular, the role of the intermediate states is amenable to direct investigation by choosing photon energies near an intermediate resonance energy. This desirable situation is peculiar to photo-ionization where the final-state energy is not restricted to coincide with a discrete energy level. Thus in Sec. 4 we present the double-photon ionization rates in the form of dispersion curves for photon energies between the two-photon threshold and the one-photon threshold. Section 2 presents the formal theory of two-photon ionization drawing heavily on the work contained in Ref. 9. In Sec. 3 the details of calculating the required dipole matrix elements are sketched.

## 2. FORMAL THEORY

The $N$-photon ionization rate has been derived in detail by Bebb and Gold.[9] From Eqs. (38) and (39) of that paper we write the integrated transition rate for two-photon ionization (in cgs units) as,

$$w_{k,g}{}^{(2)} = \frac{m/\hbar}{(2\pi)^2}(2\pi\alpha F\omega)^2 \int d\Omega_k\, |\langle \mathbf{k}\,|\,\tau^{(2)}\,|\,g\rangle|^2 k. \quad (1)$$

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* Research supported in part by the U. S. Air Force Office of Scientific Research and in part by the U. S. Army Research Office, Durham, North Carolina.

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[11] J. L. Hall, E. J. Robinson, and L. M. Branscomb, Phys. Rev. Letters **14**, 1013 (1965).

[12] S. Geltman, Phys. Letters **4**, 186 (1963). The factor of 3 is obtained after correcting some trivial arithmetic errors appearing in the original paper. See Phys. Letters **19**, 616 (E) (1965).

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[13] W. Zernik, Phys. Rev. **135**, A51 (1964; W. Zernik and R. Klopfenstein, J. Math. Phys. **6**, 262 (1965).

Here, $\alpha$ is the fine structure constant $e^2/\hbar c$, and $F$ is the photon flux in photons cm$^{-2}$ sec$^{-1}$. The integral over the solid angle $d\Omega_k$ is over all possible directions of the emitted electron. An average over the degenerate magnetic components is implied. This average will be made explicit shortly.

The transition operator $\tau^{(2)}$ is defined

$$\tau^{(2)} = \sum_\beta \frac{z|\beta\rangle\langle\beta|z}{\omega_{\beta,g} - \omega}, \qquad (2)$$

where $\beta$ denotes a set of quantum numbers defining an atomic-energy level. The quantity $\langle\mathbf{k}|\tau^{(2)}|g\rangle$ is thus just the usual second-order matrix element

$$\langle\mathbf{k}|\tau^{(2)}|g\rangle = \sum_\beta \frac{\langle\mathbf{k}|z|\beta\rangle\langle\beta|z|g\rangle}{\omega_{\beta,g} - \omega} \qquad (3)$$

between the ground state $|g\rangle$ and a continuum final state $|\mathbf{k}\rangle$. The sum over $\beta$ incorporates a complete set of states, discrete plus continuum.

Before proceeding, it is convenient to specify some notation. The one-electron alkali spectra of course display a doublet structure due to the spin-orbit splitting of each configuration. Following Condon and Shortley,[14] the terms are designated by $|nl^2L_j{}^m\rangle$, or, if no confusion arises between the $(jm)$ and $(m_l m_s)$ representations, simply by $|nljm\rangle$. In the $(m_l m_s)$ representation, the eigenstates are denoted by $|nlm_l m_s\rangle$.

Utilizing the notation of the last paragraph, we define a two-photon "ionization strength" $S^{(2)}(k; n,l,j)$ in analogy with the one-photon line strength given by Condon and Shortely.[14]

Incorporating the average over the magnetic components, we take,

$$S^{(2)} = \frac{m\hbar k}{(2\pi\hbar)^3} \frac{1}{(2j+1)} \sum_{m=-j}^{j} \int d\Omega_k |\langle\mathbf{k}|\tau^{(2)}|n,l,j,m\rangle|^2$$

$$= \frac{m\hbar k}{(2\pi\hbar)^3} \frac{1}{(2j+1)} \sum_{m=-j}^{j} |\langle\mathbf{k}|\tau^{(2)}|n,l,j,m\rangle|^2, \qquad (4)$$

where

$$|\langle k|\tau^{(2)}|nljm\rangle|^2 = \int d\Omega_k |\langle\mathbf{k}|\tau^{(2)}|n,l,j,m\rangle|^2. \qquad (5)$$

Inclusion of the density of states $m\hbar k/(2\pi\hbar)^3$ in $S^{(2)}$ makes its value independent of the normalization convention used for the continuum states. From Eq. (1), the transition rate is written in terms of the "strength" as

$$w_{k;n,l,j}{}^{(2)} = 2\pi\hbar(2\pi\alpha F\omega)^2 S^{(2)}(k; n,l,j). \qquad (6)$$

Evidently, this notation is trivially extended to arbitrary order for consideration of multiple photon ionization [cf. Eq. (16) of Ref. 9].

[14] E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge University Press, London, 1959).

