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ATOMS INTERACTING WITH ELECTROMAGNETIC FIELDS. MULTIPHOTON IONIZATION

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Abstract. - The non linear interaction between an intense laser radiation and atoms leads to ionization through the absorption of N photons from the laser radiation via laser-induced virtual states. The multiphoton ionization rate varies as a function of the laser intensity I as $I^N$. We discuss the two most important effects which govern multiphoton ionization processes: resonance effects and laser-coherence effects. In a moderate laser intensity range ($10^7 - 10^9$ W cm$^{-2}$) corresponding to the two, three or four-photon ionization of atoms, resonance effects play a dominant role while the photon statistics of the laser radiation are relatively unimportant. On the contrary, in the very high intensity range ($10^{12} - 10^{13}$ W cm$^{-2}$) required to observe large $N^{th}$-order ionization processes, coherence effects play a dominant role through $N!$ enhancement in the $N$-photon ionization rate, while resonance effects are completely damped due to the high laser intensity. We conclude by reviewing the possible applications of multiphoton absorption processes in other fields.

1. Introduction.

Multiphoton ionization of atoms is a typical example of one of the new fields of investigation in atomic physics that lasers have opened up. It is only over the past five years that considerable progress has been made in this field thanks to advances in sophisticated theoretical treatments, as well as to the possibility of conducting very accurate experiments through a better control of all the parameters of powerful pulsed lasers. As the physics of multiphoton excitation and ionization of atoms is now well understood, it is the right time to present a survey of this mature field.

It is essential to begin with the basic physics involved. Let us consider the ionization of an atom by optical radiation. The well-known photoionization of an atom takes place when the photon energy is higher than or equal the atom's ionization energy. However, an atom with an ionization energy $E_i$ can be ionized by pho-
tons with an energy $\hbar \nu$ much less than $E_i$, if the photon flux is strong enough, which, from a practical point of view, can only be achieved with laser radiation. In this case, the atom has to absorb several photons from the laser radiation in order to be ionized. This can be done using two different methods with two very different intensity ranges.

Figure 1 shows schematically the first method, using as an example the ionization of an atom through the absorption of three photons of different energies $E_1$, $E_2$, and $E_3$. Each absorbed photon matches the energy difference between two atomic states. For the different jumps, each photon has a platform to step on, which enormously facilitates the transition. The lifetime of the intermediate atomic states is typically $10^{-8}$ s. This multi-step ionization process can be performed using dye lasers delivering different laser frequencies $\nu_1$, $\nu_2$, and $\nu_3$, with an intensity of about 1 kW cm$^{-2}$.

The second method designated multiphoton ionization requires a much higher laser intensity, and can be performed with a single laser. Figure 2(a) shows schematically the four-photon ionization of an atom. The vertical arrows indicate the photons absorbed in the four-photon transition from the ground state to the continuum. One of the most essential features of a multiphoton absorption process is that it occurs through laser-induced virtual states which are not eigen states of the atom. In principle, such a multiphoton ionization process does not require any intermediate atomic state. The laser-induced virtual states related to the photon energy and its harmonics act as atomic states, the corresponding lifetimes are however much shorter. We may roughly regard the atom as spending a time $\tau$ in a laser-induced virtual excited state. This time $\tau$ is of the order of one optical cycle, typically $10^{-15}$ s. Consequently, the absorption of photons through laser-induced virtual states must occur within a time $<10^{-15}$ s. Therefore, the photon flux has to be strong enough for there to be a large number of photons within $10^{-15}$ s. We thus understand why multiphoton ionization processes can only be achieved with an intense laser radiation.

We now consider a more realistic situation because the last but one photon is absorbed in the dense part of the atomic energy spectrum. When an atomic state is located not too far from a laser-induced virtual state, the afore mentioned...
time, \( \tau \), can be determined from \( 1/\delta E \), where \( \delta E \) is the energy defect as shown in figure 2(b), i.e. \( \tau = 3 \times 10^{-11} \) s for \( \delta E = 1 \) cm\(^{-1} \). Such a quasi-resonant process requires a lower laser intensity. Furthermore, the resonant multiphoton ionization of an atom, corresponding to \( \delta E = 0 \) leads to very interesting effects which will be considered in detail in section 3.

2. Non resonant multiphoton ionization of atoms.

Non resonant multiphoton ionization of atoms is the subject of one of the chapters of volume 18, the most recent volume of the Avances in Atomic and Molecular Physics series /1/. Consequently, we will only briefly survey this topic.

The \( N \)-photon ionization rate \( W \) is given by \( W = \sigma_N I^N \), where \( \sigma_N \) is the generalized \( N \)-photon ionization cross section. \( W \) is expressed in s\(^{-1} \) units, \( \sigma_N \) is expressed in cm\(^{2N} \) s\(^{-N} \) units and the laser intensity \( I \) in photons cm\(^{-2} \) s\(^{-1} \). Multiphoton ionization cross sections have mainly been measured for alkaline atoms and rare gases with currently available solid-state laser, at a few selected wavelengths, and with laser intensities ranging from \( 10^7 \) W cm\(^{-2} \) (two-photon ionization of alkaline atoms) to \( 10^{15} \) W cm\(^{-2} \) (twenty-two-photon ionization of helium). From 1975 onwards, it has been possible to obtain accurate \( \sigma_N \) values with the availability of lasers which have good spatial and temporal coherence.

