SEARCH FOR THE "DIRECT" CHANNEL IN MULTIPHOTON DOUBLE
IONIZATION OF MAGNESIUM WITH FEMTOSECOND PULSES

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INTRODUCTION

The removal of several electrons by multiphoton absorption from the outer shell of an atom is quite easy to observe with the currently available short pulse lasers. For instance, the outer shell of xenon atoms can be completely stripped out at 10^{16} Wcm^{-2}. After the absorption of the first few photons in the discrete part of the spectrum, the atom can be (say) doubly ionized, in principle, through two quantum paths: either all the intermediate states of the multiphoton transitions are single-electron states (in this case, the electron correlations reflect only weakly in the process, and this results in the formation of the singly-charged ion in its ground state which, in turn can be ionized through only single-electron states etc...), or the multiphoton transition goes mostly through doubly-excited states up to the double ionization threshold (and is therefore more sensitive to electron correlations[1]). In the literature the first case is usually referred to as "sequential" and the second one "direct". In the perturbation picture these names are clearly improper since, strictly speaking, multiphoton absorption is always a sequential process, only one photon being absorbed at each interaction. The more appropriate names of "correlated" and "uncorrelated" have been proposed.

The probability amplitude of a real multiphoton multiple ionization is the sum of the amplitudes over the two paths and all the open channels will contribute with various branching ratios. Historically, the so-called "direct" process was at first thought to be responsible for most of the multiply charged ions. The reason was double: on the one hand, experimentally, the double (and later on) multiple ionization appeared much easier than could be predicted on the basis of single-electron, non-resonant transitions alone[2]. On the other hand, the "slopes", i.e. the power laws followed by the rates were much smaller than predicted on the same basis. It was subsequently realized that many other explanations of this unexpected behaviour could be offered: first of all, Lambropoulos[3] showed, within the framework of standard perturbation theory, that the saturation intensities of n-photon processes were rapidly increasing and then reaching an asymptotic value as a function of n (typically for n>10). The immediate implication was that a process of order say 20 would appear (and saturate) at approximately the same intensity as a process of order 10. A corollary implication was that during the rise time of a real laser pulse, the low-order processes leading to the production of the

first charge states would saturate first, thus enormously reducing the possibilities of "correlated" processes. This argument mostly applied to the multiple ionization of rare gases. Second, several experiments revealed the influence of ionic resonances in the case of alkaline-earth atoms that both increased the ionization rates and lowered the slopes thus removing most of the mysteries from the available data. For instance, in an alkaline earth atom, the absorption of the first few photons normally results in the excitation of only one of the outer electrons. Even though, for a suitably chosen wavelength, a multiphoton resonance through a doubly excited state may be forced, it will enhance essentially the production of ionic excited states through the absorption of a few "above-threshold" photons but, in general, will not lead to the double ionization threshold "directly". The second threshold is most likely to be reached through multiphoton (resonant) transitions which involve only (single-electron) ionic excited states. Actually, the "correlated" process, albeit possible in principle, is in practice competing with all the other channels and is normally responsible only for an extremely small part of the multiply charged ions. Although it has not been clearly demonstrated up to now, direct double ionization remains a fascinating goal for experiments and a potentially powerful tool to investigate multiply excited states (at least the doubly-excited states in alkaline earth atoms) and electron correlations.

In this paper, we first briefly review the methods to isolate this "correlated" process and then report the progress of the (so-far unsuccessful) quest in multiphoton double ionization of magnesium with femtosecond pulses.

