International Journal of Mass Spectrometry and Ion Processes, 78 (1987) 53–68
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

MATRIX-ASSISTED ULTRAVIOLET LASER DESORPTION OF NON-VOLATILE COMPOUNDS

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(Received 25 November 1986)

ABSTRACT

The use of a matrix for pulsed ultraviolet laser desorption mass spectrometry is shown to extend its applicability into the range of larger, thermally labile biomolecules. The matrix compounds tested show strong resonance absorption at the laser wavelength of 266 nm and can be either solid or liquid. Characteristic features of the matrix-assisted LD mass spectra are high quasimolecular ion yield with little or no fragmentation and only a few signals in the low mass range. The matrix effect is discussed in the light of three possible mechanisms: an effective and controllable energy transfer of the laser energy to the condensed phase by predominantly one-photon absorption, the creation of a uniform and soft disintegration of the condensed phase at moderate irradiances independent of the analyte's individual properties, and an enhancement of ionization yield by protonation via excited state molecules.

INTRODUCTION

The applicability of fast atom bombardment (FAB)/secondary ion mass spectrometry (SIMS) to the analysis of nearly all classes of non-volatile compounds has undoubtedly come about through the introduction of the liquid glycerol matrix [1]. A variety of liquid matrices has since been used [2] and glycerol is by far the most widely used. SIMS of solid organic samples, on the other hand, has been proven to be a very sensitive tool if used in the static mode [3], but results strongly depend on sample preparation, especially layer thickness, with best results obtained from very thin layers.

Application of laser desorption (LD) mass spectrometry to non-volatile organic compounds has so far been reported for a limited number of examples [4–16]. Generally, intercomparison of LD results is very difficult because of the wide range of experimental parameters (irradiances, laser wavelengths, pulse lengths) used by different groups; different processes in the different parameter ranges may even render attempts to develop a unified LD model futile. A thermal desorption process has, for example,

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been demonstrated for continuous-wave (cw) infrared (IR) lasers; for short-pulse ultraviolet (UV) LD, a non-equilibrium process appears to be the more appropriate model. Available experimental data do not, however, permit a clear differentiation between the two and contributions from both processes may certainly occur in a given case.

Though it seems logical to test the effect of a matrix for LD as well, only two examples have been published so far: liquid glycerol salt matrix for cw IR LD and a NH_4Cl solid matrix for pulsed (10 ns) IR LD [17,18]. In both cases, a higher quasimolecular ion yield and an "enhanced spectral quality" [17] were obtained.

In a previous paper [19], we reported that the laser wavelength becomes a parameter of decisive relevance in UV-LDMS if it leads to a resonant electronic excitation of the sample molecules. Both low threshold irradiance (E_{th}) for the detection of sample-specific ions and high yield of quasimolecular ions together with a low degree of fragmentation, as detected for resonantly absorbing amino acids and dipeptides, led to the conclusion that, at near-threshold irradiances, linear energy absorption by individual sample molecules may play an important role. Such linear processes are, in principle, easier to control with respect to the total energy deposited than the non-linear ones necessary in non-absorbing samples. As a result, the degree of internal excitation of the desorbed quasimolecular ions may remain limited. These findings led us to test whether a resonantly absorbing matrix might yield similar results, i.e. a "very soft" desorption even for molecules, lacking absorption at the wavelength used.

EXPERIMENTAL

A LAMMA-1000 instrument [20] in its usual working conditions was used for all experiments with a Q-switched frequency-quadrupled Nd-YAG laser (266 nm, 10 ns) focused by a microscope to a minimum spot size of 3 μm in diameter, or slightly defocused to spot sizes up to 30 μm. This instrument comprises a time-of-flight (TOF) system equipped with a second-order ion reflector for time focusing. All spectra were taken in the positive ion mode. Except for the CsI spectrum, the spectra presented in the following show the original signal track as registered by the transient recorder or sums of several single tracks without any electronic processing.

The following matrices were tested.

(a) Solids: tryptophane (Trp) and nicotinic acid (NicAc) as well as sucrose for the desorption of CsI;

(b) liquids: 3-nitrobenzyl alcohol (NOBA) and 2-nitrophenyl octyl ether (NPOE), introduced to FAB-MS by Meili and Seibl [21].

