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Theory of two-photon ionization of cesium

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We present a systematic theoretical analysis of two-photon ionization of cesium in the perturbation-theory regime. Matrix elements from diverse sources, such as quantum-defect theory and model potentials, as well as from experimental oscillator strengths, have been used in the calculation. The results are discussed in the context of recent measurements. In addition to total generalized cross sections (gcs) for linearly polarized light, ratios of gcs for linear to circular polarization, as well as photoelectron spin polarization, have been calculated. The various sets of matrix elements give results which are consistent, given variations that should be expected from the diversity of the sources. The disagreement with experiment, however, persists.

I. INTRODUCTION

Despite the considerable amount of existing experimental data on multiphoton ionization of atoms,[1] only a few absolute measurements of transition rates (or generalized cross sections) have been attempted. There are, of course, many good reasons for this state of affairs, having mostly to do with severe experimental complications inherent in such undertakings. Some of these difficulties are (i) the presence of molecules which also undergo multiphoton transitions, often more efficiently than the atoms, (ii) the dependence of the interaction region on laser power, and (iii) photon correlation effects. Such complications notwithstanding, absolute measurements are very important in helping assess our fundamental understanding of multiphoton ionization.

In a recent very interesting paper, Granneman and van der Wiel[2] have reported results on the measurement of absolute yields of two-photon ionization of cesium, using nine wavelengths available in the argon-ion laser (see Fig. 1). Several of these wavelengths happen to fall near a deep minimum of the total yield, at least as calculated by Bebb,[3] and most recently by Lambropoulos and Teague.[4] The experimental results are seen to be a few orders of magnitude above the predicted minimum; in fact, they do not seem to suggest a minimum at all, but a flat shape instead. Perhaps even more significant is the fact that theory and experiment disagree by at least one order of magnitude very near the $7P_{3/2}$ level.

At and very near a minimum, the transition probability is determined by a large number of matrix elements, as it is cancellation among a large number of terms that produces the minimum. The *exact* position and depth of the minimum itself can only be determined by an *exact infinite* summation of terms with *exact* matrix elements. With the exception of hydrogen, this cannot be done. For other atoms, approximate methods must be used, e.g., matrix elements derived from measured oscillator strengths or from calculations using model potentials, or a phenomenological Green's function constructed on the basis of quantum-defect theory.[5] Away from the minimum, the transition probability is not as sensitive to the exactness of the matrix elements or the completeness of the summation. It should be stressed, however, that the approximate position of the first few minima in two-photon ionization is determined by only a few matrix elements corresponding to transitions to the nearby levels. The remaining terms in the summation shift the minimum by a relatively small amount.

Near resonance with an intermediate state, the transition probability is likewise determined by only a few matrix elements, and interference plays no substantial role. It has been shown[4] for the example of the $7P$ state of cesium that the single intermediate $[7P]$-state approximation yields results within a factor of 2 of the completely converged summations for several hundred wave numbers on either side of the resonance. Finally, very near resonance, other complications doom any attempt at a simple theoretical analysis, e.g., the necessity of including the widths (both natural and induced) of the intermediate states. A more serious complication has been discussed by Beers and Armstrong,[6] who show that under certain conditions, a transition probability per unit time does not even exist as a time-independent quantity.

With the above considerations in mind, we note that all of the experimental data presented by Granneman and van der Wiel were taken at laser wavelengths sufficiently far from the minimum to pose no serious problem with respect to convergence of a partial summation in a calculation. Some, how-

