

TWO STEP LASER MASS SPECTROMETRY

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INTRODUCTION

Challenges in analytical mass spectrometry include measurement of parent molecular mass, particularly for large molecules, isomer distinction, and selective detection of trace compounds. Laser techniques can make contributions in each of these areas by providing alternative ion sources in the form of laser sample vaporization, of laser ionization, or of a combination of both /1/.

Since the first reports on the use of lasers in mass spectrometry /2-5/, the field has developed in two major directions. Two step laser mass spectrometry (L2MS), which is the subject of this review, can be distinguished from matrix assisted laser desorption ionization (MALDI). The latter technique involves a single step to both vaporize and ionize the sample

with a single laser pulse /6-8/. In L2MS laser desorption and laser ionization are two separate steps, requiring at least two different laser pulses. This separation constitutes a complication that makes the approach less adaptable to routine analysis but offers the great advantage of affording control over the ionization process. Amongst other features, this provides detection with additional selectivity by combining mass dispersion with wavelength dispersion.

In what follows we shall discuss the neutral laser desorption process, characteristics of resonant as well as non-resonant photoionization, different implementations with and without jet cooling, and specific examples.

NEUTRAL LASER DESORPTION

The process of neutral laser desorption is very poorly understood. The general idea is that fragmentation is minimized when the time scale for heating is shortened. The rates required to desorb molecules without fragmentation are of the order of 10^{11} K/sec, which corresponds to a 1000 K temperature jump in a typical 10 ns laser pulse. This observation was discussed by Hall in terms of Arrhenius type rates $k = C.P \exp(-E/RT)$ in which E represents an activation energy, P pre-exponential factor and C the surface coverage. T is the temperature and R the Boltzman constant /9/. When both E and P are larger for desorption than for thermal chemistry, desorption will dominate at higher temperatures. Thus fragmentation can be minimized by a high heating rate. Zare and Levine reached a similar conclusion with a "bottleneck" model, in which the laser energy excites the phonons of the surface, which reasonably match the frequency of the bond between the molecules and the surface, whereas the frequencies of the molecular vibrations are much higher /10./. Li *et al.* performed an elegant set of experiments on model surfaces to investigate the effect of the temporal profile of the thermal pulse on desorption /11/. Zenobi *et al.* have studied the role of surface temperatures in laser desorption /12,13/ and the energy distribution of desorbed aniline as a model molecule /14/.

For clarity it may be useful to contrast neutral laser desorption with matrix assisted laser desorption. In the latter case the analyte is mixed with a matrix compound, which serves two purposes. First the matrix absorbs the laser light and causes simultaneous vaporization of matrix and analyte. Secondly, the matrix causes ionization, usually by containing an efficient

proton donor. This approach has proven to be very useful for providing parent molecular masses of large molecules, such as biomolecules /15,16/ and polymers /17/. For routine analytical mass spectrometry this technique has become competitive with electrospray and fast atom bombardment. Recently Siegel *et al.* compared each of these techniques as well as L2MS in a side-by-side analysis of photofrin oligomers, obtaining comparable results /18/. In this context we note that in most other mass spectrometric techniques, that rely on some form of non-thermal desorption, compounds are vaporized and ionized in a single step. Prime examples are secondary ion mass spectrometry (SIMS), fast atom bombardment and (^{252}Cf) plasma desorption. Generally one may conjecture that any desorption process that produces ions, produces neutrals as well and is likely to do so with more abundant orders of magnitude. It is usually not possible to capitalize on that higher abundance for increased analytical sensitivity because of limitations in ionization efficiency. Pallix *et al.* have applied post ionization to SIMS /19/ and there have been some reports of post ionization in combination with MALDI /20/, but the major applications of photoionization are in combination with laser desorption.

PHOTOIONIZATION

Photoionization can take several forms as indicated schematically in Figure 1. The obvious first requirement is that the total photon energy exceeds the ionization potential. For single photon ionization (a) this requires wavelengths in the far UV or vacuum UV (VUV) range, that are not always conveniently produced. In spite of this technical limitation, single photon ionization can be attractive as a general soft ionization technique, as will be discussed in the next section. Most aromatic molecules can be ionized efficiently by two-photon ionization, such that a first photon excites the molecule, while a second photon ionizes by a transition from the excited state. Here we may distinguish two cases. Case (b) in Figure 1 indicates excitation to an energy at which there is a high density of intermediate states, such that the ionization process does not depend strongly on the wavelength. Case (c), on the other hand indicates the situation in which the molecule is excited to the lowest electronic singlet state, S_1 , such that ionization takes place only resonantly, i.e. when the exciting laser is tuned to vibronic resonances. Therefore scanning the laser wavelength while monitoring the

