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Dissociative proton transfer in cluster ions: clusters of aromatic carboxylic acids with amino acids

Anja Meffert, Jürgen Grotemeyer

Institut für Physikalische Chemie, Christian-Albrechts-Universität zu Kiel Olshausenstr. 40, 24098 Kiel, Germany

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Abstract

The cluster formation of several aromatic carboxylic acids ferulic acid, vanillic acid, sinapinic acid and 3,4-dihydroxybenzoic acid was investigated by means of laser desorption into a supersonic beam followed by multiphoton ionization-time-of-flight mass spectrometry. The formation of not only homogeneous clusters but also that of heterogeneous clusters with some small amino acids was studied. The different neutral clusters formed in the supersonic expansion were ionized by a multiphoton process employing either nano- or femtosecond laser pulses. Strong differences in the detection of cluster ions due to the laser pulse length employed for multiphoton ionization were observed. Only femtosecond activation led to mass spectra with intense signals of the cluster ions. In addition in the case of femtosecond ionization protonated amino acids were detected in the mass spectra. As direct ionization of the free amino acids is not possible under the chosen ionization conditions because they lack an adequate chromophore these protonated amino acids are assumed to be formed via an intracluster proton transfer in the heterogeneous dimer and subsequent decay of the ionized cluster (dissociative proton transfer). Such well-known processes for heterogeneous clusters consisting of a substituted aromatic molecule and small polar solvent molecules may be involved in the matrix-assisted laser desorption ionization ionization process. (Int J Mass Spectrom 210/211 (2001) 521–530) © 2001 Elsevier Science B.V.

Keywords: Cluster multiphoton ionization; Femtosecond activation; Time-of-flight mass spectrometry; Aromatic acids; Amino acids

1. Introduction

The formation of gas phase bimolecular clusters can be used for the understanding of intramolecular hydrogen bonding, like in biopolymers [1], or hydrophobic and hydrophilic effects in water or alcohols [2] as well as other examples [3]. Different theoretical and experimental publications have been discussed the formation of bimolecular cluster as a source for the ionization of large biomolecules through the technique of matrix assisted laser desorption ionization (MALDI). Since the introduction by Karas and Hillenkamp [4], this technique has been established as a general investigation tool for biopolymers [5–7] especially peptides [8,9] and proteins or nucleotides [10].

Despite its extensive use in various applications the mechanism of ion formation in the MALDI process has not been yet well understood. From the experimental setup the process can be roughly divided into two steps: first the analyte molecules must be desorbed from a solid crystalline matrix into the vacuum, and second, the desorption plume must be

* Corresponding author. E-mail: grote@phc.uni-kiel.de

Dedicated to Professor Nico Nibering on the occasion of his retirement.

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ionized at some point. Various studies have been performed in order to obtain experimental data which lead to an improved understanding of the fundamental aspects of desorption and ionization, such as the examination of the efficiency of various compounds as matrix substances [11–13] or velocity studies of ions formed in electric fields [14].

Several theoretical models have been developed in order to describe the desorption of large, intact molecules into the gas phase [15–18] which seem to reflect accurately the desorption step. It has become generally accepted that the matrix molecules go through a rapid phase change from the solid into the gas phase after photon absorption from the laser beam. The sublimed matrix molecules form a dense gas plume embedding the analyte molecules, which undergoes a supersonic expansion into the vacuum, in this way carrying the analyte either as neutrals or already ionized molecules into the gas phase.

However, the process leading to ionization of the analyte molecules is still a matter of research. In most applications the quasi molecular ion of the analyte molecule $[A+H]^+$ is the dominant analyte signal, involving a proton transfer to the analyte molecule in the desorption process. Several possible mechanisms for the formation of $[A+H]^+$ ions have been postulated [10]. Ehring et al. proposed that analyte ion formation in MALDI is initiated by photo ionization of the matrix molecules producing matrix radical cations. The radical cations may then react with the analyte (direct proton transfer) or first react with further matrix molecules leading to protonated matrix molecules $[M+H]^+$ which subsequently react with the analyte by proton transfer [19]. Russell et al. have postulated proton transfer reactions between electronically excited neutral matrix molecules and basic analyte molecules in the ground state. Therefore, the most useful matrices should be compounds that are strong acids in the excited state, e.g. phenols or aromatic amines [20]. Beside these postulated mechanism, also cluster formation and intracluster reactions have been discussed as possible source reactions for ionization in MALDI [21]. Nevertheless, a clear understanding of the ionization mechanism has not yet emerged.