Before giving absolute values for the non resonant multiphoton ionization cross sections of different atoms, we will present a very simple argument which leads to an order of magnitude estimate of the \( N \)-photon ionization cross section. Let us consider the simplest case, the two-photon ionization of an atom with a laser frequency \( \omega \) and an intensity \( I /2 \). If an energy-conserving first-order transition were possible, the one-photon transition would take place at a rate \( \omega = \sigma_1 I \), where \( \sigma_1 \), the one-photon absorption cross section, is typically \( 10^{-17} \) cm\(^2 \). A second photon can be absorbed if it is incident within the time \( \tau \) which is of the order of \( \omega^{-1} \), i.e. \( 10^{-15} \) s. Again, the rate of the second event is \( \sigma_1 I \), so that the overall rate for the two-photon ionization will be

\[
W \approx \sigma_1 I \omega^{-1} \sigma_1
\]

Therefore \( \sigma_2 = \frac{W}{\sigma_1} \approx 10^{-49} \) cm\(^4 \) s.

If there is an atomic state not too far from the laser-induced virtual state, we must replace \( \tau = \omega^{-1} \) by \( 1/\delta E \), where \( \delta E \) is the energy defect as shown in fig.2(b).

This estimate might be of interest to some of the readers of this paper, due to the continued interest multiphoton processes have aroused in new fields. Even though the argument leading to this crude estimate should not be taken literally, the numerical value obtained is in good agreement with experimental and theoretical data. For example, the two-photon ionization cross section of cesium atoms at 528 nm has been measured to be \( \sigma_2 = (6.7 \pm 1.9) \times 10^{-50} \) cm\(^4 \) s /3/. It is in very good agreement with different calculations /4-7/ as shown in the following table.

<table>
<thead>
<tr>
<th>Measurement</th>
<th>Calculations</th>
</tr>
</thead>
<tbody>
<tr>
<td>((6.7 \pm 1.9) \times 10^{-50} ) cm(^4 ) s at ( \lambda = 528 ) nm</td>
<td>(9 \times 10^{-50}) cm(^4 ) s</td>
</tr>
<tr>
<td></td>
<td>Crance and Aymar (1980)</td>
</tr>
<tr>
<td></td>
<td>(1.2 \times 10^{-49}) cm(^4 ) s</td>
</tr>
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two-photon ionization cross sections of singlet and triplet metastable helium atoms at 347 nm are respectively $(2.7 \pm 2) \times 10^{-49}$ and $(1.5 \pm 1.4) \times 10^{-49}$ cm$^4$ s$^{-1}$. The agreement between experimental data and calculations is very satisfying.

As far as three-photon ionization processes are concerned, let us return firstly to the simple argument which led to an order of magnitude estimate for $\sigma_2$. The overall rate for the three-photon ionization is:

$$w = \sigma_1 I \sigma_2 I \sigma_3 I$$

Therefore

$$\sigma_3 = \frac{W}{I^3} \approx 5 \times 10^{-81} \text{ cm}^6 \text{ s}^{-2}$$

This estimate is in good agreement with experimental and theoretical data on three-photon ionization cross sections of triplet and singlet metastable helium atoms which are respectively, at 6943.5 nm., $(3.0 \pm 2.2) \times 10^{-81} \text{ cm}^6 \text{ s}^{-2}$ and $(3.3 \pm 1.9) \times 10^{-80} \text{ cm}^6 \text{ s}^{-2}$ /8/. The higher value obtained for singlet states is explained by the fact that the $6^1S$ state is only 40.5 cm$^{-1}$ away from the two-photon resonance.

Two general remarks have to be made. Firstly, the multiphoton ionization cross section is very sensitive to the proximity of a resonance. For example, two of the values for $\sigma_4$ published in the literature for cesium differ by an order of magnitude at almost the same laser wavelength: $\sigma_4 = 7.5 \times 10^{-109} \text{ cm}^8 \text{ s}^3$ at 1056 nm/3/ and $\sigma_4 = 1.0 \times 10^{-107} \text{ cm}^8 \text{ s}^3$ at 1060 nm /9/. These values were obtained on either side of the resonance on the $6^2F$ state at 1059 nm. Secondly, some of the multiphoton ionization cross sections of alkaline atoms published in the literature may be somewhat misleading due to the contribution that dimers make to the atomic ion signal. This is due to the large ionization cross section of dimers relative to atoms. This problem will be considered in detail in section 4, and is especially important in the two-photon ionization of alkaline atoms, and to a lesser extent in three and four-photon ionization. From this point of view, the multiphoton ionization of rare gases at low density avoids the molecular problem completely.

Much experimental work has been undertaken on the non resonant multiphoton ionization of rare gases. However, experimental ionization cross sections can rarely be checked against theory due to the lack of relevant calculations.

In N-photon ionization with large N values (as in the case for rare gases), the N-photon ionization rate W which varies with the laser intensity I, as $I^N$, characterizes much more precisely the non-linear process than the generalized ionization cross section $\sigma_N$ defined as being independent of I. N-photon ionization of rare gases has been investigated in high laser intensity ranges, up to $10^{15}$ W cm$^{-2}$ corresponding to a laser electric field of the order of intraatomic fields. In these ultrastrong laser fields, no departure from the $I^N$ law was observed. For example, accurate measurements in 22-photon ionization of helium with a bandwidth-limited 15 ps laser pulse at 1.06 $\mu$m show a $I^{22} \pm 0.2$ intensity dependence /10/. Such an accuracy is only possible by measuring the spatial distribution of the focused laser intensity /11/. None of the experiments confirmed the tunneling ionization hypothesis /12/ which was believed to dominate over multiphoton ionization in ultrastrong fields.

