Effect of Light Polarization on Multiphoton Ionization of Atoms

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(Received 17 January 1972)

We present a theoretical interpretation of an effect recently observed in two- and three-photon ionization of Cs. We show that the total cross sections for two- and three-photon ionization of a one-electron atom depend on the polarization of the incident light. Expressions are derived for the ratio of the cross section for circularly polarized light to that for linearly polarized, and their maximum values are obtained.

In two recent experiments, Fox, Kogan, Burnham, and Robinson[1,2] have observed two- and three-photon ionization of atomic Cs using, respectively, the second harmonic and the fundamental frequency of the ruby laser. They have also reported that the measured total ionization rates for circularly polarized light are larger by the factors 1.28 (for the two-photon process) and 2.15 (for the three-photon process) than for linearly polarized light. This, as the above authors observed,[1] seems at first strange since the atoms they used were unpolarized. It is easy to show quite generally that, for unpolarized atoms, rotational invariance and parity conservation guarantee that the rate of single-photon ionization is independent of the polarization of the incident light. It appears therefore that this is a new effect peculiar to multiphoton processes. It is the purpose of this paper to show that this is indeed the case, and to provide a theoretical interpretation of the experimental results of Refs. 1 and 2.

We have calculated two-, three-, and four-photon ionization differential cross sections for a simple, one-electron model of the atom. This of course is rigorous for hydrogen and should be quite good for the ionization of Cs and the other alkali atoms. We have used the electric dipole approximation and perturbation theory of the appropriate order.[3-8] We report here the results for the two- and three-photon processes (for the case of an initial atomic state of zero angular momentum, an s state) which are pertinent to the interpretation of the results of Refs. 1 and 2. A more detailed account of this work will be presented elsewhere.

Consider a monochromatic light beam traveling along the positive z axis of an (xyz) right-handed system of Cartesian coordinates. The polarization vector of the light lies in the xy plane. The direction of emission of the photoelectron is determined by its wave vector $\vec{K}$ for which we use spherical coordinates (K, φ, θ); θ is the angle between the z axis and $\vec{K}$, and φ is the angle between the x axis and the projection of $\vec{K}$ on the xy plane. Thus the differential cross sections for the emission of the electron within a solid angle $d\Omega \equiv \sin\theta\, d\theta\, d\varphi$ will be functions of φ and θ. For n-photon ionization, this differential cross section will be denoted by $d\sigma_n/d\Omega$. The total cross section then is $\sigma_n = \int_0^{2\pi} d\varphi \int_0^{\pi} \sin\theta (d\sigma_n/d\Omega) d\theta$ Light linearly polarized along, for example, the x axis interacts with the atom[9] through the dipole operator x. Left or right circularly polarized light interacts through the operators $x \pm iy$. The angular dependence of the cross sections can be taken out of the complicated summations over all intermediate states. The resulting expressions for the cross sections contain trigonometric functions multiplied by coefficients which involve summations over radial matrix elements divided by the appropriate energy differences. (See, for example, Ref. 3.)

Two-photon ionization.—For light linearly polarized along the x axis, we obtain

$$d\sigma_2{}^x/d\Omega = a_2{}^2 + 2a_2 b_2 \sin^2\theta \cos^2\varphi + b_2{}^2 \sin^4\theta \cos^4\theta, \quad (1)$$

while for (left or right) circularly polarized light, we obtain

$$d\sigma_2{}^c/d\Omega = \tfrac{1}{4} b_2{}^2 \sin^4\theta. \quad (2)$$

Obviously, the conclusions do not depend on which axis is chosen for the polarization of the linearly polarized light. The coefficients a_2 and b_2 are functions of the frequency of the incident light. Their general structure can be found in the paper by Zernik[3] who has obtained an expression for $d\sigma_2{}^x/d\Omega$ identical to Eq. (1). He has further calculated numerical values of a_2 and b_2 for the $2S$ state of hydrogen and light wavelengths between 4556.3 and 7290.1 Å (the ruby-laser wavelength is about 6943 Å).

