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The application of ultra-short light pulses for the analysis of quickly relaxing organic molecules by means of laser mass spectrometry

Carsten Grun, Ralf Heinicke, Christian Weickhardt*, Jürgen Grotemeyer

Lehrstuhl für Physikalische Chemie und Analytik, Brandenburgische Technische Universität Cottbus, Am Technologiepark 1, D-03099 Kolkwitz, Germany

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Abstract

The combination of resonance enhanced multiphoton ionization (REMPI) and time-of-flight mass spectrometry, commonly referred to as laser mass spectrometry, has proven to be a powerful analytical tool with advantageous features for certain problems. However, these advantages are only achievable as long as the resonant intermediate level(s) being involved in the photo ionization step are long-lived on the time scale of the ionizing laser pulse. A way to overcome this problem is to apply intense ultra short laser pulses in order to finish the ionization process before relaxation in the intermediate state(s) can occur. In this paper the differences between conventional nanosecond and sub-picosecond multiphoton ionization of polyatomic organic molecules and the consequences on the laser mass spectrometry of these compounds are discussed. As examples for groups of substances for which sub-picosecond laser mass spectrometry delivers favorable results metal organic compounds, chemical warfare agents and biomolecules were chosen. It is shown that in contrast to nanosecond-REMPI the use of ultra-short laser pulses results in well interpretable mass spectra of these substances. In order to demonstrate that REMPI with ultra-short laser pulses may be employed for the detection of quickly relaxing compounds in environmental samples the quantitative analysis of a soil sample spiked with the warfare agent adamsite was performed. (Int J Mass Spectrom 185/186/187 (1999) 307–318) © 1999 Elsevier Science B.V.

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1. Introduction

Among the various ionization techniques used in mass spectrometry resonance enhanced multiphoton ionization [1,2] (REMPI) offers a number of outstanding features that make it the method of choice for

applications where high temporal resolution has to be combined with high sensitivity and selectivity. REMPI involves one or several photo absorption steps within the manifold of atomic or molecular vibronic states. As the energy of these states is a unique characteristic of a particular atomic or molecular species highly selective ionization can be achieved by choosing the proper (set of) laser wavelengths. Furthermore, REMPI turns out to be a soft ionization method for many molecular species, a feature which

* Corresponding author.

Dedicated to Professor Michael T. Bowers on the occasion of his 60th birthday.

greatly simplifies the interpretation of mass spectra of complex mixtures. However, in most cases ionic fragmentation which is often desirable in order to obtain structural information can be induced by increasing the light intensity. As REMPI is usually carried out by pulsed tunable lasers it is perfectly adapted to time-of-flight mass spectrometry [3]. This simple and robust type of mass spectrometer allows the detection of the whole mass spectrum for every single laser shot with high transmission and good mass resolution.

Though, these advantageous features of REMPI are only obtained as long as the intermediate state(s) involved in the ionization process are not significantly depleted within its duration, i.e. the duration of the laser pulse. The initial step of a multiphoton ionization process is the absorption of one or several photons transferring the molecule from its electronic ground state to an excited electronic state which in addition may be vibrationally excited. In this excited state further photon absorption has to compete with several depopulation processes [4]. Whereas fluorescence brings the molecule back to its ground state by the emission of a photon, internal conversion (IC) and inter system crossing (ISC) lead to vibrationally highly excited molecules which may subsequently dissociate. The effect of IC and ISC on the REMPI process is determined by the fact that for vibrationally highly excited states the Franck-Condon factors for absorption of a further photon are greatly reduced, thus blocking the ionization pathway. The overall effect of these relaxation processes on the laser mass spectrum is a reduced or even missing molecular ion signal and/or strong fragmentation. This means that the sensitivity of the measurement is reduced and the interpretation of the mass spectrum, namely when mixtures are to be analyzed, is complicated or even made impossible.

The rate constants that govern such energy redistribution and fragmentation processes are dependent on structure and composition of a certain molecule and the electronic structure of the excited state. As long as only the first excited singlet state of an organic molecule is involved in the REMPI process IC usually does not significantly affect the ionization yield of a conventional nanosecond laser pulse as IC rate con-

stants here do not exceed 10^6 s^{-1} . As opposed to this IC in higher singlet states is often the dominating relaxation mechanism with typical rate constants of 10^{11} to 10^{13} sec^{-1} for organic molecules.

Whereas internal conversion as mentioned above usually is not an important mechanism for the depletion of the first excited singlet state, inter system crossing can readily be the fastest process in the S_1 state. Spin-orbit-coupling is greatly enhanced by the implementation of heavy atoms, but even in molecules not containing heavy elements the ISC rate may reach values up to 10^{11} sec^{-1} , especially in systems undergoing $S_1(n, \pi^*) \rightarrow T(\pi, \pi^*)$ transitions with small energy gaps.

Examining the work performed in the field of molecular resonance enhanced multiphoton ionization it can be recognized that it was almost entirely carried out on molecules built from atomic species of the first period of the periodic table of elements and the halogen group and possessing comparatively stable excited states [5]. On the other hand it is obvious that for the large majority of technically, biologically or environmentally important substances such favorable conditions are not fulfilled. They may contain elements that give rise to large ISC rates and/or weak bonds which can easily be broken during a REMPI process. Furthermore, the first excited state of polyatomic molecules is often found to be too low in energy to be useful for a REMPI process. In such cases higher excited singlet states have to be involved which again are subject to fast internal conversion.