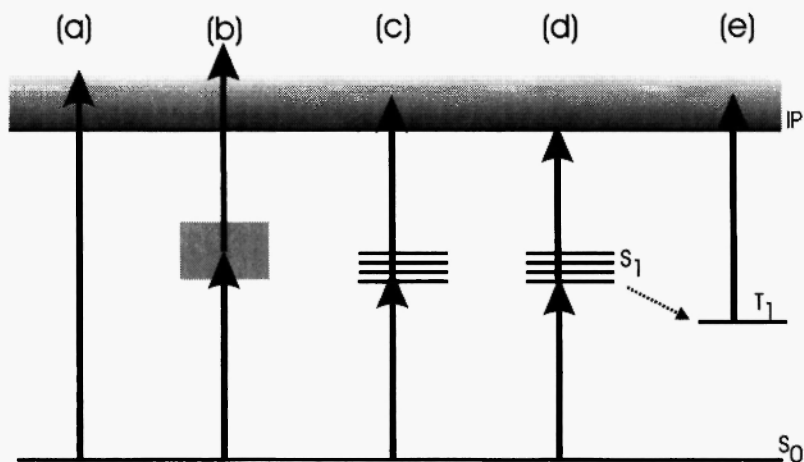


Fig. 1: Schematic diagram of photoionization.

ion signal produces an excitation spectrum. This is called resonance enhanced multiphoton ionization or REMPI [21]. In this approach we may obtain wavelength and mass information simultaneously. As will be discussed below, this powerful combination is very useful for isomer specific mass spectrometry and for trace analysis. Since the wavelength dispersion results from the first transition, the second photon need not be from the same laser. Two-color REMPI, as indicated in cases (d) and (e) in Figure 1, can offer additional enhancement in sensitivity.

MICROPROBE

A straightforward application of L2MS can be found in combinations with laser microprobe instrumentation [22-25]. This approach capitalizes on the capability to focus the desorption laser in the first step, while choosing the ionization wavelength in the second step. Typical spatial resolutions that can be obtained are limited by the diffraction limit and are of the order of microns with a UV laser and of the order of tens of microns with a CO₂ laser. The ions are usually extracted into a reflectron time of flight mass spectrometer. It is possible to produce ions with the desorption laser alone [26] but the use of the separate ionization laser introduces additional selectivity. It may be noted that separate ionization tends to degrade mass

resolution, because the place of ionization is not as sharply defined as for primary ions formed at the sample surface. This L2MS/microprobe approach works best for detection of stable aromatic compounds, particularly polycyclic aromatic hydrocarbons (PAH). Examples of applications include polymer analysis /27/ and the detection of PAHs and fullerenes in meteorites /28-30/.

JET COOLING

A most dramatic improvement on the concept of L2MS can be obtained with jet cooling. In this approach neutral laser desorbed molecules are entrained in a supersonic expansion, prior to entering the source of a time of flight mass spectrometer. A schematic diagram of a typical setup is shown in Figure 2. The main purpose of the supersonic expansion is to reduce the internal energy of the entrained molecules. As will be shown below, this

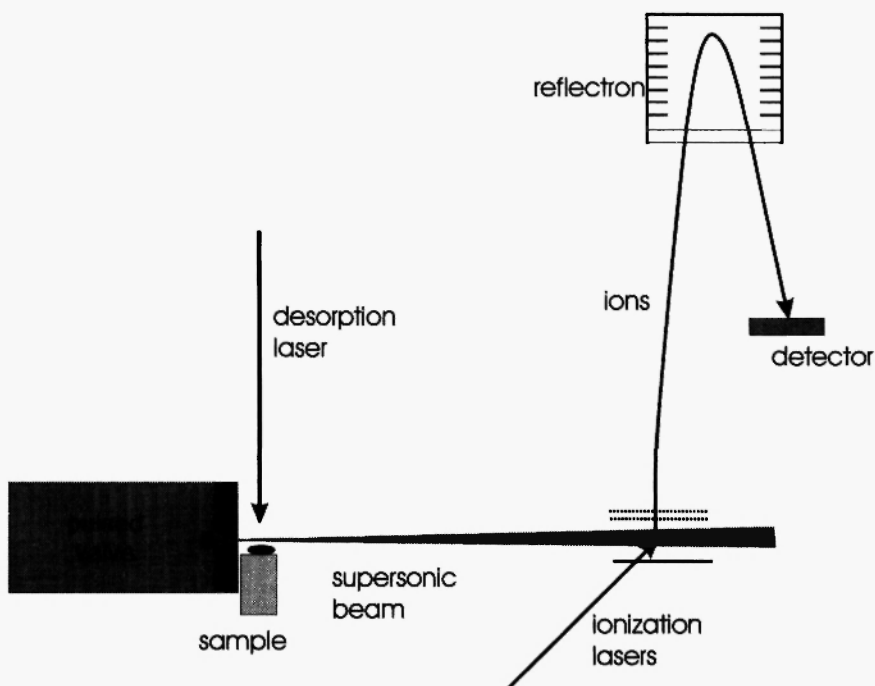


Fig. 2: Schematic diagram of jet cooling apparatus.