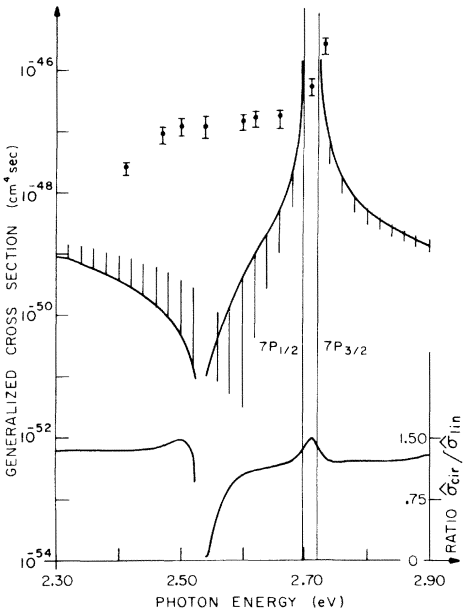

FIG. 1. Two-photon ionization of ground-state cesium near the doublet $7P$ intermediate-state resonance. The experimental points for the generalized cross section $\hat{\sigma}_{\text{lin}}$ are taken from Ref. 2. The upper solid theoretical curve was calculated using radial matrix elements from set A. The vertical bars on this curve show, for selected photon energies, the maximum variation of the calculated values for $\hat{\sigma}_{\text{lin}}$ when using any of the other five sets of matrix elements. The lower curve gives the calculated value of the ratio $\hat{\sigma}_{\text{cir}}/\hat{\sigma}_{\text{lin}}$, again using matrix elements from set A.

ever, are sufficiently close to the minimum to be useful, in principle, to test the accuracy of various sets of approximate matrix elements. Moreover, none of the points is sufficiently near resonance with an intermediate atomic state to create any of the complications inherent in resonant multiphoton ionization. In particular, none of the conditions of the model of Beers and Armstrong were satisfied in this experiment, and the transition probability per unit time is expected to be a meaningful quantity. This is the case when the detuning δ from the nearest atomic level is much larger than the corresponding Rabi frequency for the laser intensity used in the experiment, a condition met for all experimental points of Ref. 2. Then for interaction times longer than $1/\delta$ a time-independent rate exists. For the Granneman and van der Wiel experiment[2] the largest value of $1/\delta$ is of the order of 10^{-12} sec, whereas the interaction times for the experiment were of the order of 10^{-8} sec or longer. All this has been explicitly verified by numerical calculations for this case[4] using the model of Beers and Armstrong. Photon correlation effects are not expected to have had much influence on the experiment. In any case, their effect could be no more than a factor of 2 in $\hat{\sigma}$. Finally, the light intensities employed were well within the regime of applicability of perturbation theory. These experimental results, especially since they are among the first absolute measurements, are therefore ideally suited to comparison with the results of a relatively simple calculation.

The two calculations[3,4] mentioned above are based on quantum-defect theory which not only is generally approximate (especially when an S state is involved[7]), but it could also be argued that it is more so in a heavy element such as cesium, owing, for example, to spin-orbit effects and core polarization. For this reason we undertook a study of two-photon ionization in cesium using a variety of available or obtainable information on matrix elements. Thus, in addition to quantum-defect theory, model-potential results as well as experimental oscillator strengths have been employed. Our basic objective has been to assess how sensitive the calculation of two-photon ionization of cesium is to the matrix elements used, and to explain, if possible, the discrepancy between the experiment and earlier calculations.

In addition to the Granneman and van der Wiel measurement, there is already another experiment in progress.[8] Since similar experiments are likely to be undertaken in the near future, we have chosen to present most of our results in the form of tables, so that detailed comparison with experiment, as well as other calculations, is possible. We have also given ratios of transition rates for circularly polarized to linearly polarized light, as well as the photoelectron spin polarization (when circular polarization is used). Measurements of these additional quantities, although not available presently, will provide further considerable insight into the validity of the calculations.

II. THEORY

In the perturbation-theory regime, it is known[3,4,9] from the application of standard methods that the total transition probability per unit time for an atom initially in its ground state to absorb two photons of frequency ω and eject a photoelectron of energy $\hbar\omega_k$ may be written as

$$W = I^2\hat{\sigma} \ , \tag{1}$$

where I is the photon flux in $\text{cm}^{-2}\,\text{sec}^{-1}$, and the total generalized cross section (in units $\text{cm}^4\,\text{sec}$) is

$$\hat{\sigma} = \frac{a_0^4}{2}\left(\frac{\hbar}{\mathcal{R}}\right)\alpha^2\left(\frac{E}{\mathcal{R}}\right)^{1/2}\omega^2\left|T_{fi}\right|^2 \ , \tag{2}$$