TABLE 1

Molar extinction coefficients (at 266 nm) of matrix compounds

	Solvent	$\epsilon_n^{\lambda=266nm}$/l mol^{-1} cm^{-1}
Tryptophane	H_2O	4.5×10^3
Nicotinic acid	H_2O	3.4×10^3
3-Nitrobenzyl alcohol	MeOH	8.3×10^3
2-Nitrophenyl octyl ether	MeOH	2.3×10^3

Their molar extinction coefficients are shown in Table 1. Samples were used as provided commercially, usually dissolved in distilled water, for NPOE in methanol at a concentration in the range of 5×10^{-4} to 10^{-5} mol l^{-1}. A 1 : 1 mixture of sample solution with either a 10^{-2} mol l^{-1} aqueous solution of the solid matrix materials Trp and NicAc or the liquid matrices NPOE and NOBA was prepared and 2–4 μl of this mixture, containing 10^{-9} to 5×10^{-11} mol of sample were then placed on an aluminium substrate. All sample-covered substrates were transferred directly to the vacuum chamber. For Trp and NicAc, rapid vacuum evaporation of the solvent produced optically homogeneous thin layers covering some mm^2 surrounded by a thicker rim, where most of the substance is concentrated. NPOE and NOBA liquid matrices spread over a large substrate area forming a thin homogeneous layer. For CsI/sucrose, small amounts of crystalline material were placed in a droplet of water directly on the substrate and a very inhomogeneous structure was formed, varying between amorphous, microcrystalline layers and large crystals (up to 100 μm in diameter). Generally, LD spectra could be obtained from the whole sample area, if optically homogeneous, but the highest intensities were usually produced from the rim.

Out of the total amount of sample material, usually limited by the procedures of sample preparation, the volume sampled per spectrum is estimated to be in the range of 1–0.1 μm^3, i.e. 10^{-12} to 10^{-13} g, corresponding to an analyte amount of 2.5×10^{-14} to 2.5×10^{-15} g (a 20-fold molar matrix excess), depending on the ionization yield reached in a given case. This estimation of sample consumption is supported by the fact that sum spectra at threshold irradiances can be taken from the same sample spot. For all experiments, it proved to be of great advantage that the LAMMA system provides the simultaneous observation of the irradiated area through the optical microscope with a magnification of $\times$ 250. In this way, success or failure of desorption could be correlated to the microscopic sample state, i.e. homogeneity of the mixture, partial or total separation of the components, or recrystallization.

RESULTS

Threshold irradiances

As reported in a previous paper [19], Trp exhibits a low threshold irradiance (E_0^{Trp}) of about 2×10^7 W cm^{-2} for the detection of sample specific ions whereas non-absorbing amino acids require irradiances a factor of 10–12 times higher. This holds generally for all non- or weakly absorbing organic samples as, for example, the tested analytes stachyose, erythromycin, and gramicidin-S. NicAc, NPOE, and NOBA, on the other hand, needed an irradiance of a factor of 3 times that of Trp for ion formation. Their threshold-irradiance LD mass spectra are shown in Fig. 1. Whereas Trp and NicAc show quasi-molecular ions as expected, the low polarity liquid matrices show radical molecular ions (NOBA) or a fragment ion [$(M - 17)^+$ for NPOE]. As there is no hydroxyl group in NPOE, ion formation presumably involves precursor radical ions. Similar considerations hold for the peak at m/z 300 in the NOBA spectrum for which no straightforward explanation can be given. Despite the higher molar extinction coefficient of NOBA, its threshold irradiance exceeds that of Trp.

Matrix-assisted spectra were generally taken at irradiances up to 3 times the matrix threshold irradiance, corresponding to values in the range of

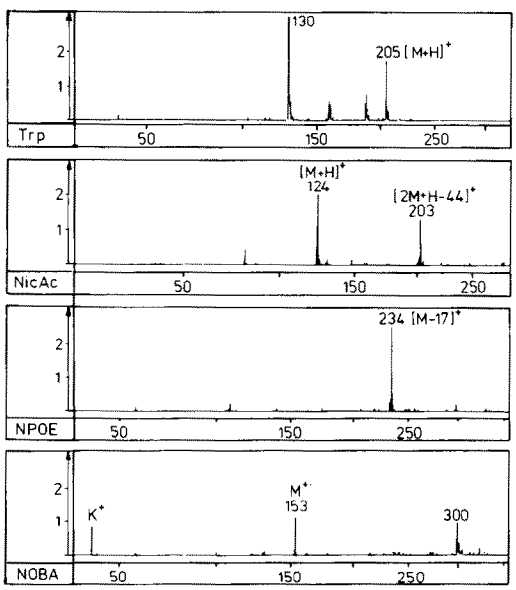

Fig. 1. Threshold irradiance LD mass spectra of the pure matrix compounds.