offers two major advantages: (i) Reduction of internal energy reduces fragmentation upon ionization and (ii) it opens the possibility of performing vibronic spectroscopy. By mapping beam profiles of laser desorbed perylene, using LIF imaging, Arrowsmith *et al.* have shown that it is possible to entrain desorbed material such that the ionization laser(s) downstream can interact with as much as 1% of the desorbed neutrals /31/. Meijer *et al.* have established an estimate of internal temperature of laser desorbed entrained molecules by analyzing the REMPI spectroscopy of anthracene and of diphenylamine, obtaining temperatures below 15 degrees Kelvin /32/. One cannot determine the temperature in the case of larger molecules for lack of spectroscopic constants. Larger numbers of internal degrees of freedom may on the one hand impede efficient cooling by requiring more collisions, but on the other hand cooling may be more efficient because the energy levels are more closely spaced.

SINGLE PHOTON IONIZATION

Although single photon ionization may appear to be a simpler concept than multiphoton ionization, most L2MS work is based on the latter for two reasons. First, it is difficult to produce photons of the required energy for single photon ionization, and secondly, the advantage of wavelength dispersion is available only when ionizing in two steps via an intermediate excited state. On the other hand, single photon ionization can offer a quite general approach to soft ionization, including for those molecules that lack a suitable chromophore for multi-photon approach.

A good example is the case of aliphatic hydrocarbons, which generally do not absorb at any convenient laser wavelength and which exhibit ionization potentials of the order of 9.5 eV. Conventional electron impact mass spectrometry yields fragment spectra that are virtually identical for all hydrocarbons of the same type, irrespective of size /33,34/. Therefore soft ionization that could produce parent molecular ions would be extremely useful, especially for the analysis of mixtures. The internal energy, E^* , of the ion, available after photoionization is

$$E^* = E_{ph} - E_{ip} - E_{el} + E_{int},$$

where E_{ph} is the photon energy, E_{ip} is the ionization potential, E_{el} is the

kinetic energy of the photoelectron, and E_{int} is the internal energy of the neutral molecule. In the case of 125 nm VUV ionization of hydrocarbons, E_{ph} is within a few tens eV of E_{ip} . Therefore, when we start with a cold molecule, implying small E_{int} , we create an ion with at most a few tenths eV of internal energy. These ions are stable and we can observe the parent mass. On the other hand, when we start with a hot molecule, E_{int} can be substantial, leading to an ion with large E^* and thus to fragmentation. This effect becomes especially pronounced for molecules of increasing size, because of their increasing number of degrees of freedom. This effect of cooling on fragmentation has been discussed by Danon *et al.* /35/.

Figure 3 shows mass spectra of squalane, a branched $\text{C}_{30}\text{H}_{62}$, ionized under different conditions. Spectra 2(a) and 2(b) result from 125 nm photoionization with optimal cooling and with partial cooling respectively. Spectrum 2(c) shows the 70 eV electron impact ionization library spectrum /33/. At conditions of optimal cooling and 9.9 eV ionization energy we obtain exclusively the parent molecular ion. In fact, we can also observe dimers and trimers that are formed in the jet expansion. This observation aids in the determination that fragmentation did not occur. At conditions of partial cooling only, the resulting photoionization mass spectrum shows a distinct fragmentation pattern. The branched alkane breaks at the branches in a non random pattern. All peaks that are marked with their mass number are the result of breaking at a branching point. Note that fragments that result from breaking towards the middle of the chain have a larger abundance than those that result from breaking at a branch on the side towards the end of the molecule. The broad peaks in the spectrum are the result of metastable decay in the flight path of the reflectron time of flight mass spectrometer. Without any cooling the spectrum is identical to that of electron impact in figure 2(c). By controlling the internal temperature it is thus possible to obtain the parent molecular mass and also to obtain structural information from partial fragmentation.

