A Method of Increasing the Sensitivity for Laser Desorption in an Ion Trap Mass Spectrometer

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Laser desorption in an ion trap mass spectrometer shows significant promise for both qualitative and trace analysis. In this work, we explore various combinations of time-varying DC and radiofrequency (RF) fields in order to optimize laser-generated signals. By judicious choice of timing between the laser desorption pulse and the rise in the applied RF trapping potential, we observed over an order of magnitude enhancement in the trapped ion signal. This new method for laser desorption has enabled us to observe mass spectra of many compounds (e.g., pyrene, dichlorobenzene, and ferrocene) that are barely detectable using previous laser desorption methods. Effects of laser timing and the magnitude of the steady-state RF potential are discussed. (*J Am Soc Mass Spectrom* 1993, 4, 706–709)

The coupling of laser desorption with mass spectral detection has produced a powerful method for the analysis of complex liquid and solid samples [1–7] and has found diverse areas of application, from analysis of superconductors [8] to complex biomolecules [9]. Laser desorption typically involves the direct production of ionized species as a result of the interaction of a high-power ($\geq 10^6$ W/cm²) laser pulse with a solid surface, matrix, or sample adsorbed on the surface.

Laser desorption/ionization techniques have been combined with virtually all types of mass analyzers [4], but because of the relatively low duty cycle associated with pulsed lasers (typically 10 Hz–1 kHz), most work has been done with mass spectrometers that use multiplex detection. Because of their potentially higher resolution, ion cyclotron resonance (ICR) and quadrupole ion traps are often used in preference to time-of-flight instruments.

The combination of laser desorption (LD)/ionization techniques with ICR and ion trap (IT) mass spectrometers provides an easy way to combine several spectroscopy and mass spectrometry techniques into a single analytical sequence. Lasers have long been used with ICR mass spectrometers for desorption [10,11] and for photodissociation studies [12]. More recently, IT mass spectrometry (IT/MS) detection has been used for LD [5, 13–21] and photodissociation studies [22, 23].

There is a fundamental problem in trapping ions formed either external to the trap or at the interior electrode surfaces of the trap. The radiofrequency (RF) voltage applied to the ring electrode produces a sub-

stantial effective potential barrier for injection of ions into the trap [24]. In general, ions either have insufficient energy to enter the trap or, if they do, they pass through the trap by traveling over the top of the potential barrier on the other side. Debye shielding of the ion cloud may partially compensate for this problem [25]; electrons injected with the ions may partially shield the cloud from the full effect of the potential barrier. After entry, the electrons find themselves in unstable orbits and are immediately ejected, whereas the naked ions are left with insufficient energy to leave the trap. Trapping is also assisted by collisional processes within the trap [26] that will slightly reduce the kinetic energy of injected ions, damp their motion [22], and increase the probability of trapping.

In this work we describe the use of laser ablation, carefully timed with respect to the finite risetime of the RF potential in the Finnigan-MAT IT/MS apparatus. Laser-desorbed ions, produced when the RF potential is low, can penetrate the trap but are unable to escape because the RF increases sufficiently to produce a deeper trapping well by the time they have passed the center of the trap. Several investigators have explored theoretically the possibility of increasing the trapping efficiency by gating the RF potential "on" after the ions have entered the trap [27]. Prior to our work, there was only one report using this method [13], and in that case no systematic study of parameters was attempted.

Experimental

The combined LD/IT apparatus has been previously described [22]. The apparatus is based on a Finnigan-MAT (San Jose, CA) IT mass spectrometer and a

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Questek XeCl excimer laser. The IT was modified for desorption experiments by drilling opposed (180°) 2.5-mm holes in the ring electrode, as previously described by Heller et al. [14].

Samples were introduced with a direct insertion probe guided through one of the holes. The probe tip (304L stainless steel; 2.2-mm diameter) was in contact with the ring electrode and thus at the ring potential. The material on the probe tip was desorbed by the laser beam, which entered through the opposite hole. The probe position was adjusted to maximize the observed ion signals. This resulted in the probe tip being recessed approximately 1 mm behind the inner surface of the ring electrode. The ablation laser beam (308 nm; 15 ns) was attenuated to approximately 100 μ J and focused by a 60-cm lens to a spot approximately 1×2 mm (3×10^5 W/cm²). Helium, at an uncorrected ion gauge pressure of $1\text{--}2 \times 10^{-5}$ torr, was used as a buffer gas. The laser was fired during the rising edge of the trapping RF potential, as shown in Figure 1, and at random phase with respect to the fundamental RF. The RF potential rises to a maximum of V_{max} , the size of the RF potential step, with a time constant of approximately 175 μ s. More recent measurements indicate that the observed signal is also dependent on the laser-to-RF phase. These experiments will be reported elsewhere [28].