The eigenstates of the alkali atoms have been discussed extensively by Condon and Shortley. Since considerable use will be made of these, a brief review of their characterization seems appropriate. The $(jm)$ eigenstates are given in terms of the $(m_l m_s)$ eigenstates by the Clebsch-Gordan (CG) series,

$$|nljm\rangle = \sum_{m_l, m_s} \langle lsm_l m_s|jm\rangle|nlm_l m_s\rangle. \qquad (7)$$

The CG coefficients contain the factor $\delta(m_l + m_s, m)$ reducing the double sum over $m_l$, $m_s$ to a sum over $m_s$. Utilizing the tabulated values for the CG coefficients, Condon and Shortely record explicit expressions for the $(jm)$ functions,

$$|nl^2L_{l+1/2}{}^m\rangle = \left[\frac{l+m+\frac{1}{2}}{2l+1}\right]^{1/2} |n, l, m-\tfrac{1}{2}, \tfrac{1}{2}\rangle$$

$$+ \left[\frac{l-m+\frac{1}{2}}{2l+1}\right]^{1/2} |n, l, m+\tfrac{1}{2}, -\tfrac{1}{2}\rangle$$

$$|nl^2L_{l-1/2}{}^m\rangle = \left[\frac{l-m+\frac{1}{2}}{2l+1}\right]^{1/2} |n, l, m-\tfrac{1}{2}, \tfrac{1}{2}\rangle$$

$$- \left[\frac{l+m+\frac{1}{2}}{2l+1}\right]^{1/2} |n, l, m+\tfrac{1}{2}, -\tfrac{1}{2}\rangle, \qquad (8)$$

where $m_l$ is replaced by $m-m_s$ in the $(m_l m_s)$ functions. For $S$ states, Eqs. (8) reduce to $|ns^2S_{1/2}{}^m\rangle = |n,s,0,m_s(=m)\rangle$.

Formally the transformation given by Eqs. (8) is appropriate to both the discrete and continuum parts of the spectra. However, the effect of the spin-orbit splitting on the continuum states is certainly small and and the use of $(m_l m_s)$ functions should introduce little error. In this approximation the final-state continuum functions are conveniently taken in the form of a partial wave expansion,

$$|\mathbf{k}\rangle = 4\pi \sum_{m_s} \sum_l \sum_{m_l} i^l e^{i\eta_l} R_l(k,r) Y_l{}^{m_l}(\theta,\phi) Y_l{}^{m_l*}(\theta_k,\phi_k)\chi(m_s)$$

$$= 4\pi \sum_{m_s} \sum_l \sum_{m_l} i^l e^{i\eta_l} Y_l{}^{m_l*}(\theta_k,\phi_k) |k,l,m_l,m_s\rangle. \qquad (9)$$

The asymptotic form of the radial function is

$$R_l(k,r) \underset{kr\to\infty}{\sim} (kr)^{-1} \sin(x + \delta(k^2)),$$

where

$$x = kr + k^{-1}\ln(2kr) - \tfrac{1}{2}l\pi + \eta_l.$$

The phase $\eta_l$ is chosen with the "ingoing" wave modification

$$\eta_l = \arg\Gamma(l+1 - i/k).$$

The additional phase $\delta(k^2)$ accounts for the "quantum defect" distortion of the continuum functions. It is defined in terms of the extrapolated quantum defect,

$\mu(k^2)$, for the associated $nl$ series by $\delta(k^2) = \pi\mu(k^2)$. References and additional discussion appear in Sec. 3.

It is, of course, not surprising that the ground-state $S$-functions and the continuum final-state functions of the alkalies should be formally analogous to the hydrogenic functions. Drawing on this analogy we can immediately write the second-order "ionization strength" as

$$S^{(2)}(k;n,s,\tfrac{1}{2}) = \frac{m\hbar k}{(2\pi\hbar)^3} \frac{(4\pi)^2}{(2j+1)}$$
$$\times \sum_{m} \sum_{l',m_l',m_s'} |\langle kl'm_l'm_s'|\tau^{(2)}|ns0m\rangle|^2 \quad (10)$$

by comparing Eq. (37) of Ref. 9. The trivial algebraic steps in obtaining Eq. (10) from Eq. (4) are exactly analogous to the derivation sketched in that paper.

For simplicity, it is expedient to incorporate the various selection rules at the earliest opportunity rather than to derive elaborate general formulae to be simplified in the final step. In this spirit, we observe that the transition operator $\tau^{(2)}$ transforms as $z^2$. This is most easily demonstrated by defining an average frequency $\bar\omega^2$. This is most easily demonstrated by defining an average frequency $\bar\omega_v$ such that

$$\tau^{(2)} = \sum_{\beta} \frac{z|\beta\rangle\langle\beta|z}{\omega_{\beta,g}-\omega} = \frac{\sum_{\beta}(z|\beta\rangle\langle\beta|z)}{\bar\omega_v-\omega}.$$

Clearly there exists some $\bar\omega_v$ such that the matrix element of the right hand expression is equal to the matrix element of $\tau^{(2)}$ as given by Eq. (2). Then, since the states $|\beta\rangle$ form a complete set, $\sum_{\beta}|\beta\rangle\langle\beta| = 1$, and $\tau^{(2)}$ becomes

$$\tau^{(2)} = z^2/(\bar\omega_v-\omega),$$

explicitly revealing the transformation properties[14a] of $\tau^{(2)}$. It follows in an elementary manner that $l' = l$, $l\pm 2$, and $m_l' = m_l = 0$ in Eq. (10). Further, from the orthonormality of the spin functions, $m_s' = m_s = m$. Employing these selection rules in Eq. (10), the "ionization strength" reduces to

$$S^{(2)}(k;n,s,\tfrac{1}{2}) = \frac{(m\hbar k)(4\pi)^2}{(2\pi\hbar)^3(2j+1)}$$
$$\times \sum_{m=-j}^{j} \sum_{l'=s,d} |\langle k,l',0,m|\tau^{(2)}|n,s,0,m\rangle|^2. \quad (11)$$

To complete the evaluation of the "ionization strength," we apply the unitary transformation given in Eq. (7) to the intermediate states appearing in the matrix element

$$\langle k,l',0,m|\tau^{(2)}|n,s,0,m\rangle$$
$$= \sum_{n''j''} \frac{\langle k,l',0,m|z|n''p^2P_{j''}{}^m\rangle\langle n''p^2P_{j''}{}^m|z|n,s,0,m\rangle}{\omega_{n'',p,j'';n,s}-\omega},$$
$$(12)$$

In writing (12) immediate use has again been made of the selection rules appropriate to the first-order dipole matrix element $\langle n''p^2P_{j''}{}^m|z|n,s,0,m\rangle$. Only the $p$-series states act as intermediate states for second-order processes in the alkalies.