Figure 4 shows a jet cooling VUV ionization mass spectrum of a roughly equimolar mixture of n-alkanes in order to illustrate two observations. First we note the fact that by recording parent masses we can analyze complex mixtures. Secondly we note that we do *not* observe any significant decrease of ionization efficiency with increasing size /36/. Other applications include polymer mass spectrometry /37/ and hydrocarbon analysis /38/.

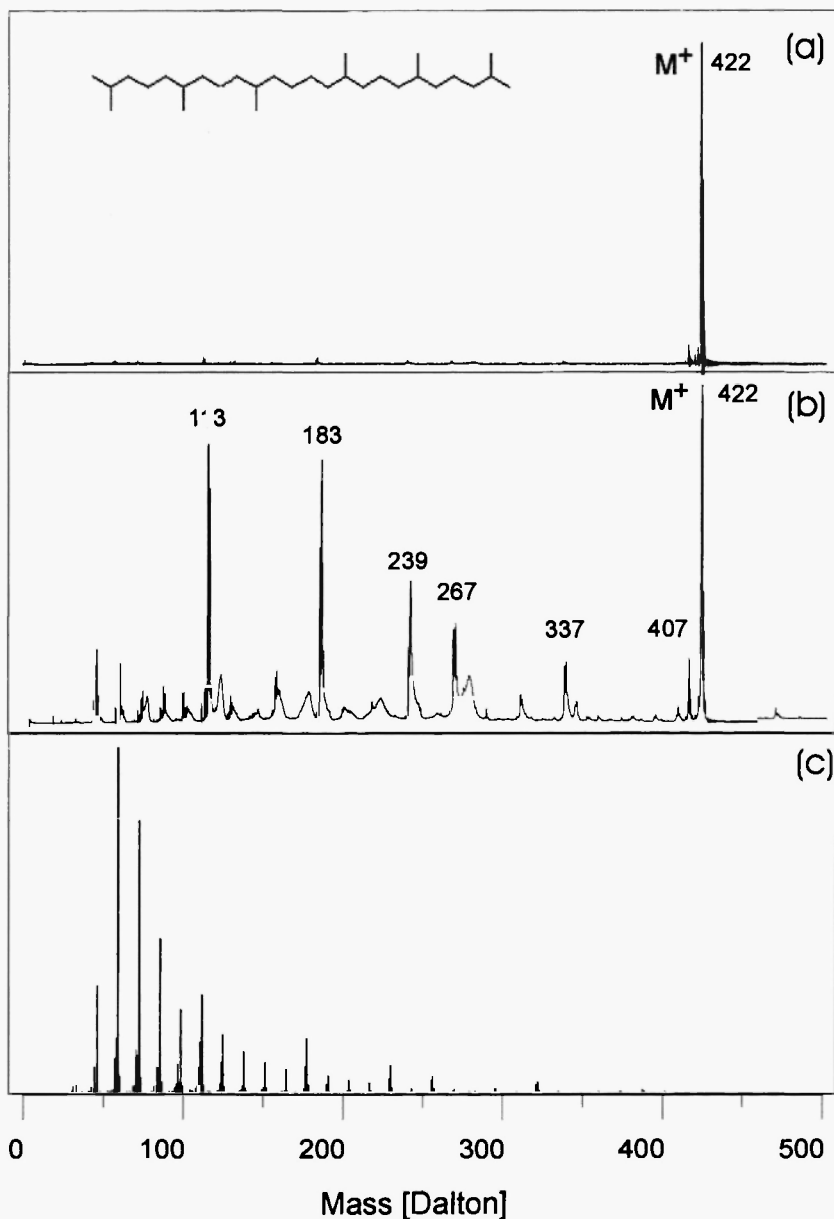


Fig. 3: Squalane mass spectra obtained under different conditions. Spectra 2(a) and 2(b) result from laser desorption with 125 nm photoionization with optimal cooling and with partial cooling respectively. Spectrum 2(c) shows the 70 eV electron impact ionization spectrum.