The total cross sections $\sigma_2{}^x$ and $\sigma_2{}^c$ as obtained from Eqs. (1) and (2) are

$$\sigma_2{}^x = \tfrac{40}{15}\pi b_2{}^2(1.5p^2 + p + 0.3), \qquad (3)$$

$$\sigma_2{}^c = \tfrac{8}{15}\pi b_2{}^2, \qquad (4)$$

where we have introduced the dimensionless parameter $p \equiv a_2/b_2$. The ratio of the two cross sections is then given by

$$\mu_2 \equiv \sigma_2{}^c/\sigma_2{}^x = (7.5p^2 + 5p + 1.5)^{-1}. \qquad (5)$$

The denominator of the right-hand side of Eq. (5) is positive for all real values of p. It has a minimum at $p = -\frac{1}{3}$, where its value is ~0.667. The maximum value that μ_2 can attain therefore is $1/0.667 = 1.5$. Clearly, for a given atom, p and consequently μ_2 depend on the frequency of the light. Estimates indicate that p will usually vary between about -1.5 and $+1.5$, which means that μ_2 will usually vary between 1.5 and 0.04, a rather wide range of values. One can show that μ_2 follows the peaks and valleys of the cross section $\sigma_2{}^x$ as a function of the photon frequency, and that for frequencies in near resonance with intermediate states, μ_2 will be near its maximum. These conclusions are in perfect agreement with Zernik's[3] numerical results. For ruby-laser light and the $2S$ state of hydrogen, using Zernik's values for a_2 and b_2, we find $\mu_2 \cong 1.4$. This is very interesting because the situation is similar to what one would expect in the case of two-photon ionization of Cs by the second harmonic of the ruby laser. It is similar in the sense that in both cases the light frequency is sufficiently close to a resonance for two or three intermediate states to give a good estimate of the cross section. Note that the frequency of the second harmonic of ruby is ~28 800 cm^{-1}, while the energy differences between the ground state[10] $6S_{1/2}$ of Cs and its excited states $10P_{1/2}$ and $10P_{3/2}$ are 28 727.09 and 28 753.93, respectively. Such an estimate leads to a value of μ_2 similar to that for hydrogen, i.e., about 1.4, which is in remarkable agreement with the value 1.28 ± 0.2 reported by Kogan *et al.*[2]

Three-photon ionization.—For light linearly polarized along the x axis, we obtain

$$d\sigma_3{}^x/d\Omega = 16\pi \sin^2\theta \cos^2\varphi\,(a_3{}^2 + 2a_3b_3 \sin^2\theta \cos^2\varphi + b_3{}^2 \sin^4\theta \cos^4\varphi), \qquad (6)$$

while for circularly polarized, we obtain

$$d\sigma_3{}^c/d\Omega = 2\pi b_3{}^2 \sin^6\theta. \qquad (7)$$

The corresponding total cross sections are

$$\sigma_3{}^x = \tfrac{64}{3}\pi^2 b_3{}^2(q^2 + 1.2q + 0.428), \qquad (8)$$

$$\sigma_3{}^c = \tfrac{128}{35}\pi^2 b_3{}^2, \qquad (9)$$

where we have again introduced the dimensionless parameter $q \equiv a_3/b_3$. Thus we now have the ratio

$$\mu_3 \equiv \sigma_3{}^c/\sigma_3{}^x = (5.83q^2 + 7q + 1.363)^{-1}. \qquad (10)$$

The coefficients a_3 and b_3 are complicated expressions this time involving double summations of products of radial matrix elements.

The denominator in the right-hand side of Eq. (10) is again positive for all real values of q and has a minimum at -0.6. As a result, μ_3 has a maximum at the same point. This maximum value is ~2.5. In three-photon ionization one can have resonance with either one or two intermediate states. One such resonance or near resonance can occur if there exists an intermediate state that favors a double photon absorption, and then ionization. This is the case (near resonance) in Cs for the ruby-laser frequency, 14 400 cm^{-1}, because the excited levels $9D_{3/2}$ and $9D_{5/2}$ have energy differences of 28 836.06 and 28 828 cm^{-1}, respectively, from the ground state $6S_{1/2}$. Under such conditions one can show that μ_3 also follows the shape of the cross section $\sigma_3{}^x$ and that it should be near its maximum value 2.5. Note that the measured value reported by Fox, Kogan, and Robinson[1] is 2.15 ± 0.4. Numerical calculations of the coefficients a_3 and b_3 do not seem to have appeared in the literature. To our knowledge, there has not even appeared an explicit calculation of the form of $d\sigma_3{}^x/d\Omega$, although general theorems[11] and calculations for total cross sections do exist.[4,6]

The examination of a simple model for multiphoton ionization of atoms has shown that the total cross sections for linearly polarized light are in general different from the cross sections for circularly polarized light. Their ratio depends rather strongly on the frequency of the incident light and can vary by at least 2 orders of magnitude. The fact that in the measurements of Refs. 1 and 2 the ratios $\mu_{2,3}$ were found to be larger than 1 is a fortuitous combination of the wavelength of the light used and the level structure of Cs. The maxima for $\mu_{2,3}$ obtained herein are rigorous for hydrogenlike atoms, and should be quite reliable whenever a one-electron model of the process is a good approximation. For further quantitative understanding of the problem, numerical values for the coefficients occurring in the differential cross sections are much needed. Such calculations are also desirable in view of the increasing use of multiphoton transitions in spectroscopic studies.