Rewriting the transformation given in Eq. (7) to incorporate the delta function $\delta(m_l+m_s, m)$ and specializing to the $p$ states

$$|n''p^2P_{j''}{}^m\rangle = \sum_{m_s}\langle p, \tfrac{1}{2}, m-m_s, m_s|j,m\rangle$$
$$\times |n'', p, m-m_s, m_s\rangle.$$

The second-order matrix element (12) becomes

$$\langle k,l',0,m|\tau^{(2)}|n,s,0,m\rangle$$

$$= \sum_{m_s,m_s'} \sum_{n''j''} \frac{\langle p, \tfrac{1}{2}, m-m_s, m_s|j,m\rangle\langle j,m|p, \tfrac{1}{2}, m-m_s', m_s'\rangle}{\Omega(n''pj'')}\langle k,l',0,m|z|n'',p,0,m\rangle\langle n'',p,0,m|z|n,s,0,m\rangle$$

$$= \sum_{n''j''} \frac{|\langle p,\tfrac{1}{2},0,m|j'',m\rangle|^2}{\Omega(n''pj'')}\langle k,l',0,m|z|n'',p,0,m\rangle\langle n'',p,0,m|z|n,s,0,m\rangle, \quad (13)$$

where the new denominator $\Omega(n''pj'')$ is defined

$$\hbar\Omega(n''pj'') = \hbar\omega_{n''pj'';ns} - \hbar\omega.$$

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[14a] *Note added in proof.* The transition operator $\tau^{(2)}$ does not in general transform as $z^2$. The relation $\tau^{(2)} = z^2/(\bar\omega_v-\omega)$ is valid only in the "space" spanned by the eigenfunctions of the Hamiltonian, the $(jm)$ functions. In the present work, approximate $(m_l m_s)$ functions have been utilized for the continuum states and the result that $\tau^{(2)}$ transforms as $z^2$ has been used improperly causing the neglect of terms involving $m_l' = \pm 1$. Rigorously we should add to Eq. (16) the term

$$(4\pi)^2 m\hbar k/(2\pi\hbar)^3 \times \sum_{l'} \left| \sum_{n'} \left\{ \frac{(-\sqrt{2}/3)\langle kl'j|z|n''pj\rangle\langle n''pj|z|ns0\rangle}{\Omega(n'',p,\tfrac{1}{2})} + \frac{(\sqrt{2}/3)\langle k,l'j|z|n''pj\rangle\langle n''pj|z|ns0\rangle}{\Omega(n''p\tfrac{3}{2})} \right\} \right|^2.$$

However, the contribution from this new term (which goes to zero for vanishing spin-orbit coupling) is negligible even for photon energies rather near resonance, i.e., $\Omega(n'',p,j) \sim 0$. The results quoted in the text provide an excellent and useful approximation. By direct computation, the added term never contributes more than 8% to the transition rate provided $\hbar\Omega(h''pj) > 0.001$ eV.

In the last line of Eq. (13), the sum over $m_s$ and $m_s'$ is eliminated by the orthonormality of the spin functions.

The sum over $j''$ reduces to only the two values $j''=\frac{1}{2}$ and $\frac{3}{2}$ corresponding to the doublet $p$ states. Putting (13) into Eq. (11) and displaying the two $j''$ terms separately, the two-photon "ionization strength" becomes

$$S^{(2)}(k;n,s,\tfrac{1}{2})=\frac{(m\hbar k)(4\pi)^2}{(2\pi\hbar)^3(2j+1)}\sum_{m=-j}^{j}\sum_{l'}\left|\sum_{n''}\left\{\left[\frac{|\langle p,\frac{1}{2},0,m|\frac{1}{2},m\rangle|^2}{\Omega(n'',p,\frac{1}{2})}+\frac{|\langle p,\frac{1}{2},0,m|\frac{3}{2},m\rangle|^2}{\Omega(n'',p,\frac{3}{2})}\right]\right.\right.$$
$$\left.\left.\times\langle kl'0m|z|n''p0m\rangle\langle n''p0m|z|ns0m\rangle\right\}\right|^2 \quad (14)$$

for the ground state of the alkalies $j=\frac{1}{2}$. Hence, the sum over the magnetic quantum number, $m$, consists of two terms, $m=\pm\frac{1}{2}$. The two terms of the sum are equal with the resulting factor of two just canceling the denominator, $2j+1=2$. Thus the average over the magnetic components is trivial, yielding the rather simple expression

$$S^{(2)}(k;n,s,\tfrac{1}{2})=(4\pi)^2(m\hbar k)/(2\pi\hbar)^3\sum_{l'}\left|\sum_{n''}\left\{\left[\frac{\frac{1}{3}}{\Omega(n''p\frac{1}{2})}+\frac{\frac{2}{3}}{\Omega(n''p\frac{3}{2})}\right]\langle kl'0|z|n''p0\rangle\langle n''p0|z|ns0\rangle\right\}\right|^2. \quad (15)$$

In (15) the spin functions have been eliminated from the dipole matrix elements by their orthonormality.