2×10^7 to 1×10^8 W cm^{-2}. In a series of spectra, the influence of the irradiance at even higher values was also determined. For the non-absorbing system CsI/sucrose, irradiances in the range of 5×10^8 to 1×10^9 W cm^{-2} were applied. Absolute calibration of irradiances is accurate to $\pm$ 50%; the accuracy of relative irradiances in the range used is $\pm$ 20%.

Solid, resonantly absorbing matrices (Trp, NicAc)

Test substances were chosen according to their absorption at the laser wavelength and whether or not molecular ions can be obtained without a matrix.

Stachyose, a tetrasaccharide (M.W. 666), and erythromycin, an antibiotic glycoside (M.W. 733), have no appreciable absorption at 266 nm, but quasimolecular ions of these substances can also be obtained without a matrix. Figure 2 shows LD mass spectra of the pure compounds. For stachyose, thicker layers and thus 10^{-2} mol l^{-1} concentrations were needed, whereas 5×10^{-4} mol l^{-1} sufficed for erythromycin. The corresponding matrix-LD spectra are shown in Figs. 3 and 4. Spectra were taken in a slightly defocused mode (laser spot diameter about 10 μm) at about equal irradiances that are a factor of 4 below that of the pure substances. As is demonstrated in the mass spectra, the increase in quasimolecular ion abundances is approximately a factor of 3 but, at the same time, the reproducibility is remarkably improved. Whereas the pure substance spectra show the

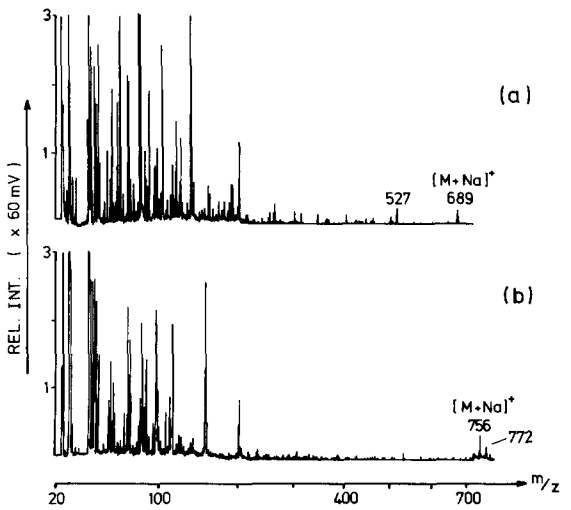

Fig. 2. LD spectra of (a) stachyose, 10^{-2} mol l^{-1} aqueous solution, and (b) erythromycin, 5×10^{-4} mol l^{-1} (without matrix).

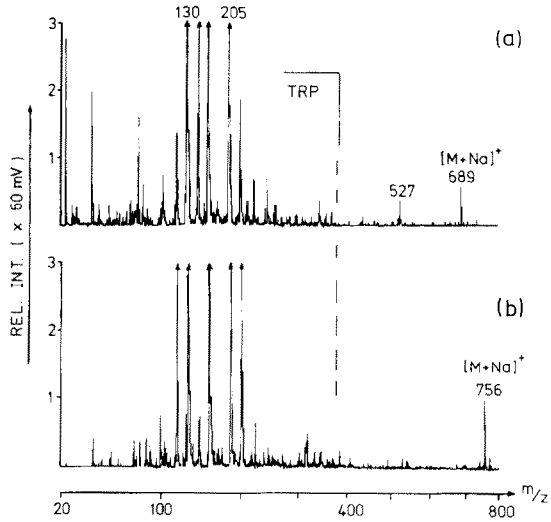

Fig. 3. Matrix-LD spectra of (a) stachyose and (b) erythromycin out of a Trp matrix; the mass peaks at 205 and 130 represent the Trp $(M+H)^+$ and the aromatic residue ion, respectively.

best possible results and appear in comparable intensities only at approximately every tenth laser shot, molecular ion abundances of matrix-assisted spectra vary from shot to shot within $\pm$ 20%, which is approximately the

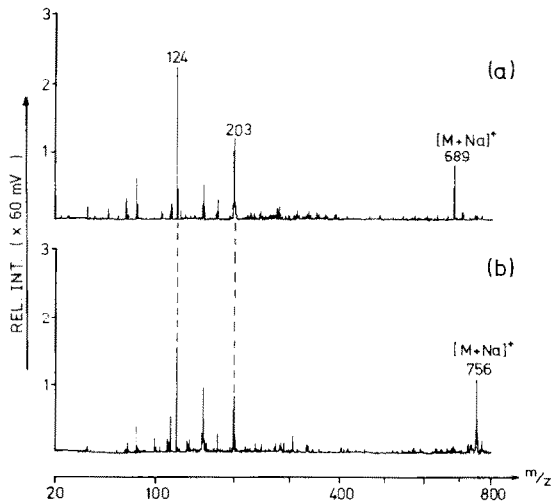

Fig. 4. Matrix-LD spectra of (a) stachyose and (b) erythromycin out of a NicAc matrix; the mass peaks at 124 and 203 represent a $(M+H)^+$ and $(2M+H-44)^+$ ion of NicAc, respectively.

