ATOMIC MULTI-PHOTON PROCESSES

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1. Introduction, Historical Background, Basic Multiphoton Processes

In this review we aim to provide an introduction to all the main areas of multiphoton studies to date. This aim will be only partially accomplished, of course. We have been unable to avoid biases. Our concentration is almost exclusively with multiphoton processes in atoms. This is compensated on the one hand by the other excellent reviews in this volume that deal with molecular multiphoton processes and multiphoton chemistry, and is justified on the other hand by the principal contributions made to the early work in the field by atomic spectroscopists.

A number of reviews of atomic multiphoton processes have already appeared.[1] We have not attempted to re-review areas that have been well-covered previously, in the sense that we have not made exhaustive reference to the original literature in those areas. In the case of topics of historical interest, a greater density of citations may be noticed. In making these decisions about citations we have been more concerned with presenting a clear elementary picture, and less concerned about giving credit, than reviewers can usually permit themselves to be. This is because there exists[2] the series of annual Multiphoton Bibliographies for all years since 1970.

The review is organized into eight areas, beginning with an historical introduction and a discussion of considerations in two-photon physics. Higher than second order processes, with an emphasis on ionization, are next described in terms of conventional rate formulas, $W^{(N)} = \sigma_N I^N$. Effects that can cause deviations from such conventional multiphoton behavior are then identified. The remainder of the review concentrates on the most important of these effects.

Most optical effects studied in the past can be attributed to single photon processes. These processes, such as emission, absorption, refraction, photoeffect, etc., can be understood at an elementary level as results of the interaction between a photon and an atom, or more precisely between a photon and an electron. Single photon processes are typical for low intensity light where the electron interacts with a single photon at a time and the probability that other photons arrive during the interaction time is low. By increasing the intensity of a light beam one can observe more and more events where an electron will be perturbed by the electric field of more than one photon at a time. The intensities required to observe such "multiphoton" effects are high and rather difficult to obtain from classical light sources. Wide ranging experimental investigations of these multiphoton processes in the optical frequency range became possible only after the development of the laser.

All of these processes have many common features. For the sake of the greatest simplicity, in this introductory chapter only inelastic processes in atoms will be discussed. In the later chapters a variety of multiphoton phenomena are described. The simplest among the multiphoton effects and those having the longest history, are two photon processes. These were discussed systematically in two well-known papers by Göppert-Mayer[3] in 1929 and 1931. A two photon transition is illustrated in Fig. 1. The energy separation $E_3 - E_1$ is equal to

$$\hbar\omega_1 + \hbar\omega_2$$

where ω_1 and ω_2 are the photon frequencies. Levels E_3 and E_1 have the same parity.

By applying second order time dependent perturbation theory[4-6] one can obtain the probability per unit time that a system makes a two-photon transition, absorbing photons at frequency ω_1 and ω_2 with total energy $E = \hbar(\omega_1 + \omega_2)$. This is given by:

$$W^{(2)}(E) = \frac{8\pi^3}{\hbar}\,\rho(E)\,\frac{1}{\eta_1^2\eta_2^2}\,\frac{n_1\hbar\omega_1}{V}\,\frac{n_2\hbar\omega_2}{V}\left|A_{31}^{(2)}\right|^2 \qquad (1.1)$$

where $\rho(E)$ is the energy density of final states of the absorber, n_1/V and n_2/V are the photon densities in the absorber volume V, and η_1 and η_2 are refractive indexes of the absorber respectively. $A_{31}^{(2)}$ is the usual two photon amplitude

$$A_{31}^{(2)} = \sum_n \left[\frac{(\vec{P}_{3n}\cdot\vec{\varepsilon}_1)(\vec{P}_{n1}\cdot\vec{\varepsilon}_2)}{\hbar(\omega_n - \omega_2)} + \frac{(\vec{P}_{3n}\cdot\vec{\varepsilon}_2)(\vec{P}_{n1}\cdot\vec{\varepsilon}_1)}{\hbar(\omega_n - \omega_1)}\right] \qquad (1.2)$$

where the matrix elements P_{3n} and P_{n1} are of the dipole operator $\vec{P} = -\sum_i e\vec{r}_i$ for given pairs of states of H_{atom}.

The two-photon transition can be thought of as a pair of two consecutive single photon transitions - the first one leading from the initial state to a virtual state and the next one from the virtual state to the final state. In order to complete the transition the second photon has to arrive within the lifetime of the virtual state after the absorption of the first photon. Thus the probability of two-photon absorption at low light intensity is very low. The virtual level is formed of all levels for which the single photon transition from the initial state and to the final state is allowed. All of these levels are taken into account with their respective detunings ΔE. The Göppert-Mayer theory[3] describes two-photon effects of various kinds including even Raman scattering.

Taking into account that the photon flux Φ *is given by*

$$\Phi = cn/\eta V \tag{1.3}$$

and that the energy density $\rho(E)$ is equal to $Ng(\nu)/2\pi\hbar$, where $g(\nu)$ is the lineshape, one can see that the two photon absorption rate is proportional to the product of the photon fluxes and to the number of absorbing centers N. Collecting all the remaining constants into one constant, denoted $\sigma(\omega_1, \omega_2)$, *one can describe the probability by the formula*

$$W^{(2)}(E) = \sigma(\omega_1, \omega_2)N\Phi_1\Phi_2 \quad , \tag{1.4}$$

or, for $\omega_1 = \omega_2$:

$$W^{(2)}(E) = \sigma(\omega)N\Phi^2 \quad . \tag{1.5}$$

The constant σ *is the two-photon absorption cross section.*

Let us assume that an experiment is made by means of two different light sources, one strong at frequency ω_1 and the other weak at frequency ω_2. By dividing the rate $W^{(2)}(E)$ by the photon flux $\Phi = cn_2/\eta_2 V$ at the frequency ω_2 we obtain the absorption constant $\gamma^{(2)}$ induced by the strong beam

$$\gamma^{(2)} = \frac{8\pi^3}{\hbar}\, \rho(E)\, \frac{1}{\eta_2 \eta_1^2}\, \frac{n_1 \hbar\omega_1}{V}\, \frac{\hbar\omega_2}{c}\, \left| A_{31}^{(2)} \right|^2 \quad . \tag{1.6}$$

As (1.6) shows, the absorption constant depends on the intensity of the strong beam.

In a more general case the absorber has N_1 atoms in the ground state and N_3 atoms in the excited state. Now the problem is more complicated since the field reacts with the atoms in several different ways. One can distinguish:

- stimulated transitions from the state 1 to the state 3, which is two-photon absorption;

- stimulated transitions from the state 3 to the state 1, which is two-photon stimulated emission;

- stimulated transitions from the state 3 to a virtual state, followed by a spontaneous transition from the virtual state to state 1;

- spontaneous transition from the state 3 to the virtual state, followed by another spontaneous transition to the state 1, which is two-photon spontaneous emission.

An analysis of all these processes can be easily made using second-order perturbation theory.[4-6] One finds that in the general case the two-photon transition rate for one photon with the frequency ω_1 and the second photon having the complementary frequency is given by the formula:

$$dN_3/dt = -\,\alpha\left[(n_1 + 1)(n_2 + 1)N_3 - n_1 n_2 N_1\right] \tag{1.7}$$

where the rate coefficient α is given by the two-photon amplitude $A_{31}^{(2)}$ as in (1.2) and appropriate constants.

A number of important special cases of expression (1.7) can now be identified. For example, in the case where the radiation field does not exist, i.e., $n_1 = n_2 = 0$, expression (1.7) reduces to

$$dN_3/dt = -\,\alpha N_3 \tag{1.8}$$

and it describes spontaneous two-photon emission.

In the case of strong optical fields at frequencies ω_1 and ω_2, i.e., $n_1 >> 1$ and $n_2 >> 1$, Eq. (1.7) describes stimulated two-photon processes.

$$dN_3/dt = \alpha(N_1 - N_3)n_1n_2 \quad . \tag{1.9}$$

For $N_1 > N_3$ the equation describes two-photon absorption. The case of $N_3 > N_1$ corresponds to two-photon stimulated emission. For $N_3 = 0$ the equation is identical to Eq. (1.1).

In cases where the atoms are in a strong optical field at either frequency ω_1 or ω_2, we have so called enhanced two-photon processes. These processes, where only modes at one of the two frequencies are strongly excited, do not have a single photon equivalent. In such a case $n_1 >> 1$ and $n_2 = 0$ (or $n_2 >> 1$ and $n_1 = 0$). For a normal population $N_3 = 0$ and the field at ω_1 cannot populate the excited state. However if a light from a weak broad band source is transmitted through the sample simultaneously with the strong field at ω_1 one can detect a new absorption line of frequency $\omega_2 = (E_3 - E_1)/\hbar - \omega_1$. In this way a strong field at ω_1, by "populating" virtual states, increases the probability of absorption at the complementary frequency ω_2. One can also detect a new absorption band at $\omega_2 = (E_3-E_1)/\hbar + \omega_1$ due to the Raman effect.

In a similar way when $N_3 > 0$ the strong field at ω_1 acts as a primer for two-photon emission. The decay process can be described by

$$dN_3/dt = -\alpha n_1 N_3 \tag{1.10}$$

and it is proportional to the intensity n_1. In emission one would see the photons at frequency ω_1 propagating coherently with the stimulating field, and the photons at frequency ω_2 behaving like photons emitted spontaneously. As the result of this interaction one would observe gain of the enhancing field and an increase of the n_2 intensity. For the population inversion case where $N_3 > N_1$ a fast increase of both intensities is possible and n_2 can become very large. Such a case was mentioned before as two-photon stimulated emission. For a case without population inversion the decay rate is determined by two competing processes: enhanced two-photon emission for which $dN_3/dt = -\alpha N_3 n_1$, and two-photon absorption for which $dN_3/dt = \alpha (N_1 - N_3) n_1 \cdot n_2$. One can show that there is a limit for intensity n_2 equal to $N_3/(N_1 - N_3)$.

