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Abstract

Resonant multiphoton ionization of laser desorbed non-volatile samples has been achieved in a Fourier transform ion cyclotron resonance mass spectrometer (FTICR). The detection of iron at the 100 parts-per-million doping level in an InP compound semiconductor sample and the production of molecular ions for a hexapeptide have been observed in a modified FTICR analyzer cell. A unique three laser experiment has been devised in which infrared multiphoton dissociation of laser desorbed dipeptide ions, formed by resonant multiphoton ionization of laser desorbed neutrals, is performed.

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Introduction

Multiphoton ionization (MPI) (1-3) of neutral molecules has been widely studied in recent years as high-powered pulsed lasers with tunable output in the ultraviolet wavelength range have become commercially available. Both resonant (REMPI) and non-resonant MPI can be used to ionize species of interest, with the former yielding wavelength-selective formation of (primarily) parent ions at low laser power, and increasing numbers of fragment ions as the laser power is increased. At high laser powers non-resonant MPI can be used to produce ionization from all molecules present in the focal volume of the laser, although wavelength selectivity is sacrificed and far fewer parent ions are usually formed (4,5). The use of MPI to ionize neutral molecules which have been desorbed from solid surfaces has been shown to be a powerful analytical technique by several groups. In this approach the ability to separate the desorption and ionization steps and the advantages of MPI outlined above have resulted in unique capabilities for analysis of solid samples.

All earlier experiments have utilized time-of-flight (TOF) mass spectrometers for mass analysis, because these pulsed instruments couple well with the pulsed lasers used for laser desorption and MPI. The groups of both Grotemeyer and Schlag (6, 7) and Lubman (8, 9) have used a supersonic expansion to entrain CO₂ laser-desorbed neutrals before MPI. This approach helps to provide a spatially well-defined beam of neutrals prior to ionization (enhancing sensitivity and mass resolution when using TOF ion analysis) and at least partially cools internal degrees of freedom of the neutral molecules, thus increasing the number of molecules in the states accessed by the MPI laser. A wide range of compounds, including many of biological interest, have been studied by these groups. Zare and coworkers (10,11) have recently used a similar approach, but without supersonic expansion of the laser-desorbed neutrals, to analyze carbonaceous deposits in meteorites.

Our laboratory has been actively engaged in coupling lasers (12-15) to Fourier transform ion cyclotron resonance (FTICR) mass spectrometers (16-20) for a number of years. Of particular interest are the direct formation of ions by CO₂ laser desorption (14,21-23), and the use of a second laser to induce fragmentation of these ions via infrared multiphoton dissociation (IRMPD) (14,20). Since FTICR utilizes pulsed ion
formation and detection, it should couple with (pulsed) laser desorption of neutral molecules followed by (pulsed) multiphoton ionization in as facile a manner as do TOF mass spectrometers.

At least two additional advantages should be realized when using FTICR mass analysis to study ions formed by MPI of laser-desorbed neutrals. The first is much higher resolution than is possible with TOF mass spectrometers, even those equipped with reflectrons (24). The highest mass resolution of any type of mass spectrometer has been routinely demonstrated (25) by FTICR mass spectrometers, and such high resolution can often be valuable in distinguishing ion structures of the same nominal mass or in separating different isotopes of certain elements which overlap in mass. A second advantage of FTICR mass analysis is the ability to subject trapped ions to further analysis, studying their reactivity in ion/molecule reactions (26), and/or inducing fragmentation by collisional (27) or photon (28) activation.

While to our knowledge no group has demonstrated MPI of laser desorbed neutrals in an FTICR mass spectrometer, several have reported MPI of molecules introduced into the ICR mass spectrometer directly in the gaseous state (29-31). Laser desorbed neutrals have been ionized by methods other than MPI, such as electron impact (32) and chemical ionization (33). We report here the successful MPI formation of ions from laser desorbed neutral molecules in a FTICR mass spectrometer. Ions formed in this way can be detected using the high mass resolution capabilities of the FTICR technique. We have also exploited the ability to subject the ions produced and trapped in this manner to laser photodissociation in a unique 3-laser experiment in which a third (gated, continuous-wave (cw) CO₂) laser has been used to dissociate small oligopeptide ions.