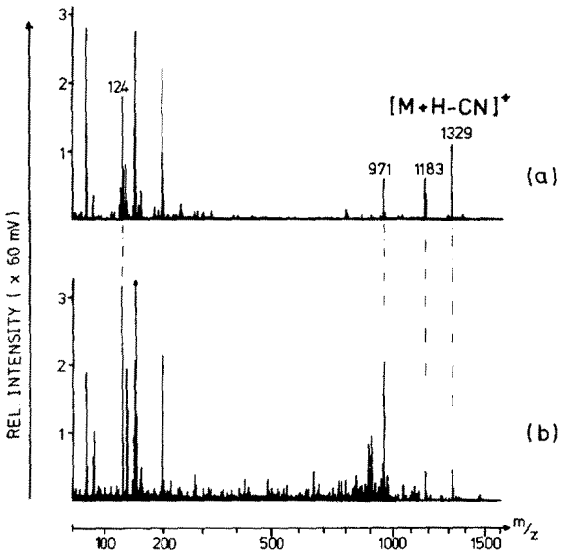

Fig. 5. Matrix-LD of vitamin B_{12}/NicAc at varying irradiance. (a) Threshold irradiance $E_0 = E_0^{NicAc}$ and (b) 3 times E_0.

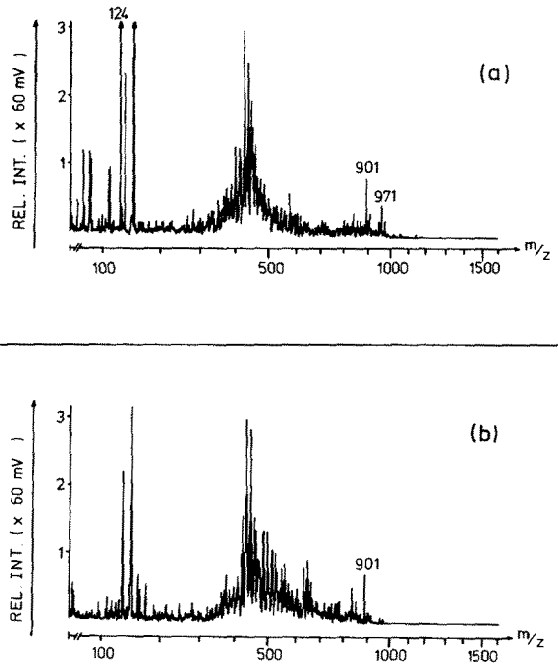

Fig. 6. Matrix-LD spectra of vitamin B_{12} at 10 E_0 (a) with NicAc matrix and (b) without matrix.

variation of the laser energy from shot to shot, provided the focusing of the laser is not changed between the shots. The signal-to-noise ratio typically amounts to 10–50 for single-shot spectra. The matrix-LD spectra differ considerably in the intensities of the matrix peaks. Whereas the threshold irradiances for matrix and analyte ionization coincide in the case of NicAc, E_0^{Trp} is somewhat below that necessary to generate sample ions and, consequently, intense matrix background cannot be avoided in this case. For stachyose, a fragment ion at m/z 527 resulting from the cleavage of one sugar molecule is observed for a Trp matrix but not when dissolved in NicAc. The spectra presented were taken from a sample–matrix molar ratio of 1 : 20, which proved to be the best ratio for maximum ion yield. However, there is a broad range (of 1 : 5 to 1 : 500) where analyte ions are observed.

Figure 5(a) and (b) and Fig. 6(a) demonstrate the influence of the irradiance on the NicAc–matrix LD for the example of vitamin B_{12} (M.W. 1355), which shows a strong absorption at 266 nm and for which quasi-molecular ions cannot be obtained without a matrix. At threshold irradiance E_0, abundant $(M + H - CN)^+$ ions and only two fragment ions are observed originating from the loss of dimethylbenzimidazol, yielding m/z 1183, and losses of sugar and phosphate groups yielding m/z 971 [Fig. 5(a)]. With increasing irradiance, the abundances of the lower mass ions increase at the expense of that of the higher mass ions [Fig. 5(b)] until, at $E = 10E_0$, a group of intense signals between 400 and 900 Daltons appear, probably indicative of a strong fragmentation of the corrin system [Fig. 6(a)]. This mass spectrum is very similar to that observed for a vitamin B_{12} sample without matrix, as shown in Fig. 6(b), taken at about the same irradiance. Signals of the Co center ion were not observed at the low irradiances used for LD spectra in Fig. 5(a) and (b); at higher irradiances [Fig. 6(a) and (b)], m/z 59 is registered, but this may also represent an organic fragment ion. The above example proves that matrix LD can also be successfully applied to samples containing absorption centers themselves.