where E is the kinetic energy of the photoelectron,

a_0 is the Bohr radius, $\mathcal{R}$ the Rydberg energy, $\alpha \approx 1/137$, and

$$T_{fi} = \sum_n \frac{(\hat{\epsilon}\cdot\vec{r})_{fn}(\hat{\epsilon}\cdot\vec{r})_{ni}}{\omega_n - \omega_i - \omega} , \tag{3}$$

where $\hat{\epsilon}$ is the polarization vector of the absorbed photons. In (3), the matrix elements $\vec{r}_{jk}$ are in units of the Bohr radius, and all frequencies are measured in kaysers (cm^{-1}). Furthermore, the energy denominator in (3) does not contain widths for the intermediate states, because in this paper we consider a situation in which the first absorbed photon does not produce an exact or near intermediate-state resonance.

Angular momentum techniques may be applied to reduce the right-hand side of (3) to a summation over radial dipole matrix elements of the form

$$R^{n'l'(j')}_{nl(j)} = \int_0^\infty r^2 dr R_{n'l'(j')} r R_{nl(j)} . \tag{4}$$

This has been done in detail in a previous paper by Lambropoulos and Teague[4] for the case of two-photon ionization, and by Teague and Lambropoulos[10] for the case of three-photon ionization. In those papers, spin-orbit effects are taken completely into account, and explicit formulas are given for total generalized cross sections (for linear and circular polarization) and for angular distributions and spin polarization of the ejected photoelectron. For now we need only remind ourselves that in cesium the initial state is $6S_{1/2}$ and dipole selection rules allow only states $nP_{1/2}$ and $nP_{3/2}$ as intermediate states. The final state is then a superposition of an S wave and D wave for linearly polarized light, and only a D wave for circularly polarized light.

Thus the crucial element in calculating transition rates is to have an accurate set of radial dipole matrix elements which is extensive enough to allow adequate convergence to be obtained when the infinite summations in (3) are truncated. We have been careful to keep truncation errors in this calculation to the order of a few percent. In view of the present large discrepancy between theory and experiment, it was not deemed worthwhile to pursue the calculations to better accuracy at this point.

III. RADIAL MATRIX ELEMENTS

Six different sets of radial matrix elements were used in the present work. These are summarized in Table I.

Sets A and B, while both are based on quantum-defect theory (QDT), lead to slightly different results, due to the fact that for set B the bound-bound matrix elements were obtained using a different criterion for terminating asymptotic series required in evaluating certain integrals than used in earlier work.[11,12] Improved quantum-defect formulas for bound-free transitions[17] were also used in selected calculations instead of the formulas from Ref. 13. The results were nowhere outside the range spanned by the other results.

The model potential calculations used in sets C, D, and E were all based on solutions of a one-particle Schrödinger equation for the valence electron of cesium, with the potential being chosen so as to reproduce the observed term values. They differ, however, in several respects. While all three model potentials incorporated the effect of core polarization, in one case[14] this was only implicit, while in the other two[15,16] a dipole potential with the correct asymptotic form was explicitly included. In all three calculations, the effect of the spin-orbit interaction was included: in two[14,15] with the potential $(1/r)(\partial V/\partial r)$, where V is the nonrelativistic potential, and an attempt to approximate the Dirac equations near the origin, but in the third[16] with the use of a potential ξ/r^3 throughout, where ξ was determined semiempirically. Finally, the effect of core polarization was not included in the calculation of the matrix elements (as distinguished from the potential) in one case,[14] but was in the other two.[15,16]

The experimental data used in set F are probably not as accurate as more recent measurements.[18,19] If these latter were used instead in set F, the results would differ very little from those obtained using set D, since the agreement between these

TABLE I. Sources of radial dipole matrix elements used. QDT refers to quantum defect theory, MPT refers to model-potential theory.