**Experimental Section**

The Fourier transform ion cyclotron resonance mass spectrometer used in this work consisted of a Nicolet (34) FTMS-1000 data system, a prototype Nicolet 2.0 tesla magnet and a home-built/assembled vacuum system (this system is described in detail in Reference 35). The main vacuum chamber was a 15 cm inside diameter (id) stainless steel cylinder which was mounted inside the 20 cm bore of the 2.0 tesla superconducting magnet. Two oil diffusion pumps (36), with pumping speeds of 700 L/s and 300 L/s
were used to evacuate the vacuum chamber. Multiple windows were mounted on the end flanges to facilitate various laser-related experiments.

Several modifications of the existing FTMS-1000 analyzer cell were necessary in order to permit entry of the beams from more than one laser (see Figure 1). In all experiments an excimer laser (37) operating in the pulsed CO$_2$ mode (10.6 μm wavelength, pulse length ca. 1 μs, approximately 0.75 mJ/pulse entering the vacuum chamber) was used to desorb a solid sample mounted on a probe tip (38). The laser beam passed through a ZnSe window into the vacuum chamber and was focussed by a 7.62 cm focal length ZnSe lens. The focussed beam entered a small hole in the front trap plate of the FTICR cell, traversed the cell and exited the back trap plate through a 1 cm diameter mesh-covered opening, then irradiating the sample. Post-ionization of the neutrals desorbed by the first laser was achieved using the fourth harmonic, 266 nm, of a Nd:YAG laser (39) or by the tunable output of a dye laser pumped by the second harmonic of the Nd:YAG laser. The output from rhodamine dyes 610 and 590 (40) were doubled to obtain wavelengths between 305 and 280 nm. The UV beam entered the vacuum chamber through a 1 cm sapphire window and for the majority of the studies passed through a 90° fused quartz turning prism and was focussed by a 2.54 cm focal length cylindrical lens through a cut-out section of the machinable ceramic cell support/insulator at the solids probe end of the cell. This positioned the focal point several millimeters from the probe tip and directly between the tip and the cell. Alternatively, some early studies were performed by passing the unfocussed beam through 1 cm diameter holes in the excite plates (similar to the cw-laser pathway shown in Figure 1), thus allowing the beam to travel through the center of the cell. Typical UV laser pulse energies were on the order of 50-100 mJ/pulse at 266 nm and 5-10 mJ for the (tuned) wavelengths from 280 - 305 nm. The output of the third laser, a gated cw-CO$_2$ laser (41), also entered the vacuum chamber through a ZnSe window and was turned by a plated gold mirror mounted to one of the excite plates. The beam entered the cell through a 1.25 cm hole and reflected from the opposite (parallel) plate, giving a second pass of this laser beam.

The FTICR pulse sequence employed is shown schematically in Figure 2. It was necessary to adjust the pulse sequence to a period of 989.5 ms in order to conform to
the triggering requirements of the Nd:YAG laser. Coupling of the FTICR electronics and
the Nd:YAG laser was accomplished by a home-built microcomputer interface (42). Using
this program it was possible to trigger the laser q-switch only every ninth firing of the
flashlamps, thus allowing a longer FTICR pulse repetition period (which corresponded to
a rate of ca. 1 Hz as opposed to the normal 10 Hz laser firing repetition rate) and
permitting greater freedom in designing the pulse sequence shown in Figure 2.

The pulsed CO$_2$ laser was triggered directly after a quench pulse expelled all ions
from the cell, but did not fire until an additional 44.1 ms after triggering due to internal
timing constraints. After pulsed laser desorption of neutral molecules the Nd:YAG was
fired a variable time period, 5 to 50 $\mu$s, later. The timing between the two lasers was
controlled by varying the delay between the quench pulse and the first eject pulse,
maintaining a fixed length for the entire sequence. The time between the two laser pulses
was monitored by using the sync output from the CO$_2$ laser and the signal from a fast
photodiode which picked up scattered light from the Nd:YAG laser beam. Jitter between
laser pulses was $\pm$ 4 $\mu$s.

Because of timing restrictions the Nd:YAG laser was not triggered during the pulse
sequence in which it fired, but instead during the preceding sequence and was "wrapped"
around to the next pulse sequence. In the 3-laser experiments the cw-CO$_2$ laser was
gated on for a variable time after a series of three ejection events, thus irradiating the
trapped ions formed by MPI of laser-desorbed neutrals. Following this the usual FTICR
excitation and detection process took place.