The effect of the spin-orbit splitting of the principal series enters in an almost obvious manner. When the spin-orbit splitting is negligible, e.g., Li, the frequency denominators become equal, $\Omega(n'',p,\frac{1}{2})=\Omega(n'',p,\frac{3}{2})$. Then the two terms involving the frequencies $\Omega(n'',p,j'')$ collapse to $1/\Omega(n'',p)$ which does not depend on $j''$. We thereby recover the results quoted in Eqs. (39) and (40) of Ref. 9 appropriate to $(m_l m_s)$ functions.

It would appear that the spin-orbit splitting has little influence on the results except for photon energies very nearly in resonance with one of the intermediate state energies. This is not necessarily the case because of the effect of the spin-orbit interaction on the radial wave functions. It is well known that the observed intensity ratios of the $p$-series doublets of the alkalies are not two to one as predicted by the simple theory. Fermi[15] first recognized the importance of spin-orbit perturbation on the wave functions. The radial integrals for the $j=\frac{1}{2}$ and $\frac{3}{2}$ cannot be assumed identical; thus our reduction of the "ionization strength" is not quite correct. Instead of factoring out the matrix elements as in Eqs. (14) and (15), they should be retained in correspondence to the $j''=\frac{1}{2}$ and $j''=\frac{3}{2}$ terms. A more careful treatment of the second-order matrix element, starting from Eq. (13), yields

$$S^{(2)}(k;n,s,\tfrac{1}{2})=(4\pi)^2 m\hbar k/(2\pi\hbar)^3$$

$$\times\sum_{l'}\left|\sum_{n''}\left\{\frac{(1/3)\langle kl'0|z|n''p0\rangle\langle n''p0|z|ns0\rangle}{\Omega(n'',p,\frac{1}{2})}+\frac{(2/3)\langle kl'0|z|n''p0\rangle\langle n''p0|z|ns0\rangle}{\Omega(n'',p,\frac{3}{2})}\right\}\right|^2, \quad (16)$$

in place of Eq. (15). In (16), it is implied that the radial integrals must be evaluated using the appropriate spin-orbit perturbed wave functions corresponding to the $j''=\frac{1}{2}$ and $\frac{3}{2}$ energy levels.

## 3. EVALUATION OF DIPOLE MATRIX ELEMENTS

Considerable attention has been given to selection of the most suitable wave functions for use in evaluating the radial dipole matrix elements appearing in Eq. (16). We concluded that quantum defect Coulomb functions could be most satisfactorily employed for the bound-state functions as well as for the continuum functions. The Coulomb functions are simple enough to allow evaluation of the large number of matrix elements needed while still providing reliable results. Comparison with experiment suggests that for simpler systems, e.g., alkalies, Coulomb functions give better results for dipole matrix elements than numerical techniques (i.e., Hartree-Fock functions).

Bates and Damgaard[16] have applied the Coulomb

functions to evaluate dipole matrix elements for a wide range of quantum numbers. Their tables, however, are not extensive enough to cover the present application. Hence, a Fortran computer program was written to evaluate the matrix elements using a slight rearrangement and correction[17] of their formulas. The asymptotic expansion used to evaluate the radial matrix elements is given in the appendix. The numerical results differ slightly from those normally quoted for the quantum defect method because of the use of a different criterion for terminating the series [see Eq. (A3)]. In particular, the matrix elements between the ground state and the higher lying $p$ states of cesium proved somewhat sensitive to the number of terms included in the summation.[18]

In order to utilize the quantum defect Coulomb functions, the effective principal quantum number $n^*$

[15] E. Fermi, Z. Physik **59**, 680 (1929).
[16] D. R. Bates and A. Damgaard, Phil. Trans. **A242**, 101 (1949).

[17] A. Burgess and J. J. Seaton, Monthly Notices Roy. Astron. Soc. **120**, 121 (1960). The asymptotic Coulomb function quoted in this reference corrects some trivial errors appearing in the normalization factor recorded in Ref. 16 (see also Appendix).
[18] See comment in last paragraph beginning on page 127 of Ref. 17.

TABLE I. Energy levels and quantum defects for the ground states and the principal series of the alkali atoms. The data are taken from the Moore tables, (Ref. 19). The conversion factor from reciprocal centimeters to electron volts is taken as $1.239529\times10^{-4}$ eV cm.