Set	Bound-bound	Bound-free
A	QDT, using Refs. 11 and 12	QDT, using Ref. 13
B	QDT, Ref. 3	QDT, using Ref. 13
C	MPT, Ref. 14	QDT, using Ref. 13
D	MPT, Ref 15	MPT, present calculations
E	MPT, Ref. 16	MPT, present calculations
F	Experimental data cited in Ref. 15	MPT, present calculations

TABLE II. Two-photon ionization of ground-state cesium in the region of the doublet $7P$ resonance. The subscripts on the total generalized cross section $\hat{\sigma}$ indicate linearly and circularly polarized light. P is the photoelectron spin polarization for right circularly polarized light. The notation $A\ -a$ means $A\times10^{-a}$.

λ^{-1} (cm^{-1})	$\hat{\sigma}_{lin}$ (cm^4 sec)	$\hat{\sigma}_{cir}/\hat{\sigma}_{lin}$	P
19 436.35 [a]	7.90 −50	1.19	−0.06
19 932.23 [a]	4.62 −50	1.18	−0.10
20 140.99 [a]	3.39 −50	1.18	−0.13
20 491.80 [a]	1.54 −50	1.19	−0.23
20 986.36 [a]	3.81 −52	1.39	0.82
21 150	6.89 −51	1.15	0.36
21 155.07 [a]	7.34 −51	1.15	0.34
21 200	1.23 −50	1.14	0.24
21 300	3.26 −50	1.15	0.09
21 400	7.79 −50	1.15	−0.03
21 468.44 [a]	1.41 −49	1.15	−0.11
21 500	1.88 −49	1.15	−0.15
21 600	5.25 −49	1.16	−0.32
21 700	2.87 −48	1.20	−0.58
21 750	4.14 −47	1.29	−0.66
21 760	3.06 −46	1.32	−0.63
21 765 [b]	2.28 −44	1.33	−0.60
21 770	5.00 −46	1.35	−0.57
21 780	4.53 −47	1.39	−0.46
21 790	1.60 −47	1.43	−0.31
21 800	8.52 −48	1.47	−0.10
21 810	5.72 −48	1.49	0.13
21 820	4.54 −48	1.50	0.37
21 830	4.12 −48	1.49	0.59
21 838.83 [a]	4.14 −48	1.47	0.74
21 840	4.17 −48	1.46	0.76
21 850	4.59 −48	1.43	0.88
21 860	5.41 −48	1.39	0.96
21 870	6.78 −48	1.36	0.99
21 880	8.97 −48	1.33	1.00
21 890	1.26 −47	1.31	0.99
21 900	1.90 −47	1.29	0.97
21 910	3.15 −47	1.27	0.94
21 920	6.14 −47	1.25	0.91
21 930	1.62 −46	1.24	0.87
21 940	1.05 −45	1.23	0.84
21 945 [c]	1.72 −44	1.23	0.82
21 950	4.28 −45	1.22	0.81
21 975	6.43 −47	1.21	0.73
22 000	1.97 −47	1.19	0.67
22 002.20 [a]	1.81 −47	1.19	0.66
22 100	3.00 −48	1.17	0.49
22 200	1.32 −48	1.16	0.40
22 300	7.95 −49	1.15	0.32
22 400	5.52 −49	1.15	0.28
22 500	4.16 −49	1.15	0.25

[a] Argon-ion laser frequency.
[b] Near $7P_{1/2}$ resonance ($E_{7P_{1/2}}-E_{6S_{1/2}}=21\,765.65$ cm^{-1}).
[c] Near $7P_{3/2}$ resonance ($E_{7P_{3/2}}-E_{6S_{1/2}}=21\,946.66$ cm^{-1}).

measurements and the calculated[15] oscillator strengths is excellent.

In general, the various sets of bound-bound matrix elements differ by a few percent for transitions to the low-lying npj states, but by large factors for the higher states, particularly for $j=\frac{1}{2}$. We expect the results using set D to be the most accurate overall.

IV. RESULTS

In Tables II–IV we present results for two-photon ionization of ground-state cesium obtained using the matrix elements from set D (Table I). Table II covers in detail the region near the doublet $7P$

TABLE III. Two-photon ionization of ground-state cesium in the region of the doublet $8P$ resonance. $A\ -a$ means $A\times10^{-a}$.