Emphasis should be given to the fact that N-photon ionization with large N values can be observed by simply increasing the laser intensity. As an example, figure 3 shows that, by using a coherent laser pulse at 1.06 $\mu$m, the 4-photon ionization of cesium occurs at $10^{10}$ W cm$^{-2}$, the 11-photon ionization of xenon at $10^{13}$ W cm$^{-2}$ and the 22-photon ionization of helium at $10^{15}$ W cm$^{-2}$, for the same ionization rate $W = 10^8$ s$^{-1}$.
3. Resonance effects in multiphoton ionization of atoms.

By tuning the laser frequency, the multiphoton ionization rate of atoms can be made to exhibit a typical resonant character when the energy of an integral number of photons approaches the energy of an atomic state. This occurs in the W expression when we sum all the intermediate states with resonance detunings in the denominator. W increases dramatically while retaining a finite value due to damping terms arising from the coupling of the resonant state with the ground state and the continuum.

3.1. Resonance effects in a moderate laser intensity range (10^7-10^9 W cm^-2)

The characteristics of the resonance effects have been extensively investigated in the four-photon ionization of Cs atoms with a Nd-glass laser pulse and the tuning of the frequency through the resonant three-photon transition 6S→6F. This example has been chosen for two reasons. Firstly, calculations can be carried out with a high degree of accuracy for Cs atoms. Secondly, the Nd-glass laser is very well suited to perform this experiment at 1059 nm because it can deliver a coherent pulse and the wavelength can be tuned within the 1052-1065 nm range. It is of interest to use a coherent pulse because resonance effects can be investigated without any mixing with laser coherence effects and laser bandwidth effects so that a direct comparison with theory can easily be made. Furthermore, it should be pointed out that a few years ago coherent pulses from high-power dye lasers were not available.

As we have seen previously, the ionization time of an off-resonance multiphoton ionization process is given by 1/ΔE, i.e., 10^-11 sec for ΔE = 3 cm^-1. Here we are concerned with resonance processes at a laser intensity of 10^8 W cm^-2; the ionization time is much longer and is given by the lifetime of the resonant state induced by the laser field. With our experimental conditions, the 6F resonant state is much more strongly coupled to the continuum than to the ground state. This means that the photoionization rate from the 6F level is much greater than the decay rate to the ground state due to stimulated emission. At the exact resonance, the ionization time τ = 1/(σI), where σ = 1.4x10^-18 cm^2 is the photoionization cross section of the 6F level. τ ≈ 10^-9 sec for I = 10^8 W cm^-2. Thus the resonant multiphoton ionization process requires a laser intensity, roughly 100 times lower than for the off-resonance process, in agreement with the ratio of the aforementioned times (10^-9/10^-11). This point is verified by the results shown in Fig. 4, which shows the laser intensity I required to form 10^4 ions as a function of reso-
Resonance detuning. The full curve is derived from a theoretical calculation /20/ and the experimental points have been obtained using a single-mode laser pulse /14/.

Conversely, if the laser intensity is kept fixed, resonance effects will be expressed as an enhancement in the number of ions at the resonance frequency, as shown in Fig. 5. This result was obtained using a bandwidth-limited 15-psec laser pulse /16/. It clearly demonstrates a shift in the resonance profiles when the laser intensity is increased from $10^8$ to $10^9$ W cm$^{-2}$. As is well known, the exchange of photons between laser radiation and atoms shifts and broadens atomic levels. These effects have been well described within the framework of the dressed atom theory /21/. Atomic level shifts induce a resonance shift as shown in Fig. 5. This resonance shift is linear with respect to the laser intensity $I$, $\Delta = \propto I$ with $\propto = 2$ cm$^{-1}$/GW cm$^{-2}$, in excellent agreement with calculations /20, 23/. As the resonance shift is linear as a function of the laser intensity; this means that a photon is absorbed and reemitted in addition to the four-photon absorption leading to the ionization of the atom.

The importance of atomic level shifts induced by the laser field is also emphasized through the law describing the variation in the number of ions $N_i$ as a function of the laser intensity $I$ very near to the resonance. Let us consider a laser frequency that gives rise to a small static resonance detuning $\Delta E = E_{6F} - E_{6S} - 3E_p$, where $E_p$ is the photon energy. Atomic level shifts bring about a dynamic resonance detuning $\Delta E = \Delta E + \propto I$, which can tune the resonance to be closer or farther away, depending upon whether $\Delta E$ is positive or negative. Consequently, the variation in the number of ions formed will be faster or slower than the simple $I^4$ law. We observed indeed an $I^K$ law. Figure 6 shows the variation of $K = (\log N_i)/(\log I)$ as a function of $\Delta E$. This result has been obtained using a single-mode Nd:glass laser pulse /14/. In this representation, a resonance appears as a sharp phenomenon marked by a dramatic change.
in the nonlinear order $K$, which no longer corresponds to the number of photons absorbed by the atom. For $\Delta E$ values larger than 10 cm$^{-1}$, atomic level shifts become insignificant, compared to $\Delta E$, and the $I^4$ law is again valid and characterizes the off-resonance four-photon ionization process.