FAVORING AND DETECTING THE MULTIPHOTON "CORRELATED" DOUBLE IONIZATION

Isolated Core Excitation (ICE) scheme

The doubly excited states (n_1l_1, n_2l_2), which normally lie above the first threshold, can be roughly classified in categories according to the expectation values of the radial coordinates $<r_1>$ and $<r_2>$. If $<r_1> >> <r_2>$ and $<r_2> \cong 1$ a.u. the outer electron is far away from the core and the corresponding energy region is between the singly-charged ion ground state and its first excited states. In this case n_1 is large and n_2 is small. These states form Rydberg series converging to the low-lying ionic excited states. If $<r_1> >> <r_2>$ and $<r_2> >> 1$ a.u. they form Rydberg series converging to the highly excited ionic states. Finally if $<r_1> \cong <r_2> >> 1$ a.u. the states are located just below the double ionization threshold and are sometimes referred to as Wannier states. In order to study the "correlated" process, one might be attempted to try the technique known as the ICE method[4] which has been extensively used to study the autoionizing region of the spectrum. A first laser (or possibly two lasers) resonantly excites one of the two electrons on a Rydberg bound state ns md for example. It is then far enough from the core to remain spectator while another laser excites the core electron to a p state resulting in, say, a np md autoionizing state. Although extremely efficient to produce cleanly low-lying autoionizing Rydberg series, this method, from its very principle, is not likely to allow driving the atom above the double ionization threshold or even to the Wannier region[5]. Actually, it will lead to mostly low lying states of the singly charged ion and, consequently to virtually no "correlated" double ionization.

Non-Resonant multiphoton transitions

Taking an opposite strategy, one may try to force a completely non-resonant multiphoton transition from the atom ground state up to the Wannier region and above. This works for instance in the XUV range, for single-photon double ionization[6]. However, this method fails too in the case of multiphoton transitions with low-energy (visible) photons. The

experiments show that, because of the high density of autoionizing states just above the single ionization threshold, there is a very large branching ratio for channels leading again to the formation of low-lying excited ionic states

Symmetric resonant channels

An alternate route seems to be multiphoton transitions resonant only with strongly correlated states in which the two electrons have the same principal quantum numbers (although it is not clear in this case that n_1 and n_2 always remain good quantum numbers). This is not easy in practice however, since the energies of these states are largely unknown, and their ability to enhance multiphoton transitions is also unknown. Nevertheless, some observations[7] seem to indicate that this is the right way to go in the case of magnesium where a transition resonant with the $3p^2$ was found to lead to highly excited states of the ion, only one photon (2 eV) below the double ionization threshold.

Short pulses versus long pulses

The other experimental parameter is the pulse duration. There are at least two arguments in favor of short pulses. Since one wants to enhance the highest-order channel it is natural to take pulses as short as possible to increase the corresponding saturation intensity. Further, the shorter the pulse is the less "sequential" (in the sense of the two electrons being emitted independently of each other) the process can be, especially under the conditions where the first emitted electron has a low kinetic energy and the second a higher one. The electron-electron Coulomb interaction seems bound to play an important role in this case. However, the drawback of short pulses is that the threshold shifts are not fully compensated by the ponderomotive effect, and the photoelectron energies depend on the intensity at which they are released thereby shifting and broadening the electron peaks. This complicates, in the non-resonant case, the interpretation of the electron energy spectra which, as discussed in the next section remain potentially the best possible signature for the "correlated" process.

Electron energy spectra vs ionization rates measurements

One (and historically the first) way, to study multiphoton multiple ionization is to detect the ions produced and to analyze their charge state in a time-of-flight spectrometer. Then plotting the various rates as a function of intensity could in principle reveal the correlated channel, at least when it requires a different number of photons than the sum of the photon numbers required for the sequential steps. However, the difference is at most 1 and therefore the slope measurements must be extremely accurate, a difficult condition to meet, particularly for large slopes. Electron spectra, on the contrary, are easy to record and potentially contain a very clear signature since the "uncorrelated" process leads to discrete peaks while the "correlated" one produces, in principle, a continuous spectrum according to the condition:

$$E_1 + E_2 = Nh\nu - IP_1 - IP_2 \tag{1}$$

where E_1 and E_2 are the kinetic energies of the photoelectrons released in the "correlated" process, IP_1, IP_2 the atom and ion ionization potentials respectively and $h\nu$ the photon energy. It is likely, however, that this continuous spectrum can easily be buried in the wings of the large discrete peaks corresponding to the various uncorrelated channels and the associated ATI spectra.