| P states | | Li $E_I=5.39036$ $\mu_g=0.41189$ | | Na $E_I=5.13780$ $\mu_g=1.3733$ | | K $E_I=4.33956$ $\mu_g=2.2300$ | | Rb $E_I=4.17610$ $\mu_g=3.1957$ | | Cs $E_I=3.89295$ $\mu_g=4.1312$ | |
| n | j | E (eV) | μ | E (eV) | μ | E (eV) | μ | E (eV) | μ | E (eV) | μ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 2 | 1/2 3/2 | 1.84735 | 0.04114 | | | | | | | | |
| 3 | 1/2 3/2 | 3.83329 | 0.04515 | 2.10177 2.10390 | 0.88390 316 | | | | | | |
| 4 | 1/2 3/2 | 4.52051 | 0.04665 | 3.75167 3.75236 | 0.86825 746 | 1.60955 1.61670 | 1.76845 552 | | | | |
| 5 | 1/2 3/2 | 4.83609 | 0.04746 | 4.34334 4.34365 | 331 249 | 3.06181 3.06414 | 1.73813 516 | 1.55920 1.58865 | 2.72073 2.70779 | | |
| 6 | 1/2 3/2 | 5.00656 | 0.04837 | 4.62301 4.62317 | 107 029 | 3.59455 3.59559 | 1.72824 525 | 2.93957 2.94917 | 2.68421 7126 | 1.38557 1.45426 | 3.67148 3.63892 |
| 7 | 1/2 3/2 | 5.10901 | 0.04874 | 4.77719 4.77729 | 0.85997 919 | 3.85121 3.85177 | 376 076 | 3.45023 3.45458 | 7225 5923 | 2.69791 2.72035 | 3.62714 3.59502 |
| 8 | 1/2 3/2 | 5.17524 | 0.05047 | 4.87117 4.87123 | 948 870 | 3.99468 3.99502 | 152 1.71847 | 3.69813 3.70047 | 6678 5369 | 3.18672 3.19697 | 3.61251 3.58034 |
| 9 | 1/2 3/2 | 5.22068 | 0.04899 | 4.93265 4.93271 | 959 843 | 4.08305 4.08327 | 994 688 | 3.83745 3.83885 | 6401 5089 | 3.42572 3.43126 | 3.60584 3.57359 |
| 10 | 1/2 3/2 | | | | | 4.14131 4.14146 | 910 600 | 3.92421 3.92450 | 5343 4925 | 3.56081 3.56413 | 3.60229 3.57000 |
| 11 | 1/2 3/2 | | | | | | | 3.98057 3.98119 | 6156 4839 | 3.64467 3.64683 | 3.60024 3.56785 |
| 12 | 1/2 3/2 | | | | | | | 4.02023 4.02066 | 6093 4775 | 3.70035 3.70182 | 3.59853 3.56625 |

for the relevant energy levels must be determined. Table I gives, for the alkali atoms, the ground and excited $p$-series energy levels[19] (in eV) and the corresponding quantum defect $\mu$. The effective quantum number is, of course, just $n^*=n-\mu$. In Table II, the resulting values of the $\langle n',p|r|n,s\rangle$ radial dipole matrix elements are recorded for the alkali atoms.

Oscillator strengths for cesium predicted from the tabulated matrix elements compare favorably with the experimental values of Kvater and Meister[20] though they deviate somewhat from the values calculated by Stone.[21] Also the ratios of the doublet intensities for the $p$ series are found to increase monotonically from 2 for the $6s$-$6p$ doublet up to 7.2 for the $6s$-$12p$ doublet. This would seem to be more in line with the experimental results than Stone's calculations (which predicts a ratio of 33.5 for the $12p$ doublet) but the variation between experimenters is too great to draw any firm conclusions.[21] In any case, the quantum defect method clearly accounts for the effects of the spin-orbit interaction on the wave function to a reasonable degree and gives an excellent approximation of the radial bound-bound matrix elements. The results for the lighter alkalies should prove even better.

Burgress and Seaton[17] have applied the quantum-defect method to derive simple expressions for bound-free dipole matrix elements. Their results account for the distortion of the continuum Coulomb functions through extrapolation (or interpolation) of the quantum

TABLE II. Radial dipole integrals for the alkalies. The signs of the matrix elements have been corrected to account for the proper number of nodes for each of the wave functions. The sign of the Coulomb functions given by Ref. 16 are in error by the factor, $(-1)^{n-l-1}$.

| Intermediate state n' | j' | $(-1)\times\langle n',p|r|n,s\rangle$ (in Bohr radii) | | | | |
| | | Li (2s) | Na (3s) | K (4s) | Rb (5s) | Cs (6s) |
|---|---|---|---|---|---|---|
| 2 | 1/2 3/2 | 4.06 | | | | |
| 3 | 1/2 3/2 | −0.216 | 4.25 4.25 | | | |
| 4 | 1/2 3/2 | −0.191 | 0.398 0.401 | 5.00 4.99 | | |
| 5 | 1/2 3/2 | −0.143 | 0.148 0.150 | 0.451 0.464 | 5.16 5.14 | |
| 6 | 1/2 3/2 | −0.111 | 0.0809 0.0820 | 0.180 0.188 | 0.559 0.813 | 5.42 5.38 |
| 7 | 1/2 3/2 | −0.0887 | 0.0527 0.0535 | 0.105 0.110 | 0.244 0.276 | 0.500 0.644 |
| 8 | 1/2 3/2 | −0.0738 | 0.0378 0.0384 | 0.0712 0.0749 | 0.149 0.170 | 0.193 0.277 |
| 9 | 1/2 3/2 | −0.0610 | 0.0296 0.0295 | 0.0532 0.0561 | 0.104 0.120 | 0.104 0.162 |
| 10 | 1/2 3/2 | | | 0.0418 0.0442 | 0.0874 0.0920 | 0.0648 0.109 |
| 11 | 1/2 3/2 | | | | 0.0627 0.0727 | 0.0438 0.0785 |
| 12 | 1/2 3/2 | | | | 0.0516 0.0600 | 0.0316 0.0600 |

[19] The atomic energy levels are taken from *Atomic Energy Levels*, edited by C. E. Moore, Nat. Bur. Std. (U. S.) Circ. No. 467 (U. S. Government Printing Office, Washington, D. C., 1949). The conversion factor from reciprocal centimeters to electron volts is taken as $1.239529\times10^{-4}$ eV cm.

[20] G. Kvater and T. Meister, Leningrad Univ. Vestnik No. 9, 137 (1952). See Ref. 21.