λ^{-1} (cm^{-1})	$\hat{\sigma}_{lin}$ (cm^4 sec)	$\sigma_{cir}/\sigma_{lin}$	P
25 400	4.26 −51	1.11	−0.38
25 500	3.00 −52	1.43	−0.15
25 600	1.44 −50	1.11	0.10
25 650	8.11 −50	1.11	−0.26
25 700	3.07 −48	1.23	−0.67
25 704	9.46 −48	1.26	−0.66
25 708 [a]	1.89 −46	1.30	−0.62
25 710 [a]	3.25 −46	1.32	−0.59
25 714	1.02 −47	1.36	−0.49
25 718	3.16 −48	1.41	−0.35
25 722	1.59 −48	1.45	−0.16
25 726	1.03 −48	1.48	0.06
25 730	7.93 −49	1.50	0.28
25 734	6.93 −49	1.49	0.49
25 738	6.72 −49	1.47	0.67
25 742	7.05 −49	1.44	0.81
25 746	7.87 −49	1.41	0.90
25 750	9.23 −49	1.37	0.96
25 754	1.13 −48	1.34	0.99
25 758	1.43 −48	1.31	1.00
25 762	1.89 −48	1.29	1.00
25 766	2.60 −48	1.27	0.98
25 770	3.77 −48	1.25	0.96
25 774	5.87 −48	1.23	0.94
25 778	1.02 −47	1.22	0.91
25 782	2.09 −47	1.21	0.88
25 786	6.23 −47	1.20	0.86
25 790	6.84 −46	1.19	0.83
25 792 [b]	4.44 −44	1.18	0.82
25 794	4.54 −46	1.18	0.80
25 798	6.01 −47	1.17	0.78
25 800	3.50 −47	1.17	0.77
25 810	7.79 −48	1.16	0.71
25 850	1.04 −48	1.13	0.55
25 900	4.08 −49	1.12	0.44
26 000	1.77 −49	1.10	0.31

[a] Near the $8P_{1/2}$ resonance at 25 709.14 cm^{-1}.
[b] Near the $8P_{3/2}$ resonance at 25 791.78 cm^{-1}.

TABLE IV. Two-photon ionization of ground-state cesium from threshold to the $10P$ resonance. $A\ -a$ means $A \times 10^{-a}$.