MULTIPHOTON IONIZATION OF MAGNESIUM WITH FEMTOSECOND PULSES

For magnesium, which was chosen for this study, $IP_1 = 7.55$ eV and $IP_2 = 15$ eV. Around 590 nm, the single ionization requires 4 - photon
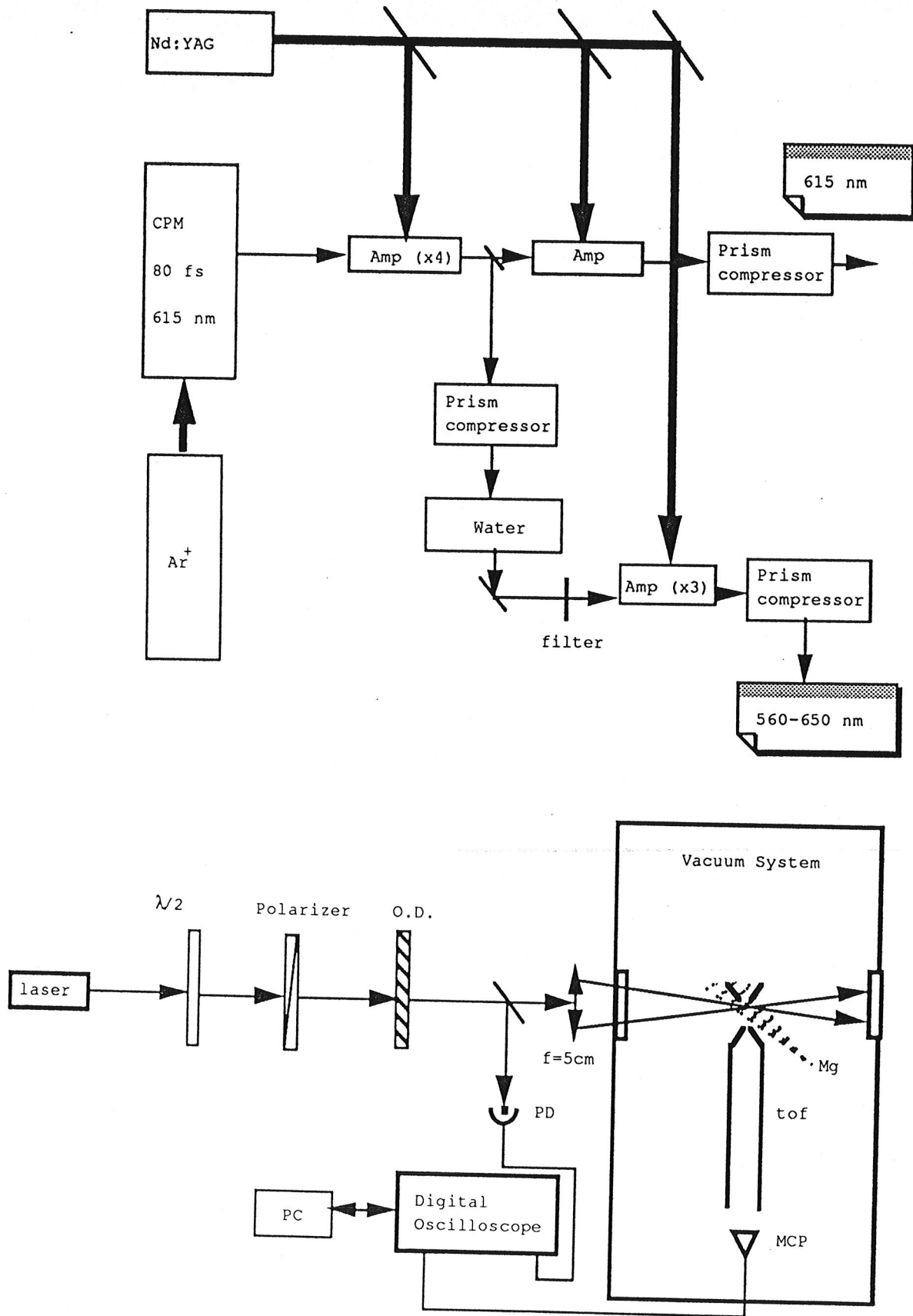
Nd:YAG

615 nm

CPM
80 fs
615 nm

Ar$^+$

Amp (x4)

Amp

Prism
compressor

Prism
compressor

Water

filter

Amp (x3)

Prism
compressor

560-650 nm

Vacuum System

λ/2

Polarizer

O.D.

laser

f=5cm

PD

Mg

tof

MCP

PC

Digital
Oscilloscope

Fig. 1 Experimental setup

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absorption while the "uncorrelated" and "correlated" double ionization require 12-photon absorption. Previous studies[7] in the picosecond regime have shown that it was possible to force (with a branching ratio of a few percent) 9- or 10-photon transitions to reach the 4p and 5p thresholds if the laser was tuned to the four-photon resonance with the $3p^2$ ^1S state.