Results and Discussion

Trimethylphenyl ammonium iodide was studied first as a benchmark compound. Initial LD/IT mass spectra of this compound were obtained by firing the laser at long delay times (after the RF potential reached V_{max}) and were in qualitative agreement with previous work [15]. Peaks were observed at m/z 136 (the intact cation), as well as at lower and higher masses.

Figure 1. Depicts the timing sequence for mass spectral analysis by LD IT MS. The horizontal axis represents time; the expanded region in the middle trace shows that the voltage rise is not instantaneous but has a finite time constant (approximately 175 μ s) associated with the apparatus.

Figure 2. Signal detected for several ions as a function of delay between initiation of the RF trapping potential and firing of the ablation laser, V_{max} , the steady-state RF potential, was 508 V, which results in ejection and, hence, no detection of ions below a mass of 40 Da.

We then explored the effect of timing between the laser ablation event and various combinations of time-varying DC and RF potentials on the ring electrode. In general, we found that firing the laser on the increasing edge of the RF trapping potential, as shown in Figure 1, significantly increased the observed signal level, relative to firing the laser either before the application of the trapping potential or after the potential reached V_{max} . Typical results are shown in Figure 2, where the detected signal for several masses is plotted as a function of delay between turn-on of the RF potential and firing the laser. The most prominent masses observed above the parent ion mass correspond to the combination of mass 76 with the 121-Da ion. Ion signals observed at 197, 271, and 273 Da are comparable in intensity to the 121-Da ion signal. We observed peaks up to 577 Da, corresponding to the 121-Da ion in combination with six 76-Da fragments.

The observed signals are strongest in the delay time range 40–150 μ s. The optimum delay time depends on both ion mass and V_{max} . Figure 3 shows the time delay at which the maximum signal occurs (i.e., the maxima of the curves in Figure 2) as a function of V_{max} and for a number of different masses. The maximum trapping efficiency occurs at longer delays for heavier ions. This also corresponds to higher RF potentials because the RF potential is closer to reaching V_{max} at long delay times.

If the delay times on the y axis in Figure 3 are converted to RF potential at that instant, the data still retain some of the curvature shown. That is, the optimum signal depends on both the magnitude of the RF when the laser fires and the rate at which the RF voltage is changing. This can be understood in a qualitative sense as follows. Early in the formation of the trapping field, an ion is presented with a relatively low

Figure 3. Delay time for maximum signal $T_{\max}$ as a function of $V_{\max}$ (RF $V_{o-p} = 12.5 \times \text{Da}$) for ions having mass-to-charge ratios indicated.

barrier to entry into the trap, and the trapping well is not very deep. During the time that the ion is traversing the trap (10–50 μs , based on both modeling studies and on other measurements of the velocity of laser-desorbed ions), the amplitude of the field increases, and the ion is presented with a much deeper well from which to escape. That is, the kinetic energy gained by the ion as it travels to the center of the trap is less than the kinetic energy it needs to escape if the RF is ramped. The effect on trapping efficiency of lower RF potential when the laser fires can be partially compensated by a faster rise of the RF potential (i.e., higher $V_{\max}$).

We did not use well depth in Figures 2 and 3 because there are some difficulties in applying the pseudopotential model of an effective potential well [24] quantitatively. First, the pseudopotential model is most applicable under steady-state conditions near the center of the trap. The model fails near the electrodes where the trapping field changes rapidly on the scale of ion motion during a single RF cycle [24a]. Second, to calculate the potential barrier versus delay time, we must accurately know the RF potential at each delay time. The RF potential rises with a time constant that is dependent on $V_{\max}$ (10–90% risetimes of 171 and 185 μs for RF steps from 0 to 250 and 1250 V_{o-p} , respectively), and we noted small deviations in the risetime of the RF from day to day (resulting in an error in the delay time-to-RF potential conversion).

It should be noted that in most of the earlier experiments cited above, the laser was not fired until many milliseconds after the trapping potential had been applied (after the RF reached $V_{\max}$); typically this potential corresponded to a low-mass cutoff of 20–40 Da. At these delay times and for all of the RF step sizes studied, the signals in this work have reduced to a very small fraction of the value exhibited at optimal

delay times. The signal observed by triggering on the leading edge of the RF potential is at least an order of magnitude larger than that observed by firing the laser after the RF reaches $V_{\max}$.

Using the LD/dynamic trapping method described above, we also observed mass spectra from samples of pyrene, anthracene, ferrocene and dichlorobenzene and mixtures of polycyclic aromatic hydrocarbons. In contrast, no signal could be obtained from these samples if the laser was fired after the RF reached $V_{\max}$. In the future we will report the effect on trapping efficiency of LD/IT/MS parameters, such as buffer gas pressure and composition, ring electrode DC potential, and phase locking the RF voltage and laser pulse.

Conclusions

The combination of laser sampling and IT/MS promises to be a powerful analytical technique for the direct analysis of complex samples. The work presented here demonstrates that the sensitivity of this method can be increased significantly by firing the laser and injecting ions into the trap, on the rising edge of the RF waveform, before the RF potential is fully developed.

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