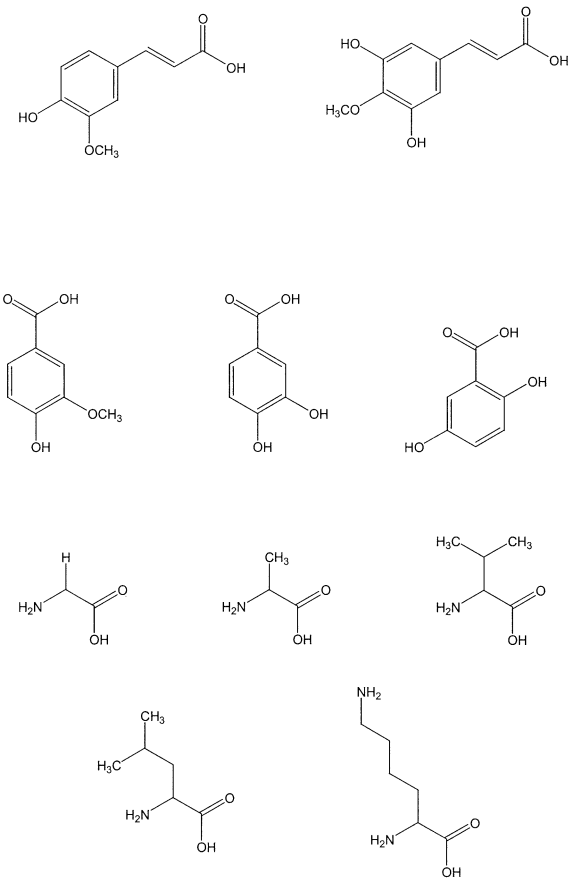

Fig. 1. Molecular structures of the MALDI matrix substances and amino acids under investigation.

Although the measurement conditions may vary in a wide range, one common point of all used matrices is their chemical structure. They contain an aromatic ring, acting as a chromophore for the absorption of photons, and a substructure that delivers labile or better acidic protons. This group is believed to be the source for protonation of the analyte.

In this work, we have investigated the cluster formation between typical MALDI matrices and amino acids by means of laser desorption into a supersonic beam followed by multiphoton ionization [22]. This mass spectrometric technique allows the separation of desorption and ionization processes in time and space. The investigated samples are displayed in Fig. 1.

Our interest is here focused on the question

whether cluster formation is been observed, and even reactions in the ionized clusters can be detected. Beyond this question, the influence of the laser pulse width will be addressed in order to investigate the influence of excited electronic states to the ionization process.

2. Experimental

The experiments were performed in a reflectron time-of-flight (RETOF) mass spectrometer (Bruker TOF1) and described in detail elsewhere [23]. In our investigations concerning heterogeneous cluster formation the MALDI matrix substance and the respective amino acid were mixed in equal molar parts. Polyethylene was used as further matrix material. The resulting probe mixtures were pressed to pellets and applied to the probe tip. Desorption of the sample molecules out of a matrix into a supersonic beam of argon was performed with the help of a pulsed CO_2 laser (10.6 μm). The probe tip is placed in a vertical distance of approximately 1 mm in front and a horizontal distance of 0.5 mm below the nozzle of the pulsed valve the in the desorption chamber. The supersonic beam of argon provides cooling of the internal degrees of freedom of the sample molecules as a consequence of multiple collisions, and this cooling makes possible the formation of neutral clusters during such collisions. In our experiments we applied a backpressure of about 3 bar argon. With this setup the typical temperature of the neutrals is around 5 K, 25 K and more than 50 K in the translational, rotational and vibrational modes of freedom, respectively. The neutral sample molecules and neutral clusters were transported through a skimmer approximately 10 cm into the ion source of the RETOF mass spectrometer, where they were post-ionized with multiphoton ionization (MUPI). Preformed ions originating from the desorption process are prevented from getting into the ion source by the fact that the neutral beam enters the ion source through the charged repeller. MUPI was performed using 500fs laser pulses as well as nanosecond laser pulses (8ns duration) for comparison. The femtosecond laser pulses were generated with the help of a dye laser system that was pumped by a XeCl excimer laser ($\lambda \sim 260$ nm, pulse length 500 fs, energy/pulse $10-15$ μJ). For the ionization with nanosecond laser pulses the frequency doubled output of a Nd:yttrium-aluminum-garnet (YAG) pumped dye laser system was used ($\lambda=260$ nm, pulse length 8 ns, energy/pulse $\sim$500 μJ). Both laser beams are introduced rectangular to the neutral beam as well as the resulting ion beam from opposite sides into the ion source.

