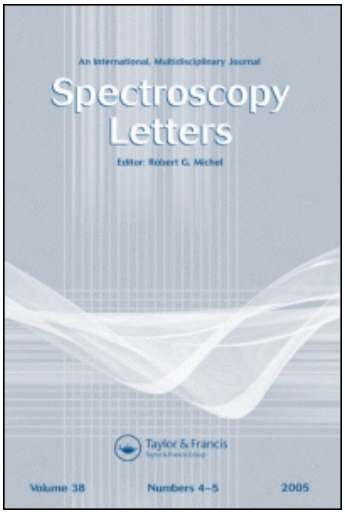


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# Laser Desorption Mass Spectrometry of Some Organic Acids

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# LASER DESORPTION MASS SPECTROMETRY OF SOME ORGANIC ACIDS

KEY WORDS: Laser desorption, mass spectrometry, LAMMA, negative ions, organic acids

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ABSTRACT

Positive and negative ion laser desorption (LD) mass spectra of organic acids are characterized by the emission of the quasimolecular ions $(M+H)^+$ and $(M-H)^-$. Generation of $(M+H)^+$ ions is interpreted as evidence for the occurence of high pressure proton transfer reactions in LD. Fragment ions can be rationalized by loss of stable neutral molecules from quasimolecular ions although decomposition may also be occuring prior to ionization. Features unique to LD, including the detection of pyrolysis products along with ions characteristic of the sample, are discussed in terms of the internal energy distribution in the irradiated microvolume. Negative ion

mass spectra of acids are dominated by $(M-H)^-$, while positive ion spectra contain abundant fragment ions, underlining the utility of detecting negative ions for acidic compounds.

## INTRODUCTION

Laser desorption (LD) is rapidly becoming an established method for the generation of ions from organic solids. LD mass spectra of a wide variety of compounds have been reported, including biologically important materials such as carbohydrates and drugs.[1-8] Since laser irradiation generates quasimolecular ions analogous to those formed during chemical ionization (CI), it is of interest to establish the similarities and differences between mass spectra obtained using LD and those obtained following chemical ionization.

It is helpful that mass spectrometry/mass spectrometry (MS/MS) has been used recently to characterize the dissociation chemistry of protonated molecules extracted from conventional CI sources.[9-11] Studies of this type provide a basis for comparison with results obtained using other ionization methods. The CI studies concluded that $(M+H)^+$ ions fragment by loss of stable neutral molecules via rearrangement reactions. Alkane and alkene eliminations dominated the reactions of parent species, but electron unpairing with alkyl radical loss was also observed. Elimination of neutrals containing

a heteroatom was observed, including loss of water and aldehydes from protonated ketones and loss of simple ethers and alcohols from protonated ethers. For protonated amines and esters, neutral losses included amines, ammonia and acids in addition to alkyl radical, alkane and alkene losses. We report here positive and negative ion LD mass spectra for a series of acids. The results are discussed in terms of the fragmentation processes that take place and are compared to results obtained using CI.



## EXPERIMENTAL

All experiments were performed using a Laser Microprobe Mass Analyzer (Leybold-Heraeus LAMMA-500) equipped with a Q-switched frequency quadrupled Nd-YAG Laser having a pulse width of approximately 15ns (265nm) and having the -90/90 geometry.[12] Ions are accelerated into a time-of-flight mass spectrometer with a 2m drift tube. An ion reflector compensates for the initial spread in ion energy and mass resolution in the range 800-1000 $m/\Delta m$ is attainable.[13] The output from a 17 stage venetian blind electron multiplier was collected by a transient recorder (Biomation) using sampling intervals of 10, 20, or 50ns and output to a strip chart recorder (Gould Accuchart). Mass assignments were determined by measurement and hand calculation based on the relationship $\ell=k\sqrt{m}$ where

$\ell$ = distance and k is a constant. Samples were deposited as powders onto copper grids. Following evacuation of the analysis chamber, the sample was oriented using micrometers to focus a He-Ne alignment laser on the desired particle. Small crystals were totally destroyed by the Nd-YAG laser pulse, while the beam desorbed portions of large crystals. Power densities were typically $10^7$-$10^9$ W/cm$^2$. Samples were reagent grade materials obtained commercially and were used without further purification.