It should be pointed out that a very good agreement between theory and experiment is obtained as far as the preceding result (Fig. 6) is concerned, provided all the experimental parameters are brought into the calculations. Let us give an example concerning the laser intensity. $K$ is calculated from $K = (h \Delta \log N_i) / (\delta \log I)$, and the number of ions, $N_i$, is derived from the very simple expression

$$N_i = (a I^4) / \left( (\Delta E + \sigma I)^2 + (\sigma I)^2 \right),$$

Let us consider a fixed laser intensity that is assumed to be homogeneous in the interaction volume. In the vicinity of the resonance, the variation of $K$ exhibits positive and negative values, which are inconsistent with the experimental results shown in Fig. 6. The assumption of a homogeneous laser intensity in the interaction volume is unrealistic, because this ideal condition is never fulfilled in experiments. The experimental spatial distribution function of the laser intensity is Gaussian in most cases, so that the laser intensity $I$ can be written

$$I = I_M \exp \left( -\frac{(r/r_0)^2}{2} \right).$$

When this Gaussian distribution is introduced, negative values of $K$ are no longer observed, which is in good agreement with all experimental results on resonance effects in the multiphoton ionization of atoms.

Such considerations must be extended, because the experimental results shown in Fig. 6 were not obtained at a fixed laser intensity but for a fixed number of ions. By fulfilling this additional requirement, Gontier and Trahin /23/ have calculated the variation of $K$ in the vicinity of the resonance, which is in very good agreement with experimental results.

As far as the width (FWHM) of the resonance profile is concerned. Fig. 5 shows a width of 1 cm$^{-1}$ governed by the broad laser bandwidth (1.4 cm$^{-1}$) of the 1.5 $\times$ 10$^{-11}$ sec pulse. The situation is different when a single-mode laser pulse with a duration of 3 $\times$ 10$^{-8}$ sec and a narrow bandwidth of 20 MHz is used. Figure 7 obtained with such a laser pulse shows four resonance peaks due to a 0.3 cm$^{-1}$ hyperfine structure of the 6S ground state of the Cs atom and to a 0.1 cm$^{-1}$ fine structure of the 6F resonant state /15/. The width of each of the four resonance peaks is 600 MHz, much broader than the 20-MHz laser bandwidth. This is due to both an intensity independent Doppler broadening, which contributes 300 MHz, and an intensity dependent broadening due to the fact that the laser intensity is inhomogeneous in the ionization region. There is a distribution of intensity between zero and a maximum value.

As the resonance shift is linear with respect to the laser intensity, we also have
a large distribution in the shifts, which appears as a broadening in the resonance profiles and contributes 300 MHz for $I = 2 \times 10^7 \, \text{W cm}^{-2}$. This intensity dependent broadening increases when the laser intensity is increased, as shown in Fig. 7, in good agreement with a calculation performed by Gontier and Trahin /17/.

3.2. Temporal effects in resonant multiphoton ionization processes.

Temporal aspects induced by the laser pulse duration play an important role in resonance effects. Figure 8(a) shows schematically the time evolution of the population of the resonant state $n_r$ /10/. Figure 8(b) shows the time evolution of the corresponding multiphoton ionization probability $P$. Both figures exhibit three successive temporal regions. The population of the resonant state $n_r$ increases as $t^2$ in region I, reaches a stationary regime in region II, and decays exponentially to zero in region III. As far as the ionization probability $P$ is concerned, the temporal evolution obeys a $t^3$ law in the first region and a linear law in the second region before reaching an ionic saturation (due to the total ionization of all the atoms) in region III. It should be pointed out that a time-independent ionization rate, i.e., an ionization probability per unit time, can be defined only in the second region.

The separation between regions I and II allows us to define a characteristic time:

$$T = \frac{\sigma I}{(\delta E)^2 + (\sigma I)^2}$$

3.3 Resonance effects in a high laser intensity ($10^{13} \, \text{W cm}^{-2}$)

Resonance effects in the $10^{13} \, \text{W cm}^{-2}$ intensity range can be investigated in the multiphoton ionization of rare gases using a tunable-wavelength coherent Nd:glass laser pulse. We consider the twelve-photon ionization of krypton when a resonance occurs on a 5d or 4d' state with the penultimate photon absorbed. When the laser intensity used is high enough, no significant enhancement in the number of ions $N_i$ is observed, although the resonance effects exhibit a large variation in the effective order of nonlinearity $K = (\delta \log N_i) / (\delta \log I)$ very near to the resonance /10/.

In contrast with the very good agreement between theoretical and experimental results on resonance effects in the four-photon ionization of Cs in the intensity range of $10^7 - 10^9 \, \text{W cm}^{-2}$, the experimental results on resonance effects for the twelve-photon ionization of krypton at $10^{13} \, \text{W cm}^{-2}$ cannot, as yet, be quantitatively explained due to the lack of relevant calculations. The absence of such calculations is mainly due to the lack of atomic data and especially oscillator strengths for rare gases. However, we can give a qualitative explanation in terms of the
A characteristic ionization time $T$ in the close vicinity of the resonance. The photoionization cross section of the resonant state, $\sigma$, is not known with any accuracy for 5d or 4d' states in krypton. It is estimated to be between $10^{-20}$ and $10^{-19}$ cm$^2$. As the resonant multiphoton ionization rate is proportional to $T$, the variation of $T$ as a function of $\delta E$ should give valuable information on the resonance profile. In Fig. 9, $T$ is plotted for $10^{12}$ and $10^{13}$ W cm$^{-2}$, assuming a photoionization cross section $\sigma = 10^{-20}$ cm$^2$. For $I = 10^{13}$ W cm$^{-2}$, no significant enhancement of $T$ is observed, which explains why no significant resonance profile is experimentally observed under the same conditions. This flattening of the resonance profile arises from the dominant contribution of the $(\sigma I)^2$ term due to the high $I$ value over the $(\delta E)^2$ term throughout a very broad resonance detuning. Conversely, if we consider examples with a significant weaker value of laser intensity or a resonant state in which the photoionization cross section is smaller, a resonance profile with a small amplitude might still be observed, as in a previous experiment on the eleven-photon ionization of Xe performed at the Lebedev Institute by Alimov and Delone [24].