The mass spectra were recorded using a 200 MHz transient digitizer and the evaluation of the registered data was performed on a VME bus computer. Each spectrum represents the sum of 25 laser shots. A more detailed description of the experimental setup has already been given in the literature [24].

All matrix compounds (ferulic acid, vanillic acid, sinapinic acid, 3,4-dihydroxy-benzoic acid and 2,5-dihydroxy benzoic acid) as well as the employed amino acids (glycine, leucine and lysine) were purchased from Sigma Aldrich Chemistry and used without further purification.

3. Results and discussion

3.1. Aromatic carboxylic acids

In first set of experiments, the pure MALDI matrix compounds were investigated by means of laser desorption multiphoton ionization time-of-flight mass spectrometry. In Fig. 2 the time-of-flight mass spectra of ferulic acid, sinapinic acid and vanillic acid obtained with multiphoton ionization using nanosecond laser pulses at $\lambda = 260$ nm are presented. With the exception of the vanillic acid very little intensity is observed on the molecular ion of the ferulic and sinapinic acid under these conditions. The main signal in both cases is due to the loss of the carboxylic acid function. In the case of the ferulic acid this leads to the signal at mass 150 and with sinapinic acid the signal is found at mass 180. It can be argued that the source of these signals is due to a neutral fragmentation in the desorption step leading to the decarboxylized compound which is than ionized by the two

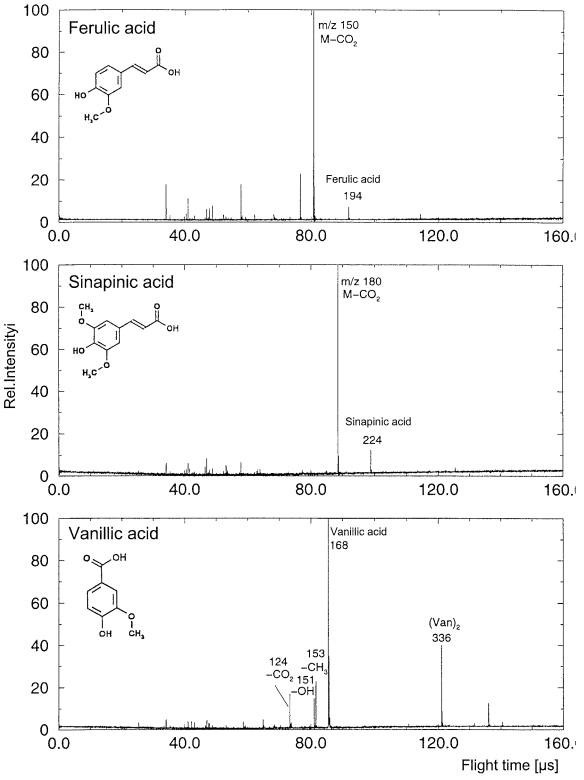

Fig. 2. Time-of-flight mass spectra of ferulic acid, sinapinic acid and vanillic acid. Ionization performed with 8 ns laser pulses, λ =260 nm, energy/pulse ~500 μJ.

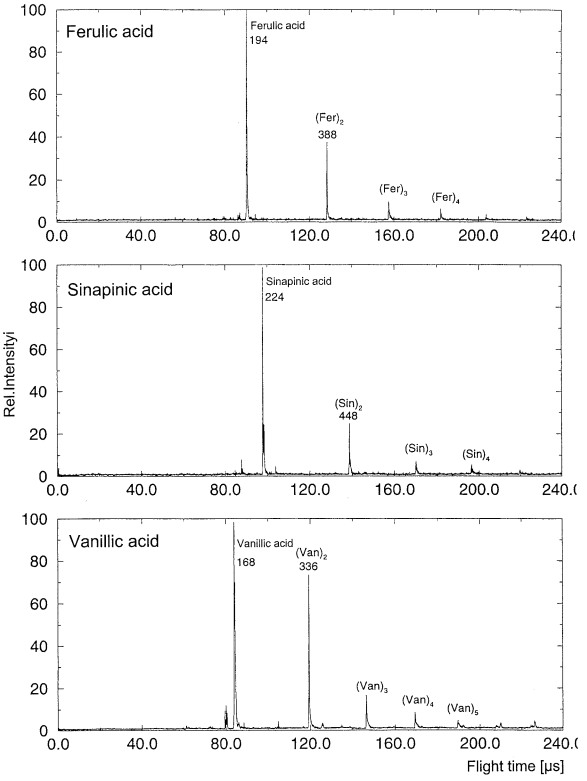

Fig. 3. Time-of-flight mass spectra of ferulic acid, sinapinic acid and vanillic acid. Ionization performed with 500 fs laser pulses, λ =260 nm, energy/pulse ~80 μJ.

photon absorption in the activation step. The argument is supported by the fact that the 0–0 transition in both substances is around 350 nm and the transition probability at 260 nm is very small as observed in the UV spectra [27]. Furthermore, also low mass fragments are detected with nanosecond activation.