For most experiments, the mass spectrometer was operated in its standard
broadband (2.67 MHz to 10 kHz) mode using frequency chirp excitation. Heterodyne
detection of the transient signal was used when required for accurate mass analysis. Typically,
10 to 50 transient signals, each consisting of 16384 data points, were acquired
and averaged. The averaged time-domain transient was apodized (43) and zero-filled
once prior to Fourier transformation. The size of the individual transient signal could be
increased from 16k to 64k data points as necessary to increase the mass resolution. Only
positive ions were observed following multiphoton ionization, and a trapping voltage of 2
volts was used for most experiments. The trapping voltage was reduced to 0.5 volts
during heterodyne detection experiments.
A clean stainless steel probe tip was used to generate the Fe signal as was an InP wafer doped to the 100 ppm level. Coronene (Aldrich) and peptide samples (Chemical Dynamics Corporation) were used without additional purification. Sample purity was assessed using broadband laser desorption mass spectrometry. The samples (0.5 to 5 mg) were mixed with methanol (3 to 5 ml) and a small portion of the resulting slurry was deposited on a stainless steel probe tip using a micropipette. The sample coating typically appeared opaque and was much thicker than that normally used for laser desorption. The solids probe tip was mounted such that rotation of the probe exposed a fresh surface for laser desorption of neutrals. Depending on sample preparation, a single spot produced signal for 100 to 500 laser pulses.

Results and Discussion

Post-Ionization of Laser Desorbed Neutrals in the FTICR. The first attempts at multiphoton ionization of laser desorbed neutrals were made with coronene. Care was taken to use sufficiently low desorption laser power that no ions were produced directly. Postionization was achieved with an unfocussed (frequency doubled) dye laser beam of 300 nm wavelength (solution $\lambda_{\text{max}}$ of coronene is 302 nm) which passed through the center of the cell in a similar path as the IR laser beam in Figure 1. A maximum m/z = 300 parent ion signal was observed when the delay between the desorption and ionization lasers was set to 60 $\mu$s, but ions were still formed with a delay time of up to 150 $\mu$s.

Multiphoton ionization of laser desorbed iron atoms was performed using a similar procedure and experimental configuration to that for coronene. Iron and other neutrals were desorbed from a 304 stainless steel probe tip with postionization achieved by 302.1 nm light, the first photon resonant with the $^5\Delta_3 \rightarrow ^5\Delta_2$ transition and the second exciting into the ionization continuum. Light of several other wavelengths corresponding to transitions originating from the $^5\Delta_2$ state (298.4, 296.7, and 293.7 nm) also produced ionization. However, no signal could be produced from other higher lying $^5\Delta_2$ states. This indicates that significant populations of even low-lying excited states (0.05 eV and 0.11 eV above the ground state) of the Fe atoms were either not produced or were quenched en route to the cell center. These results are quite different from the resonant ionization lines observed in a glow discharge (44), where numerous examples of excitation
from the higher excited states were observed. Figure 3 shows the Fe\textsuperscript{+} signal produced by 302.1 nm resonant, two photon ionization as a function of the velocity the neutral iron atoms would obtain if desorbed from the surface during the desorption laser beam pulse. The experimental distribution does not fit Boltzmann velocity distributions at 2,700 °C (the boiling point of 302 stainless steel) or 10,000 °C. A substantial signal is observed at both velocities much slower than neutrals desorbed at 2,700 °C would acquire and much faster than those formed at a temperature of 10,000 °C. This indicates that either the iron atoms are desorbed with a wide distribution of kinetic energies or that the desorption process proceeds gradually with atoms emitted tens of microseconds after the laser energy has been deposited.

Significant iron signals were also produced when the doubled dye laser beam was focussed by the cylindrical lens and ionization took place quite close to the probe tip. At a distance between the probe tip and ionization laser focal point of approximately 2 mm the strongest ion signals were found at a laser delay of 7 µs and no observable signal was seen at either 4 or 10 µs. Jitter in the timing prevented a detailed study of neutral velocities; however, the narrow distribution of desorbed iron atoms found close to the probe tip (as opposed to a wide distribution seen at the cell center) indicates an virtually instantaneous desorption process with the resulting atoms desorbed with a wide range of velocities.