A logic and straight forward attempt to become independent of relaxation processes while performing REMPI is to carry it out on a time scale too short for these processes to occur significantly [6]. This can be achieved by the use of ultrashort light pulses, say in the picosecond range. As in this case the light field is switched off before the onset of intramolecular processes an irradiated molecule is either ionized intact and with little vibrational excess energy or stays neutral and thus invisible to the mass spectrometer [7]. Recently, Ledingham and Singhal published an excellent review [8] of the work performed and the molecular systems studied by laser mass spectrometry with ultra-short and intense light pulses.

In order to maintain the high ionization efficiency typical for REMPI and desirable in almost every analytical application the laser pulse energies used in nanosecond experiments have to be compressed into these ultrashort pulses resulting in high light intensities. This factor increases the probability for non-resonant multiphoton processes which result in unselective ionization. As shown in previous work [9] such effects which counteract one of the most useful features of analytical REMPI, i.e. the ability to species selective ionization, are not significant at the laser intensities used in this work (10^{10} to 10^{11} W/cm²). These light intensities correspond to electric field amplitudes in the range of 2×10^8 to 6×10^8 V/m. Thus, tunnel ionization can be ruled out as such field strengths are lower than typical intramolecular values by three orders of magnitude. However, if much higher laser intensities are applied non-resonant ionization may take over, making ps-REMPI an ionization method with a tunable degree of selectivity. It depends on the specific analytical problem whether a high degree of selectivity is preferred or whether a multi-component overview is to be obtained. Using REMPI both scenarios can be realized by choice of the proper laser intensity [9,10].

Yet, another factor exists which may reduce the selectivity in a ps-REMPI experiment. According to Fourier transform a very narrow pulse in time as well as a very short-lived excitation is inherently correlated with a large spectral bandwidth. For the case of REMPI of quickly relaxing molecules this means that on the one hand side the excitation is performed by a pulse with increased linewidth into a state with a lifetime broadened absorption line. This factor too may increase the probability of simultaneous ionization of two or more species present in a mixture to be analyzed. Again, the question whether this can disturb a certain measurement or whether it is desirable in the sense of multi component detection has to be answered for each specific case.

In this work we demonstrate how fast relaxation processes can influence the laser mass spectrometry of polyatomic organic molecules and show cases for which the use of ultrashort laser pulses is essential in order to obtain interpretable mass spectra. For the

case of aromatic compounds containing elements of the fifth group of the periodic system (chemical warfare agents) and several metal organic substances we will discuss the influence of the reduced binding energy when involving atoms of increased size. Biomolecules will serve as examples for molecules undergoing fast internal conversion processes and finally the effect of fast ISC will be investigated using aromatic ketones. As will be shown in all these cases the use of nanosecond-REMPI does not lead to satisfying results or is even not applicable at all. The substances were chosen as examples because of their relevance in analytical contexts which favor the use of laser mass spectrometry. It was the main goal of this work to characterize the changes in the mass spectra which are observed when the duration of the pulses is shortened and to demonstrate how ultra-short laser pulses can be advantageously used for the detection of a pollutant in a realistic environmental matrix (here: humous soil).

2. Experimental

The experimental setup used for the measurements reported here is described in more detail elsewhere [11] and will be discussed here only in brief. The experiments were performed using a commercial reflectron time-of-flight mass spectrometer (Bruker TOF 1) equipped with a home built molecular beam inlet system to which a laser desorption device is coupled. Neutral laser desorption with a CO₂ laser (wavelength 10.6 μ m) is used to vaporize substances with an insufficient vapor pressure at room temperature and introduce them into the supersonic beam expansion. A draft of the experimental setup is shown in Fig. 1. For multiphoton ionization of the sample molecules in the ion source either the frequency doubled output of a Nd:YAG pumped dye laser system (Lambda Physik FL 3001) or an excimer pumped femtosecond dye laser system (Laserlabor Göttingen) was used. Whereas the first one produced UV pulses with energies up to 500 μ J distributed over a pulse duration of 6 ns, the latter delivered 0.5 ps pulses with energies of ~ 40 μ J. Both laser beams could be focussed into the ionization region simultaneously thereby ensuring equal conditions regarding

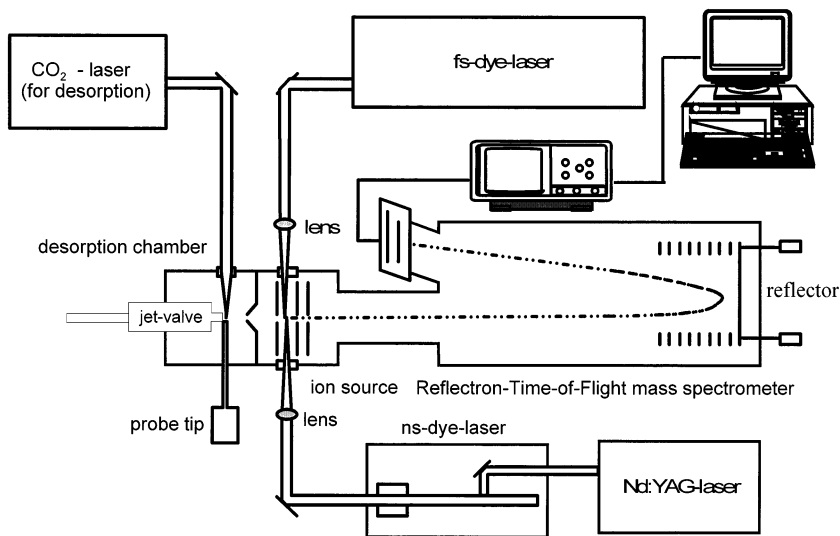


Fig. 1. Experimental setup consisting of a reflectron time-of-flight mass spectrometer including a laser desorption molecular beam inlet system and a nanosecond, resp. sub-picosecond laser system for multiphoton ionization.