On the other hand there are some indications that these substances can be desorbed intact and the small intensity on the molecular ion can be accounted for other reasons. It is well known in multiphoton ionization that the intermediate excited electronic state of a molecule can undergo different other photo physical processes, such as intersystem crossing into a different electronic state or even neutral fragmentation reactions beside the normal absorption of a second photon. From investigations of α–β unsaturated carbonyl compounds such as benzalacetones and benzalaldehydes it is known that these compounds undergo a very fast intersystem crossing into a different excited electronic state. By using ultra short laser pulses, it is possible to overcome this photo physical process thus forming the molecular ion nearly exclusively.

In case of ferulic and sinapinic acid this behavior is also observed. As shown in Fig. 3, femtosecond activation of the carboxylic acids leads nearly the exclusive formation of the molecular ion. No other fragmentation products can be observed. This result demonstrates that the observation of the decarboxylation products cannot be accounted to neutral fragmentation in the desorption step. Otherwise one would observe these fragments also with the femtosecond laser pulses at the same wavelength.

In addition to this difference between nano- and femtosecond laser pulses, homogeneous clusters in all aromatic acids are observed. As already published

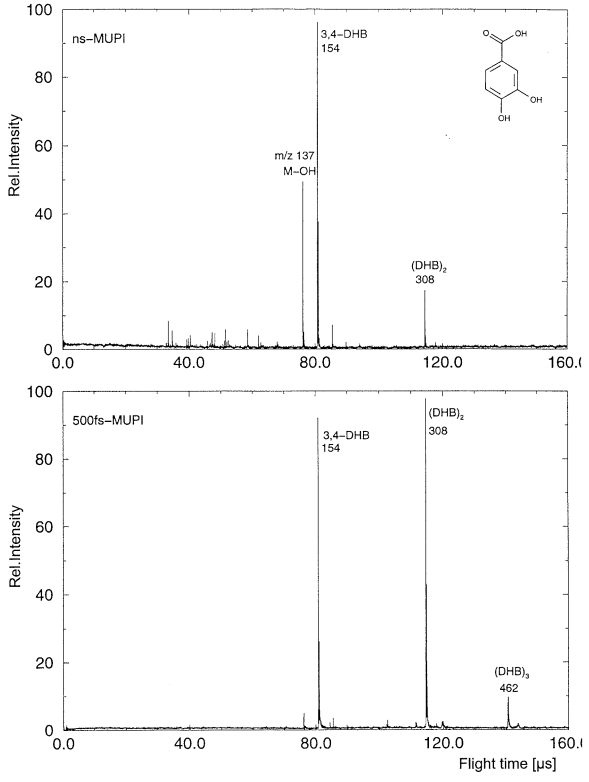

Fig. 4. Time-of-flight mass spectra of pure 3,4-dihydroxy-benzoic acid. Top spectrum: Ionization performed with 8 ns laser pulses, $\lambda = 260$ nm, energy/pulse ~500 μJ. Bottom spectrum: Ionization performed with 500 fs laser pulses, $\lambda = 260$ nm, energy/pulse ~80 μJ.

[25] homogeneous clusters of theses different matrix substances can be observed up the tetramer or pentamer or even larger.

The same behavior is observed for 3,4-dihydroxy-benzoic acid as demonstrated in Fig. 4. In this case the molecular ion is already observed in the nanosecond multiphoton ionization mass spectrum. In contrast to the other samples this substance show also cluster formation already with the nanosecond activation. But the tendency to form homogeneous cluster is strongly reinforced if femtosecond laser pulses are applied. As seen from Fig. 4 the intensity of the dimer cluster exceeds the intensity of the monomer. This is a direct result of the pulse duration. By using 500 fs laser pulses pumping of the intermediate state of the dimer-cluster, as well as of larger clusters is faster than any fragmentation of the excited neutral state, thus leading to an increased observable intensity of these clusters.