The aim of the present work is to test the influence of the pulse duration in the subpicosecond regime and to try the covariant mapping technique to extract information from the energy spectra.

Experimental setup

The laser is an amplified 80 fs CPM dye laser and provides either 1 mJ, 615 nm pulses or, after continuum generation, wavelength selection, amplification and compression 200 to 400 µJ, 100 fs pulses in the range 560-650 nm. The beams are focused by a f=5 cm achromat between the poles of a magnetic-bottle spectrometer where it crosses a magnesium effusive thermal beam. Ions can be charge-analyzed and electrons energy-analyzed in a time-of-flight tube and detected on a twin channel-plates device. The signals are collected by a digital oscilloscope and processed by a computer. The laser energy is monitored by a fast photocell whose signal is used to bin the laser shots and the corresponding spectra into narrow laser intensity windows (Fig. 1). The pulse energy is varied either through natural fluctuations or through variations controlled by a polarizer-half wave plate device and optical density filters.

Ion detection: saturation and doubly to singly charged ions ratio

Fig. 2 shows the Mg^+ and Mg^{++} signals as a function of the laser pulse energy at 590 nm. Single ionization saturates around 4 mJ and the Mg^{++}/Mg^+ maximum ratio is about .1

Tuning the wavelength between 580 and 605 nm results in the Mg^+ and Mg^{++} lineshapes shown in Fig.3. The tuning range was here limited to the Rhodamine 6G & 610 range used in the amplifiers. It could be easily extended by using other dyes.
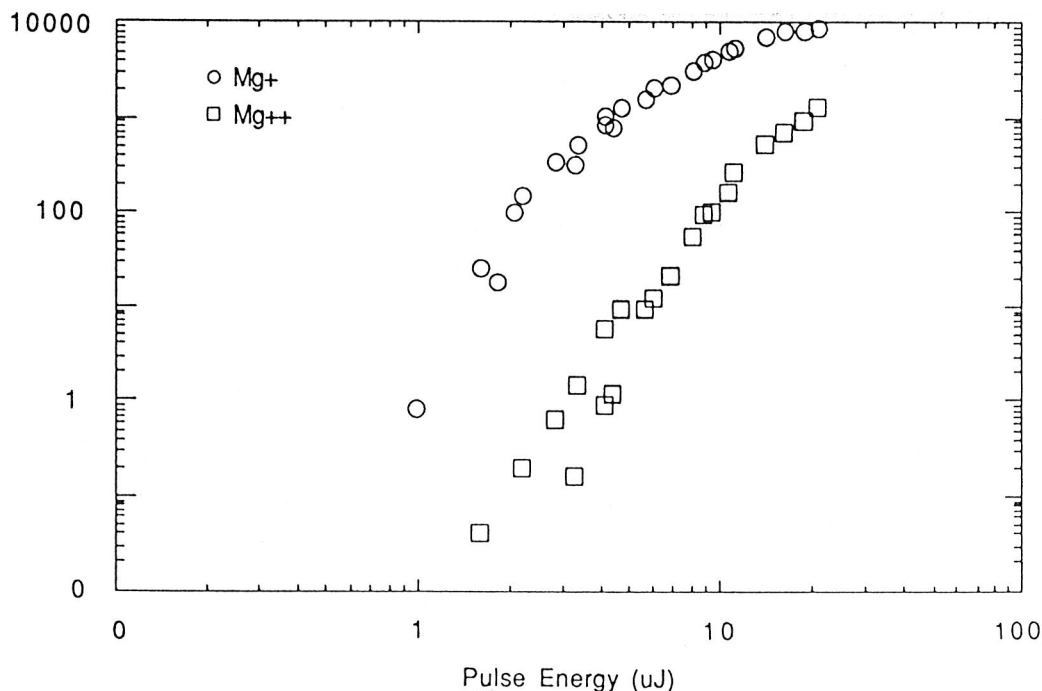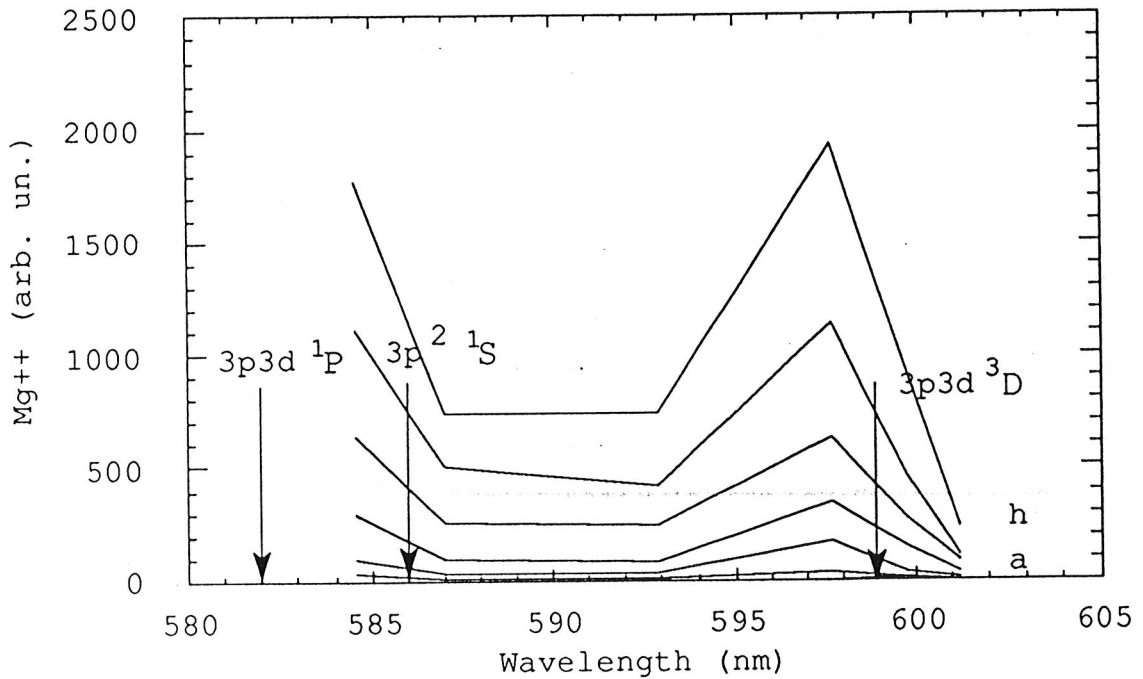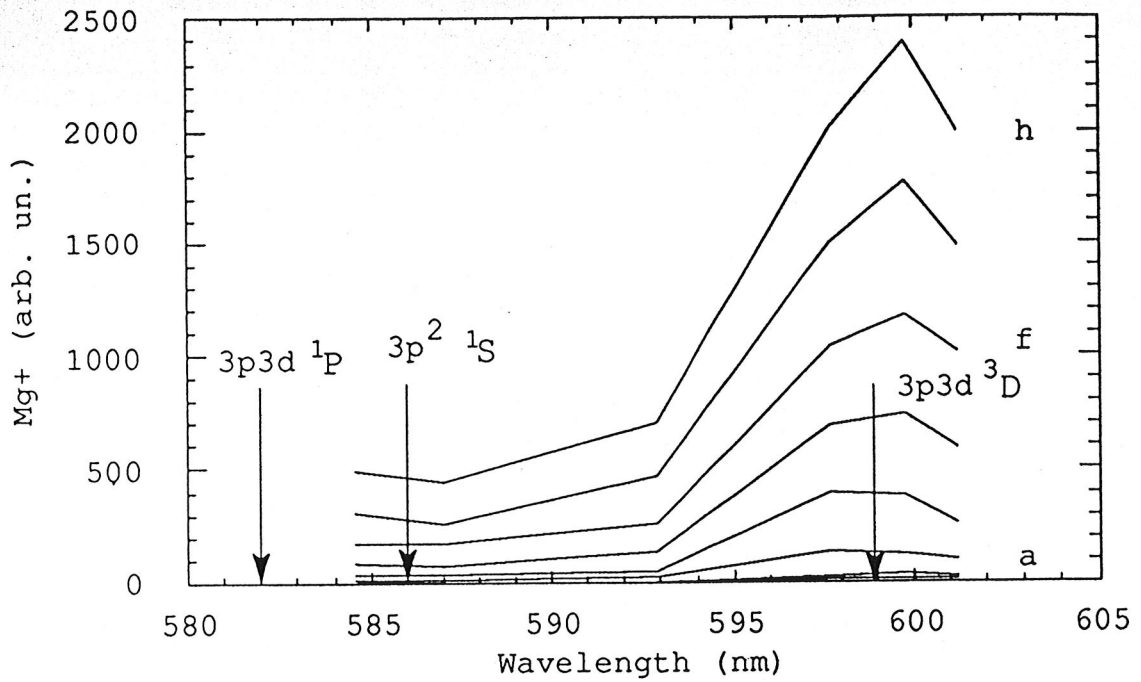