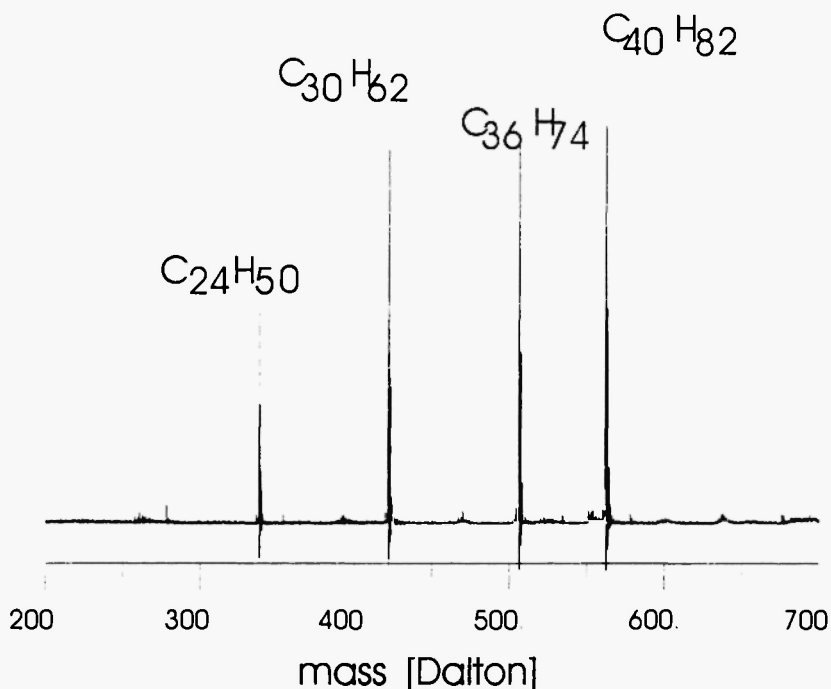


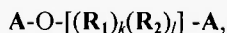
Fig. 4: Laser desorption jet cooling VUV ionization mass spectrum of a roughly equimolar mixture of n-alkanes.

NON-RESONANT TWO-PHOTON IONIZATION

In two-photon ionization without vibronic spectroscopy we deal with excitation to a quasi-continuum intermediate state, consisting of a high density of vibronic states. This is the situation for many aromatic molecules, when ionized by 266 nm light from a quadrupled YAG laser or by 193 nm light from an excimer laser. A number of authors have used this approach in combination with jet cooling [1,39-41]. The picture that emerges is that fragmentation can be controlled by proper choice of wavelength and of laser fluence. For example, Tembreull and Lubman have shown that many small biomolecules can be ionized effectively at 280 nm while fragmentation increases at shorter wavelengths [42]. Grotemeyer *et al.* have shown that fragmentation can be controlled by the ionization laser fluence [43,44]. It is often possible to obtain parent masses at low fluence and partial fragmentation at higher fluence. This control can be used to the advantage of

structural analysis. Lockyer and Vickerman have shown that fragmentation is a function of laser pulse width and can be better controlled with femtosecond pulses than with nanosecond pulses /45/.

A prerequisite for two-photon ionization is that the molecule contains a suitable chromophore. This fact can be used to analytical advantage by comparing single-photon with two-photon ionization. The former can ionize both aliphatic and aromatic species, while the latter is blind for aliphatic molecules. Thus by applying both approaches to an unknown sample it is possible to characterize the observed parent molecular mass as due to either aromatic or aliphatic molecules. Another possibility is the use of aromatic substituents in order to label molecules for detection by two-photon ionization. An example appears in Figure 5 showing a jet cooling L2MS spectrum of a labeled perfluorinated polyether co-polymer of the type:



where R_i represent two different repeat groups and A represents an end-group containing an alcohol. The polymer was labeled by esterification to

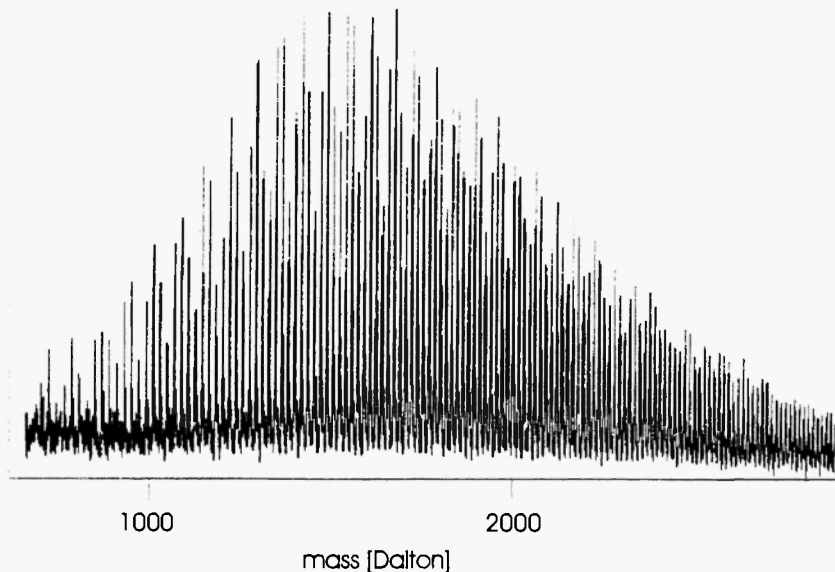


Fig. 5: Laser desorption jet cooling spectrum of a labeled perfluorinated polyether co-polymer, ionized by two photon ionization of the end group chromophores.

carry piperonyl end groups that could be two-photon ionized at 193 nm. Every peak in this mass spectrum corresponds to a parent mass with one of the possible combinations of k and l . The accurate determination of molecular weight distributions is one of the main challenges in polymer analysis. Other applications include aerosol analysis /46,47/.