There is a competition between enhanced two-photon emission and the spontaneous anti-Stokes Raman effect (see Fig. 1.1). For the Raman effect the photons at ω_1 would be absorbed and spontaneous emission would be observed at $\omega_2 = (E_3 - E_1)/h + \omega_1$. Since the typical density of energy levels increases for increasing energy, the probability of emitting the spontaneous anti-Stokes Raman line is usually larger than the probability of two-photon emission. Resonant enhancement of the two-photon emission can, of course, change this relationship.

Two quantum absorption was observed experimentally for the first time by Hughes and Grabner in 1950.[7] These authors reported an unpredicted line group in the spectrum of $Rb^{85}F$ molecules studied by an electric resonance method in the radio frequency range. The group was observed at one-half the frequency of one of the line groups of the molecule. A theoretical model of the observed two quantum transitions was also given by Grabner and Hughes.[7] Radiofrequency two quantum transitions were also observed in double resonance experiments in atoms[8,9] and Autler and Townes observed and explained multi-photon effects in rf-microwave double resonance experiments with OCS molecules.[10] A fully quantized field description of Autler-Townes type atomic states "dressed" by an intense radiation field was given in 1963 by Jaynes and Cummings.[11]

The first optical two quantum absorption experiment was performed by Kaiser and Garret in 1961.[12] The authors observed blue fluorescence from a Europium doped CaF_2 crystal irradiated by a red ruby laser beam. The results were in good agreement with a theoretical analysis by Kleinman[13] who estimated the signal strength. Almost simultaneously Franken, et al., observed second harmonic generation in the optical range.[14] These first nonlinear optical experiments started an avalanche of further research. At this time there were no lasers tunable in a broad frequency range so excitation of isolated narrow atomic lines was rather difficult. Most of the experiments were performed on organic materials and doped crystals having broad absorption lines. For this same reason multiphoton ionization was also popular. The first observation of a double quantum transition between narrow atomic levels was reported by Abella in 1962.[15] He observed the $6^2S_{1/2} \rightarrow 9^2D_{3/2}$ transition in Cs vapor excited by a ruby laser. The laser was temperature tuned to the transition frequency and the absorption was detected by observing the $9^2D_{3/2} \rightarrow 6^2P_{3/2}$ fluorescence. Geltman[16] treated theoretically the relatively simple case of negative ion electron detachment, and experimental studies were carried out shortly afterwards by Hall, et al.[17]

For some time multiphoton absorption and optical nonlinear effects such as second harmonic generation were treated as separate subjects. In 1965 Terhune, et al.,[18] treated two-photon absorption using standard nonlinear optics theory. In this case, the Fourier amplitude of the polarisation at an optical frequency can be expressed as the power series expansion

$$P = \chi_1 E + \chi_2 E^2 + \chi_3 E^3 + \ldots \qquad (1.12)$$

and two-photon absorption processes are governed by the imaginary part of the χ_3 susceptibility. It is now common to recognize the close similarities between the theories of nonlinear optics and of multiphoton processes.

Another application of multiphoton processes, in addition to nonlinear optics, was in atomic spectroscopy. It is now well-known that the effect of Doppler broadening on spectral lines can be eliminated in first order, using two-photon absorption. This technique is the basis for so-called Doppler-free multiphoton spectroscopy. The method of two photon Doppler-free spectroscopy was proposed by Vasilenko et al. in 1970[19] and the first experiments were done in 1974.[20,21]

2. Two-Photon Processes

We assume that the energies of all intermediate levels are much greater than the energies of either ω_1 or ω_2 optical photons, and that their total oscillator strength to the initial and to the final state is equal to one.[13] This assumption is equivalent to a situation with a single intermediate state

ω_1 and both dipole elements P_{3n} and P_{n1} equal to $e\sqrt{\hbar/2m\omega_1}$. Taking into account that $\rho(E) = Ng(\nu)/2\pi\hbar$ and assuming $\eta_1 = \eta_2 = \eta$ one can obtain the induced absorption constant given by the formula

$$\gamma^{(2)} = 8\pi^2 g(\nu) N \frac{1}{\eta^2} \frac{e^4}{m^2c^2} \frac{\nu_1\nu_2}{\nu_I^4} \Phi \tag{2.1}$$

where Φ is the photon flux, N is the number of absorbing atoms in the light beam and $g(\nu)$ is the lineshape function.

For a laser generating one joule of light energy in a 30 ns pulse, the photon flux is in the order of 10^{26} phot/cm^{2}s for the beam cross section equal to 1 cm^2. For such a photon flux (corresponding to 300 MW/cm^2 power density) the induced absorption constant is on the order of 0.01 to 1 cm^{-1} depending on the position of the intermediate level ω_1 in respect to the laser and probe frequency and on the concentration of the absorbing atoms. For a lower power density two-photon absorption is rather difficult to detect in a direct absorption measurement since the weak absorption introduces very small relative changes of intensity of the light beam. However, the total number of absorbed photons can still be very large. The absorption event is usually followed by radiative emission at some frequency which is neither ω_1 nor ω_2 and is characteristic of the sample. This fluorescence can be separated by means of suitable filters and can be used as a measure of the absorption. In this case the detecting capabilities are greatly improved.

A similar calculation can be performed in order to estimate the order of magnitude of the two-photon absorption cross-section $\sigma(\omega_1, \omega_2)$. In the first approximation σ is intensity independent and for a typical absorber with all intermediate levels far off resonance σ is on the order of 10^{-48} cm^{4}s.

If a two-photon absorption experiment is performed so that the total absorption is weak and the population of the excited state is low, i.e., $N_3 \ll N_1$, one can use the simple formula (1.5) in order to compute the absorption rate. However, the photon flux changes during the pulse duration and there is an intensity distribution across the laser beam. Assuming validity of the formula (1.5) within a small elementary volumes dV and taking into account that number of atoms dN in dV is equal to $c \cdot dV$ where c is the concentration of the absorbing centers, we can express the total number of absorbed photons in the form

$$n = \sigma c \int I^2 dv dt \quad . \tag{2.2}$$

The integration is performed over volume of the sample and time. For a two-photon absorption cross section $\sigma = 10^{-48}$ $cm^4 s$, the number of absorbing centers in the sample equal to 10^{21}, and the laser beam of 1 cm^2 cross section, the laser power required to obtain 1% absorption is as high as 40 MW. The cross section for two-photon absorption is much larger in the case of intermediate resonances.[22] In such cases one can even saturate the transition at much lower power than computed above.[23]

Even very weak lasers can be used in multiphoton experiments, and two-photon absorption can be detected with very good signal to noise ratio.[24] This is not surprising if one takes into account that the power density at the focus of a high numerical aperature and well corrected lens can reach 100 MW/cm^2 even with a 50 mW laser as light source. The sensitivity of an optimized system for studying two-photon absorption can be very high. Two-photon absorption has been observed[25] at laser power as low as 10 mW, which means that the improvement of sensitivity obtained since the first experiment of Kaiser and Garret[12] was close to 10^{10}.

The presence of a strong optical field at frequency ω_1, according to Eq. (1.7), or in the more general case (1.8), increases the probability of transition at frequency ω_2, where $\omega_1 + \omega_2 = (E_3 - E_1)/\hbar$. Thus in the presence of a strong optical field at ω_1 a new absorption line at ω_2 is created and it can be used to determine the structure and other properties of the E_3 level. This fact was very important before 1970[26] since most of the lasers used at that time lacked tunability. It suggested the following technique, which makes possible the investigation of two-photon absorption over a broad frequency range. For the first time two-photon absorption spectra were investigated without limits caused by the tunability range of the lasers.

Figure 2.1 shows a typical experimental setup. The sample is irradicated by a strong, usually a Q switched, laser beam and by a flashlamp with a broad continuum spectrum. Figure 2.2 shows the experimental signals. Figure 2.2a gives the flashlamp pulse detected by the Ph2 detector without the laser pulse. Figure 2.2b shows the laser pulse detected by the Ph1 detector. If the sample is illuminated simultaneously by the laser and the flashlamp, an intensity decrease of the transmitted flashlamp pulse is observed during the laser pulse as shown in Fig. 2.2c. The decrease is caused by absorption of pairs of photons with one photon from the laser beam and the other one from the flashlamp. By tuning the monochromator and repeating the experiment one can obtain a two-photon absorption spectrum of the sample. Since only the laser field is strong in these experiments the observed absorption is rather weak and the detecting system has to be able to measure very small changes of the flashlamp beam intensity. The laser power required to observe the absorption is as high as 10^8 W/cm^2 and at this power density the two-photon absorption is usually observed together with other nonlinear effects, mainly with long lived absorption due to suspended submicron particles.[27] The last effect is difficult to avoid and it requires very long and careful preparation of the sample in order to remove the small particles. The spectral resolution of the method is limited by the resolution of the monochromator. The method has become much less popular, following the development of broadly tunable lasers.

A pulsed tunable dye laser operating at a high repetition rate, pumped by a nitrogen or an excimer laser, is a much more convenient source for multiphoton spectroscopy. Such a laser, with a pulse energy of about 1 mJ and several nanoseconds pulse duration, can generate in a focused beam a power density which saturates two-photon absorption and is large enough to investigate absorption of more than two photons. The tunability of such a laser makes investigation of a spectrum much easier and the narrow linewidth assures high spectral resolution.