As a further example, mellitin, a linear unprotected polypeptide of 26 amino acids (M.W. 2843), one of them a strongly absorbing Trp, was

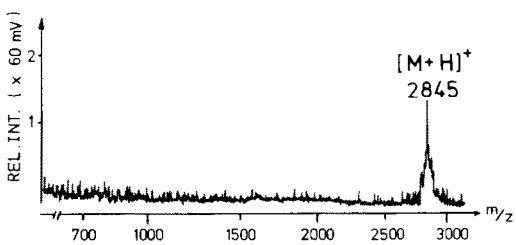

Fig. 7. Matrix-LD spectra of mellitin/NicAc accumulated from 12 single laser shots.

chosen. Figure 7 shows the sum spectrum of 12 single matrix-LD spectra. A protonated molecule with no fragment ions above m/z 600 is the only signal.

Liquid, resonantly absorbing matrices (NPOE, NOBA)

Among the numerous matrices applied in FABMS [2], only NPOE and NOBA contain aromatic groups that show resonant absorption at 266 nm. Figure 8 shows the matrix-LD spectrum of gramicidin-S, a cyclic decapeptide (M.W. 1140) out of a NPOE matrix. At threshold irradiance [Fig. 8(a)], abundant cationized sample molecules are the only ions observed, neither matrix nor alkaline ions appear in the spectrum. With increasing irradiance [Fig. 8(b)], a high-abundance protonated molecule appears in addition, accompanied by a matrix peak at m/z 234. It cannot be decided whether the latter ion is formed by loss of H_2O from a protonated molecule or by loss of OH from a molecular radical ion. The latter process seems to be

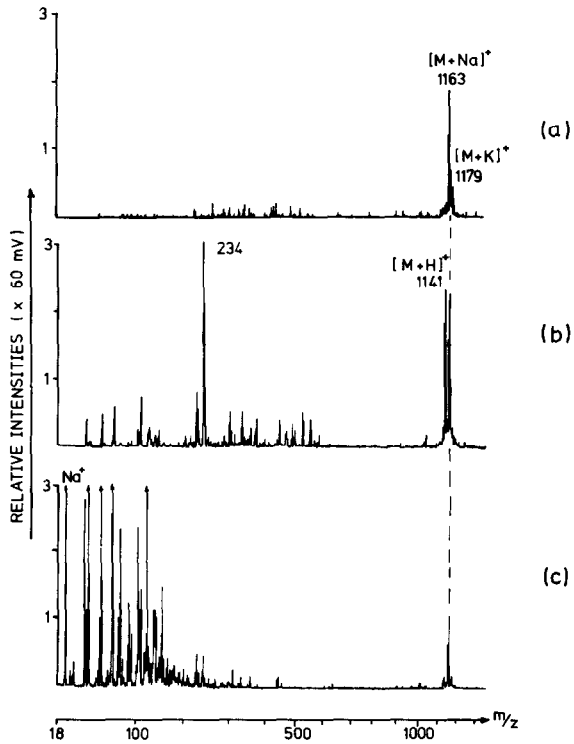

Fig. 8. Matrix-LD spectra of gramicidin-S/NPOE at increasing irradiance. (a) Threshold irradiance, E_0, (b) 3 times E_0 and (c) 10 times E_0.

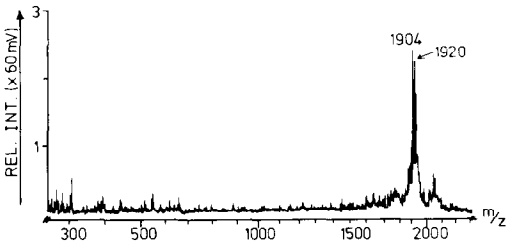

Fig. 9. Matrix-LD spectrum (mass range above m/z 250) of gramicidin accumulated from 5 single spectra.

more probable because of the low polarity of the matrix compound. Above 10 E_0 [Fig. 8(c)] the intensity of the analyte ions decreases and a strong fragmentation of the matrix is observed.