Fig. 2 Ions signals vs pulse energy

Fig. 3. Mg⁺ (top) & Mg⁺⁺ (bottom) ion signals vs wavelength. The curves a-f are for increasing laser pulse energy over a range of a few microjoules. The arrows indicate resonances for 4-photon absorption to the $3p^2$ ^1S autoionizing state and 5-photon absorption to the two 3p3d states.

Electron energy spectra: shifts, covariance mapping

Electron spectra

Fig. 4 shows some electron energy spectra at 590 nm. The most prominent peaks correspond to the 4-photon (0.75 eV) ionization of Mg and the first ATI order. Several other transitions may be recognized (and will not be
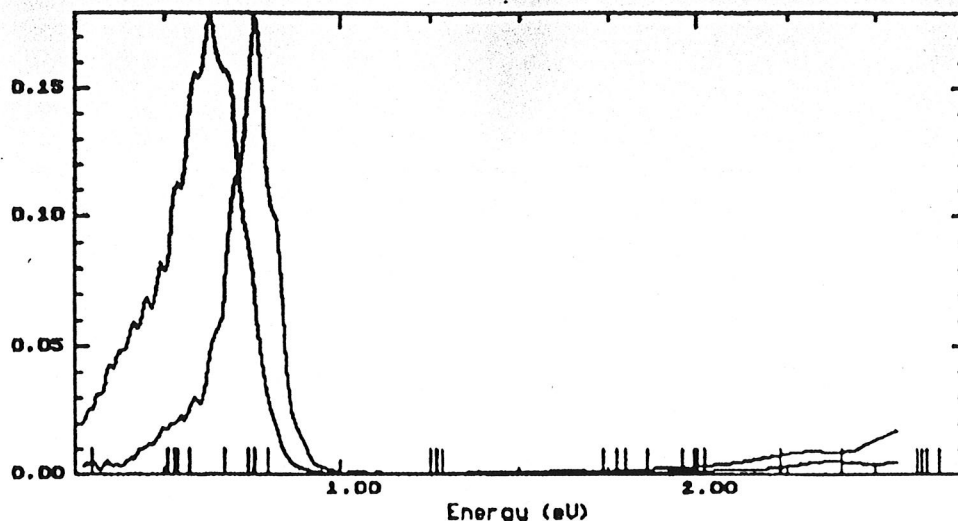
Fig. 4 Electron energy spectrum at 590 nm For two different intensities. The shift of the 0.75 eV peak is clearly visible.

commented upon here), but essentially no trace of the continuum due the correlated process can be identified. The 0.75 eV peak is shifting as a function of the pulse energy as expected for short pulses and nonresonant ionization.