λ^{-1} (cm^{-1})	δ_{lin} (cm^4 sec)	$\delta_{cir}/\delta_{lin}$	P	λ^{-1} (cm^{-1})	δ_{lin} (cm^4 sec)	$\delta_{cir}/\delta_{lin}$	P
16 000	8.10 −49	1.22	.04	24 200	5.84 −50	1.12	0.05
16 500	5.86 −49	1.21	.03	24 300	5.38 −50	1.12	0.04
17 000	4.26 −49	1.21	.02	24 400	4.93 −50	1.12	0.03
17 500	3.11 −49	1.20	.01	24 500	4.51 −50	1.11	0.02
18 000	2.26 −49	1.20	.00	24 600	4.10 −50	1.11	0.01
18 500	1.63 −49	1.20	−0.02	24 700	3.70 −50	1.11	0.00
19 000	1.14 −49	1.19	−0.03	24 800	3.29 −50	1.11	−0.02
19 500	7.45 −50	1.19	−0.06	24 900	2.88 −50	1.11	−0.03
20 000	4.21 −50	1.18	−0.11	25 000	2.45 −50	1.11	−0.06
20 100	3.63 −50	1.18	−0.13	25 100	2.00 −50	1.10	−0.09
20 200	3.06 −50	1.18	−0.14	25 200	1.51 −50	1.10	−0.13
20 300	3.51 −50	1.18	−0.17	25 300	9.82 −51	1.10	−0.21
20 400	1.99 −50	1.19	−0.19	25 400	4.26 −51	1.11	0.38
20 500	1.50 −50	1.19	−0.23	25 500	3.00 −52	1.43	−0.15
20 600	1.04 −50	1.19	−0.28	25 600	1.44 −50	1.11	−0.10
20 700	6.31 −51	1.20	−0.36	25 700	3.07 −48	1.23	−0.67
20 800	2.97 −51	1.23	−0.50	25 800	3.50 −47	1.17	0.77
20 900	7.89 −52	1.35	−0.66	25 900	4.08 −49	1.12	0.46
21 000	4.92 −52	1.31	.98	26 000	1.77 −49	1.10	0.31
21 100	3.45 −51	1.15	.53	26 100	1.15 −49	1.10	0.25
21 200	1.23 −50	1.14	.24	26 200	8.71 −50	1.09	0.21
21 300	3.26 −50	1.14	.09	26 300	7.10 −50	1.09	0.18
21 400	7.79 −50	1.15	−0.03	26 400	6.02 −50	1.09	0.16
21 500	1.88 −49	1.15	−0.15	26 500	5.24 −50	1.09	0.14
21 600	5.25 −49	1.16	−0.32	26 600	4.62 −50	1.09	0.12
21 700	2.87 −48	1.20	−0.58	26 700	4.12 −50	1.09	0.10
21 800	8.52 −48	1.47	−0.10	26 800	3.72 −50	1.09	0.09
21 900	1.90 −47	1.29	0.97	26 900	3.35 −50	1.08	0.07
22 000	1.95 −47	1.19	0.67	27 000	3.00 −50	1.07	0.05
22 100	3.00 −48	1.17	0.49	27 100	2.65 −50	1.06	0.03
22 200	1.32 −48	1.15	0.32	27 200	2.25 −50	1.06	0.00
22 300	7.95 −49	1.15	0.28	27 300	1.80 −50	1.06	−0.04
22 400	5.52 −49	1.15	0.28	27 400	1.22 −50	1.06	−0.12
22 500	4.16 −49	1.15	0.25	27 487.63 [a]	5.51 −51	1.06	−0.31
22 600	3.31 −49	1.14	0.22	27 500	4.43 −51	1.07	−0.37
22 700	2.73 −49	1.14	0.20	27 600	1.11 −50	1.09	0.10
22 800	2.31 −49	1.14	0.18	27 700	1.32 −48	1.12	0.66
22 900	2.00 −49	1.14	0.17	27 800	9.94 −50	1.08	0.33
23 000	1.75 −49	1.14	0.15	27 900	5.76 −50	1.07	0.24
23 100	1.55 −49	1.14	0.14	28 000	4.35 −50	1.06	0.19
23 200	1.39 −49	1.13	0.13	28 100	3.60 −50	1.06	0.15
23 300	1.26 −49	1.13	0.12	28 200	3.08 −50	1.06	0.12
23 400	1.14 −49	1.13	0.11	28 300	2.65 −50	1.06	0.10
23 500	1.04 −49	1.13	0.10	28 400	2.24 −50	1.05	0.06
23 600	9.53 −50	1.13	0.09	28 481.91 [a]	1.87 −50	1.05	0.02
23 700	8.75 −50	1.13	0.09	28 500	1.78 −50	1.05	0.01
23 800	8.06 −50	1.12	0.08	28 600	1.09 −50	1.05	−0.11
23 900	7.43 −50	1.12	0.07	28 700	1.03 −51	1.24	0.93
24 000	6.86 −50	1.12	0.06	28 800	1.16 −49	1.07	0.43
24 100	6.33 −50	1.12	0.06	28 900	4.27 −50	1.05	0.25

[a] Argon-ion laser frequency.