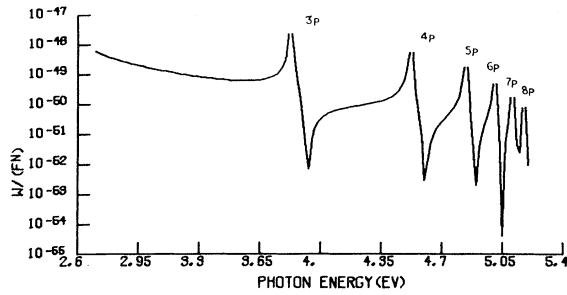[21] P. M. Stone, Phys. Rev. **127**, 1151 (1962).

FIG. 1. Dispersion for two-photon ionization rate of Li. The transition rate for the second harmonic of ruby, $\hbar\omega = 3.57$ eV is $w = 7.8 \times 10^{-50}F^2$. The symbol $W/(F^N)$ should be interpreted as $w/F^2$.

defect for the associated $nl$ series. In the present application, the $p$-series intermediate states couple $s$ and $d$ continuum states. The quantum defect was extrapolated into the continuum by fitting an energy-dependent quantum defect $\mu(\epsilon) = \mu^0 + \mu'\epsilon$ to the negative-energy $s$ and $d$ states. For the $d$ states there are of course two series corresponding to the two $j$ values $\frac{3}{2}$ and $\frac{5}{2}$ of the doublets. The results however were found to be completely insensitive to which term of the doublet was used and in fact independent of the values of the energy dependent term $\mu'\epsilon$ (within reasonable limits). The sensitivity of the latter was checked by comparing results using the calculated values for $\mu'$ and setting $\mu'$ equal to zero. Changes appeared in the third significant figure.

As on additonal check, several matrix elements were compared to the exact solutions of Bebb[22] at integral values of $n^*$ with the extrapolated quantum defect $\mu(\epsilon)$ set to zero. Typically, the results of Burgess and Seaton[17] are a few percent smaller than the exact values but certainly the agreement is satisfactory.[23]
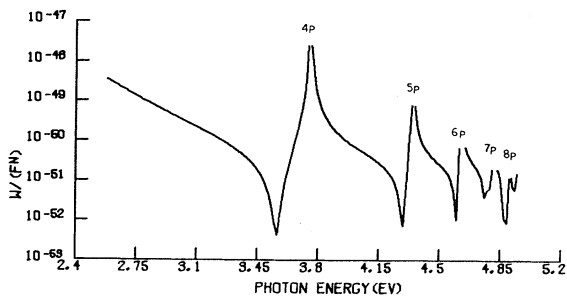


FIG. 2. Dispersion for two-photon ionization rate of Na. The ruby second-harmonic photon energy falls in the deep "valley" at 3.57 eV. The transition rate $\sim 6 \times 10^{-53} \times F^2$ for $\hbar\omega = 3.57$ eV is three orders of magnitude smaller than for the other alkalies.

[22] H. B. Bebb, J. Math. Phys. (to be published).
[23] The normalization convention of Burgess and Seaton differs from that implied in Eq. (9) of the present work. To bring their results into correspondence with the present convention, the quantity $g(\nu l; \epsilon'l')$ defined in Eqs. (23) and (59) of Ref. 17 is multiplied by $(-1)^{n-l-1}(I_{nl})^{-1}k^{-1/2} = (-1)^{n-l-1}(n^*)^2/k^{1/2}$. The factor $(-1)^{n-l-1}$ accounts for the fact that the bound-state Coulomb functions do not have the correct number of nodes (see caption of Table II).

TABLE III. Quantum defect parameters of the $s$ and $d$ series of the alkalies. The quantum defect $\mu(\epsilon)$ is $\mu(\epsilon) = \mu^0 + \mu'\epsilon$ with $\epsilon$ measured in small Rydberg units, i.e., $\epsilon = -(n^*)^{-2}$ for the negative energy states and $\epsilon = k^2$ (with $k$ in inverse Bohr radii) for positive energy states.

| Atom | Quantum defect parameters | | | |
|------|---------|---------|---------|---------|
|      | $\mu_s{}^0$ | $\mu_s{}'$ | $\mu_d{}^0$ | $\mu_d{}'$ |
| Li   | 0.4024  | −0.0028 | 0.0064  | 0.0872  |
| Na   | 1.3521  | −0.130  | 0.01752 | 0.0728  |
| K    | 2.1819  | −0.130  | 0.2812  | 1.120   |
| Rb   | 3.1342  | −0.158  | 1.351   | 0.743   |
| Cs   | 4.0512  | −0.240  | 2.47    | 0.041   |

Because of the simplicity of the formulas given by Burgess and Seaton for the bound-free matrix elements, the extensive tabulation necessary to list the numerical values does not seem warranted. In Table III, the quantum defects for the $s$ and $d$ series are given. For the $d$ series the tabulated values correspond to the $j = \frac{5}{2}$ terms. With these parameters and the values of the bound-bound matrix elements given in Table II, it is a trivial task to compute the second order matrix element given in Eq. (16) for photon energies near some intermediate resonance, i.e. when $\Omega(n'',p,j'')$ approaches zero the sum over $n''$ can be accurately replaced by keeping only the near resonant term[9] [see also the numerical formula, Eq. (43) of Ref. 9].