Covariance mapping

To investigate the relationships between various electron peaks in a multiphoton ionization spectrum we employ the technique of covariance mapping. This technique has been applied to multiphoton molecular fragmentation[8] yielding insights into the photofragmentation process which were unavailable by previous experimental techniques. The idea is that the measurement of higher order moments of a physical process yields more information concerning the probability distribution function for that process than does a simple measurement of the first order moment (i.e., the average signal).

The electrons removed from different atoms are identically but independently distributed in energy, giving a distribution function for the ensemble of electrons which is the product of the individual probability functions. In such case there is no correlation in the distribution function, and the sample covariance tends to zero. If, however, two electrons derive from the same atom then the sum of their energies is constrained by the number of photons absorbed by the atom and by the final internal state of the ion. Moreover, there is a correlation between them. The probablility distribution function representing these two electrons includes a correlation term, and the computed sample covariance will be nonzero. It is the relationship between electrons emanating from a single atom that give rise to nonzero covariances. Even if several atoms are ionized at each laser shot the independent events will tend to a sample covariance of zero, and only correlated energies yield nonzero values. Of course, the noise level of the system will place a lower limit on a significant correlation, and detector efficiency will place an upper limit on the sample covariance given a particular value of the correlation.

If we consider two small ranges of energy then we can associate with each range an average rate, variance, and correlation. The distribution function for the pair is the bivariate normal distribution. And in general, for n variates (energy ranges) we have the multivariate normal distribution:

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$$p(X) = \frac{1}{\sqrt{2\pi}^N \sqrt{|K|}} \exp\left\{-\frac{1}{2}(X^t K^{-1} X)\right\} \tag{2}$$

where $X = (x_1-m_1, x_2-m_2, \ldots, x_N-m_N)$ is a column vector of the rates minus their averages, X^t is its transpose row vector, and K^{-1} is the inverse of
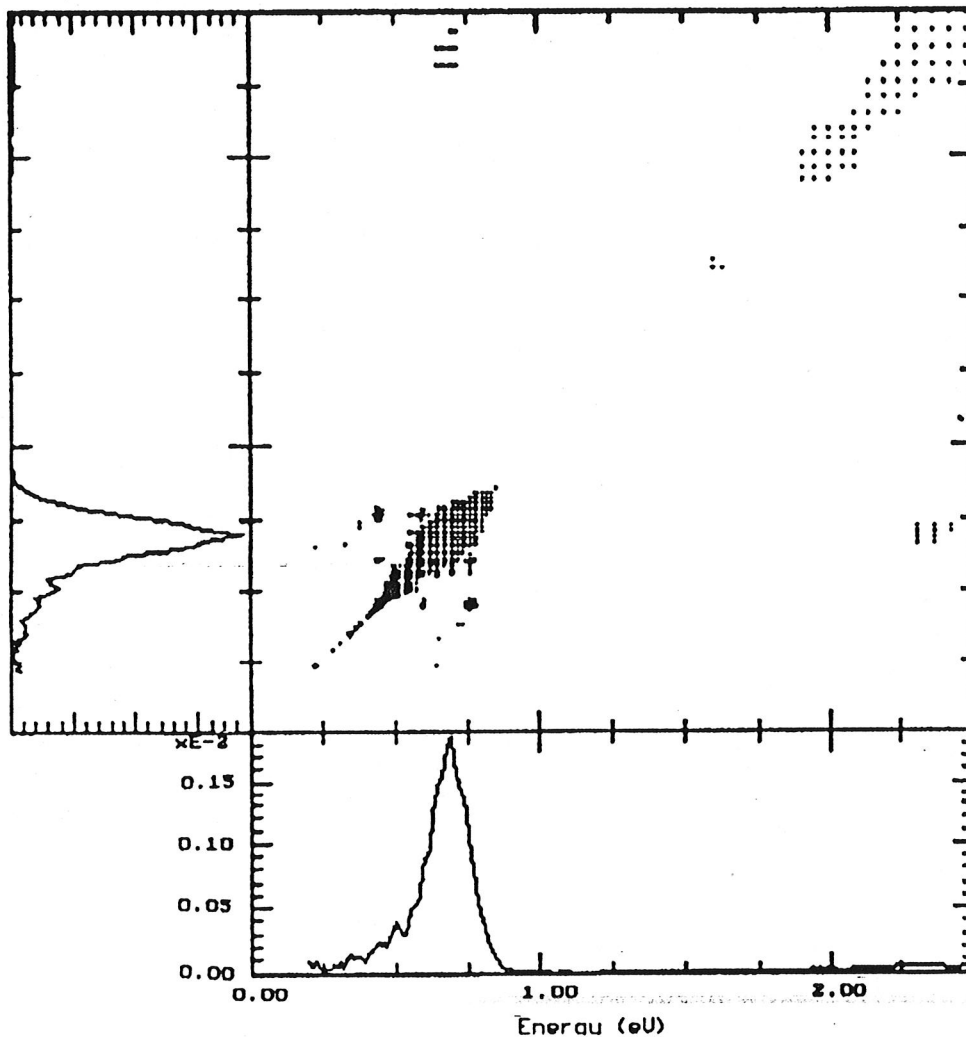