Since by using circularly polarized light, one can at best gain factors of 1.5 and 2.5 for two- and three-photon ionization, respectively, but lose a factor of 10^{-2} at a different wavelength, it is safer to use linearly polarized light when in doubt. It should perhaps be noted that the cross sections for unpolarized light cannot be obtained from the cross sections for either linearly or circularly polarized light. For this, one would have to combine the polarization vectors for two mutually perpendicular axes within the transition amplitudes, take the square of the absolute value, and then average over all directions of polarization of each photon separately. The resulting cross sections for unpolarized light are different from either of the other two cases. This is yet another difference between single and multiphoton ionization.

The effect discussed in this paper is related to the effect of field correlations on multiphoton processes.[12-15] They both arise from the fact that, even in the dipole approximation, the transition amplitudes for multiphoton processes depend nonlinearly on the vectors of the radiation field. The nonlinearity in the field amplitude leads to rates depending on correlation functions of the field instead of just the absolute value of its amplitude. The nonlinearity in the polarization vector of the field leads to the present effect, because when the circular polarization vector $\epsilon_x \pm i\epsilon_y$ is inserted in the expression for the transition amplitude, cross products of matrix elements involving the orthogonal components ϵ_x and ϵ_y occur. Such cross products (which do not occur in single-photon processes) lead to total cross sections depending on the polarization of the light. It may be said that the rates depend on correlation functions of the polarization vectors.

Note added in proof.—After submission of this Letter, a paper by Hernandez and Gold[16] was brought to my attention. These authors have calculated rates for two-photon absorption in anthracene for elliptically polarized light. They find that the ratio of the rate for elliptical polarization to that for linear varies from 1 to 1.5 as the ellipticity parameter varies from 0 (linear polarization) to 1 (circular polarization). The fact that they find a maximum value for the ratio equal to ours, results from their intial (molecular) state being totally symmetric as is ours.

I wish to express my appreciation to Dr. P. Braunlich for bringing the above reference to my attention.

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[1] R. A. Fox, R. M. Kogan, and E. J. Robinson, Phys. Rev. Lett. 26, 1416 (1971).

[2] R. M. Kogan, R. A. Fox, G. T. Burnham, and E. J. Robinson, Bull. Amer. Phys. Soc. 16, 1411 (1971).

[3] W. Zernik, Phys. Rev. 135, A51 (1964). Strictly speaking, the second term in my Eq. (1) should be multiplied by $\cos(\delta_2 - \delta_0)$, where δ_l is the phase shift of the lth partial wave of the final state. For hydrogen, this is the phase shift of the Coulomb-modified plane wave. For Cs, it can be obtained from quantum-defect theory. For the purposes of this Letter, we have taken $|\cos(\delta_2 - \delta_0)| \simeq 1$. This does not affect the subsequent conclusions about the maxima of the ratios and is a very good approximation for Cs and ruby-laser light. A similar remark applies to the equation for three-photon ionization.

[4] H. B. Bebb and A. Gold, Phys. Rev. 143, 1 (1966).

[5] H. B. Bebb, Phys. Rev. 149, 25 (1966), and 153, 23 (1967).

[6] Y. Gontier and M. Trahin, Phys. Rev. 172, 83 (1968).

[7] J. Cooper and R. N. Zare, in *Lectures in Theoretical Physics*, edited by S. Geltman, K. T. Mahantahappa, and W. E. Brittin (Gordon and Breach, New York, 1969), Vol. XI-C, pp. 317–337.

[8] J. C. Tully, R. S. Berry, and B. J. Dalton, Phys. Rev. 176, 95 (1968).

[9] See, for example, A. Messiah, *Quantum Mechanics* (Wiley, New York, 1965), Vol. II, p. 1032.

[10] C. E. Moore, *Atomic Energy Levels as Derived from Analyses of Optical Spectra,* National Bureau of Standards Circular No. 467 (U. S. GPO, Washington, D. C., 1958), Vol. III, p. 125.

[11] C. N. Yang, Phys. Rev. 74, 764 (1948).

[12] P. Lambropoulos, Phys. Rev. 168, 1418 (1968), and 144, 1081 (1966).

[13] B. R. Mollow, Phys. Rev. 175, 1555 (1968).

[14] G. S. Agrawal, Phys. Rev. A 1, 1445 (1970).

[15] F. Shiga and S. Imamura, Phys. Lett. 25A, 706 (1967).

[16] J. P. Hernandez and A. Gold, Phys. Rev. 156, 26 (1967).