Attempts to analyse vitamin B_{12} in a NPOE matrix failed. This failure is attributed to a segregation of the sample and matrix components upon evaporation of the methanol solvent, apparent as red crystalline islands in the microscope. The problem of insufficient solubility of the more polar samples in this matrix has also been mentioned by Meili and Seibl [21]. This may also explain why gramicidin, a natural mixture of different linear polypeptides, yielded only a low intensity for high-mass ions with NPOE, whereas intense signals of gramicidin-S were detected. Better results were obtained with NOBA. Figure 9 shows the sum spectrum of five spectra, showing abundant ions at m/z 1904 and 1920, representing the alkali-cationized molecules of the main constituent valine-gramicidin-A (M.W. 1880). Below m/z 300, intense matrix peaks are registered.

The system CsI / sucrose

Whereas pulsed-UV LD of pure alkaline salts produces only a very narrow cluster ion $[(CsI)_nCs^+]$ distribution up to $n = 4$ with a steep exponential decay [22], admixture of sucrose dramatically enhances the formation of large cluster ions, with $n = 57$ still clearly detectable above noise level. Because of the limited memory space of the transient recorder used, only a limited time (mass) window per laser shot could be recorded at a given time resolution. The spectrum shown in Fig. 10 is therefore composed of six overlapping sections obtained from successive laser shots. Because of the relatively large fluctuations in ion abundances from shot to shot and from spot to spot on the rather inhomogeneous sample, the signal heights in successive time slots were normalized to those of the preceding ones in the overlap region. This rather severely limits the accuracy of the absolute magnitude of cluster ions in the spectrum shown. The spectrum is, therefore,

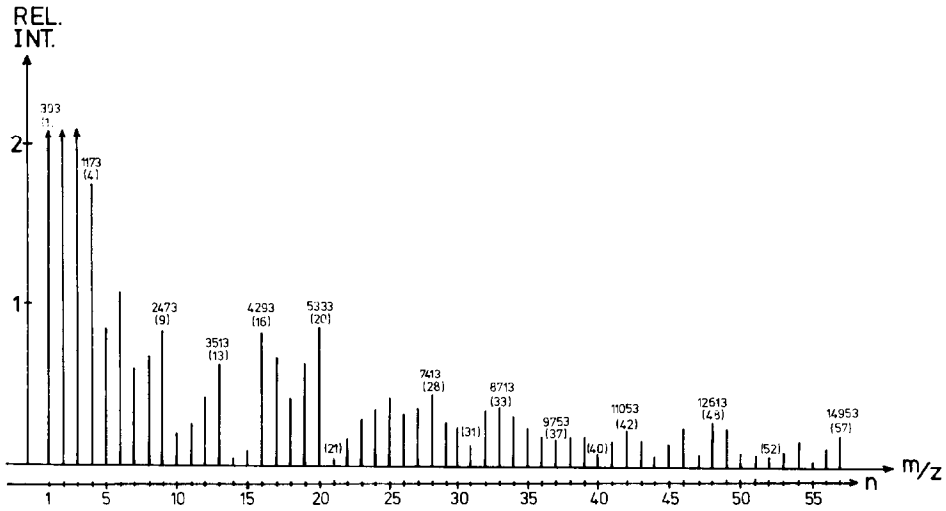

Fig. 10. LD spectrum of a CsI/sucrose 1:1 mixture added from single spectra of increasing mass ranges.

mainly presented as a demonstration for the strong influence of matrix effects on cluster distributions. The exact course of signal intensities particularly above $n = 25$, however, awaits careful determination. The observed cluster ion distribution with a rather linear decay above $n = 4$ also shows "magic numbers" at $n = 13$ (high intensity) and $n = 31$ (low intensity) as observed for SIMS (see, for example refs. 23–25), but distinct differences in the range of $n = 20$–23 are also apparent. Altogether, the variation of intensities seems to be not as pronounced for LD as for SIMS. Adduct ions between sucrose and CsI clusters were not observed.

DISCUSSION

Results show that the use of a matrix can usefully improve desorption of non-volatiles in pulsed-UV LD, particularly in cases in which no quasi-molecular ions are detected without a matrix. The matrix may facilitate a soft desorption process by several mechanisms.

(1) The resonantly absorbing matrix enables an effective and controllable coupling of the laser energy into the condensed phase. At moderate irradiances, an appropriate amount of energy per unit volume (E_a/V) is deposited, inducing disintegration of the condensed phase.

(2) Ionization may occur by chemical reactions between excited-state and ground-state matrix and/or analyte molecules.