In case the excited state is populated ($N_3 > 0$) one can observe, in the presence of a strong optical field, an enhanced two-photon emission. Enhanced two-photon emission was observed for the first time by Yatsiv, Rokni and Barak in 1968.[28] The authors used ruby laser radiation together with the Stokes shifted component of stimulated Raman emission in nitrobenzene for pumping the 6S level of potassium by simultaneous absorption of photons from the two beams. The enhancing field was generated by stimulated atomic Raman scattering in potassium. The Raman component at 2729 cm^{-1} was generated due to interaction with the $4P_{3/2}$ excited potassium level. The complementary emission frequency ω_2 is only 10 cm^{-1} larger than the $5P_{3/2}4S$ resonance line frequency. For such a small detuning the coefficient in Eq. (1.2) is close to resonance. The observed enhanced emission at $\omega_2 = 24730\ cm^{-1}$ satisfies the equation $\hbar(\omega_1 + \omega_2) = E_{6S} - E_{4S}$.

Similar effects were observed by and Braunlich et al.[29] in Deuterium atoms. The atoms were initially excited to the 2S metastable level. A pulsed Nd-glass laser was used for the stimulation and no intermediate resonances were present. Photons at the complementary frequency were observed and the signal strength was compared with the theory.

Harris[30] proposed the use of enhanced two-photon emission (as well as the spontaneous anti-Stokes Raman effect) for generation of VUV or soft X-ray radiation. The emission would start from a metastable level where some atomic population would be stored. For a tunable laser starting the transition, the enhanced spontaneous radiation at the complementary would be tunable.

In the recent experiment of Zych et al.[31] measurements of the characteristics of such a source were performed. Both enhanced emission and spontaneous anti-Stokes Raman sidebands were observed from 2s1S Helium atoms irradiated by a mode locked Nd:YAG laser. The energy at the metastable Helium level corresponds to 601A and the sidebands were observed at 569A and 637A. The spectral brightness of the laser-induced anti-Stokes radiation was found to be 140 times greater than that of the 584A He resonance line. The 637A enhanced line was found to be about ten times weaker than the anti-Stokes line.

3. Higher than Second-Order Ionization Processes

After the development of the giant pulse ruby laser, dielectric breakdown of air and the creation of plasma in a focused laser beam were commonly observed. Such effects cannot be due to the absorption of only one or two optical photons. These experiments provided the first major stimulus for interest in the theory of multiphoton processes, since multiphoton ionization was one of several possible mechanisms responsible for the breakdown. One of the first theoretical discussions was an attempt to bridge the gap between multiphoton and tunneling approaches to breakdown.

In 1966 Bebb and Gold[32] extended the usual techniques of perturbation theory to the computation of N photon ionization rates of noble gas atoms. The N photon transition probability was obtained in the form

$$W_{f,g}^{(N)} = \alpha I^N | K_{f,g}^{(N)} |^2 \rho(E) \tag{3.1}$$

where α is a constant, I is the light beam intensity, ρ is the atomic density of states and $K_{f,g}$ is the N-th order matrix element.

The main difficulty in calculating the transition probability is the evaluation of the matrix element $K^{(N)}$, which contains many infinite summations over electronic eigenstates, with intermediate state denominators of the form

$$\frac{1}{\omega(a_\nu,a_g) - \nu\omega_L + i\gamma_\nu/2} \tag{3.2}$$

where $\nu < N$ is the intermediate photon number, ω_L is the laser frequency, and $\omega(a_\nu,a_g)$ is the transition frequency between states a_ν and a_g. Bebb and Gold eliminated the sums by defining an average frequency $\bar{\omega}(\nu)$ independent of the atomic states to replace the atomic frequencies $\omega(a_\nu,a_g)$. In this way the matrix element in (3.1) can be written in the form

$$K_{f,g}^{(N)} = \frac{\langle a_f | Z^N | a_g \rangle}{\prod_{\nu=1}^{N} \left(\bar{\omega}(\nu) - \nu\omega_L + i\gamma_\nu/2\right)} \quad . \tag{3.3}$$

The equality is still retained since obviously there is a set of frequencies $\bar{\omega}(\nu)$ such that the two matrix elements are equal. Additional reduction is possible by assuming that there exists a single average frequency $\bar{\omega}$, independent of the order ν. Then the N-th order matrix element is given by

$$K^{(N)}_{f,g} = \frac{\langle a_f | Z^N | a_g \rangle}{\prod_{\nu=1}^{N} (\bar{\omega} - \nu\omega_L + i\gamma/2)} \quad . \tag{3.4}$$

An exact evaluation of $K^{(N)}_{f,g}$ still involves an infinite sum. However the number of matrix elements to compute has been reduced. The authors finally set $\bar{\omega}$ equal to the first excited level frequency and they computed the ionization cross sections of Xe, Kr, Ar, Ne and He for 7, 8, 9, 13 and 14 photon excitation respectively. Since the work of Bebb and Gold many other methods of calculation of the multiphoton cross section have been proposed.[33-36] One can show that the contribution to the cross section decreases for high atomic states. Thus, one can obtain a good approximation with only a modest number of lower-lying states.[37,38]

Theoretical predictions of the dependence of the ionization yield on the intensity of the laser and on its frequency, based on formulas (3.1) and (3.4), are generally in rough agreement with experiment. These formulas invoke sophisticated approximation methods for evaluating various contributions to the total, but they are still all based on the lowest relevant order of perturbation theory (N-th order for N-photon ionization). They all lead to the proportional relationship:

$$W^{(N)} = \sigma_N \, I^N \tag{3.5}$$

where σ_N is a generalized (N-photon) cross section. Examples of the kind of confirmation of perturbation theory that is possible by multiphoton ionization experiments have been given by many authors[39] and have been well-reviewed. A very recent case has been reported by Morellec, et al.[40] Careful measurements of two-photon ionization of cesium were carried out over a range of frequencies around the interference minimum between the 6P and 7P intermediate states. With a laser intensity of approximately 10 GW/cm^2, these experiments confirmed the existence and position of the minimum (see Fig. 3.1), and showed that earlier experiments carried out with lasers 5-6 orders less intense were apparently severely compromised by the contributions of cesium dimers.

Another active area of multiphoton ionization work concerns the spin polarization and angular distribution of the ionized photo-electrons. For example, recently Matthias, et al.[41], have used angular distributions in three-photon ionization of Ba atoms as a probe of configuration mixing in intermediate states. Figure 3.2 shows some of their experimental results. A brief review was given in 1977 by Van der Wiel and Granneman.[42] More recent work has been reported by Leuchs, et al.,[43,44] and by Dixit, et al.,[45,46] and additional references can be found in those papers.

Multiphoton excitation of autoionization resonances has led to a wealth of new information about states above the ionization threshold, particularly even parity states formerly inaccessible by one photon excitation.[47,48] In the same vein, spectroscopic information about elements other than the alkali atoms has been greatly increased by multiphoton methods. Such work was reviewed, for example, by Wynne[49] and by Solarz[50] in 1977.

One of the most evident indications that a multiphoton process deviates from the perturbative predictions of (3.1) and (3.4) is obtained when a plot of $\log W^{(N)}$, as a function of $\log I$, does not have slope N. It has become customary to discuss such situations within the same framework as the "normal" results for which the slope is N, by re-writing Eq. (3.5) as an arbitrary power law equation:

$$W^{(N)} = \sigma_N \, I^k \quad . \tag{3.6}$$

The power law index k equals N in perturbative situations, but is in general a function of the parameters of the multiphoton process.

There are a number of reasons why one might expect, in certain cases, deviations from predictions based on perturbation theory. Among these reasons we can list the following: Initial and final level positions may experience I-dependent shifts; the final level width may depend on I; the nature of an experiment may require I to be treated statistically (quantum effects may be important, the laser pulse intensity may vary from shot to shot, etc.); various laser parameters, such as frequency, pulse shape, and intensity may be significantly time-dependent during a single laser pulse; intermediate q-photon ($q < N$) transitions may be near enough to resonance to permit population to reach intermediate levels; and final-state interactions may alter the nature of the transition. The remainder of this review is devoted to brief discussions of these non-perturbative effects.

4. Laser-Induced Shifts and Widths

The principal effect of off-resonant one photon intermediate states on a two-photon transition is to shift the energies of the initial and final atomic levels. This shift is second order in the laser field strength (linear in the intensity) and is called the ac Stark shift in analogy to the familiar quadratic Stark shift induced by a static electric field. The expression for the ac Stark shift of the initial level is given by (with $\hbar = 1$)

$$\Delta E_1 = s_1 \, I \tag{4.1}$$

where

$$s_1 = -\,2\pi\left(\frac{e^2}{c}\right)\sum_n |\vec{r}_{m1}\cdot\hat{\varepsilon}|^2\left[\frac{1}{\omega_{m1}-\omega_L}+\frac{1}{\omega_{m1}+\omega_L}\right] \tag{4.2}$$

where m indexes the intermediate levels. Also, $\omega_{m1} = (E_m - E_1)/\hbar$ is the unperturbed transition frequency between initial and intermediate levels, and $\vec{r}_{m1}$ is the corresponding dipole transition matrix element. The electric field and the intensity are given by

$$E(t) = \hat{\varepsilon}\,\mathcal{E}\,e^{-i\omega_L t} + \text{c.c.} \tag{4.3a}$$

and

$$I = (c/2\pi)|\mathcal{E}|^2 \quad . \tag{4.3b}$$

If there is one intermediate state much closer to resonance than any other, it will dominate (4.2). This was the case in the two-photon absorption experiments of Liao and Bjorkholm,[51] in which the ac Stark shift was measured.