REMPI

The greatest strength of L2MS is in the possibility to vary the ionization wavelength, such that mass spectrometry and optical spectroscopy can be obtained simultaneously, creating in effect a truly hybrid technique. This situation is indicated in Figure 1 (c). A first tunable photon excites the molecule to a vibronic resonance, usually in the first excited electronic singlet state, S_1 . A second photon ionizes only those molecules that are excited by the first photon. This second photon can be of the same wavelength as the first, in which case only one ionization laser is required, producing one-color two-photon ionization. The color must be such that the photon energy equals at least half of the ionization energy. The second photon can also be derived from an additional laser. In that case, two-color ionization, the second photon can also be tunable, it can be more energetic than the first, and it can be applied with a delay in order to ionize from a triplet state and in order to investigate the lifetime of the S_1 state (see Figure 1 (d-e)). REMPI and its associated techniques have been developed originally for spectroscopic studies of relatively high vapor pressure compounds that can be seeded in a supersonic molecular beam /21,48/. Another important application of these techniques is in the study of molecular clusters /49/. The combination with laser desorption of neutral molecules has now made it possible to apply REMPI techniques also in mass spectrometry of larger compounds.

Cable *et al.* studied tryptophan di- and tripeptides by REMPI as well as by laser induced fluorescence, following laser desorption /50,51/. Li and Lubman demonstrated for laser desorbed tyrosine and related structural analogs that electronic spectroscopy can be a sensitive probe of small structural changes in related biological compounds /52/. Meijer *et al.* applied the technique to clusters of para amino benzoic acid /53/. More recent applications have been reported, amongst others by Fiona and Jones /54/ and by Dale *et al.* /55/.

ISOMER DISTINCTION.

One of the advantages of wavelength resolved L2MS is the potential of separating and identifying structural isomers. We wish to illustrate this here with two examples: (a) dipeptides with different sequences and (b) nucleoside isomers.

(a) Dipeptides with different sequences.

In Figure 6 we compare the spectrum of tyrosine with two dipeptides that contain tyrosine as a chromophore, Tyr-Ala and Ala-Tyr. The structure in the spectra is due to multiple conformations, indicated by capitals, and to very low energy vibrations, indicated by lower case letters and by lines that show vibrational sequences. The possible conformations for tyrosine and its derivatives have been discussed by several authors /56-60/. When comparing with the dipeptides, we observe changes in the frequencies of torsional sequences as well as conformational changes. We associate the peaks marked with E with conformations with the carboxyl group in the *ante* position and those are not changed appreciably for either dipeptide. On the other hand the red-most peaks, which we associate with conformations in which the carboxyl group can interact with the aromatic ring, are very sensitive to the dipeptide sequence. Those peaks change much more dramatically for Tyr-ala than for Ala-Tyr because in the former case the peptide bond occurs on the carboxyl terminus. Thus we notice the tremendous isomeric distinction that can be obtained by wavelength dispersion in addition to mass spectral detection.

(b) Nucleoside isomers.

Figure 7 shows the REMPI spectra of laser desorbed guanosine (Gs), 2'deoxyguanosine (2'dGs), and 3'deoxyguanosine (3'dGs). The latter two compounds are isomers that cannot be distinguished on the basis of their mass. However the combination of optical dispersion with mass dispersion allows for clear distinction. The spectral difference is the result of the occurrence of two possible conformers in guanine, one of which is stabilized by a hydrogen bridge involve the 2'OH group. This conformer is absent in 2'dGs but present in 3'dGs, leading to the distinctive detection of these two isomers.