the beam of neutrals and the mass spectrometer. Thus, a direct comparison of the ionization processes induced by two different lasers was possible. Both laser systems were operated within the wavelength range 250 nm to 264 nm in which all compounds under investigation are ionized after absorption of two photons. Chemicals, except warfare agents, were purchased commercially in technical quality and used without further purification. CLARK I and Adamsite were obtained from the Wehrtechnisches Institut für Schutztechnologien, Munster, Germany, as extracted from a World War I shell. For laser desorption the technically pure substances were mixed with polyethylene and pressed to pallets. Soil samples were dried by applying vacuum for one hour at room temperature and homogenized in a mortar before pressing.

3. Results and discussion

In order to study the effect of an increased size of the central atom on the laser mass spectra of aromatic molecules under nanosecond and picosecond conditions the triphenyl derivatives of all elements of the fifth group of the periodic table were investigated. In Fig. 2 the laser mass spectra obtained with 6 ns pulses

are compared to those produced with 0.5 ps pulses under otherwise equal conditions. Inspecting the ns-spectra it can be recognized that while for triphenylphosphine the signal of the molecular ion is still the dominant peak, already for triphenylarsine its relative abundance is greatly reduced and it is completely missing in the spectra of triphenylantimony and triphenylbismuth. All the ns-spectra are characterized by strong fragmentation leading to intense and unspecific signals in the low mass range. Typical fragmentation reactions are the loss of one or several phenyl ligands and the formation of the phenyl and the biphenyl cation. The spectra are an expression of the reduction in bond strength when going to heavier atoms within a group of the periodic table of elements giving rise to stronger fragmentation.

The situation is completely different in the case of picosecond multiphoton ionization. Here, the molecular ion signal dominates the spectrum and only few and structural specific fragments are observed except in the case of triphenylbismuth. These dissociation products result from the loss of one or several ligands of the central atom. It is evident that for the heavier central atoms only the ionization by ultra short laser pulses allows the clear mass spectrometric identification of the compound.

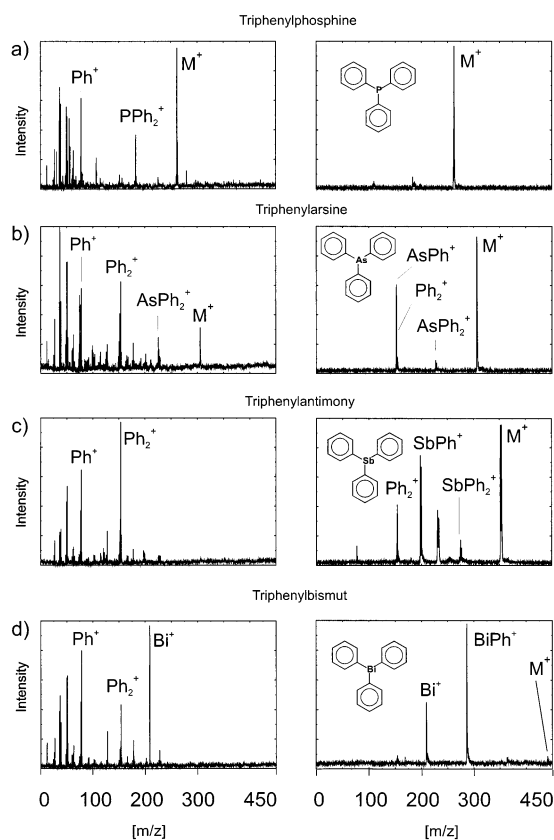


Fig. 2. Comparison of the time-of-flight mass spectra obtained with 5 ns laser pulses (left column) and 0.5 ps laser pulses (right column) of a) triphenylphosphine, b) triphenylarsine, c) triphenylantimony, d) triphenylbismuth. Note the increasing degree of fragmentation as the size of the central atom increases. Laser wavelength: 251.5 nm.

In the case of organic compounds containing a heavy metal atom this effect is even enhanced. This can be seen from the spectra of a few organic mercury, platinum, and cobalt compounds plotted in Fig. 3. Except for diphenylmercury the nanosecond spectra of these compounds do not even exhibit organic fragments, but are dominated by the metal ion signal. For biphenylmercury the formation of the biphenyl cation and aromatic fragments is observed as was the case for the group V triphenyl compounds. Picosecond REMPI also here results mainly in the formation of the molecular ion besides fragments originating from ligand losses. All these examples demonstrate that by the use of ultrashort laser pulses it is possible to overcome the problems related to fast