The ultimate intent of these atomic post-ionization experiments with FTICR mass analysis was the detection of trace impurities while taking advantage of the technique's high resolution. Iron at a 100 ppm doping level in an InP compound semiconductor substrate was observed using the experimental configuration discussed above and shown in Figure 1. The signal was maximized at a 10 µs delay time between the two lasers (slightly longer than with Fe from the stainless steel substrate) at a 2 mm probe to focal point distance, which permitted a major portion of the desorbed neutrals to be intersected by the focussed ionization laser. A small In\textsuperscript{+} peak is also observed at m/z = 115, since it was difficult to produce desorption without the formation of In\textsuperscript{+}. The FTICR mass spectrum obtained is shown in Figure 4. A maximum mass resolution of 11,400 using 64 K data points was obtained. This resolution, which is much lower what is normally experienced using FTICR, may be the result from the high translational energy these ions
possess (in addition to a wide distribution of energies) and the inability to thermalize the ions with a neutral gas because of resulting loss of signal strength.

**Infrared Multiphoton Dissociation (IRMPD) of Oligopeptide Ions** Previously (14,21) we have coupled direct laser desorption with infrared multiphoton dissociation to study a wide variety of interesting chemical systems. The coupling of these two laser experiments yields a technique that is capable of producing molecular weight information because of the "soft" ionization nature of laser desorption yet also provides useful structural information from the fragments produced by IRMPD.

A study of alkyl-substituted pyridinium salts (21) demonstrated that laser desorption of these compounds readily forms intact positive ions in the gas phase which undergo fragmentation following collisionally activated dissociation (CAD) (using argon as a collision gas) or IRMPD when irradiated by a cw CO₂ laser. An advantage that photodissociation may have over collisionally activated dissociation is that as the molecular weight of the ion of interest increases collisional processes may impart insufficient energy to the ion due to the reduced momentum transfer of a massive ion colliding with a small neutral molecule. Further studies of IRMPD on ions in the molecular weight range 300 to 1400 (14) showed that these larger ions readily undergo fragmentation when "activated" by absorption of infrared photons.

Often direct laser desorption produces a pseudo-molecular ion which is formed by attachment of a cation such as K⁺ or Na⁺ to the intact neutral molecule. Unfortunately, the main fragmentation pathway observed with IRMPD is quite often (the structurally uninformative) loss of the neutral molecule.

\[(M+K)⁺ + n\nu \rightarrow M + K⁺\]

Such behavior is not seen when working with negative ions, where (M-H)⁻ ions are most often formed, but it can be quite limiting when examining positive ions. Production of such pseudo-molecular ions is particularly undesirable when using laser desorption and IRMPD to study peptide ions where cleavage of amide linkages and not M - K⁺ bonds is sought.

Based on the results of other workers (12) using low-powered laser desorption and multiphoton ionization for ion production in time-of-flight investigations the laser desorbed neutral peptide provides an abundance of ions that are potentially useful for structural
identification. Peptides containing a strongly UV absorbing amino acid residue, such as phenylalanine ($\lambda_{\text{max}} = 268$ nm), tyrosine ($\lambda_{\text{max}} = 272.7$ nm), tryptophan ($\lambda_{\text{max}} = 286.0$ nm), or histidine ($\lambda_{\text{max}} = 250.0$ nm) are easily ionized by resonant multiphoton ionization often producing a characteristic molecular or pseudomolecular ion.

Consider, for example, the laser desorption/multiphoton ionization spectrum of the hexapeptide LeuTrpMetArgPheAla. This molecule undergoes facile ionization when irradiated with 266 nm light producing a molecular ion and numerous fragment ions. These ions provide useful molecular weight and structural information. An abundant fragment peak is observed for each of the possible sequence ions as shown in Figure 5. The labeled peaks represent fragmentation from the C-terminus end of the molecule. Additional fragment ions resulting from N-terminus cleavages and loss of side alkyl groups are present in lesser abundance.

Although the amount of fragmentation observed following MPI can sometimes be controlled by varying the energy of the ionization laser, quantitative control of the amount of fragmentation is often quite difficult. One answer to this problem is to irradiate ions trapped in the FTICR analyzer cell with infrared radiation. The laser desorption/multiphoton ionization mass spectrum of the dipeptide tryptophanglycine (TrpGly) is shown in the top of Figure 6 (all ions, including a large intensity ion at m/z = 130, below m/z = 150 are ejected in this spectrum). This dipeptide forms a pseudomolecular ion m/z = 244 ([M-OH]$^+$ as determined by accurate mass analysis). This ion dissociates when irradiated with a gated pulse of light from a continuous wave carbon dioxide laser, forming two fragment ions at m/z = 200 and 171. Double resonance experiments (m/z = 200 is ejected during the cw CO$_2$ laser pulse) confirm this to be a competing and not a sequential (m/z = 200 $\rightarrow$ m/z = 171) reaction. The amount of fragmentation is easily controlled by varying either the cw-CO$_2$ laser power or the length of the irradiation period. A plot of the normalized abundance for the parent and daughter ions as a function of the cw-CO$_2$ laser pulse energy is shown in Figure 7. The daughter ion intensity increases smoothly as the amount of IR irradiation increases.