Again the shortening of the pulse duration leads to less fragmentation of the molecular ion. In the case of the 3,4-dihydroxy-benzoic acid the signal for the loss of the hydroxy group disappears by the shortening of the laser pulse. It should be noted that this behavior is not a result of the different energies of the laser pulses, but only due to the laser pulse width. In every case presented in this paper the energy per pulse or better the number of photons delivered to the sample is the same in both nano- and femtosecond activation.

In general the presented data demonstrate that all aromatic carboxylic acids and their cluster formation can be investigated successfully with ultra short laser pulses.

3.2. Clusters from carboxylic acids and amino acids

In the following experiments, we employed small, nonaromatic amino acids (Fig.1) in clustering experiments with the different carboxylic acids. These investigations are motivated on one hand by the fact that these clusters and their structures have some interesting elementary reactions one other hand motivated by the fact that amino acids are the constituents of peptides which represent one of the most important class of analyte molecules investigated by MALDI spectroscopy.

In Fig. 5 the cluster mass spectra from leucine codesorbed with 3,4-dihydroxy-benzoic (DHB) acid with different pulse durations are shown. As already discussed with the pure aromatic carboxylic acids strong differences in the mass spectra are observed in changing between 8 ns and 500 fs laser pulses.

The nanosecond mass spectrum [Fig. 5(a)] of this mixture displays mainly the same signals for the aromatic carboxylic acid and its dimer cluster accompanied by a signal for the protonated amino acid leucine. To reiterate the experimental setup prevents the measurement of ions formed in the desorption step nor the amino acid is ionized directly by the multiphoton procedure. This can easily be proven by the investigation of the pure amino acids. Under the same

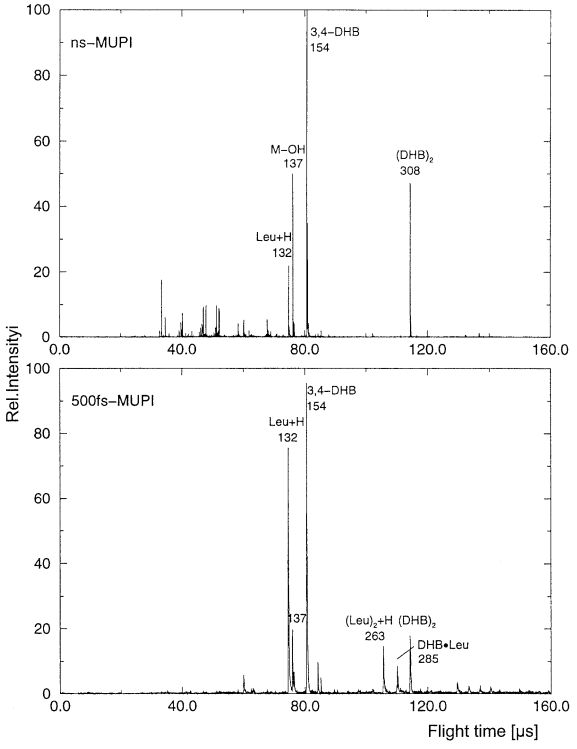

Fig. 5. Time-of-flight mass spectra obtained for 3,4-dihydroxy-benzoic acid mixed with leucine. Top spectrum: Ionization performed with 8 ns laser pulses, $\lambda = 260$ nm, energy/pulse ~500 μJ. Bottom spectrum: Ionization performed with 500 fs laser pulses, $\lambda = 260$ nm, energy/pulse ~80 μJ.

conditions the mass spectrum exhibits no ion signal at all. This means that the protonated amino acids can only be detected in the presence of the dihydroxy-benzoic acid where the formation of heterogeneous clusters of matrix and amino acid can occur. As a result the signal for the protonated amino acid can only be produced by an intracluster reaction between the 3,4-dihydroxy-benzoic acid and leucine. The appearance of this signal at mass 132 can be explained by formation of a neutral cluster in the supersonic beam, which than ionized by absorption of photons in the aromatic moiety of the benzoic acid.