The ac Stark effect can have a major non-perturbative influence on a given multiphoton transition. For example, due to the ac Stark effect the atomic frequency $\bar{\omega}(a_\nu, a_g)$ in Eq. (3.2) is a function of laser intensity because the ground level (and perhaps others) will experience an ac Stark shift:

$$\omega(a_\nu,a_g;\ I) = \omega(a_\nu,a_g;\ I=0) + s_g I \quad . \tag{4.4}$$

Thus the resonance denominators in σ_N of (3.2) may themselves be sensitive functions of I. This appears to be the explanation for consistent observations of non-perturbative behavior [$k \neq N$ in (3.5)] by the Saclay group over a number of years.[52] We mention here particularly their studies of four-photon ionization of cesium with a three-photon intermediate resonance at the 6F level. In Fig. 4.1 one sees the experimental data for k plotted as a function of detuning from the 6F level. It is dramatically clear that k can be greatly different from its perturbative value if an intermediate resonance is approached. It is also clear that the data approach the perturbative prediction $k \approx 4$ far enough away from resonance.

We note that very simple theories of near-resonance effects the SRA (single rate approximation) theory of Petite, Morellec and Normand,[52] and the ETL (extended two-level) theory of Eberly[53] are able to predict very large positive k values comparable to those shown in Fig. 4.1 simply on the basis of the ac Stark shift of the cesium ground level. In this case the Stark shift is sufficient to alter the on-resonance/off-resonance character of the three photon 6S-6F transition completely, in the neighborhood of resonance. However, both simple theories also predict significant negative values for k which are not shown in Fig. 4.1. This is apparently also the case with much more elaborate theories, such as that of Gontier and Trahin.[54]

Agreement with the data shown in Fig. 4.1 is obtained only by recognizing that the experimental method prevented observation of $k < 0$.[52] Thus it is a task remaining to observe negative k values in such experiments (although, see Fig. 11 in a report of three-photon ionization experiments by Lambropoulos and Moody[55]). Finally it should be emphasized that the ac Stark shift given in (3.1) and (3.2) is itself a perturbative approximate result. In principle one should write

$$E_1 = \sum_{n=1}^{\infty} s_1^{(n)} I^n \quad , \tag{4.5}$$

but systematic methods for calculating the higher order Stark coefficients for

$n > 1$ have been followed carefully in very few cases.[54,56] However, closely related effects that depend on all (infinitely many) powers of I are the subject of Sec. V.

Any process that removes population from an atomic level decreases the effective lifetime of the level. This is well-known, of course, in connection with spontaneous emission. In the same way, stimulated processes can decrease the effective lifetime of excited bound level p if they are irreversible.[56,57] An example occurs frequently in bound-bound transitions excited by a powerful laser. It is almost certain that the laser photons will ionize at least a fraction of the atoms that reach the excited bound state p. In the absence of complications, the ionization of level p is well-described by a single number, the ionization rate (3.5), and it is certainly irreversible. Thus the lifetime of level p can be written

$$\frac{1}{\tau_p} = \sum_{k<p} A_{pk} + \sigma_p I^p \tag{4.6}$$

where A_{pk} is the spontaneous decay rate from level p to level k. Such a contribution to lifetime shortening also appears in the effective linewidth of level p, of course.

Lifetime shortening of this type was probably present in the data of Moody and Lambropoulos.[55] Excitation of the 3S-3P one-photon resonance in sodium vapor, using one of two lasers (say laser A), was followed by two-photon ionization of 3P. This two-photon ionization was arranged to occur through a higher quadrupole intermediate resonant state. It almost certainly also occurred via many off-resonance dipole intermediate states. The quadrupole resonance was arranged with photons from the other laser (laser B). It is interesting that for sufficiently high powers in these experiments the ionization signal decreased with increasing power in laser A. In other words, the multiphoton power law index k took on negative values.

Very simple considerations can easily be sufficient for a qualitative understanding of such findings. In the case mentioned above the ionization from 3P can become rapid enough to shorten the 3P lifetime. The consequent 3P broadening is the same as a decrease in the density of final states in the

3S-3P transition. Thus the first excitation step from 3S to 3P becomes weaker for higher powers. This naturally reduces the production of ions.[55] Detailed discussions of such effects, which amount basically to saturation effects in an intermediate resonance, have been given for different regimes of laser intensity in a number of theoretical treatments of multiphoton ionization.[56-59]

5. Coherent Strong-Field Effects

We emphasized in Sec. IV that the ac Stark shift, proportional to intensity I, is the first order correction in a perturbative series, and we implied that higher order corrections had been calculated only rarely. In fact, calculations to all orders in I have been made and the consequent predictions have, in many cases, been closely verified in experimental work. The point is that one views an atomic transition entirely differently as soon as higher order terms begin to be important. Higher order terms become important when there is significant probability that the optical electron occupies any level other than the initial one, and one becomes immediately interested in all-orders effects rather than in the next one or two higher perturbative corrections. These effects have been reviewed by Knight and Milonni.[1]

In this section we will examine such all-order effects, by considering an explicit solution of Schrödinger's equation that for a two-level atom, i.e., we consider only one level other than the initial one. The probability of transferring the atomic electron into the excited level (level 2) at time t is well-known[60] to be given by:

$$p_2(t) = |\Omega/\Omega'|^2 \sin^2 (\Omega' t/2) \quad . \tag{5.1}$$

As (5.1) indicates and Fig. 5.1 shows, the probability of reaching the excited level oscillates perfectly periodically at the frequency $\Omega' = (\Omega^2 + \Delta^2)$. This oscillation has highest amplitude at exact resonance, when $\Omega' = \Omega$. This is the true significance of Ω as a frequency. Some early optical observations equivalent to (5.1) were made by Gibbs.[61]

The change in point of view mentioned at the start of this section is now evident. We can no longer speak of a transition rate for population transfer from one level to the other, but of an oscillation rate at which the electron shuttles back and forth between the levels. It must not be thought that these rates are simply different ways of expressing the same behavior. They are not. Note, for example that the solution given in (5.1) is perfectly finite at exact resonance, even without introducing level widths.

The appearance here of the Rabi frequency $\Omega = 2e(\vec{r}_{21} \cdot \vec{\varepsilon})\mathcal{E}/\hbar$ as a parameter of significance is partially due to one "oversight" in our present treatment of Schrödinger's equation: we have included no linewidth or density of final states in our formulation of the dynamics. It shoud be clear from this fact alone that Ω and Ω' are fundamentally distinct from transition rates such as (3.4) although dimensionally the same (sec^{-1}), of course.

From our discussion it now appears that the empirical addition of level widths to resonance denominators, such as in (3.4), is unnecessary. The existence of the Rabi frequency appears to eliminate the need to worry about resonance divergences. This is true, although it is far from the whole story. In a recent review Knight and Milonni[1] explore thoroughly the role of Rabi frequency in optical spectroscopy. It is also sometimes useful to recognize that the RWA method demonstrated here has a very important antecedent in the Landau-Zener method.[62]

In summary of the main theoretical point, in an atomic transition for which a finite level width γ is given, a completely satisfactory qualitative rule that takes account of the Rabi frequency can be stated as follows. When $\gamma >> \Omega$, then the transition is characterized by smooth linear growth of population in the final level, and the growth rate is given by the usual Fermi golden rule value for the transition rate. However, when $\Omega >> \gamma$, then the transition is characterized by periodic oscillations of probability from one level to the other, at the oscillation frequency Ω', and not by smooth monotonic population transfer.

For reference, a laser intensity of only several Watts/cm^2 acting on an atomic transition with unit oscillator strength can produce a Rabi frequency in the range 0.1-1 GHz, not much smaller than a typical atomic/optical Doppler width.

The two-level method for dealing with resonance also applies to a multiphoton resonance. There is a well-defined N-photon Rabi frequency[63] for that case. Two photon Rabi oscillations have been observed indirectly by Tan-no, Yokoto and Inaba.[64] Multiple-photon oscillations of population in multi-level atomic and molecular systems have been studied extensively in a wide range of theoretical models,[65] but very little contact with experimental absorption data has been possible.

On the other hand, many experimental observations of strong-field all-orders effects, using pump-probe methods, have been successful. The first observations were perhaps those of Autler and Townes using microwave probes of rf molecular saturation effects.[10] We can also mention the observation of the optical strong-field resonance fluorescence spectrum, first achieved in 1974 by Schuda, Stroud and Hercher.[66]

Strong-field effects can also influence the center of mass motion of an atom, even though the radiative interaction of the atom is with its dipole moment, a strictly internal atomic coordinate. A qualitative explanation is that all of the photons absorbed from the laser by the atom have the same momentum, but a certain fraction of those re-radiated will be scattered incoherently, with all directions of re-radiation equally likely. The difference in net momentum absorbed and emitted in the resonance radiation process gives rise to a drift of the atom as a whole.[67] A related process gives rise to the Kapitza-Dirac effect,[68] which occurs in a standing-wave field. In this effect all absorptions and emissions are stimulated, but some involve photons in the right-moving wave and others involve photons in the left-moving wave. Both kinds of photon give rise to the same internal transition in the atoms, but they obviously impart different momenta. These effects have been advanced as the basis for a variety of applications, including isotope separation, neutral atom traps, and atomic cooling.

In 1978 two sets of experiments[69] demonstrated cooling, and recently Pritchard and collaborators have reported[70] atomic deflection with the signature of Kapitza-Dirac scattering. A variety of other observations of strong-field all-orders interactions related to Rabi oscillations have been reviewed by Knight and Milonni.[1]

6. Light Fluctuation Effects in Multiphoton Processes

According to formula (2.2) the total number of absorbed photons due to two photon absorption can be described as $n = c\sigma_2 \int I^2 dVdt$. In the case of N-photon absorption one can, taking (3.9) into account, describe the number of absorbed photons in a form similar to (2.2):

$$n = c\sigma_N \int I^N dVdt \quad , \qquad (6.1)$$

where c is the concentration of atoms, σ_N is the N-photon cross section, and I is the instantaneous intensity at a given point (r, t) in space and time.