(3) Favourable prerequisites are created by isolating analyte molecules, or

small clusters thereof, in the excess matrix. The disintegration of the condensed phase after laser irradiation will be controlled by the matrix structure.

In the following, the reported results will be discussed in the light of these three hypotheses.

(1) If the laser wavelength (266 nm) coincides with a resonance absorption band of the matrix, each photon absorbed will create an excited-state matrix molecule. As reported in a previous paper [19], the energy deposited per single molecule in the top molecular layer of Trp by this classical absorption (calculated from Beer's law for the molar extinction at the laser wavelength, pulse duration of the laser and the irradiance used) amounts to 20 eV or 4–5 photons at threshold irradiance. (Non-linear effects like excited-state absorption cannot be excluded but can be neglected for an estimate of the energy deposited.) The energy primarily stored by electronically excited bulk molecules (excitons) will be quickly dissipated into vibrational bands of phonons to a large extent. Thus, a high energy per unit volume is built up, provoking a strong perturbation of the solid-state structure. As a result, a rapid disintegration of the condensed phase takes place before equilibration of the energy into all degrees of freedom would lead to a destruction of thermally labile biomolecules. Thus, the process of disintegration has to be understood as a non-equilibrium process. One of the advantages of resonant absorption is that the amount of energy deposition (E_a/V) can easily be controlled by variation of the laser irradiance. In contrast to this, energy deposition into non-absorbing samples requires a minimum, usually high irradiance and the induced transition into a strongly absorbing state leaves only limited controllability of energy deposition. Irradiance-controlled energy deposition is exemplified in the Results section both for vitamin B_{12} out of a NicAc matrix and for gramicidin-S out of a liquid matrix. Highest yields of quasimolecular ions are, in all cases, registered at threshold irradiances or in a small region above, indicating that "thermal" stress on matrix and analyte molecules also increases strongly with increasing energy deposited.

This description also holds if the analyte molecules contain single chromophores, resonantly absorbing at the laser wavelength, as, for example, vitamin B_{12} or mellitin. For such large molecules, the energy deposited per unit volume or per polar binding site to the surroundings will be much lower compared with the small, strongly absorbing matrix molecules. The overall energy deposition will be still controlled by the matrix. Without an absorbing matrix, a single chromophore like a Trp in the polypeptide mellitin or also larger chromophores as in vitamin B_{12} do not suffice to deposit enough energy per molecule by linear transfer processes within the laser-pulse time and desorption fails [Fig. 6(b)].

The irradiance necessary for non-linear (two-photon) absorption, usually leads to the formation of a "hot spot", a highly excited volume in the center of the laser-irradiated sample region. Quasi-molecular ions, if present at all, are thought to result from a rim around the "hot spot" [8]. In the mass spectra, the "hot spot" is documented by abundant low-mass (≤ 150 Daltons) unspecific fragment ions [see the mass spectra of the pure substances in Figs. 2 and 6(b)]. Whereas the destructive disintegration is the dominant process for non-linear multiphoton energy deposition in the UV region, disintegration into intact molecular constituents (of matrix and analyte) may dominate for resonant energy transfer at threshold irradiances.

In a mass spectrometer, only processes leading to charged species will be registered. The generated ions may be preformed and set free within the process of disintegration of the irradiated microvolume if the binding forces are not too high. In the case of matrix LD, formation of matrix ions should therefore not be a prerequisite for analyte ion desorption. This is fulfilled, for example, in the case of an NPOE matrix where, at threshold irradiance, only cationized analyte molecules are observed. It is a unique feature of matrix-UV LD, compared with most other desorption techniques, that, under favourable conditions, high-intensity quasimolecular ions can be desorbed without *any* significant matrix or chemical noise signals [Fig. 8(a)].

Differences in matrix-LD characteristics between Trp and NicAc mainly show up as high-intensity matrix signals in the case of Trp, even at low irradiances. Thus, NicAc is advantageous because of low matrix signals and because less excitation is transferred to the analyte molecules, as shown by the absence of fragmented stachyose ions (m/z 527). Whereas both have nearly the same molar extinction coefficient at 266 nm, the laser wavelength nearly matches the absorption peak of NicAc, excitation of Trp takes place at a wavelength considerably below the absorption peak wavelength at 285 nm. For Trp, the excess vibrational excitation transferred with each photon could be the reason for the higher degree of fragmentation of both matrix and analyte ions in the case of Trp.