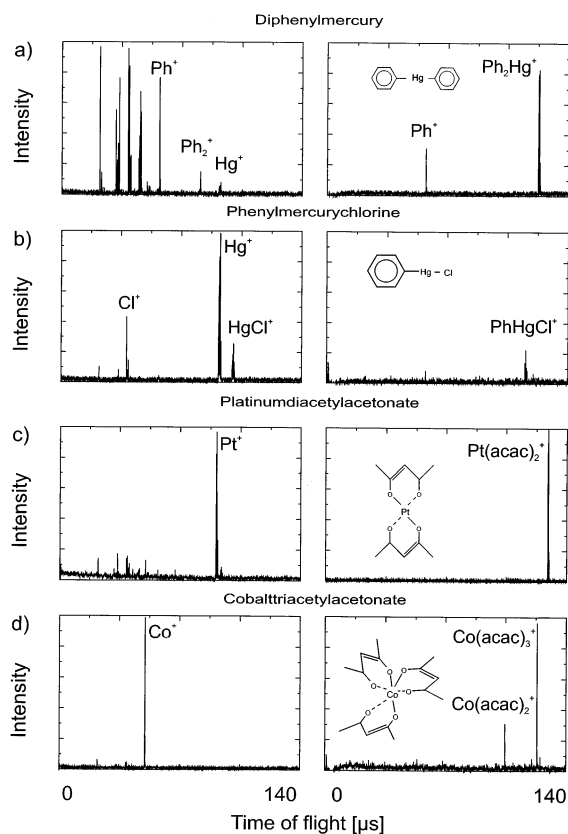


Fig. 3. Comparison of the time-of-flight mass spectra of some heavy metal containing organic compounds obtained with nanosecond REMPI (left column) and sub-picosecond REMPI (right column). a) diphenylmercury, b) phenylmercurychlorine, c) platinumdiacetylacetonate, d) cobalttriacetylacetonate. Laser wavelength: 250 nm.

dissociation processes of the excited molecules. In previous work [12] we showed that this is even true for the multiphoton ionization of metal carbonyls which exhibit the highest dissociation rate constants known for organic molecules so far. Time-resolved experiments on $\text{Fe}(\text{CO})_5$, a molecule extensively studied because of its role in catalytic processes as well as in surface technology and discussed as a prototype for photoinduced dissociation, yielded fragmentation time constants on the order of 100 fs [13].

It could be argued that the intense fragmentation resulting from nanosecond REMPI of these compounds is due to a too high laser intensity and could be avoided by establishing more moderate conditions.

This was checked by reducing the laser intensity down to a level where the ion signals were only about a factor of 10 above the background noise. While for some substances a slight reduction of the degree of fragmentation could be observed, for none of them the characteristics of the mass spectra changed in a significant way. Anyhow, such low laser intensities are not useful in real analytical applications because the sensitivity of the whole technique would be reduced to an unacceptable level.

As mentioned above a further important process which can cause problems to conventional nanosecond laser mass spectrometry is inter system crossing (ISC). Particularly the multiphoton ionization of aromatic ketones and compounds containing heavy elements can be influenced by this radiationless process. A molecule well known for possessing an extremely high ISC rate constant in the order of 10^{11} s^{-1} is benzophenone [14]. According to the discussion above we would expect a molecule which underwent ISC to be vibrationally highly excited and therefore to exhibit vanishing Franck-Condon factors for the absorption of further photons. In total this should result in a reduced ionization yield. As can be seen from Fig. 4a this is exactly what is observed in the case of benzophenone. Using a nanosecond laser at moderate intensities for ionization it is not possible to observe any molecular ion signal at all. Only at high laser intensities small fragment ions down to C^+ probably resulting from an interplay of fast fragmentation and subsequent photon absorption of the fragments, known as “ladder switching” [15], first neutral then ionic, can be detected. But similar to the fast dissociation processes it is also possible to ionize the molecules by ultra short laser pulses before the ISC process sets in. In this way an intense molecular ion signal is obtained for benzophenone [Fig. 4(b)]. Fragmentation of the molecular ion is mainly prevented because of the absence of ionic ladder switching due to the short pulse duration and the absence of ladder climbing due to the moderate laser intensity. Also the benzophenone dimer formed in the supersonic jet expansion is detected in the picosecond-REMPI case.

Biomolecules possessing a large number of internal degrees of freedom and of (avoided) crossings of

potential energy surfaces represent an excellent example to demonstrate the effect of internal conversion processes on the resonant multiphoton ionization. The ionization and dissociation of large molecular systems is still an issue of ongoing research with important consequences for pharmaceutical and biochemical mass spectrometry. The problems related to the mass spectrometry of biomolecules are mainly due to the fact that the conventional ionization methods as electron ionization but also multiphoton ionization with nanosecond laser pulses exhibit a drastic loss in efficiency with increasing molecular mass [16]. Thus, special techniques, namely matrix assisted laser desorption/ionization [17] (MALDI) and electrospray [18] were developed. However, certain features of resonant multiphoton ionization—particularly its selectivity—would be of great advantage especially in medical and pharmaceutical applications of mass spectrometry. This goal is interfered with the high probability for internal conversion and possibly successive dissociation in such systems. When performed by nanosecond laser pulses the results are mass spectra as that of β -carotene shown in Fig. 5a. While the molecular ion is totally missing, the only signals observed belong to unspecific small fragments in the range CH_n^+ to C_6H_n^+ . But this problem too can be solved using laser pulses which finish the ionization before IC and subsequent dissociation can occur on a significant scale. The corresponding mass spectrum (Fig. 5b) is characterized by an intense molecular ion signal. In other cases, as e.g. for the polypeptide gramicidin D, the molecular ion signal may be detectable even when REMPI is carried out by nanosecond pulses [see Fig. 6(a)] but also here the use of picosecond laser pulses leads to a significant improvement of the mass spectrum [Fig. 6(b)].