## RESULTS AND DISCUSSION

Laser desorption of hippuric acid gave rise to the results shown in Figure 1. $(M-H)^-$ ions dominate the negative ion mass spectrum, the major fragmentation being loss of $CO_2$ to yield m/z 134. It is interesting that in a CI/MS/MS study of hippuric acid, negative ion fragments were observed at m/z 121 and 73 as well as 134.[14] These species were detected only in LD mass spectra obtained using higher laser power densities such that abundant $C_nH^-$ and $C_n^-$ cluster species were formed. These results are striking in that both fragment ions m/z 121 and 73 and cluster ions were generated during the same 15ns laser pulse, even though significantly more energy is required for formation of carbon cluster species. One explanation for these observations

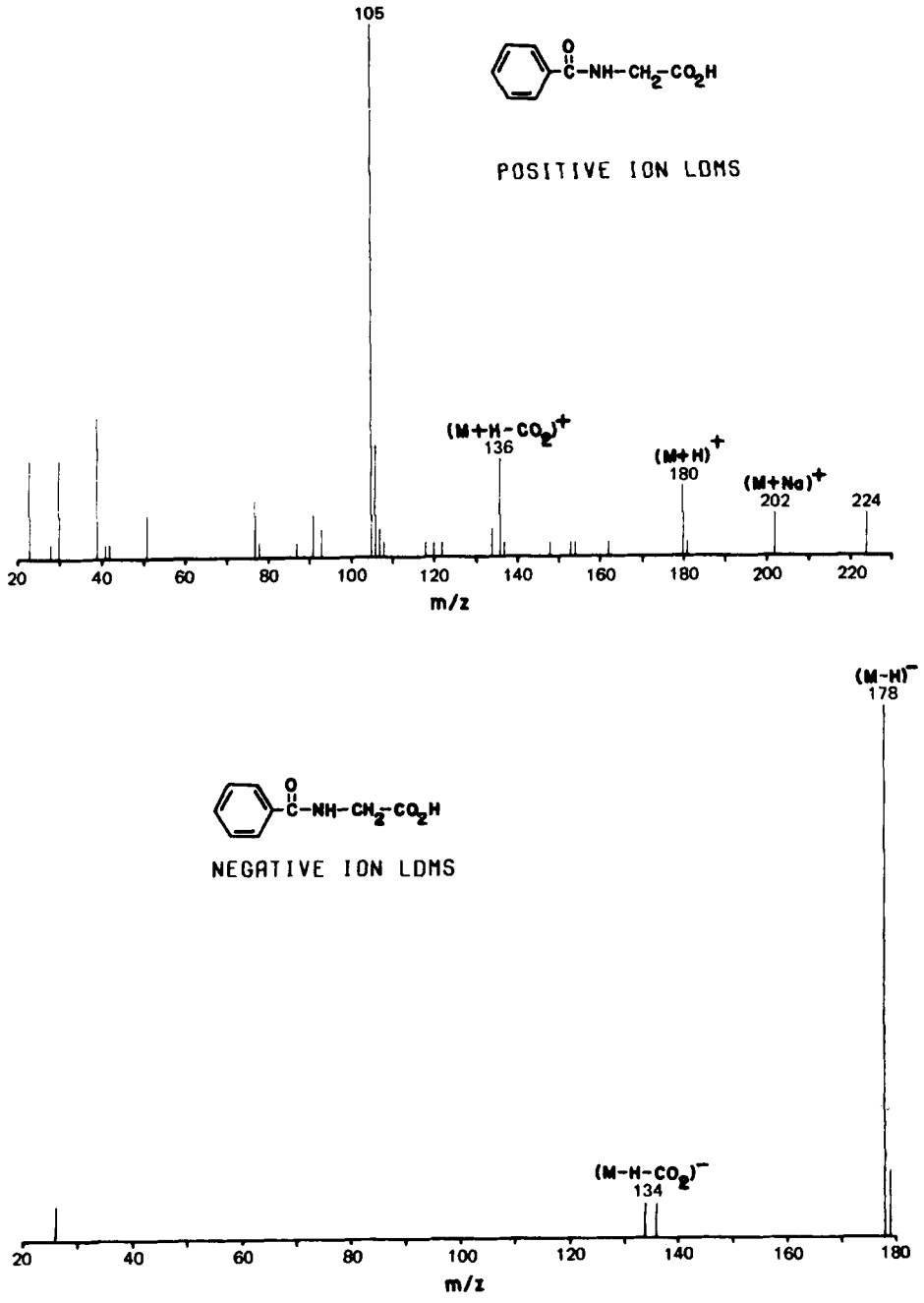



FIG. 1. Laser desorption mass spectra of hippuric acid.

is discussed along with the LD mass spectrum of citric acid, below. Ions at m/z 136 probably arise from an impurity since they did not follow the fluctuations in sample ion abundances observed from repetitive laser shots. The positive ion LD mass spectrum of hippuric acid (Figure 1) shows emission of the protonated molecule at m/z 180, sodium cationized species $(M+Na)^+$ at m/z 202, and sodium cationization of the sodium salt at m/z 224. Similar cationized salt species have been generated by ion bombardment of p-aminobenzoic acid/LiCl mixtures, in which the ions $(M-1+2Li)^+$ and $(M-2+3Li)^+$ were observed in the SIMS spectrum.