In this experiment, a resonance profile was observed with an enhancement of ten at the most. The measurement of such a resonance profile, together with a knowledge of the laser intensity as an absolute value, would allow us to determine with accuracy the photoionization cross section for a given atomic state. Such data are often missing in the literature.

The dramatic change in the effective order of non linearity $K = (\delta \log N_i)/(\delta \log I)$ is also observed very near to a resonance in krypton at $10^{13}$ W cm$^{-2}$, even when the resonance profile is too flat to be measured. The variation of $K$ is explained, as for Cs at $10^8$ W cm$^{-2}$, in terms of atomic level shifts induced by the laser field. However at $10^{13}$ W cm$^{-2}$, calculations would have to take into account not only the linear term $\alpha I$ but also higher-order terms $\beta I^2, \gamma I^3, \ldots$, which are expected to limit shift values.

4. Antiresonance effects in two-photon ionization of Cs atoms.

As is well known, the two-photon ionization cross section $\sigma_2$ at laser frequency $\omega$ is given by second-order perturbation theory.
and it is necessary to sum all the intermediate states $|n\rangle$ of energy $h\nu_n$. Figure 10 shows the variation of the two-photon ionization cross section for Cs atoms, calculated by Bebb /4/, as a function of the photon energy. The variation of $\sigma_2$ exhibits both successive resonance profiles arising from minima in the denominator of the expression for $\sigma_2$, and deep minima due to destructive interference among the terms of the sum. Second-order perturbation theory predicts a first minimum for a 2.6 eV photon energy, i.e. about 480 nm, arising from cancellation of the $6P$ and the other $nP$ states with a main contribution from the $7P$ states.

It was expected that this minimum in the two-photon ionization cross section for Cs atoms would be difficult to investigate experimentally due to the contribution dimers make to the $Cs^+$ signal through processes such as

$$
Cs_2 + 2 h\nu \rightarrow Cs^+ + e
$$

followed by $Cs_2^+ + h\nu \rightarrow Cs^+ + Cs$
together with the two-photon dissociation of $Cs_2$. As the density of resonant states is high, such processes can be enhanced resonantly, especially at laser wavelengths in the 480 nm region where there is a strong $Cs_2$ absorption band: $^1\Sigma_g^- \rightarrow ^1\Sigma_g^+$. Atomic $Cs^+$ ions resulting from these molecular processes are indistinguishable.
Fig. 10 -- from Cs$^+$ ions originating from the two-photon ionization of Cs atoms. The molecular density $n_{Cs^2}$ is much lower than the atomic density $n_{Cs}$, typically $n_{Cs^2} = 5 \times 10^{-4}$. However, the two-photon ionization and dissociation rates for Cs$_2$ are much higher than the two-photon ionization rate for Cs atoms. Consequently, it is necessary to minimize the dimer density. This can be partially achieved through a thermal dissociation in a superheater. The molecular component reduction factor is roughly ten /25/. There is no possibility whatsoever of dissociating all the dimers by this process.

The most important parameter which makes this experiment feasible is the laser intensity. It has been clearly demonstrated in a previous experiment on four-photon ionization of Cs atoms at 1.06 $\mu$m, that the contribution dimers make to the Cs$^+$ signal plays a dominant role with laser intensities less than $10^7$ W cm$^{-2}$ /26/. It is therefore necessary to use a high intensity in the $10^9$ - $10^{10}$ W cm$^{-2}$ range. The problem can be solved by taking advantage of the different intensity dependencies of the number of atomic Cs ions produced by the two-photon ionization of Cs atoms that obey a $I^2$ law, and the number of atomic Cs ions originating from the different molecular channels that become saturated at high laser intensity and obey an $I^K$ law, with $K < 1$. The contribution dimers make to the Cs$^+$ signal therefore dominates completely in the low laser intensity range, while the Cs$^+$ signal originating from the two-photon ionization of Cs atoms dominates the dimer contribution when the laser intensity is higher than $10^9$ W cm$^{-2}$.

The two-photon ionization cross section of atomic cesium was measured in the 460-540 nm range in an experiment that fulfills the following two requirements: a laser intensity of $10^{10}$ W cm$^{-2}$, and a partial thermal dissociation of dimers in a superheater /25/. Figure 11 shows that $\sigma_2$ exhibits a deep minimum, as predicted by second-order perturbation theory. This result has two important consequences:

- Firstly, it confirms the validity of second-order perturbation theory, and clarifies a puzzling situation which arose from a previous experiment in which there was no minimum in the two-photon ionization cross section of cesium and in which ionization cross section values up to four orders of magnitude higher than theoretical values occurred /27, 28/. This result can be explained because the experiment was performed in a very low intensity range ($10^4$ - $10^5$ W cm$^{-2}$) where the
contribution dimers make to the Cs+ signal dominates completely the Cs+ signal originating from the two-photon ionization of Cs atoms. However, this result brought about a confused situation /29/ and even led some theoretical physicists to question the validity of perturbation theory. Finally, the observation of the minimum, in the two-photon ionization cross section of Cs atoms shown in Fig.11, as well as in the three-photon ionization of K atoms /30/ makes the situation clear and confirms once and for all the validity of perturbation theory.