None of the molecules studied in this work exhibited a significant wavelength dependence neither of the ionization efficiency nor of the fragmentation pattern within the wavelength range 250 to 255 nm. This can be expected because of the fast relaxation processes occurring in their excited states and because the accessible laser wavelengths excite these substances to higher singlet states where the density of states is high.

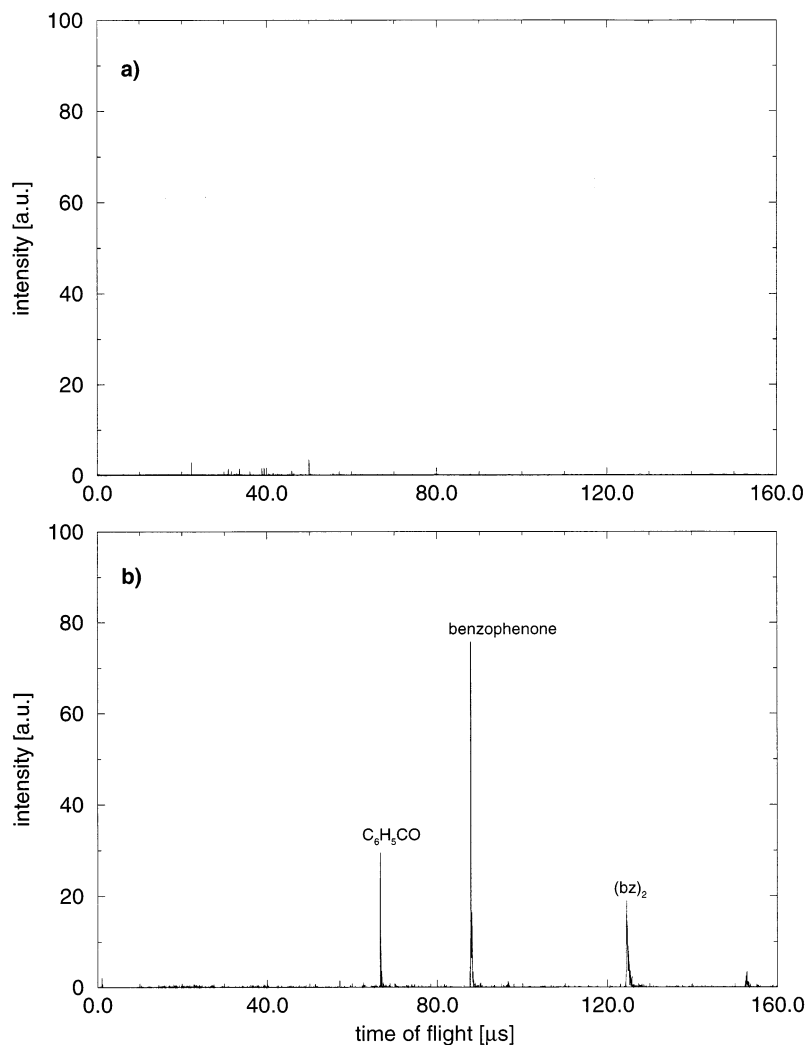


Fig. 4. Time-of-flight mass spectra of benzophenone which undergoes fast ISC in its S_2 state. Whereas nanosecond REMPI only produces small fragment ion signals (a), the sub-picosecond spectra are characterized by the molecular ion as well as structure specific fragments (b).

Besides the changes in the appearance of the mass spectra the higher intensity of the ultra-short laser pulses directs the branching ratio of molecules in the excited state towards higher ionization efficiency. This can be illustrated employing a simple kinetic model in which the relaxation processes are characterized by a rate constant k_R and the probability for further photon absorption by the product of the absorption cross section σ and the photon flux $\Phi_{\text{ph}} = I/(h \cdot \nu)$. In Table 1 the share of the ionization in the total depopulation of the excited intermediate level is

calculated for several values of k_R and the laser intensities of our nanosecond and subpicosecond laser system ($8 \times 10^6 \text{ W/cm}^2$ and 10^{10} W/cm^2 , resp.). For the absorption cross section from the excited state to the ionization continuum a typical value of 10^{-18} cm^2 was assumed. These results show that shorter pulses make a more economic use of the laser pulse energy as far as multiphoton ionization is concerned.

The major goal of our work on picosecond laser mass spectrometry is to apply this technique for the fast and advantageous analysis of environmental and