In most cases the spatial and temporal dependence of the light intensity from a pulsed laser is not known because of very rapid temporal and spatial variations. For this reason it is usually convenient to consider the intensity as a statistical quantity and deal with various averages. Space-time integrals such as in (6.1) can be replaced by intensity integrals. We write the space-time average as:

$$(VT)^{-1} \int I^N(r, t) d^3r dt = \int_0^\infty I^N p(I) dI \quad , \qquad (6.2)$$

where $p(I)dI$ is the probability that, at any given (r, t) during the pulse, the intensity lies between I and $I + dI$.

There are important situations where the exact pulse shape $I(t)$ is not possible to determine, but where $p(I)$ can be predicted fairly reliably. For example, a multi-mode laser may have unknown intensity variations on a picosecond time scale; but if enough modes are involved the statistical properties of the light are likely to be close to Gaussian (thermal). In this case one can use[71-73]

$$p_{thm}(I) = (1/\langle I \rangle) e^{-I/\langle I \rangle} \qquad (6.3a)$$

and easily compute

$$\langle I^N \rangle = N! \langle I \rangle^N \quad . \qquad (6.3b)$$

A contrasting situation occurs with single mode cw laser light, which we call purely coherent:

$$p_{coh}(I) = \sigma(I - \langle I \rangle) \tag{6.4a}$$

$$\langle I^N \rangle = (\langle I \rangle)^N \quad . \tag{6.4b}$$

This shows that light with thermal fluctuations is N! times more efficient in N-photon absorption processes than non-fluctuating coherent light.

We have treated the laser field as a statistical but not quantum mechanical object above, and such a treatment is usually satisfactory. Quantum mechanical statistical effects have been reviewed by Loudon[74] and by Walls.[75]

A similar averaging procedure can be carried out for the spatial distribution. Here one would compare plane wave illumination to spatially incoherent illumination. The averaging procedure leads again to an N! factor for a Gaussian speckle pattern and a factor of 1 for a coherent plane wave. In any real case, since both spatial and temporal effects are included in the formula (6.1), both temporal and spatial variations are important. However most laser sources generate TEM_{00} modes with a well-known spatial dependence of intensity and in such a case only temporal effects have to be treated in average terms.

The first discussion of statistical effects was given by Bonch-Bruevich and Khodovoi[76] in 1965. They showed, using a semiclassical approach, that the probability of two-photon absorption depends on a fourth order electric field correlation function. Lambropoulos, et al.,[77] found theoretically that the two-photon absorption rate depends on the statistical properties of the light and the absorption probability for thermal light should be twice that of coherent light. Almost at the same time Teich and Wolga[78] found the same results. The problem was investigated further by Shen[79] and Mollow.[80] Propagation effects and the relation between the laser and the absorber bandwidth were discussed. Agarwal[81] in 1970 computed the influence of the field correlation effects in multiphoton absorption, obtaining the N! factor for N-photon absorption.

The first experimental demonstration of coherence effects in second-order processes was completed by Teich, et al., in 1970.[82] The second harmonic generation efficiency of 10.6 μm single mode CO_2 laser light in a tellurium crystal was measured. The spatial coherence of the beam was changed by a diffuser and agreement with the theory was observed.

In 1974 two experiments were reported[83,84] in which temporal coherence was changed by controlling the number of axial modes in the laser. A single mode laser was assumed to be a coherent source, and a multimode laser was assumed to have independent modes so that its light could be assumed incoherent. Krasinski's experiments[83] used a c.w. excited two-photon absorption and Lecompte's[84] used a pulsed laser and eleven-photon ionization. In both cases agreement with theory was found. Lecompte, et al., reported a particularly strong influence of the statistical properties of the light because of the very large value of 11!

7. Time and Bandwidth Effects

The most obvious effect of laser temporal fluctuations is to give the laser a finite bandwidth.[56] Burshtein[85] and his collaborators were the first to treat strong laser-atom interactions with temporal fluctuations. Burshtein used generalized random telegraph models of phase, frequency, and amplitude fluctuations, and developed a statistical master equation for important atomic variables - inversion, polarization, dipole correlations, etc.

Wide interest in laser fluctuation processes began in 1976-77 with the publications[86] of Agarwal, Eberly, Zoller, Avan and Cohen-Tannoudji, and Kimble and Mandel, in which the Wiener-Levy model of phase fluctuations was widely invoked, mostly for the purpose of studying laser fluctuation effects on two-level-atom strong-field resonance fluorescence where new experimental data was available.[66] More general problems of multiphoton excitation and ionization were considered soon afterward.[87,88]

The simplicity of the Wiener-Levy model is important because, within the model, a class of noise processes can be treated exactly from the dynamical standpoint, without short-time or Fermi Golden Rule approximations. An important consequence of the model, roughly equivalent to the fact that the model implies a Lorentzian bandshape for the laser field, is a set of "substitution rules" first described by Wódkiewicz.[87,88] Wódkiewicz has shown that, *under near-resonance conditions when the effect of slow phase diffusion will* be most pronounced, the single-time density matrix elements referring to level population, inversion, and dipole coherence will behave exactly as they would *in the absence of Wiener-Levy phase diffusion, except that their resonance* relaxation rate $1/T_1$ and $1/T_2$ must be replaced by the new rates $1/T_1$ and $1/T_2+\gamma^{\ell}$. In other words, the Wiener-Levy model of phase diffusion leads to an enhanced "transverse" or off-diagonal relaxation, without affecting the rate of diagonal relaxation. No comparable rule is known for any other relaxation model, and the same rule is known not to apply to multi-time variables (correlations of density matrix elements, for example) even within the Wiener-Levy model.

Georges and Lambropoulos[87] were the first to emphasize that the Lorentzian shape laser spectrum of the Wiener-Levy phase model does not agree with actual laser bandshapes, and to suggest that existing experimental data[89] could be explained by laser fluctuations if the laser band shape were more accurately reflected in the theory. An extended phase fluctuation model exists,[90] in which ϕ is still statistically Gaussian, but the auto-correlation is no longer purely exponential:

$$\langle e^{i\phi(t_1)} e^{-i\phi(t_2)}\rangle = e^{-\gamma^{\ell}[T-(1-e^{-\beta T})/\beta]} \tag{7.1}$$

where $T\equiv|t_1-t_2|$, *and* β *is a new lineshape cutoff parameter. If* $\beta \gg \gamma^{\ell}$, then (7.1) becomes

$$\langle e^{i\phi(t_1)} e^{-i\phi(t_2)}\rangle \sim e^{-\frac{1}{2}\gamma^{\ell}\beta T^2} \quad . \tag{7.2}$$

The Fourier transform of (7.2) is no longer Lorentzian, but Gaussian, implying that the laser bandshape changes to a narrower peak [with width $\sqrt{(\beta\gamma^{\ell})}$ instead of γ^{ℓ}], and the wings of the spectrum are more sharply cut off.

This second phase model is known as the Ornstein-Uhlenbeck model, and was applied by Zoller and Lambropoulos[90] to double-resonance data of Smith, et al.,[89] obtaining reasonable agreement. Predictions of other multiphoton effects such as multiphoton ionization which depend not only on laser linewidth but also on line shape have been made,[115] and other experimental tests have been carried out.[92]

Stochastic temporal fluctuations of laser intensity lead to some of the same effects (finite bandwidth, obviously) as phase and frequency fluctuations. There is, however, no easily tractable mathematical model of intensity fluctuations able to play a role comparable to the Wiener-Levy phase model. The most common assumptions have been either that the electric field amplitude is itself a zero-mean Gaussian white noise process (infinite-bandwidth thermal light), or that the intensity exhibits white noise fluctuations in magnitude about a finite average value.[93]

An entirely different set of considerations arises if the laser light is not stochastic but still time-dependent. Some theoretical studies of the effects of laser pulse shape have been made.[94] The effect on the multiphoton index k can be inferred from Fig. 7.1, taken from Gontier and Trahin.[94] In addition, laser pulse time dependence and its effect on two-photon absorption has been experimentally investigated by Allen and his collaborators[95] for low and high intensities. Agreement with theoretical predictions, including resonant effects, saturation, Stark shifts, spontaneous emission and finite laser bandwidths was found. Some of these are discussed by Allen and Stroud.[1]

8. Dressed Free Electron Interactions

The action of intense radiation fields on atomic and molecular systems is observed in a variety of ways, as we have discussed elsewhere in this review. An important part of the analysis of the measured data is an assumption, often implicit, about the nature of the initial and final states of the atomic and molecular systems. It is obvious that when the radiation field is extremely strong it may not only create observable transitions but also change the character of the system's states. This possibility was first discussed widely in the context of strong-field scattering of free electrons,[96] using the long-known Volkov solutions for the wave function of an electron in a plane-wave radiation field.

In the non-relativistic limit, and ignoring spin, as is usually appropriate for optical frequencies, the Volkov wave function is:

$$\psi(\vec{r}, t) = \exp -i[(p^2/2m)t - \vec{p}\cdot\vec{r} + \phi_p(t)] \quad , \tag{8.1}$$

where the phase function is an integral over the interaction part of the electron Hamiltonian.

The electron wave function $\psi(\vec{r}, t)$ contains all possible harmonics of the radiation field. That is, the electron wave function is "dressed" by the electron's nonlinear interaction with the radiation field.