As the nonaromatic amino acids do not absorb the irradiated laser light, the ionization process of neutral clusters formed in the supersonic beam are dominated by the matrix compound. The absence of cluster ions in the mass spectra when nanosecond laser pulses are used for ionization indicates a short lifetime of the excited states of the formed matrix clusters. This argument would indicate that already the electronic excited neutral state of the DHB is transferring the proton to the amino acid as already discussed in the literature [26] or the electronic excited state of the cluster undergo very fast dissociation into the respective monomeric constituents. A further explanation could be that competing processes like internal conversion, intersystem crossing or fragmentation lead to depopulation of the excited state of the benzoic acid before absorption of the second photon leading to ionization can take place. This is supported by the observation that in the case of nanosecond ionization a more intense fragmentation corresponding to the loss of CO_2 (fragment ion at *m/z* 150) is observed. Only when short laser pulses (in this case 500 fs) are used these processes may be avoided and the clusters as well as a higher amount of matrix molecules are ionized. To distinguish between these both possibilities evidence can be extracted from the experiments.

Inspecting closely the protonated amino acid signal not only in case of the leucine but also in all other investigated amino acid samples, one can see a metastable broadening of this signal [25,27]. As a result the heterogeneous cluster must be formed but the different reactions must be faster than the laser pulse width. This experimental finding can easily be proved by the use of ultra short laser pulses.

Investigating this mixture with femtosecond activation, the resulting mass spectrum (Fig. 5(b)) displays still the molecular ion information as well as the main fragmentation of the benzoic acid. It should be noted that the intensities of these signals as well as for the protonated amino acid are distinctive different from the nanosecond mass spectra as explained already above by faster pumping of the intermediate electronic state. The main difference to the nanosecond mass spectrum is in the high mass region. Here the signals for a protonated leucine dimer and the heterogeneous cluster form the benzoic acid and the leucine are observed.

These results clearly demonstrate that the protonated amino acid is formed from the heterogeneous dimer as a result of intracluster processes after ion-

ization of the cluster. In the ionized heterogeneous dimer a proton is transferred from the matrix molecule to the amino acid. Subsequently, the cluster ion decays releasing the protonated amino acid and the corresponding matrix radical [Matrix−H]$^{\cdot}$. This intracluster reaction may be described schematically as

$$[M \cdot A] \xrightarrow{h \cdot \nu} [M^{+\cdot} \cdot A] \rightarrow (M - H)^{\cdot} + (A + H)^{+}$$

where M is the carboxylic acid and A is the amino acid.

Such intracluster reactions are well-known for mixed clusters of substituted aromatic compounds like for example toluene and small polar solvent molecules like H_2O and NH_3 [28–30] as dissociative proton transfer (dPT). The reaction here is assumed to take place in an analogous way for all investigated systems below consisting of matrix compound and small amino acids. The systems investigated in our study resemble the systems for which dissociative proton transfer has already been shown as the employed matrix compounds represent only more complex substituted aromatic compounds and the small amino acids contain the basic amino group.

It should be emphasized that the appearance of any cluster from the amino acids and the different benzoic acids are not due to the preparation conditions. As shown previously [25], the relative amounts of both substances to each other or the preparation of the mixture on the probe tip yield no differences in the spectra. Therefore, the formation of the protonated amino acid must be a gas phase process.

Analogous experiments performed with the other matrix compounds under investigation led to concurring results. The results are shown in Figs. 6 and 7 as well as in Table 1. In Fig. 6 the cluster mass spectra of different amino acids with sinapinic acid taken with 500 fs laser pulse duration is shown. As seen from this mass spectra strong signals for the monomeric unit of the organic acid as well as the homogenous clusters are observed. Beside these signals the cluster formation of the sinapinic acid with the different amino acids alanine, valine and lysine is seen. In case of the alanine and the lysine only the heterogeneous dimer

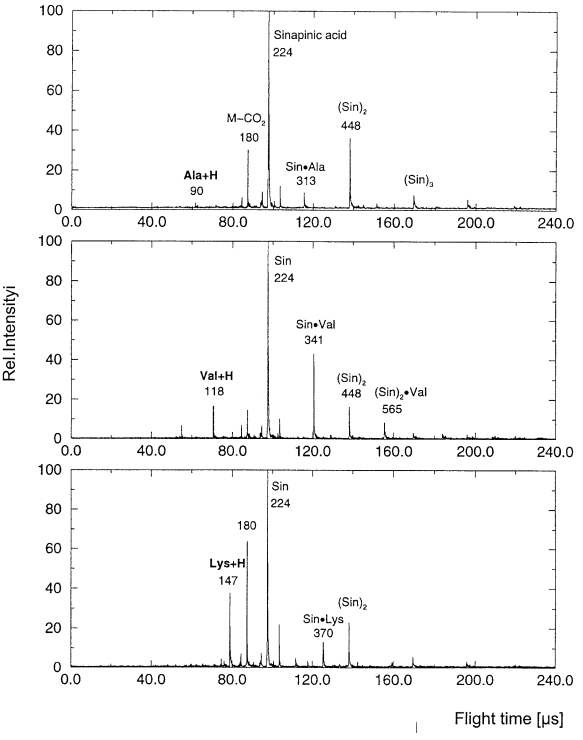

Fig. 6. Cluster formation of sinapinic acid with some small amino acids: top spectrum alanine, middle spectrum valine, and bottom spectrum lysine. Ionization performed in all cases with 500 fs laser pulses, $\lambda = 260$ nm, energy/pulse $\sim$80 μJ.