Fig. 5 Sample of covariance map for the electron energy spectrum at 590 nm.

the covariance matrix. For a collection of observations, the probability of observing that particular collection is the product of the individual probabilities. For M observations, the probability is

$$P = \frac{1}{(\sqrt{2\pi})^{MN} (\sqrt{|K|})^M} \exp\left\{-\frac{1}{2} \sum X^t K^{-1} X\right\} \tag{3}$$

Since the argument of the exponential is a 1x1 matrix it is the same as the trace of the 1x1 matrix. A property of the trace of a product of matrices is that it is preserved under commutation of the product. Thus

$$\sum X^t K^{-1} X = tr\left(\sum X^t K^{-1} X\right) = tr\left(K^{-1} \sum X X^t\right) = tr(K^{-1} S) \tag{4}$$

where $S = \sum X X^t$ is a square matrix for which an individual element is $(S)_{ij} = \sum (x_i-m_i)(x_j-m_j)$ the sample covariance. If we require that the above probability be unconditionally maximized, i.e., we invoke the property of maximum likelyhood, we find that the distribution covariance

which maximizes the probability is the one which is equal to the sample covariance.[9]

A serious problem arises when a third independent parameter correlates two electron energies which would otherwise be independent in the absence of the mutual correlation to the third parameter. The intensity of the laser light is just such a parameter. Laser fluctuations induce fluctuations in the electron production thereby inducing correlations among all of the electron peaks. This is a catastrophic effect because these artificial correlations can overwhelm the single-atom correlations. To circumvent this problem, one must take pains to reduce to a minimum the fluctuations of the laser intensity.

In the best case, our laser fluctuates by 10 percent from shot to shot. This level of fluctation is much too important and the consequent induced correlations can easily overwhelm the real correlations which we seek. One solution to this problem is to window the data collection by laser intensity. In this way, the laser fluctuations for a particular data set can be reduced to below the one percent level (the lower limit is set by the 8 bit resolution of the oscilloscope) and since the data is binned by laser intensity, one collects covariance data over a range of intensities. The residual correlation left in the data due to laser fluctuation can be treated by computing a partial covariance which mathematically freezes out the effect of the fluctuating laser. This technique is of limited utility since it removes only linear cross correlations[10].

An example covariance map is shown in figure 6. On the sides of the figure are shown the average electron spectra from which one can identify the peaks giving rise to covariance islands in the central part of the figure. Unfortunately the structure shown on the map is not readily explained by the energy level diagram for magnesium. The covariances are small and the correlations induced by laser fluctuations are not completely removed. This points to the fact that our detection is inefficient and that the range of allowed laser fluctuation is too large. We are currently improving the system and hope to present better maps soon.

CONCLUSION

In conclusion, the multiphoton double ionization of magnesium atoms by visible subpicosecond pulses still does not show substantial trace of the "correlated" process in the electron energy spectra. The more sophisticated technique of covariant mapping has been attempted but without conclusive result so far. More experimental effort is required, especially the spectroscopy of high-lying autoionizing states, to increase the chances to observe this rather elusive process.

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