Keldysh[97] was the first to exploit such state-dressing in multiphoton ionization theory. He considered the final-state ionized electron to be described by Volkov states, thus incorporating (to all orders in perturbation theory) a part of the field-atom interaction into the final state. The atomic transition itself was then treated in first order. The Keldysh theory is an attempt to bridge the gap between the high frequency "multiphoton" regime and the "tunneling" regime of quasi-static incident fields. Keldysh predicted that the ionization rate would exhibit tunneling behavior or multiphoton behavior depending on the size of the parameter:

$$\gamma_k = \hbar\omega / nea_0E \tag{8.2}$$

where ω and E are the frequency and the field strength of the laser, ea_0 is the Bohr dipole moment, and n is the principal quantum number of the ionizing level.

Soon afterward other calculations with different results appeared.[98] A surprising variety of papers followed during the next decade in which the approximations of Keldysh were questioned and alternatives were proposed both to this method and result. Finally in 1979 Brandi and Davidovich[99] began to establish connections among these calculations. They identified different approximations made in applying the method of steepest descents to the final state sum as the origin of the divergence among several of the predictions, and were also able to show that some apparently different predictions were simply gauge transformations of each other.

All of these predictions, however, are extremely difficult to subject to careful experimental test, because they all involve the very small free electron Thomson scattering cross section $d\sigma_T$ in one way or another. The electromagnetic radius of a free electron is too small for effective probing by optical means.

However, an electron in the presence of an external potential, for example one undergoing scattering from an atom or molecule, has a much larger effective structure. In 1973 Kroll and Watson[100] showed that electronic free-free transitions in scattering from atoms in the presence of an intense laser field were governed by the cross section:

$$d\sigma_n = d\sigma_{el}\ \Lambda(p_f,\ p_i)\ J_n{}^2(\mu\vec{K}_n \cdot \vec{\varepsilon}/k) \quad , \tag{8.3}$$

where Λ is a phase space factor, and $d\sigma_{el}$ is the elastic cross section, which is many orders of magnitude larger than $d\sigma_T$, and n is the number of photons participating in the electron scattering.

Weingartshofer and his collaborators have made beautiful measurements[101] of free-free cross sections, and have observed the Bessel function behavior predicted in (8.3) for values of n much different from $n = 0$. Thus they have observed the basic multiphoton "dressing" of the electronic state contained in the phase ϕ_p of (8.1). Figure 8.1 shows the results of Weingartshofer, et al., for electron scattering from Argon.

The verification of the Kroll-Watson dressed cross section obtained by Weingartshofer is obviously complete in many important details, while the dressed transition rates for ionization derived by Keldysh and others have been very resistant to experimental study. Ionization processes can be strongly dominated by the bound-state wave functions involved (except for extremely high laser intensities). This means that any multiphoton dressing of the ionized free electron is a minor effect overall. By contrast, in electron-atom scattering the electron is always free, to a first approximation. Any multiphoton dressing of the electron will have directly observable consequences, as Weingartshofer[101] has shown.

Acknowledgements

The authors acknowledge partial support from the U.S. AFOSR, U.S. ARO-D, U.S. DOE, and U.S. ONR. Part of the work was completed while JK was visiting the Institute of Optics, University of Rochester, and JE was visiting the Physics Department, Imperial College. We are grateful for the hospitality of these institutions. JE acknowledges receipt of an SERC Visiting Fellowship during July and August 1983.

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Figure Captions

Fig. 1.1 (a) Energy levels and frequencies of the radiation field taking part in a two-photon transition, and

(b) same diagram for very closely related Raman effect.

Fig. 2.1 Experimental setup

Fig. 2.2 (a) The flashlamp pulse.

(b) The laser pulse.

(c) The flashlamp pulse with a dip due to two photon absorption. The position of the dip coincides with the position of the laser pulse.

Fig. 3.1 The interference minimum predicted by perturbative calculations of the multiphoton cross section for two photon ionization of Cs with photon energies near to the 6S-7P resonance [from Morellec, et al., Ref. 40].

Fig. 3.2 Angular distributions of multiphoton ionized electrons, [from Matthias, et al., Ref. 41].

Fig. 4.1 Order of nonlinearity K for four-photon ionization of Cs as a function of detuning. The full curve is obtained for constant intensity $I = 10^7$ W/cm^2. The dotted line corresponds to collection of 10^3 ions [from Petite, et al., Ref. 52].

Fig. 5.1 The Rabi solution (5.1), showing the inversion as a function of time, and the effects of detuning. The highest curve shows the inversion of an atom exactly on resonance, and the curve lying only slightly below it is detuned from resonance by 0.2 times the on-resonance Rabi frequency Ω. The next lower pair of curves are for atoms detuned by 1.0 and 1.2 times Ω; and the bottom pair of curves are for atoms detuned by 2.0 and 2.2 times Ω [from Allen and Eberly, Ref. 60].

Fig. 7.1a Illustration of the space-time region of integration, to account for real pulse-shape effects. (Gontier and Trahin, Ref. 94).

Fig. 7.1b Four-photon ionization of Cs. Total ion number calculated within the geometry shown in Fig. 6.1a bove. (Gontier and Trahin, Ref. 94).

Fig. 8.1 Photon "replica" states exhibited in electron scattering data of Weingartshofer, et al.[101]