Secondly, the accuracy of the results shown in Fig.11 allows very profitable comparisons to be made with several calculations using second-order perturbation theory. It should be pointed out that in the close vicinity of a resonance with an intermediate state, the two-photon ionization cross section is determined from only a few matrix elements. For example, in the resonant two-photon ionization of Cs atoms on the 7P state, it has been shown that the single intermediate 7P state approximation yields results within a factor of 2 of the completely converged summations over several hundred wavenumbers on either side of the resonance /31/. At, or very near to a minimum, the two-photon ionization cross section is determined from a large number of matrix elements, as a large number of terms manifest cancellation producing the minimum. The exact position and depth of the minimum can only be determined by an exact infinite summation of terms with exact matrix elements. All the calculations published in the literature predict a minimum in the two-photon ionization cross section of Cs atoms, but they disagree on the position and the depth of the minimum. Therefore, the experimental result can be a very sensitive test of the accuracy of the different calculation models. The comparison of the experimental results (dotted line) with calculations /5, 31-33/, is shown in Fig. 12. This figure demonstrates that the model potential theory (curve C /5/ and D /33/ in full line) gives much more accurate results than the quantum defect theory (curve A /31/ and B /32/ in dashed line). This is because the first P levels give the main contribution to \( \sigma_2 \) at the minimum, while the quantum defect method gives matrix elements of poor accuracy for the first P levels. Furthermore, a good agreement between experimental result and the model potential theory is obtained by taking into account the continuum contribution.

5. Laser temporal coherence effects

5.1. - Coherence effects in non resonant multiphoton ionization
Multiphoton ionization of atoms is an inherently non-linear process and as such depends not simply on the laser intensity but also on its coherence properties. Many multiphoton ionization experiments reported in the literature have been performed with incoherent laser pulses generated by multimode Q-switched lasers which had spectral bandwidths of about 1 cm⁻¹ and strong temporal fluctuations. The duration of these peak intensities is given by 1/\(b\) where \(b\) is the spectral bandwidth of the laser pulse, i.e. 30 ps for \(b = 1\) cm⁻¹. As was shown in the introduction, the characteristic ionization time of non-resonant multiphoton ionization of atoms can be as short as \(10^{-15}\) s. As a result, atoms "see" the fluctuations in the "arrival" of photons and respond not only to the average number of photons per unit time but also to the way this number fluctuates. Photons arrive bunched in an incoherent laser pulse Fig. 13(a), while they arrive in single file in a coherent laser pulse as shown in Figure 13(b). This is referred to as the effect of correlations or photon statistics.

The study of the effects of intensity fluctuations or photon statistics began as early as 1964 in non-linear optical processes /34/ and 1966 on two-photon absorption /35/. Specific calculations on coherence effects in multiphoton ionization have been performed later /36, 37/. The fundamental result of these calculations is that the rate of non-resonant \(N\)-photon ionization with chaotic light is larger by a factor \(N!\) than with purely coherent light.

Let us describe the temporal fluctuations of a laser pulse used for multiphoton ionization experiments. The instantaneous laser intensity seen by atoms can be expressed in the form:

\[
I(t) = \overline{I_M} \cdot G(t) \cdot i(t)
\]
where $\overline{I}$ is the maximum time-averaged intensity. $G(t)$ is the normalized temporal distribution function envelope of the laser intensity, its duration is about $10^{-8}$ sec for a Q-switched laser pulse. $i(t)$ is a periodic function, which will play a very fundamental role in this study. It has a stochastic pattern which depends on the number of modes and on both relative phases and amplitudes of modes. We generally measure only the time-averaged intensity

$$\overline{I}(t) = \overline{I}_M \cdot G(t)$$

without taking into account peak intensity function $i(t)$. Whereas multiphoton ionization of atoms is a highly non linear process which is very sensitive to peak intensity function since the $N$-photon ionization rate is proportional to the $N^{th}$ power of the instantaneous intensity, $i(t)$ shall be called the peak intensity function.

Let us define the $N^{th}$ order time-independent peak intensity moment, by

$$f_N = \langle I^N \rangle$$

where the bracket stands for the ensemble average. $f_N$ which readily characterizes the statistics of the laser pulse can be easily related with multiphoton ionization. The number of ions induced by a multimode laser pulse is:

$$N_m = \beta \int \overline{I}^N(t)dt = \beta \int I^N(t) \cdot i^N(t)dt$$

The number of ions induced by a single-mode laser pulse having the same average intensity is:

$$N_1 = \beta \int \overline{I}^N(t)dt = \beta \int I^N(t)dt$$

Hence,

$$\langle \frac{N_m}{N_1} \rangle = \langle \frac{\overline{I}^N}{\overline{I}^N} \rangle = f_N$$

Thus $f_N$ may be related to multiphoton ionization very simply. It is the enhancement of the ion signal due to the multimode operation of the laser. Let us mention that two other moments have been considered in the literature $g_N$ and $b_N /37/.

$$g_N = \frac{\langle I^N \rangle}{\langle I \rangle^N}$$

$$b_N = \frac{\langle I^N \rangle}{\langle I \rangle^N}$$

![Fig.13 multimode laser pulse](image1)

![Fig.14 single mode laser pulse](image2)
The theoretical predictions of a $N!$ enhancement in the non resonant $N$-photon ionization rate have been experimentally corroborated. For example, Figure 14 shows that the non resonant four-photon ionization rate of Cs atoms induced by an incoherent 3GHz bandwidth laser pulse is enhanced by $4!$ compared to the rate induced by a single-mode laser pulse of the same average intensity /38/. Likewise, the non resonant five-photon ionization rate of Na atoms with an incoherent laser pulse is more efficient by a factor $5!$ than that encountered with a single-mode laser pulse of the same average intensity /39/.