TrpGly has been previously (45) shown to form a cyclo-dipeptide (with elimination of water), but only when a thick sample (ca. 10 $\mu$g) is subjected to laser desorption and REMPI in a similar approach to this study (where sample thickness is estimated at 0.5 -
However, accurate mass analysis identified the loss of 17 amu as OH (not H2O or NH3) in the FTICR. Subsequent losses of 44 and 73, induced by IRMPD, can be explained by the loss of CO/NH2 and NHCH2CO/NH2 from [TrpGly]+ shown in Figure 8, but would be difficult to explain if a cyclic ion was formed. Thus, by employing 3-lasers and the high resolution of FTICR to study the reaction mechanism, a different fragmentation route than that earlier predicted has been ascertained.

The LD/REMPI of several dipeptides produced intact molecular ions which were then subjected to IRMPD. The molecular ion of ProPhe (mw = 262) IR photodissociated to form m/z = 70 ([pyrrole - 1]+ (see Figure 9)), and the ArgPhe molecular ion (MW = 341) photodissociates producing fragment ions at m/z = 304 (loss of neutral OH), m/z = 245 (loss of the phenyl group), m/z = 263 (loss of NHCNHNH2) and m/z = 158 (the breaking of the peptide bond with the charge remaining on the Arginine fragment). These fragments provide practical information which is useful in structure determination. Thus, the promising results produced by the LD/REMPI/IRMPD technique suggest that it may be extended to larger molecular weight, more biologically significant oligopeptides/proteins in which direct laser desorption does not produce useful information.

**Conclusions**

Multiphoton ionization of neutral molecules formed by laser desorption has been carried out successfully in a Fourier transform ion cyclotron resonance mass spectrometer. At least two advantages of using FTICR mass spectrometric detection have been realized: high mass resolution and the ability to subject ions formed by MPI to infrared laser dissociation while they are trapped in the FTICR cell. Extensions of this technique to larger peptides, other biological samples, and to lower concentrations of dopants or contaminants in semiconductor samples are in progress.

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Figure Captions:

Figure 1. ICR cell modified to permit three laser experiments.

Figure 2. Experimental pulse sequence employed in the FTICR experiments. The cw-CO$_2$ photodissociation step was eliminated when only LD/REMPI was desired.

Figure 3. Relative intensity of Fe$^+$ formed by REMPI (302.1 nm) of laser desorbed neutral from a 304 stainless steel probe tip as a function of velocity, assuming all neutrals were desorbed during the 1 μs pulse duration of the CO$_2$ desorbing laser. Also plotted are the Boltzmann velocity distributions at 2,700 K (boiling point of stainless steel) and 10,000 K.

Figure 4. REMPI spectrum of iron doped (100 ppm) InP. Resolution (FWHH) of the Fe$^+$ peak is 11,400. A small In$^+$ ion is also observed and is formed by the desorbing laser.

Figure 5. The LD/REMPI (REMPI at 266 nm) spectrum of hexapeptide LeuTrpMetArgPheAla.

Figure 6. (a) The LD/REMPI spectrum of TrpGly (all ions under m/z = 150 are ejected. (b) The LD/REMPI/IRMPD spectrum of TrpGly showing losses of 44 and 73 amu.

Figure 7. Dependence of ion peak area vs. cw-CO$_2$ power for the photodissociation of [M - OH]$^+$ formed by LD/REMPI.

Figure 8. Possible ionization/dissociation scheme for the LD/REMPI/IRMPD of TrpGly.

Figure 9. IRMPD ions formed from the LD/REMPI produced molecular ions of (a) ProPhe and (b) ArgPhe.
pulsed CO\textsubscript{2} laser beam

ZnSe focussing lens

cw-CO\textsubscript{2} laser beam

gold plated mirror

ICR cell

cylindrical lens

90\degree turning prism

solids probe

focal point

resonant Nd:YAG laser beam
a) $[M - OH]^+$

b) $[M - OH]^+$
Dissociation Laser Power (Watts)

\[
\frac{\text{Total Peak Area}}{\text{Ion Peak Area}}
\]

- \text{m/z = 244}
- \text{m/z = 171}
- \text{m/z = 200}
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