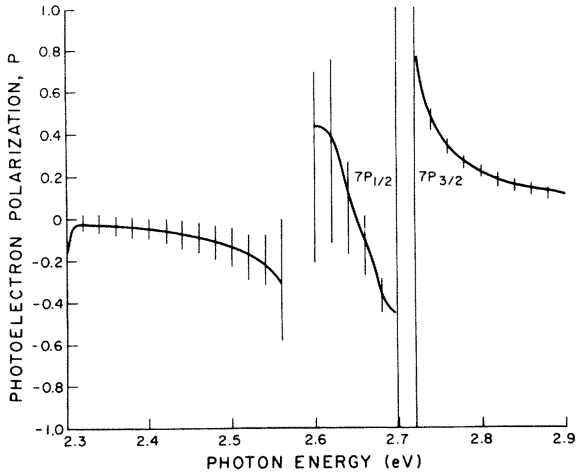

FIG. 2. Two-photon ionization of ground-state cesium near the doublet $7P$ intermediate-state resonance. The solid curve is the photoelectron spin polarization calculated using radial matrix elements from set D. The vertical bars on this curve show, for selected photon energies, the maximum variation of the calculated values for P when using any of the other five sets of matrix elements.

resonance and gives the total generalized cross section $\hat{\sigma}_{\mathrm{lin}}$ for the case of incident linearly polarized light, the ratio $\hat{\sigma}_{\mathrm{cir}}/\hat{\sigma}_{\mathrm{lin}}$, and the ejected photoelectron spin polarization P for circularly polarized light. Table III gives analogous data for the doublet $8P$ resonance, while Table IV presents data at 100-cm^{-1} intervals all the way from near threshold to the region of the doublet $10P$ resonance. Also in Table IV are results for the two uv frequencies available from an argon-ion laser, although not used by Granneman and van der Wiel.[2] While we believe the set of matrix elements used

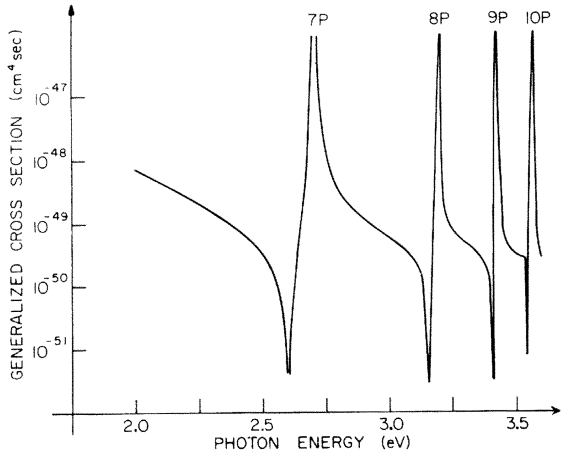

FIG. 3. Generalized cross section $\hat{\sigma}_{\mathrm{lin}}$ for two-photon ionization of ground-state cesium, based on matrix elements from set D.

to produce the tabulated results to be the most accurate of the six sets, tables of results analogous to those presented for set D are available for the other five sets on request.[20]

Finally, representative results are plotted in Figs. 1, 2, and 3. In the curves of Figs. 1 and 2 we have left a gap in the region of the minimum of the deep valley, since the calculation is expected to be much less accurate in this region. In particular, quadrupole contributions, even though off resonance, will establish the minimum of the deep valley in $\hat{\sigma}_{\mathrm{lin}}$, estimated to be about 10^{-52} cm^4 sec.

V. DISCUSSION

The amount of variation obtained among the several calculations is illustrated in Fig. 1 to facilitate visual inspection. As one might have expected, the variation is larger near the minimum, and considerably smaller away from it. All calculations produce a minimum. It is easy to recognize that as long as the two products of radial matrix elements $R^{6p}_{6s}R^{EI}_{6p}$ and $R^{7p}_{6s}R^{EI}_{7p}$ have the same algebraic sign, there will be a deep minimum below the $7P_{1/2}$ level, whose exact position and depth will depend on other details. All calculations gave the same sign (note that it is the relative sign that really matters) to the above two products, over the entire energy range of Fig. 1. In fact, for all alkalis, only in Li is there a change in sign between the matrix element connecting the ground state to the continuum via the first excited P state ($2P$) and that connecting it to the continuum via the second excited P state ($3P$) in the analogous photon energy range. For this reason, Li is the only alkali that does not exhibit[3,21,22] a minimum between the first two P states. Since in all alkalis, the $\langle n_0 S | r | nP \rangle$ matrix elements decrease rather rapidly with increasing n, the remaining terms in the summation cannot cause dramatic changes. Although the absolute values of the matrix elements are model dependent, whatever differences one finds are reflected in the results of Fig. 1. Moreover, there exist experimental values for oscillator strengths (which we have used in one set of calculations), providing a guide as to what discrepancies between calculated values one can reasonably expect.