can be found, while the clustering with valine yields also higher order heterogeneous clusters like the trimer and other. Apparently, the intensity of the signal for the protonated amino acid is for the three cases different. While the alanine show the smallest intensity for the transfer of the proton, this signal reaches over 40% with lysine. Using the amino acid glycine for clustering together with the sinapinic acid results in the observance of the heterogeneous cluster but not in any signal for the proton transfer to the amino acid.

Using vanillic acid as a proton donator the intensities for these reactions are completely changing. As seen from Fig. 7 vanillic acid shows a strong signal for the protonation of the amino acid glycine at mass *m/z* 76. Comparing the respective signal for alanine and vanillic acid with the signal obtained with sinapinic acid the formation of the protonated amino acid is

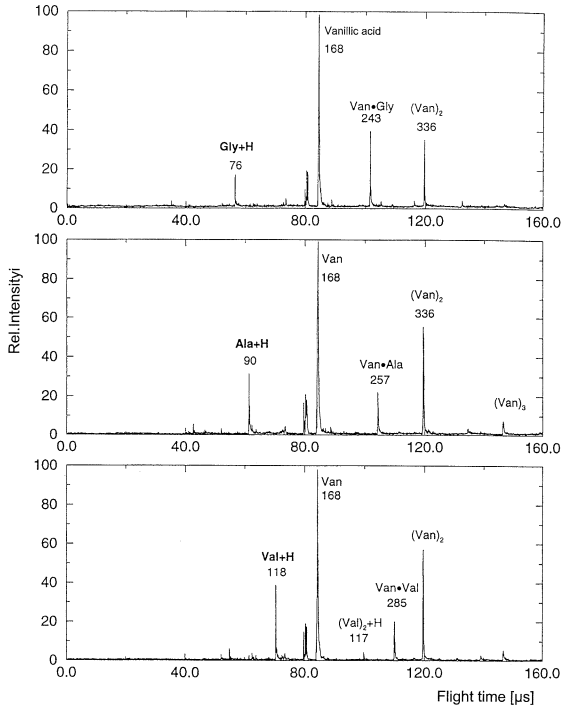

Fig. 7. Cluster formation of vanillic acid with some small amino acids: top spectrum glycine, middle spectrum alanine, and bottom spectrum valine. Ionization performed in all cases with 500 fs laser pulses, $\lambda = 260$ nm, energy/pulse $\sim$80 μJ.

in the first case much stronger. The same behavior is observed for the valine. Here the protonated amino acid signal reaches approximately 50% intensity as twice as much as observed with sinapinic acid.

In Table 1 the complete results of these investigations are summarized. Here the intensities for the signal of the protonated amino acids are compared. Clearly the most acids used as matrices yield not in a signal for any proton transfer in case of the amino acid glycine. Both the dihydroxy-benzoic acids as well as the sinapinic acid show no signal at all, while the vanillic and the ferulic acid can undergo this dissociative proton transfer reaction with medium to high intensities. Using alanine as a proton receptor again the 2,5 DHB yield no signal. In this case not even a signal for the homogenous cluster with femtosecond laser pulses could be observed. The other isomer of this benzoic acid shows a small signal for the protonated alanine like the sinapinic acid. Increasing the size of the nonaromatic residue of the amino acid or the introduction of a functionalized amino acid yield in strong signals for the protonated amino acid.

This behavior can easily understood by thermodynamics of the transfer reaction. As already shown in the literature [25] any dissociative proton transfer can occur if the following energetic requirements is fulfilled:

$$\mathrm{PA(M-H)^{\cdot}} - \mathrm{PA(A)} + \mathrm{D[M-H)^{\cdot} - (A+H)^{+}]} < 0 \text{ or } \mathrm{PA(M-H)^{\cdot}} < \mathrm{PA(A)}$$

with PA(Y): proton affinity of the respective compound and D: energy necessary to dissociate the ionic heterogeneous dimer after the proton has already been transferred to the amino acid molecule.