The most dramatic experimental demonstration of these effects has been performed in the 11-photon ionization of xenon atoms by varying the mode-structure of a Nd-glass laser pulse from a single-mode to about one hundred modes /40/. Figure 15 shows, in solid line, the enhancement of the number of ions, i.e. the experimental value of the $f_{11}$ moment when the number of modes is increased from one to one hundred for the same average laser intensity. The number of ions is enhanced by nearly $10^7$ when the number of modes is increased from one (coherence time 40 ns) to one hundred (coherence time 8 ps). As a comparison, this figure also shows in dashed line, the $f_{11}$ moment calculated in assuming that phases of the modes are independent. The difference between the experimental and the calculated $f_{11}$ moment mainly comes from the fact that the laser spectrum consisted of several bands with ten modes in each band. Therefore, the statistical properties of this laser radiation could be different from that used in calculating the $f_{11}$ moment assuming that phases of the modes are independent. As shown in figure 15, experimental and calculated $f_{11}$ values tend towards each other and are expected to become identical at an asymptotic value $11!$ for a very large number of modes.

As a conclusion, the off-resonant $N$-photon ionization rate can be written as

$$w = \sigma_N f_N I^N$$

The $N^{th}$ order peak intensity moment, or $N^{th}$ order autocorrelation function, $f_N$, is equal to unity for a single-
mode laser pulse, or a bandwidth-limited pulse that is, a pulse completely devoid of intensity modulation. In the limit of an infinite number of independent modes, \( f_N \) equals \( N! \). \( f_N \) depends both on the laser spectral bandwidth and on the order \( N \) of the non-linear process. It is a small correction factor (\( \ll 2 \)) for a two-photon process, while it has a dramatic effect in high order non-linear processes such as multiphoton ionization of rare gases. This effect can give, in many cases, the key to the explanation of discrepancies between \( \sigma_N \) calculated in assuming coherent laser radiation and \( \sigma_N \) measured with incoherent laser pulses. Conversely, multiphoton ionization processes allow us to consider an atom irradiated by a laser pulse, as an ideal photon detector concerning the statistical properties of the laser pulse. The determination of the \( N \)th order autocorrelation function of the laser peak intensity is of special interest to fully characterize a laser radiation.

5.2. Coherence effects in resonant multiphoton ionization

The characteristic ionization time in non-resonant multiphoton ionization of atoms can be as short as \( 10^{-15} \) s. As a result, atoms "see" the fluctuations in the laser intensity and are very sensitive to the statistical properties of laser radiation. In resonant multiphoton ionization of alkaline atoms in moderate laser intensity range (\( 10^7 - 10^9 \) W cm\(^{-2} \)) instead, the characteristic ionization time can be as long as \( 10^{-9} \) s. Consequently the statistical properties of laser radiation are not expected to enhance dramatically the resonant multiphoton ionization rate. However, the resonance shift due to laser-induced atomic level shifts, is linear as a function of the laser intensity and can be significantly enhanced by laser intensity fluctuations of an incoherent laser pulse. In addition, the laser bandwidth begins to play a role as soon as it becomes comparable to the resonance detuning. Therefore, laser-temporal coherence effects cannot be investigated independently of laser bandwidth effects in resonant multiphoton ionization.

In the past few years, a number of authors have investigated this problem theoretically /41-43/. It is only very recently that specific calculations have been performed /44-46/. Recently, laser coherence effects and bandwidth effects have been investigated experimentally in four-photon ionization of Cs, with a three-photon resonance on the 6F level /38/. The sophisticated laser used in this experiment allows to change both wavelength and temporal coherence by varying the number of longitudinal modes. Increasing the number of modes leads to stronger intensity fluctuations and a larger bandwidth. The resonance curves obtained with incoherent laser pulses are observed to be shifted and broadened with regard to those induced by coherent pulses with the same average intensity. The statistical enhancement of the resonance shift is shown directly in figure 16. This figure gives two resonance profiles obtained at the same laser intensity \( I = 5.6 \times 10^7 \) W cm\(^{-2} \), with a coherent pulse fig. 16(a) and an incoherent pulse fig. 16(b) which has a bandwidth \( b = 0.1 \) cm\(^{-1} \). In the resonance
profile obtained with the multimode laser pulse, the 6F fine structure is not resolved because the laser bandwidth is larger. The important result of this figure is the additional shift induced by the incoherent laser pulse.

This additional shift is 0.2 cm\(^{-1}\) expressed in terms of the energy of the three-photon transition 6S \rightarrow 6F. The statistical enhancement of the resonance shift is clearly demonstrated in figure 17 which shows the two laws of variation of the resonance shift as a function of the laser intensity, with a coherent pulse (dashed line) and an incoherent laser pulse (full line). The difference between the two lines gives the additional shift due to the laser intensity fluctuations, i.e. (3.6 ± 0.3) cm\(^{-1}\)/GW cm\(^{-2}\). This experimental result is in excellent agreement with a previous calculation /44/. Figure 17 shows that the resonance shift induced with an incoherent laser pulse is enhanced by a factor 2.8 ± 0.2 compared with the shift induced with a coherent pulse. As shown in a recent calculation /47/, it is remarkable that two laser modes of equal intensity already account for half of the enhancement of the shift obtained in a chaotic field.