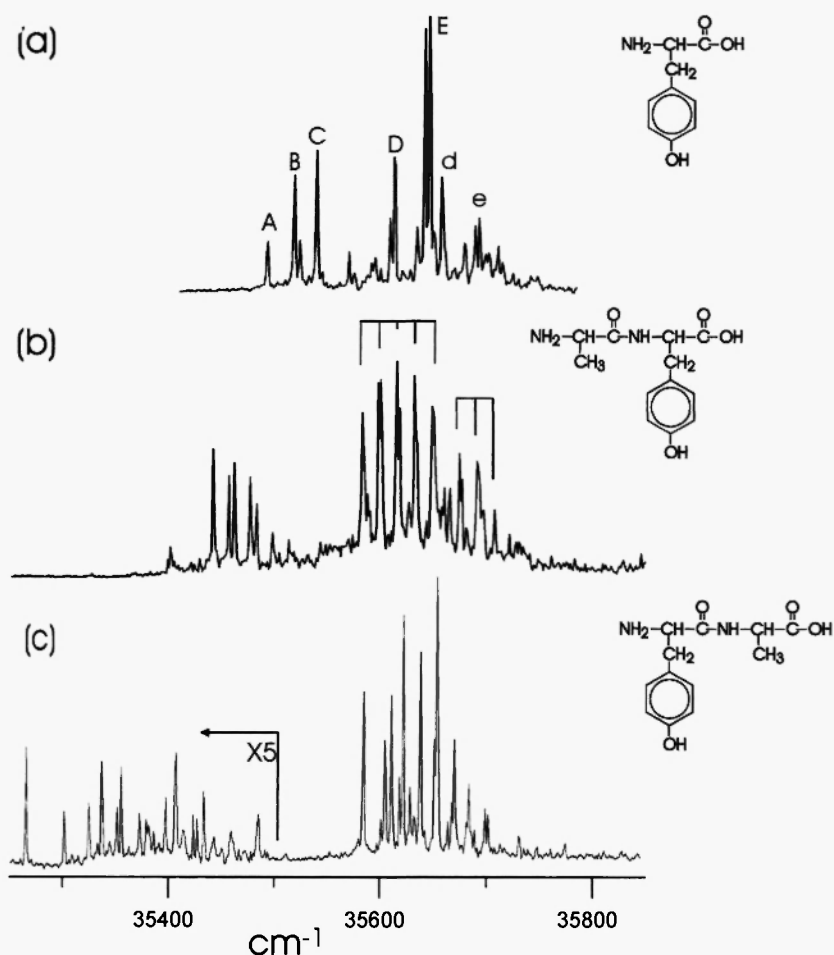


Fig. 6: L2MS/REMPI spectrum of (a) tyrosine, (b) Ala-Tyr, and (c) Tyr-Ala, offset by + 100 cm^{-1} .

TRACE ANALYSIS.

L2MS with REMPI detection provides an opportunity for trace analysis with great dynamic range. Resonant ionization requires orders of magnitude smaller laser fluences than does non resonant ionization. In many cases fluences of the order of tens of microJoules/ cm^2 suffice to obtain a resonant