(2) Besides release of preformed matrix and analyte ions within the process of disintegration, resonantly absorbing matrices may also enhance ionization by protonation or, more generally, by chemical ionization. The formation of protonated mellitin molecules can be explained by a protonating action of the matrix, which may be even more pronounced for excited-state matrix molecules because acidity may considerably change in the excited state [26]. A reaction such as

$$\mathrm{NiAc}^{*} + \mathrm{M} \rightarrow (\mathrm{M} + \mathrm{H})^{+} + (\mathrm{NicAc} - \mathrm{H})^{-}$$

may be responsible for the observed ions. Additionally, the formation of intermediate radical matrix ions can also not be excluded. As they are

formed in a high-density intermediate state of the disintegrating volume, they will immediately undergo chemical reactions such as, for example

$$NPOE^{+\cdot} + M \rightarrow (NPOE - H)^{\cdot} + (M + H)^{+}$$

A process like this may be responsible for the high yield of protonated gramicidin-S molecules in coincidence with matrix (NPOE) ions.

As these processes occur in the condensed phase, or at least in a high-density intermediate state, energetics may be different from gas-phase reactions because ionization energy may be noticeably reduced by the solvation energy of the electron and the proton affinity of a reactant or analyte molecule. The question, however, of whether these processes can really be induced by absorption of a single photon, as has been shown in photobiological systems [27], is still open. It should be noted, however, that, at the irradiances used, the probability of a second photon being absorbed via the excited state is also not negligible.

(3) The effect of changes in the solid-state structure to enable desorption is clearly demonstrated for the case of CsI/sucrose mixtures where an unusually broad cluster-ion distribution is formed. In general, UV LD often fails and only low-mass fragment ions are observed if the analyte is a salt. This indicates that the average energy (E_a/V) necessary to overcome locally strong ionic bonds is too high to produce intact quasimolecular ions in the case of organic salts or large cluster ions in the case of a pure alkaline salt. Within this frame, quaternary salts or hydrochlorides of organic bases take an intermediate position. Because of their large ionic radii their solid-state binding energy is expected to be rather low, more comparable with hydrogen-bond energies in molecular crystals of polar organic molecules. The high yield of cations or anions thus becomes understandable, especially as no distinct ionization step, i.e. protonation or alkaline ion attachment, is necessary. These effects will also hold independently of the nature of energy transfer to the sample. Thus, the role of the sucrose may be attributed to the fact that, by rapid vacuum evaporation of the solute, an amorphous mixed crystal has been formed where regions of predominantly molecular crystal character (excess of sugar) and more ionic character alternate. Within the microscopically very inhomogeneous and thick layer, small microcrystalline CsI islands (preformed clusters) may exist separated by sugar entities. The laser-induced non-equilibrium evaporation now can take place at lower E_a/V, setting free big cluster ions with low internal energy which now can decay or survive up to several ms to be registered.

In the case of biomolecules in an excess solid matrix (Trp, NicAc), the matrix determines the solid-state structure and thus the properties of the solid concerning its disintegration. Analyte molecules are expected to be dissolved in the matrix molecular lattice with the main forces being hydro-

gen bonds. This situation will not change much, even if the analyte is a salt, as long as its concentration in the host matrix stays low. Solution chemistry, especially with amphoteric NicAc may also be helpful in the formation of neutral analyte molecules. The above considerations are supported by the experimental observation that addition of excess alkaline salt suppresses desorption both of intact analyte and matrix ions [28]. In the case of liquid matrices (NPOE, NOBA), additional surface effects due to their low polarity can not be excluded. Analyte molecules may accumulate at the liquid surface, thus favouring the yield of analyte ions.

In addition, the results show that the type of condensed state, i.e. solid or liquid, of the matrix has no significant influence on the desorption characteristics. This distinguishes the LD process from the desorption process well in matrix SIMS where molecular ions could no longer be detected from a frozen glycerol matrix, whereas chemical background drastically increases [29].

According to the above considerations, a distinct E_a/V is necessary to overcome the intermolecular forces. This value will have comparable magnitude for polar molecular crystals and low vapour pressure non-polar liquids. This independence of matrix LD from the state of the sample offers a new degree of freedom for fitting a matrix to an analytical problem of interest.

CONCLUSIONS

The introduction of a matrix in pulsed-UV LD, the rather universal applicability and the desorption models discussed open new perspectives for LD. Further work on optimizing the system, e.g. by looking for additives enhancing ionization rate, adopting the matrix to the analytical problem, and investigating the detection limits, still needs to be done. The lack of chemical background as observed for NPOE may be attractive for mixture analysis. In addition, variation of the laser wavelength with tunable dye lasers offers an additional degree of freedom for optimizing the sample–matrix system to an analytical problem of interest.

ACKNOWLEDGEMENT

This work was supported by the Deutsche Forschungsgemeinschaft under grant No. Hi 285/2-5.

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