If this mechanism applies for the observed formation of protonated amino acids the important value influencing the detection of the respective protonated amino acid is the gas phase proton affinity of the employed amino acid. Only if the gas phase proton affinity of the amino acid exceeds the proton affinity of the corresponding radical $[M-H]^{\cdot}$ of the used matrix compound a proton transfer in the formed heterogeneous dimer may take place. By using experi-

Table 1
Intensities of the protonated amino acid from cluster reactions with different carboxylic acids (− not observed; ○ appearing, but weak; + intensity <15%, ++ intensity <20%; +++ intensity < 30%, ++++ intensity >30%)

	Glycine	Alanine	Valine	Leucine	Lysine
2,5 DHB	−	−	○	+	++
3,4 DHB	−	○	+	+++	+++
Sinapinic acid	−	○	+	++	+++
Vanillic acid	−	+	++	++	+++
Ferulic acid	+	+	++	+++	+++

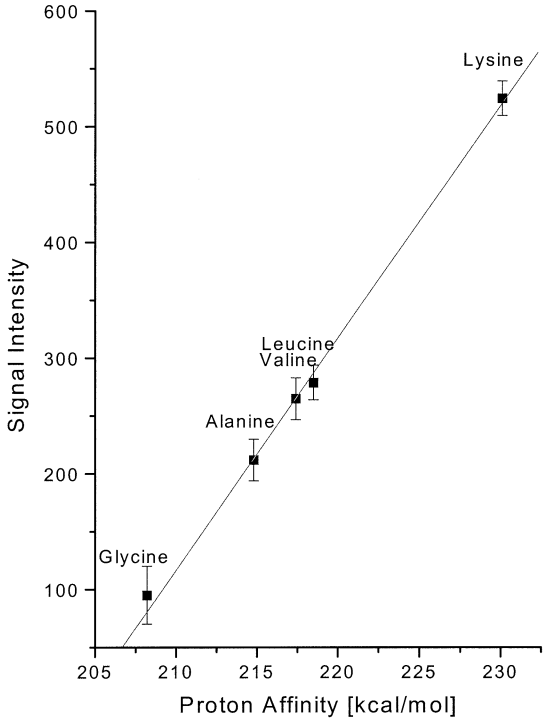

Fig. 8. Proton affinity of the amino acids versus the intensity of the protonated amino acid signal. Proton donating agent: vanillic acid. Activation with 500 fs laser pulses, energy/pulse ~80 μJ.

mental values for the proton affinities from the literature [31,32] one can compare the measured intensity for the protonated amino acid directly with the experimental values of the proton affinities. Theoretically plotting these both values should result in a straight line. As an example the intensity values obtained from the investigations with the vanillic acid are displayed in Fig. 8.

As shown in this figure the data from our experiments follow the theoretical considerations as well as the proposed mechanism. Clearly a linear relationship between the intensities for the different protonated amino acids and its proton affinities exists. This good agreement of experiment and theory gives support to the assumed dissociative proton transfer. In this diagram only the data for the vanillic acid together with the experimental error is shown. Similar results are obtained for the other benzoic acids. It should be noted that this technique allows a quick experimental estimation of the proton affinity of the deprotonated benzoic acid radical [33].

Further proof for the influence of the proton affinities of the deprotonated benzoic acid and the amino acid can be seen by using ammonia as the simplest amino acid. Since ammonia has the smallest proton affinity, no proton transfer with any of the investigated, thus the formation of NH_4^+ ions is not observed.

4. Conclusion

The gas phase behavior of some aromatic carboxylic acids were investigated by means of laser desorption multiphoton ionization time-of-flight mass spectrometry. Using femtosecond laser pulses for the ionization process intense homogeneous clustering of these compounds was observed and, when codesorbed with small polar amino acids into the supersonic beam, also the formation of heterogeneous clusters, especially heterogeneous dimers, was detected. In addition protonated amino acids were detected, which could not have been formed by direct ionization as the amino acids do not absorb laser light under the chosen ionization conditions. Most important the experimental results disclose a relation between the formation of heterogeneous dimers and protonated amino acids. On the basis of these experimental findings the protonated amino acids must be formed via proton transfer in the heterogeneous dimer ions from the carboxylic acid to the analyte molecule and subsequent decay of the dimer releasing the respective protonated amino acid, also by dissociative proton transfer. This proposed mechanism is promoted by the observed correlation of the signal intensity of the detected protonated amino acids with their gas phase proton affinities.

Acknowledgements

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