## 4. RESULTS AND DISCUSSION

The infinite sum over the intermediate states is of course the chief obstacle to calculating the "ionization strength" defined in Eq. (16). Because of the large dipole matrix element between the ground state and the lowest lying doublet $p$ states (see Table II) this difficulty is alleviated to some extent in the alkali atoms. The sum over intermediate states can be estimated to a good approximation by keeping only the lowest lying states together with those states with energies in near resonance with the photon energy, i.e., the states such that $\Omega(n'',p,j'')$ is small. In the present instance, the "strength" is approximated by summing over the finite
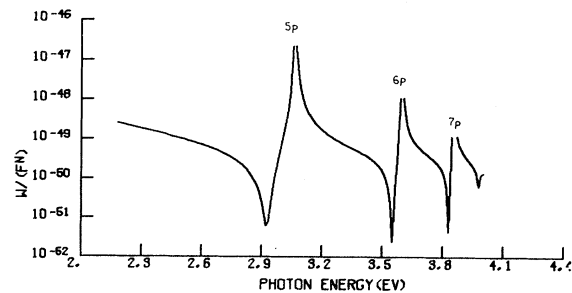


FIG. 3. Dispersion for two-photon ionization rate of $K$. The ruby second harmonic falls in a region (just below the $7p$ doublet at 3.851 eV) where the transition rate is changing rapidly with photon energy. At $\hbar\omega = 3.57$ eV, $w = 3.1 \times 10^{-50}F^2$ and at $\hbar\omega = 3.575$ eV, $w = 5.6 \times 10^{-50}F^2$. The ruby line can be thermally tuned between about $\hbar\omega = 3.57$ eV and 3.575 eV.

but relatively large number of intermediate levels listed in Table I.

The contribution from the continuum intermediate states is neglected. A careful investigation of hydrogen[9] shows that the continuum states can provide a significant "background" except for photon energies in near resonance with one of the discrete intermediate states. However, for the heavier alkalies (including lithium), the contribution from the continuum is much smaller than for hydrogen. This is most easily seen by comparing the oscillator strengths of the discrete states. The oscillator strength for the lowest lying $p$ state in hydrogen is $f(1s \rightarrow 2p) = 0.416$ and the sum over the complete discrete spectrum yields 0.565 leaving 0.435 as the continuum contribution to the total oscillator strength. For lithium the oscillator strength for the lowest lying $p$ state is 0.75 and for the heavier alkalies it exceeds 0.97. Hence, the contribution from the continuum for these atoms is surely small. In fact the main "background" to the second-order matrix elements is provided by the lowest lying $p$ doublet which is included in the present approximation.

The results are presented in Figs. 1 through 6 as dispersion curves of the transition rate per atom for unit photon flux, $w/F^2$, versus the photon energy measured in electron volts. Dispersion curves are given for photon energies from the two-photon threshold to near the one-photon threshold. It is seen that the "resolution" in Figs. 1 to 5 is not sufficient to separate the characteristic doublet structure of the alkalies. Figure 6 presents a high-resolution curve for cesium in the vicinity of the $10p$ doublet (the second harmonic of ruby falls just above the $10p\,^2P_{3/2}$ level, i.e., $\hbar\omega \sim 3.57$ eV). All of the figures are reproduced directly from the output of a Calcomp digital plotter.

The curves show several interesting features. First referring to Fig. 1 for lithium, we notice the appearance of "deep valleys" between each resonance except $2p$ and $3p$. The "valleys" are caused by the cancellation of the contributions from the energy levels above and below the photon energy. No cancellation appears for photon energies between the $2p$ and $3p$ levels of lithium because the corresponding matrix elements have opposite signs. As can be seen from Table II, no other sign changes
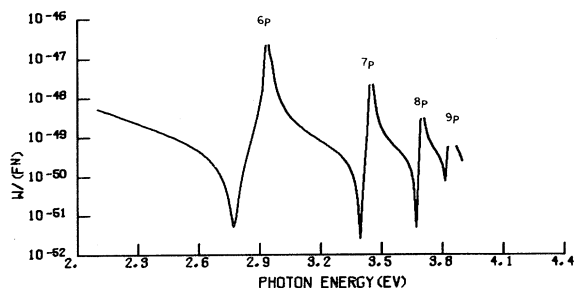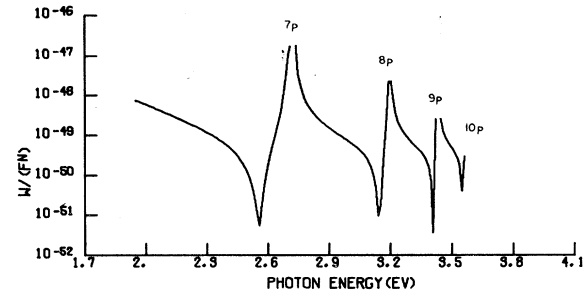


FIG. 5. Dispersion for the two-photon ionization of Cs. The second harmonic of ruby is very near the $10p\,^2P_{3/2}$ level at 3.5641 eV. Figure 6 gives a high-resolution curve for this region.

occur. The sign of the bound free matrix element does not depend on the principal quantum number over the photon-energy range considered here.