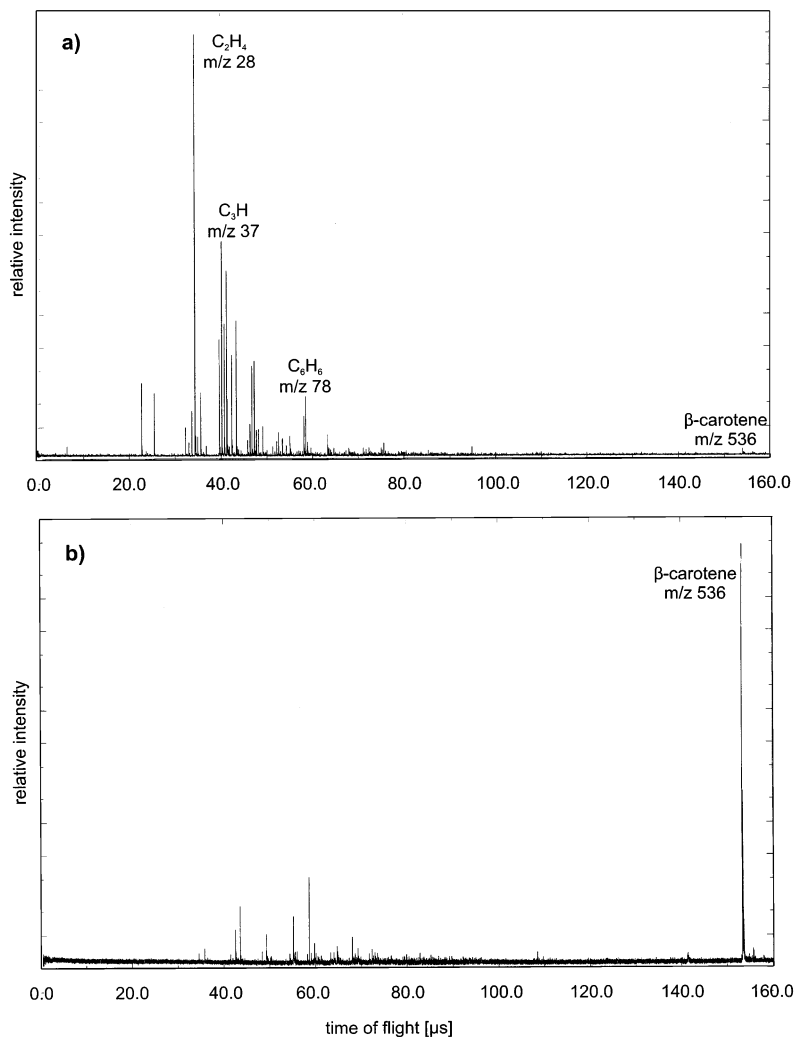


Fig. 5. Laser mass spectra of β -carotene ionized either by 5 ns laser pulses (a) or 0.5 ps pulses (b). While, due to fast internal conversion and dissociation processes no useful mass spectrometrical information is obtained in the first case, the second produces mass spectra with the features necessary for analyte identification.

technical samples. It is therefore of great importance to demonstrate that this technique is able to detect the substances of interest in realistic matrices. Regarding heavy metal containing compounds, explosives and chemical warfare agents soil is the most common matrix in which they have to be detected. In the vicinity of (former) army training areas, ammunition plants, or front lines large numbers of samples have to be taken and analyzed in order to obtain a clear basis for the decision about which areas have to be cleaned.

This adds to the total costs of such measures in a substantial way. Thus, there is a continuous demand for faster and cheaper analytical techniques. Because of its unique features, particularly the selectivity of ionization and the quickness of the analysis, resonant laser mass spectrometry is a promising candidate for this task if it can avoid the time consuming sample preparation steps. However, a prerequisite for its successful application is the use of ultrashort laser pulses in order to avoid the fast dissociation processes