The width of the resonance profiles induced by multimode laser pulses depends on the laser bandwidth, the intensity-dependent broadening and statistical broadening. Figure 18 shows the variation of the resonance widths as a function of the laser intensity, for single-mode laser pulses (a) and multimode laser pulses with bandwidths 3 \times 10^{-2} cm\(^{-1}\) (b), 8 \times 10^{-2} cm\(^{-1}\) (c) and 0.15 cm\(^{-1}\) (d). At low intensities, the resonance width is governed by the laser bandwidth while at high intensities it depends on statistical broadening. These results are in good agreement with calculations.
6. Conclusion and future prospects

The different aspects of the multiphoton ionization of atoms are now well understood, and many of them can be correctly described by rigorous theoretical models. For example, accurate measurements of absolute values of the two, three and four-photon ionization cross sections of alkaline atoms and metastable helium atoms are in good agreement with calculated values, and clearly emphasize the validity of perturbation theory. In the same way, there is also a good agreement between theoretical and experimental results on resonance effects in multiphoton ionization of cesium atoms in the moderate laser intensity range, $10^7 - 10^9 \text{ W cm}^{-2}$. Resonance effects emphasize the important role played by laser-induced atomic level shifts. Destructive interference effects, which give rise to minima in the multiphoton ionization cross sections of atoms, have been investigated with a high degree of accuracy in the two-photon ionization of Cs atoms. This effect has been successfully used to check the validity of different calculation models. Lastly, laser temporal-coherence effects increase the non resonant N-photon ionization rate by $N!$, in good agreement with theoretical calculations. Combined coherence and resonance effects yield a significant enhancement in both the laser-induced resonance shift and resonance width.

It should be pointed out that the relative influences of resonance effects and coherence effects vary with the number N of photons involved in the ionization process and consequently with the required laser intensity. In the moderate laser intensity range corresponding to two or three-photon ionization of atoms, resonance effects play a dominant role, while photon statistics of the laser radiation are relatively unimportant (they contribute a factor of two at the most in a non resonant two-photon process). On the contrary, in the very high intensity range required to observe large Nth-order ionization processes, coherence effects play a dramatic role through the $N!$ effect, while resonance effects are so highly damped as a result of the high laser intensity, that resonance profiles are no longer observed.

Now we have a synthetic understanding of multiphoton absorption processes in atoms, it would be of interest to extend it to new fields where multiphoton processes can play a role. Different topics can be considered.

- Molecular spectroscopy can now benefit considerably from multiphoton ionization processes. New states can be reached and identified, especially through the optical double resonance multiphoton ionization spectroscopy of molecules. This technique allows a significant simplification of the spectrum produced by allowing a tunable-wavelength laser to bring the molecule to a resonant intermediate state through a two or three-photon excitation process, with a second laser to provide the ionization step.

Furthermore, multiphoton processes in molecules leading to excitation, ionization or dissociation have been the subject of a great deal of experimental and theoretical work but are far from being satisfactorily understood. It is still quite an open field.

- Competition between resonant multiphoton ionization of atoms or molecules and ultraviolet odd-harmonic generation at high pressure is a new promising field. Recent experiments have shown that resonant multiphoton ionization of atoms or molecules vanishes to the benefit of a vacuum ultraviolet third-harmonic generation when the atomic or molecular pressure is above approximately 1 Torr [48]. This topic is of interest for two reasons. Firstly, from a basic point of view, it leads to an understanding of the cooperative effects involved, together with the possible optical bistability occurring in these collective atomic or molecular systems. On the other hand, such effects could lead to the production of promising sources of coherent vacuum ultraviolet light for the vacuum ultraviolet spectroscopy of molecules.

- In the lowest order perturbation theory, an atom is ionized by absorbing N photons. However, it can also be ionized through the absorption of $N+1, N+2...$ photons of the same energy. Such processes are present in every multiphoton ionization, but
being of a higher order, they require higher laser intensities to be observed. The absorption of one additional photon was observed for the first time in an experiment on six-photon ionization of xenon, by measuring the energy spectrum of electrons produced in the ionization /49/. More recently, two experiments on 11-photon ionization of xenon exhibited absorption which exceeded the minimum number eleven by seven photons /50/ and ten photons /51/. The electron energy spectrum consists of series of peaks evenly spaced in photon energy. These experiments showed that ionization must be described in terms of competing N-photon, N+1-photon, N+2-photon... transitions from the ground state of atoms up to different final states above the first ionization limit.

- The formation of doubly charged ions has been observed in the multiphoton ionization of alkaline-earth atoms at 10^{10} W cm^{-2}. Possible resonances on two-electron bound states or on autoionizing states could explain the creation of doubly charged ions /52/.

- The production of multiply charged ions formed by multiphoton absorption in rare gas atoms is a recently innovated topic. Up to quadruply charged ions can be observed with krypton atoms irradiated with a very high laser intensity. Multiply charged ions appear to be formed through direct multiphoton absorption from the atom's ground state. This leads to the challenge of calculating multiphoton ionization rates for many-electron atoms. This quite new topic could lead to interesting new developments. For example, advantage could be taken of the well known radiative properties of these ions to generate extreme ultraviolet radiation.

- Finally, multiphoton free-free transitions have been detected in the scattering of electrons on atoms or molecules, in the presence of a strong CO laser field /53/. These processes involve inverse Bremsstrahlung, as well as Bremsstrahlung, i.e. absorption or emission of several photons by free electrons in the field of an atom.

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