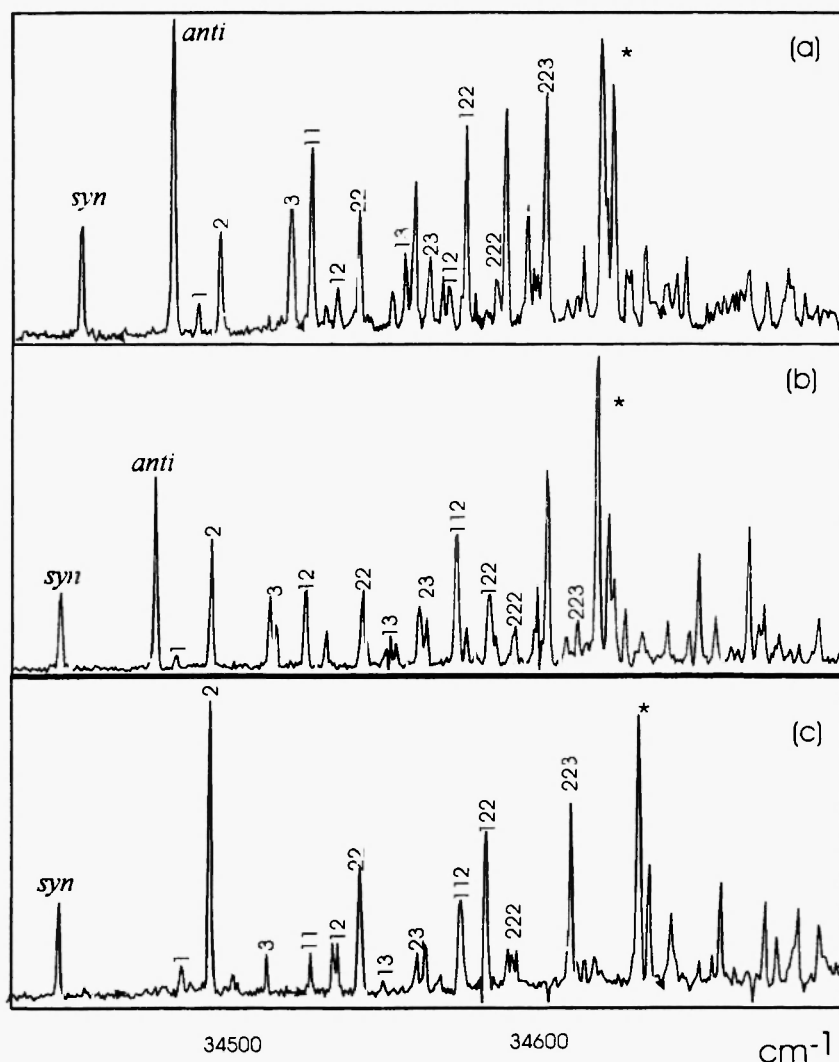


Fig. 7: REMPI spectra of laser desorbed guanosine (Gs), 2'deoxyguanosine (2'deoxyGs), and 3'deoxyguanosine (3'deoxyGs).

signal. This implies that it is possible to detect a specific species resonantly without ionizing any of the other compounds that may be present in the sample. In other words, one *can* fish a needle out of a haystack. There is the prerequisite that one must know what the needle looks like; that is to say, the spectroscopy of the trace compound must be known. With that caveat it is

possible to achieve two advantages at once for analytical mass spectrometry: species specific detection and dynamic range. The point is illustrated in Figure 8, showing two L2MS spectra of Endoc C grease ®. Panel (a) was obtained with non-resonant ionization at 193 nm, at high laser fluence, and shows all ionizable compounds in the sample. Panel (b) was obtained with resonant ionization at 308.1 nm, the 0-0 transition of diphenylamine. Less than a mJ/pulse was used, sufficient to resonantly ionize diphenylamine, but not enough to ionize any of the other compounds that were present in the sample in orders of magnitude higher abundance.

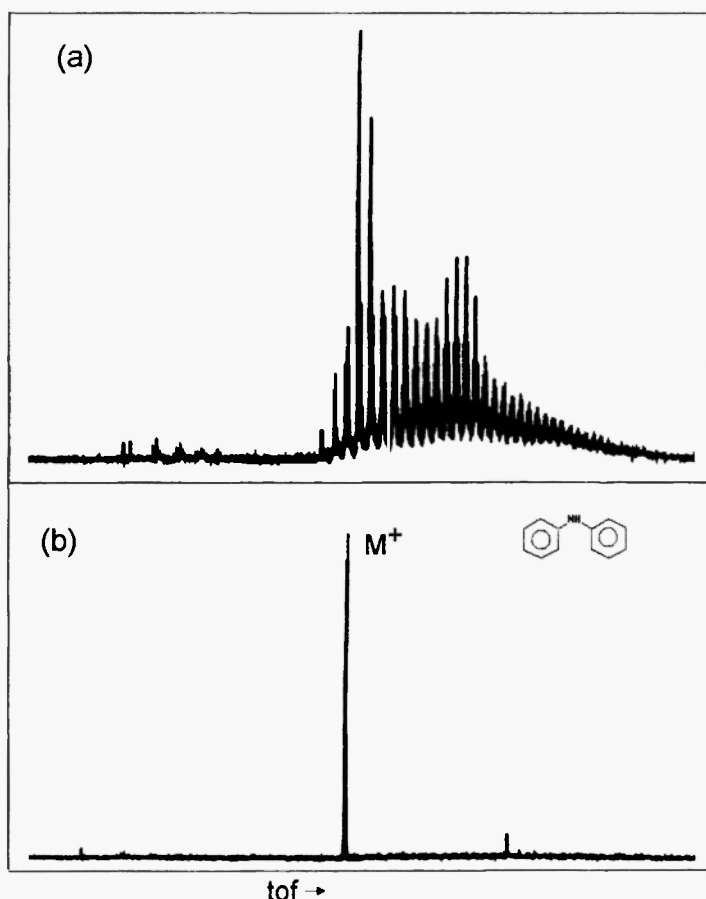


Fig. 8: L2MS spectra of Endoc C grease ®. (a) non-resonant ionization at 193 nm, (b) resonant ionization at the 0-0 transition of diphenylamine.

SUMMARY

Two-step laser mass spectrometry offers opportunities for addressing specific challenges in analytical mass spectrometry. As opposed to single step approaches, L2MS employs a separate photoionization step, which can provide additional information. This approach has been shown to be useful for measurement of parent molecular mass, particularly for large molecules. Moreover the separate photoionization step adds selective detection as a function of wavelength. In combination with resonance ionization L2MS can add spectroscopic information to the mass spectrometry, creating a truly hybrid approach. Applications include isomer distinction, and selective detection of trace compounds.

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