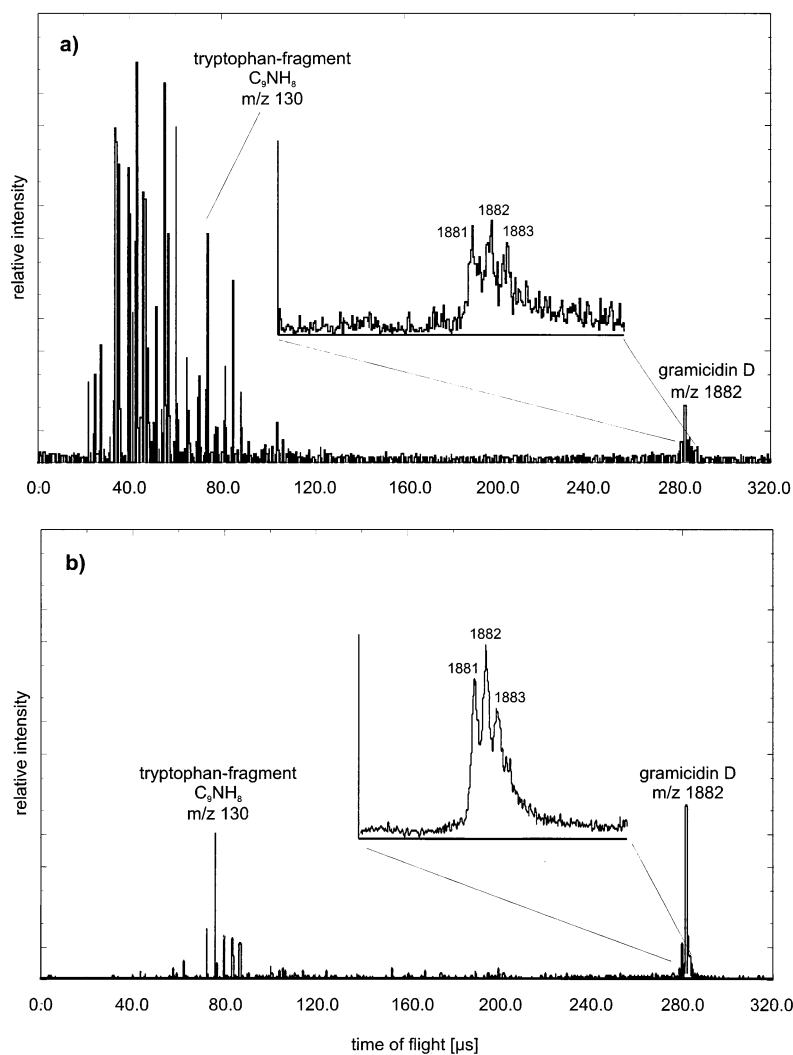


Fig. 6. Laser mass spectra of the polypeptide gramicidin D ionized either by 5 ns laser pulses (a) or 0.5 ps pulses (b). Although in this case the molecular ion can be detected in the nanosecond REMPI spectrum, ultra short pulse ionization leads to a clear improvement of the mass spectrum.

that occur in the excited states of these molecules. As an example the REMPI mass spectra of two arsenic containing chemical warfare agents, diphenylarsine-chlorine (CLARK I) and adamsite are shown in Fig. 7. These measurements once again illustrate the need of ultrashort laser pulses in order to obtain interpretable mass spectra from compounds of this type. It is only with the use of ultra-short laser pulses that the molecular ion signal is formed to a significant extend

Table 1

Percentage of excited state systems undergoing absorption of a further photon as calculated for several values of the relaxation rate constant in this excited state, and two laser intensities (I) corresponding to a typical nanosecond and a picosecond laser pulse. A value of 10^{-18} cm^2 was assumed for the absorption cross section.

	$I = 8 \times 10^6 \text{ W/cm}^2$	$I = 10^{10} \text{ W/cm}^2$
$k_R = 10^8 \text{ s}^{-1}$	9.1%	100%
$k_R = 10^9 \text{ s}^{-1}$	1.0%	93%
$k_R = 10^{12} \text{ s}^{-1}$	10 ppm	1.2%

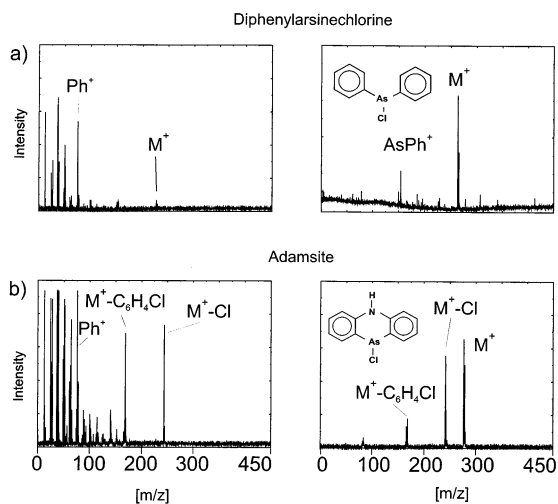


Fig. 7. Comparison of the nanosecond (left hand side) and picosecond (right hand side) REMPI mass spectra of two arsenic containing warfare agents: (a) diphenylarsinechlorine (CLARK I), and (b) adamsite. Laser wavelength: 251.5 nm.

and structural specific fragments are formed which may be used for the unambiguous identification of the compound. In order to perform a first step towards the applicability of our technique to realistic samples we spiked humous soil samples taken just from outside our lab with varying amounts of the arsenic containing warfare agent Adamsite which was produced in large amounts during World War I and still can be found in rather high concentrations in various parts of Germany. The sample preparation procedure was reduced to a half hour drying under vacuum. Afterwards the sample was pressed to a pallet and directly inserted into the mass spectrometer. Fig. 8 shows the picosecond REMPI mass spectra of the clean soil and a sample "contaminated" with an adamsite concentration of 1%. At the UV laser wavelength used the adamsite signal can clearly be identified and is not interfered with other substances present in the matrix. In some of the measurements soil components were coionized at the wavelength used [see e.g. the signal at mass 324 amu in Fig. 8(b)], but none led to interferences with the adamsite signal. Due to the inhomogeneity of the soil such signals were not observed in all sample areas where laser desorption was performed.

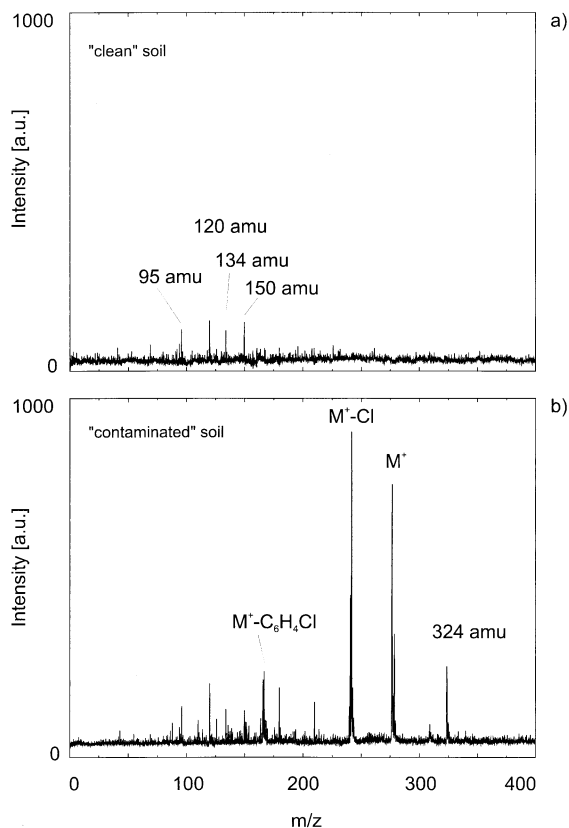


Fig. 8. Laser desorption-picosecond REMPI mass spectrum of a clean soil sample (a) and a soil sample containing 1% of adamsite (b). Laser wavelength: 250 nm.