Spin-orbit intricacies[15,16] are not expected to affect appreciably the total $6S$-nP transition probability away from resonance. We note that the models of Norcross[15] and Weisheit[16] give very similar results, although they predict different behavior for the ratio

$$\frac{\langle nP_{3/2} | r | 6S \rangle}{\langle nP_{1/2} | r | 6S \rangle} \equiv \rho$$

for large values of n. In two-photon ionization, and away from a fine-structure P doublet as in the minimum, it is the total oscillator strength (matrix element) that matters. In any case, the ratio ρ for Cs does not differ from unity appreciably for the first three or so P states, and they are the ones that have the greatest influence on the minimum of Fig. 1.

Spin-orbit details do have a significant effect on the photoelectron spin polarization, as is readily seen in Fig. 2. This therefore provides a much more refined test of calculational models, although much more difficult to measure. Note that a small influence of spin-orbit effects on the matrix elements is inherently included in quantum-defect theory, but not nearly enough for a heavy element like cesium. For this reason the polarization results obtained using the model potential bound-bound matrix elements (sets C–E), or the experimental values (set F), are much to be preferred.

Within the framework of quantum-defect theory a complete infinite summation over intermediate states can be performed through the use of an approximate phenomenological Green's function.[5] The latter can be expressed in terms of Whittaker functions for which series expansions can be used. This procedure introduces only minor corrections with respect to our quantum-defect results as we have found in previous work.[4] On the other hand, the Green's-function method presents its own difficulties (having mainly to do with the convergence of the series expansions) as we have discussed elsewhere.[10] These are more severe in processes of order higher than two, where multiple infinite summations are involved. But in any event, questions of infinite versus truncated summation do not make any substantial difference in our reported results *vis a vis* the experiment.

In addition, one must not forget the inherent limitations of quantum-defect theory, especially as it applies to cesium. Thus, the exact summation of such approximate matrix elements may not necessarily be better than an approximate summation of more accurate matrix elements. This is a choice that must always be made in multiphoton processes. The issue of the infinite summation is more crucial when the first photon brings the electron very near (just below) the continuum edge.

It should be noted that near resonance with intermediate atomic states (where only a few matrix elements matter), all calculations give results within a factor of 2 or so. This is reasonable since differences of the order of 20–30% between individual matrix elements will cause such variations in $\hat{\sigma}$. For example, for a photon of frequency 22 002.20 cm^{-1}, the ratio of the maximum to the minimum value for $\hat{\sigma}$ is 1.95. This, incidentally, is one of the experimental points of Fig. 1, the one above the $7P_{3/2}$ level. Thus it appears that there is consistency among the various models, despite their inherent differences. And yet their discrepancy with the experiment of Granneman and van der Wiel[2] is quite substantial.

On the other hand, it is perhaps worth noting that Compton *et al.*[8] have measured two-photon ionization rates for the two resonance processes $6S$-$7P_{1/2}$-continuum and $6S$-$7P_{3/2}$-continuum. They have not yet made an attempt to determine $\hat{\sigma}$. They have, however, measured the ratio 1.9 ± 0.2 for rates of the above two processes. The present calculations, when averaged over the finite experimental laser linewidth, yield the result 1.6 ± 0.9, where the uncertainty reflects the maximum deviation for the various sets of matrix elements, and that in the experimental line shape.

We have attempted to construct a fairly complete theoretical picture of two-photon ionization in cesium. Our results do not produce better agreement with experiment. In that sense we have added to the puzzle, for which we have no explanation at this time. It is hoped, however, that future experiments, involving also measurements of the other quantities (besides $\hat{\sigma}_{1i_n}$) that we have calculated, will eventually make it possible to resolve the present paradox.

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