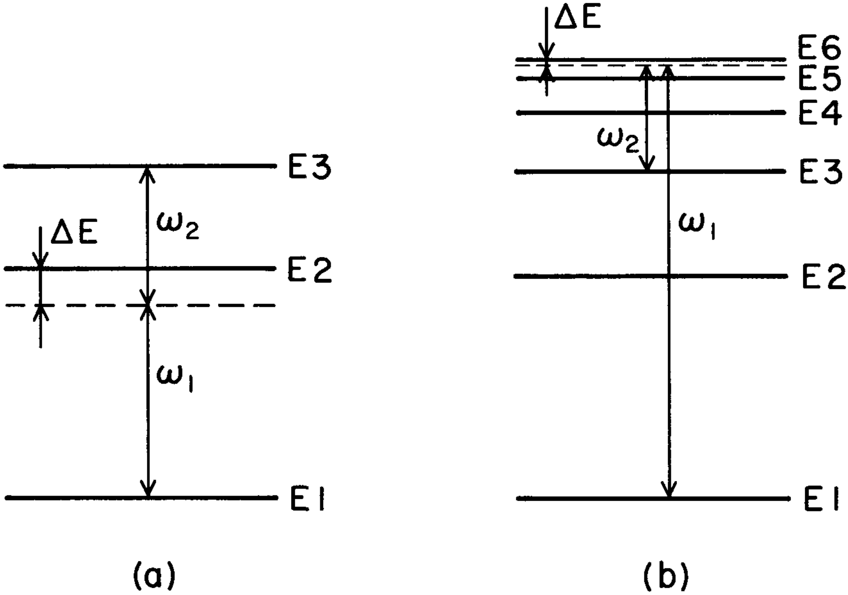


Fig. 1.1

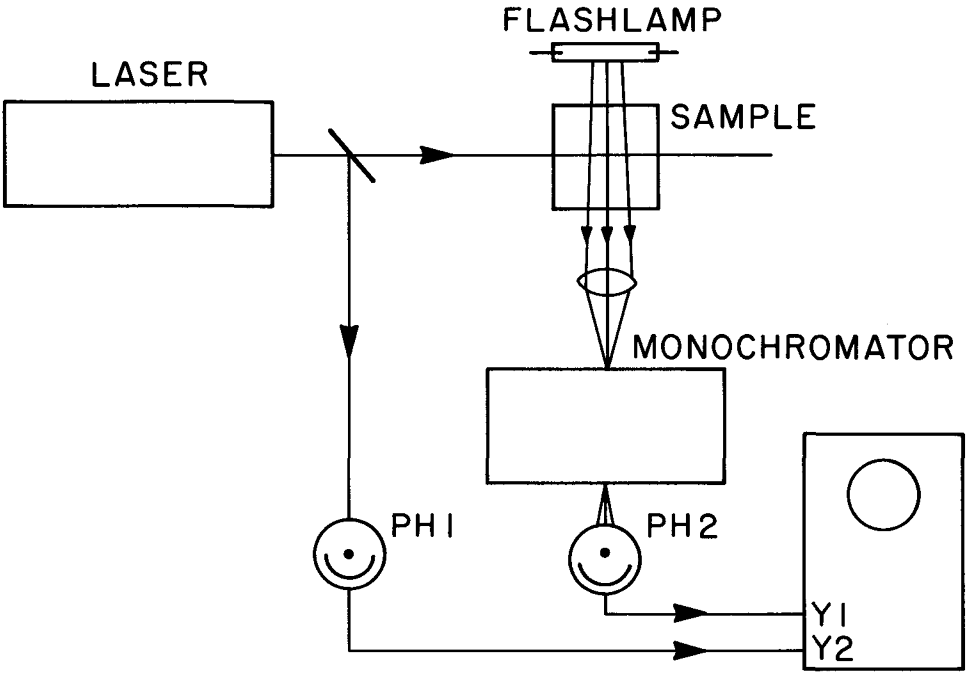


Fig. 2.1

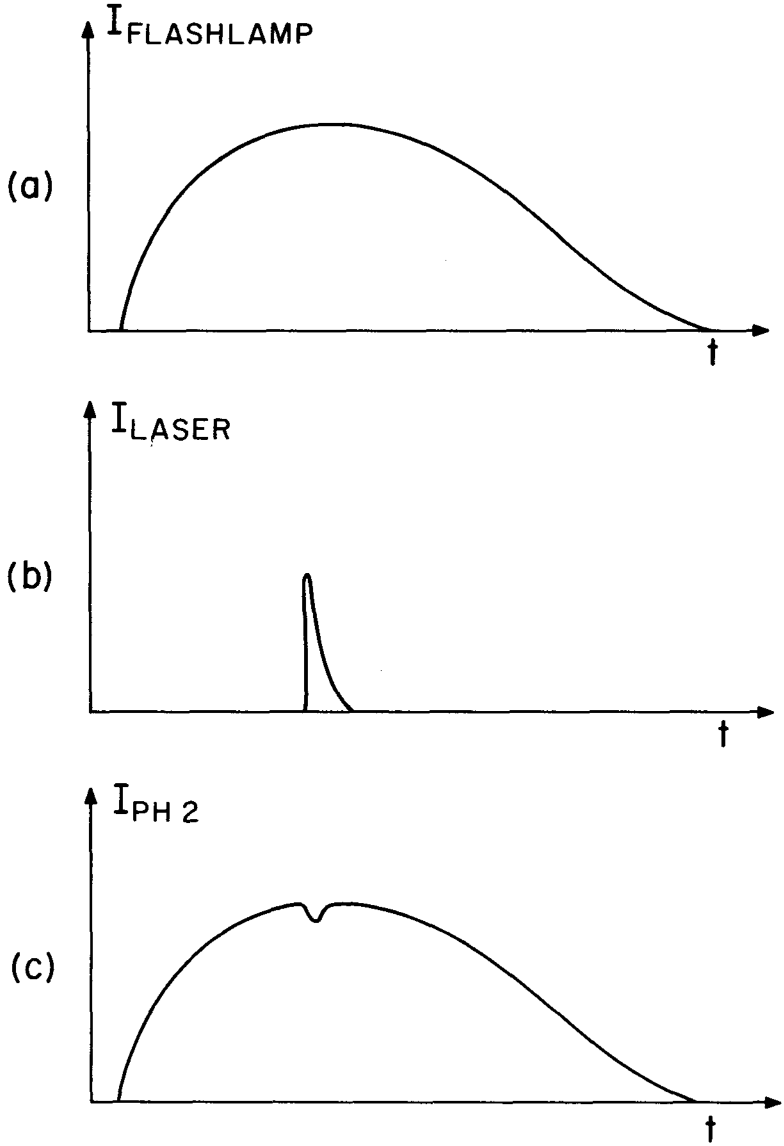


Fig. 2.2

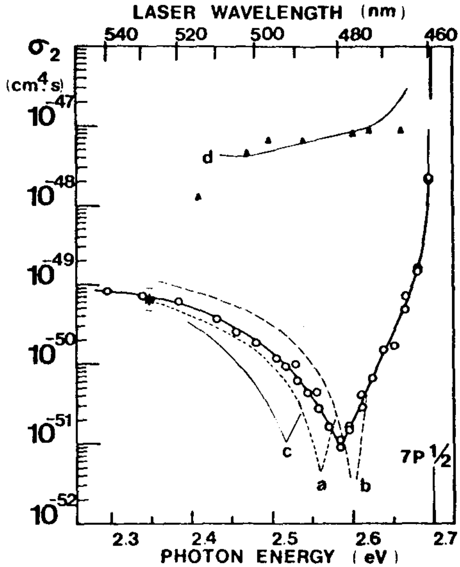

LASER WAVELENGTH (nm)
540
520
500
480
460
σ_2
($cm^4 s$)
10^{-47}
10^{-48}
10^{-49}
10^{-50}
10^{-51}
10^{-52}
d
c
a
b
7P 1/2
2.3
2.4
2.5
2.6
2.7
PHOTON ENERGY (eV)

Fig. 3.1

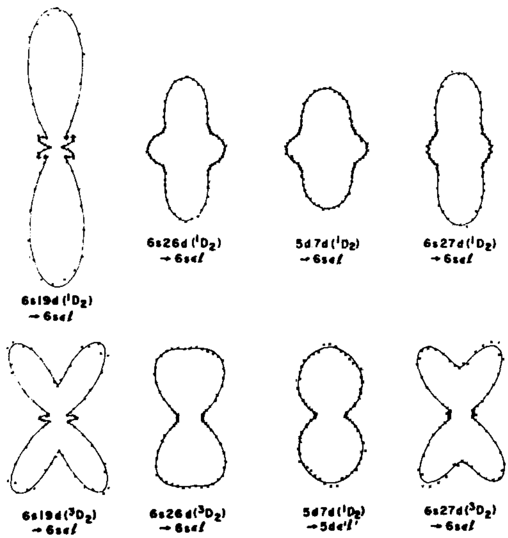

6s19d ($^1D_2$) → 6sεl
6s26d ($^1D_2$) → 6sεl
5d7d ($^1D_2$) → 6sεl
6s27d ($^1D_2$) → 6sεl
6s19d ($^3D_2$) → 6sεl
6s26d ($^3D_2$) → 6sεl
5d7d ($^1D_2$) → 5dε'l'
6s27d ($^3D_2$) → 6sεl