Six soil samples with adamsite concentrations ranging from 0 to 5% by weight were prepared and analyzed quantitatively utilizing the peak area of the molecular ion signal in the time-of-flight spectrum and using the soil sample with the highest adamsite concentration as standard. Of course, such high concentrations are not typical for real world samples but as this work focuses on the mass spectrometry of the compounds under investigation, the setup was not at all optimized in order to achieve high sensitivity. In particular an optimization of the coupling between the laser desorption and the supersonic expansion and of the transfer of the molecular beam into the ion source could be significantly improved. However, the purpose of the measurements presented here is to demonstrate that quantitative measurements are possible

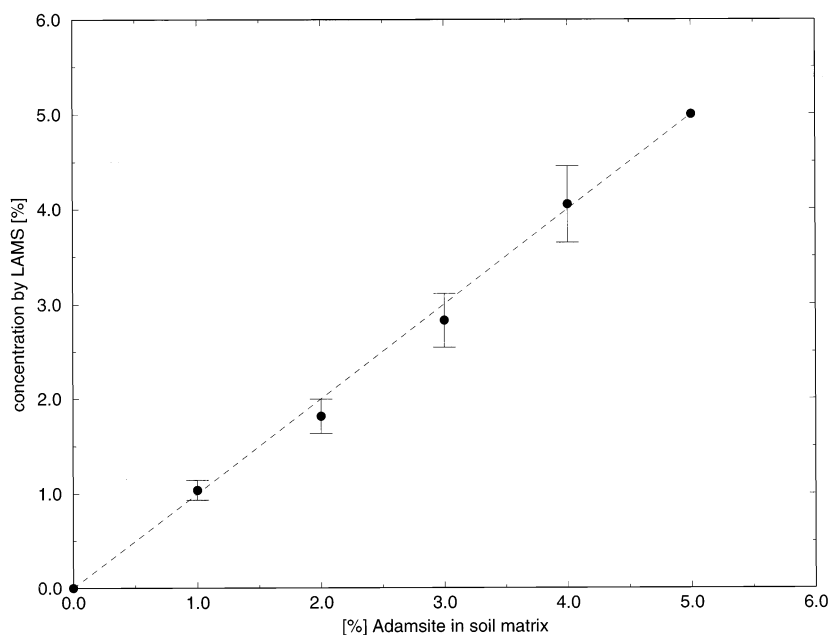


Fig. 9. Quantitative determination of the Adamsite concentration in soil samples spiked with various amounts of the war fare agent using laser desorption/picosecond REMPI mass spectrometry. The system was calibrated with the 5% sample. The solid line indicates the one-to-one correspondence of the concentrations as prepared by weighing compared to those determined by laser mass spectrometry. A $\pm 10\%$ error margin is indicated for each measurement.

in principle with laser mass spectrometry utilizing ultrashort laser pulses. In Fig. 9 the concentration values obtained in this way are compared to those established by weighing showing equality within $\pm 10\%$. Each REMPI measurement was performed during 2 seconds by averaging the mass spectra of 20 laser shots. This quickness of the analysis in connection with the very simple sample preparation are the main advantages of REMPI time-of-flight techniques for the analysis of environmental samples.

4. Conclusion

Within the frame of this work laser mass spectrometrical investigations were performed on organic compounds which undergo fast relaxation processes of several kinds in their excited states and thus cause severe problems to conventional multiphoton ionization with nanosecond laser pulses. This group of species, which seems to cover a large part of the

technically or environmentally relevant substances, contains e.g. metal organic compounds, molecules containing heavy atoms, chemical warfare agents, explosives, and biomolecules.

The mass spectra of all substances investigated depend crucially on the duration of the applied laser pulses. Whereas under nanosecond conditions only small and unspecific fragments were detected, the picosecond-REMPI mass spectra are dominated by the molecular ion signal accompanied by structure specific fragments. Only the latter case allows the unambiguous identification of the compound and may therefore be useful for analytical applications. However, it was shown in previous work that up to the laser intensities used in these experiments, a high degree of selectivity is still maintained in the ionization step [9]. As expected and demonstrated by Ledingham and coworkers [10] at even higher intensities this behavior changes and non-resonant ionization becomes the major process turning multiphoton

ionization into a rather general and unspecific ionization technique. Furthermore, this group showed that by varying the laser wavelength at high intensities the degree of fragmentation can be tuned. Summarizing these observations it can be stated that multiphoton ionization with ultra-short laser pulses in the picosecond range offers a unique ionization technique which allows the independent tuning of the degree of selectivity and fragmentation over wide ranges, is not restricted to certain groups of substances and is able to deliver well interpretable mass spectra even for very labile molecules.

On the negative side it has to be mentioned that short pulse laser systems are still very expensive and sensitive devices. However, the field of laser technology in general and that of short pulse lasers in particular are in a state of dramatic developments. If this trend continues it will only be a couple of years that such systems are in the reach for analytical applications from the financial as well as from the technological point of view.

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