Cesium is the only alkali atom having an atomic-energy level very nearly in resonance with the second-harmonic ruby photon energy with the $10p\,^2P_{3/2}$ level at 3.56413 eV. From Fig. 6, we see that the predicted transition rate is about $w = 2.6 \times 10^{-49} F^2$ for $\hbar\omega = 3.57$ eV.[24] This near resonance provides a unique opportunity to investigate the role of higher order contributions to the transition rate. In the first approximation, these contributions will add a complex, flux-dependent damping parameter $\gamma + i\gamma'$ to the energy denominators of the second-order matrix elements causing both a shift[25] and broadening[13] of the resonance lines. This in turn will cause the transition rate to deviate from the $F^2$ flux dependence given by the present theory. These effects are not expected to be noticeable for photon fluxes below $10^{29}$ or $10^{30}$ photon cm$^{-2}$ sec$^{-1}$ and only then for photon energies in near resonance with an intermediate level; however, they may be of possible experimental interest for higher fluxes.
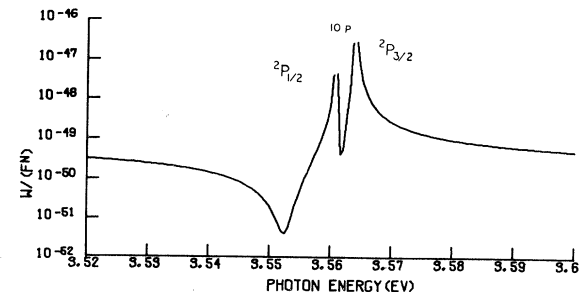
## ACKNOWLEDGMENTS

FIG. 6. High-resolution dispersion curve for Cs showing the $10p$ doublet. The transition rate at $\hbar\omega = 3.57$ eV is $w = 2.6 \times 10^{-49} F^2$.

[24] Some very interesting preliminary theoretical and experimental results obtained by John L. Hall for cesium are in good agreement with the present estimate though his results suggest a slightly smaller transition rate at the second harmonic of ruby (private communication).

[25] M. Mizushima, Phys. Rev. **133**, A414 (1964).



FIG. 4. Dispersion for the two-photon ionization rate of Rb. The transition rate at $\hbar\omega = 3.57$ eV is $w = 5.1 \times 10^{-50} F^2$.

critical reading of the manuscript. The author is also grateful for several useful and stimulating discussions with Dr. John L. Hall concerning his calculations and experiments on cesium.

## APPENDIX

In this Appendix, the Bates and Damgaard[13] method of evaluating dipole radial matrix elements is generalized to include matrix elements of $r^m$. In addition the results are put into a form more suitable for careful numerical computations.

The bound state Coulomb functions are given by

$$P_{n*,l}(r) = Ne^{-r/n*} \sum_{t=0} a_t r^{n*-t}, \qquad (A1a)$$

where

$$N = (-1)^{n-l-1}(2/n*)^{n*}$$
$$\times [\rho(n*)n^{*2}\Gamma(n*+l+1)\Gamma(n*-l)]^{-1/2}, \quad (A1b)$$

where $n*=n-\mu$; $n*$ is the effective principal number, $n$ is the principal quantum number, and $\mu$ is the quantum defect. The quantity $\rho(n*)$ is a correction different from one only if the quantum defect changes significantly with $n$. It is defined[17]

$$\rho(n*) = 1 + \partial\mu/\partial n*. \qquad (A1c)$$

The coefficients $a_t$ are given by

$$a_0 = 1, \quad a_t = a_{t-1}(n*/2t)[l(l+1) - (n*-t)(n*-t-1)]. \qquad (A1d)$$

The phase factor $(-1)^{n-l-1}$ is incorporated to insure that the tail of the function approaches zero with the proper sign. (The Coulomb functions do not in general have the correct number of nodes due to their devious behavior near the origin.)

The matrix element $\langle n',l'|r^m|n,l\rangle$ is given by the integral

$$\int_0^\infty P_{n*',l'}(r)r^m P_{n*,l}(r)dr = \int_0^\infty G(r)dr,$$

where

$$G(r) = P_{n*',l'}(r)r^m P_{n*l}(r)$$

$$= N'N \exp\left[-\left(\frac{1}{n*'}+\frac{1}{n*}\right)r\right]r^\nu \sum_{t,t'=0} a_{t'}a_t r^{-(t+t')}$$

and

$$\nu = n*'+n*+m.$$

The function $G(r)$ is put into the form of an asymptotic series by setting $t+t'=p$ and defining

$$A_p = \sum_{\substack{t,t' \\ \text{for } t+t'=p}} a_{t'}a_t = \sum_{t=0}^{P} a_t a_{P-t}.$$

Then,

$$G(r) = N'N \exp\left[-\left(\frac{1}{n*'}+\frac{1}{n*}\right)r\right]r^\nu \sum_{P=0}^{P_0} A_p r^{-p}.$$

While the above transformation of $G(r)$ is nothing but a rearrangement of terms, it is important in considering criteria for terminating the expansion. Bates and Damgaard imposed the condition that $\nu-p \geqslant 2$. However, the first neglected term is not always small compared to the sum of the others and more careful consideration must be given to the termination procedure.

The integral of $G(r)$ is trivial, giving

$$\langle n',l'|r^m|n,l\rangle$$

$$= \int_0^\infty G(r)dr = N'N \sum_{P=0}^{P_0} A_p(1/n*'+1/n*)^{-(\nu-p+1)}$$

$$\times\Gamma(\nu-p+1) = N'N \sum_{P=0}^{P_0} F(P). \quad (A2)$$

In choosing a criterion for evaluating the asymptotic expansion, the behavior of $F(P)$ was investigated. Normally for small $P$, the sign of $F(P)$ alternates. Then for some value of $P$, $F(P)$ begins to approach zero (keeping the same sign) to a minimum term, $F(P_{min})$, and then changes sign. It was decided to terminate the series before the minimum term, $P_0 = P_{min}-1$ and add the average of the next two terms (which have opposite signs). Thus,

$$\langle n',l'|r^m|n,l\rangle$$

$$= N'N\{ \sum_{P=0}^{P_{min}-1} F(P) + \tfrac{1}{2}[F(P_{min})+F(P_{min}+1)]\}. \qquad (A3)$$

The technique is justified by yielding improved agreement with empirical results.