Fig. 3.2

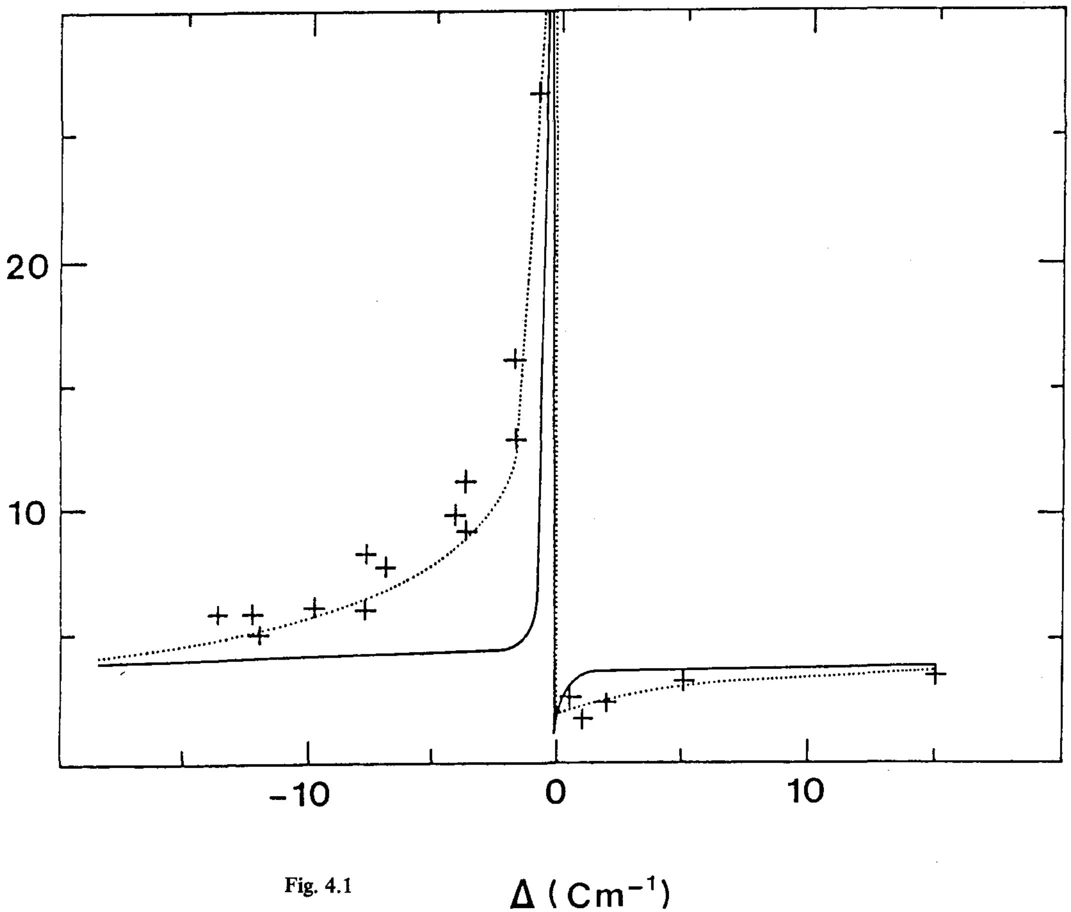


Fig. 4.1

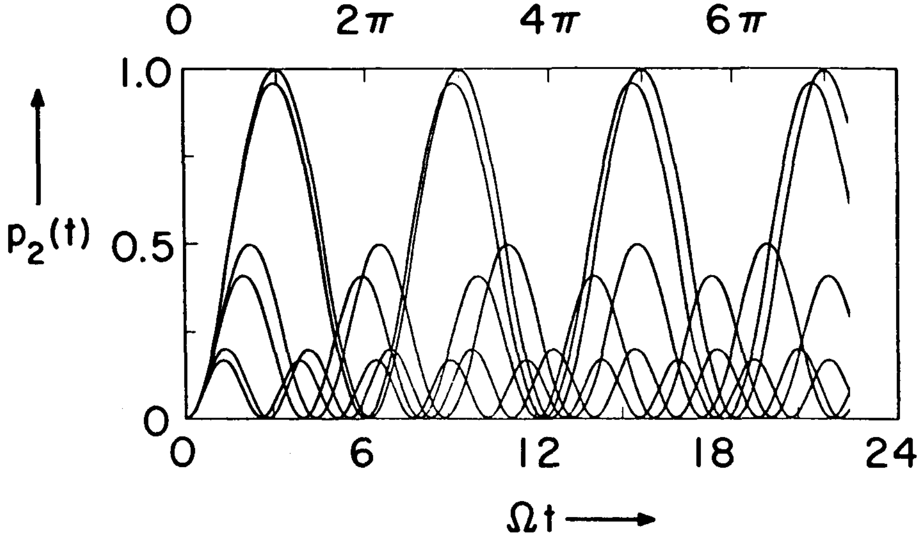


Fig. 5.1

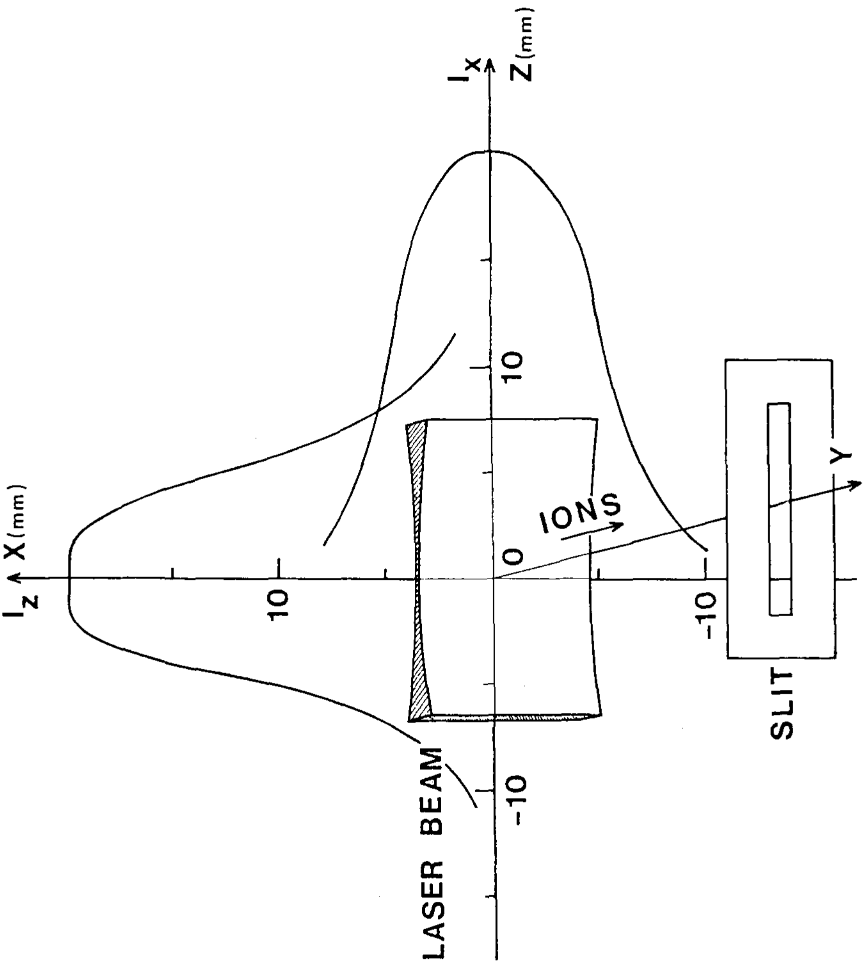
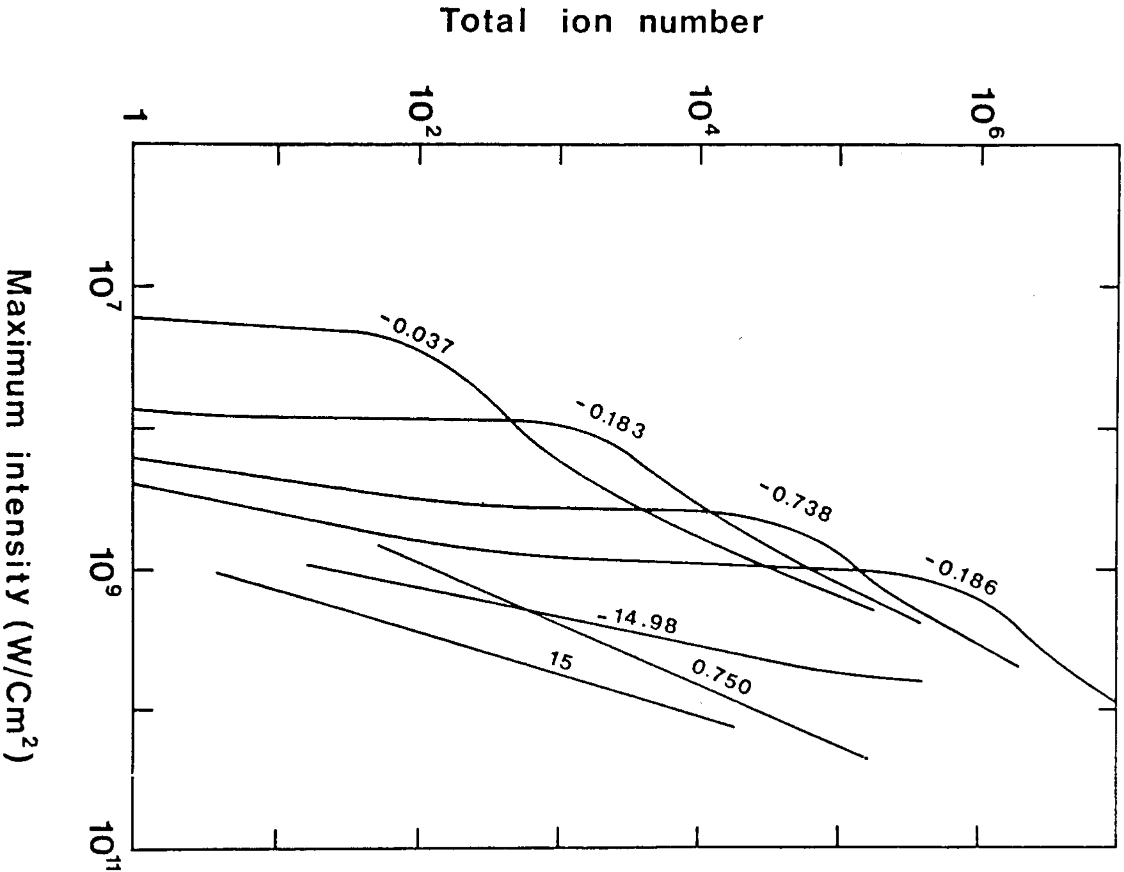
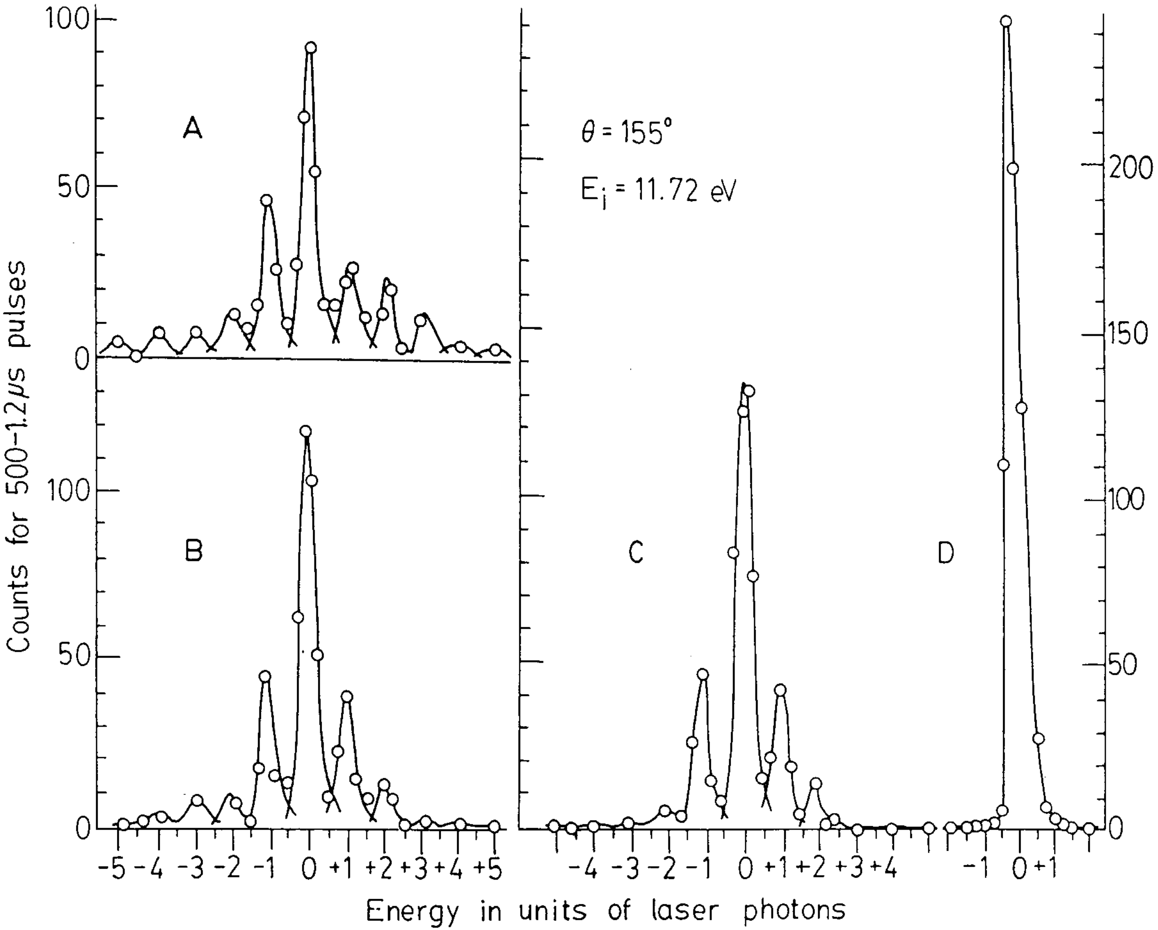


Fig. 7.1(a)



Total ion number
1
10^2
10^4
10^6
Maximum intensity (W/Cm^2)
10^7
10^9
10^11
-0.037
-0.183
-0.738
-0.186
-14.98
15
0.750

Fig. 7.1(b)



A
B
C
D
θ = 155°
E_j = 11.72 eV
Counts for 500–1.2 μs pulses
Energy in units of laser photons

Fig. 8.1