[15] Loss of $CO_2$ from $(M+H)^+$ gives rise to ions at m/z 136. Ions at m/z 105 correspond to the benzoyl cation and can be rationalized as loss of formic acid and methyleneimine ($CH_2=NH$) from the protonated molecule, or alternatively as loss of an intact glycine unit by cleavage of the C-N bond following N-protonation. Ions at m/z 77 and 51 are indicative of the aromatic ring and are observed in EI and CI mass spectra of aromatic compounds.

Laser desorption of citric acid yields results similar to those for hippuric acid (Table I, Figure 2). In addition to $(M+Na)^+$, m/z 215, and $(M+H)^+$, m/z 193, a number of fragment ions were detected in the positive ion LD mass spectrum. These can all be rationalized as losses of water and formic

TABLE I
Positive and Negative Ion Laser Desorption Mass Spectra of Acids

| Positive ions | | Negative ions |
|---|---|---|
| | Hippuric acid | |
| m/z | | m/z |
| 224 | $(M+2Na-H)^+$ | 178 $(M-H)^-$ |
| 202 | $(M+Na)^+$ | 134 $(M-H-CO_2)^-$ |
| 180 | $(M+H)^+$ | |
| 162 | $(M+H-H_2O)^+$ | |
| 136 | $(M+H-C_2H_5NO_2)^+$ | |
| 105 | $(M+H-C_2H_5NO_2)^+$ | |
| 91 | $C_7H_7^+$ | |
| 77 | $C_6H_5^+$ | |
| 51 | $C_4H_3^+$ | |
| | Citric acid | |
| m/z | | m/z |
| 215 | $(M+Na)^+$ | 191 $(M-H)^-$ |
| 193 | $(M+H)^+$ | 111 $(M-H-CO_2-2H_2O)^-$ |
| 175 | $(M+H-H_2O)^+$ | 87 $(M-H-CO_2-HOAc)^-$ |
| 157 | $(M+H-2H_2O)^+$ | 85 $(M-H-H_2CO_2-HOAc)^-$ |
| 147 | $(M+H-H_2CO_2)^+$ | 59 $CH_3CO_2^-$ |
| 139 | $(M+H-3H_2O)^+$ | 57 $(M-H-2CO_2-H_2CO_2)^-$ |
| 129 | $(M+H-H_2O-H_2CO_2)^+$ | |
| 111 | $(M+H-2H_2O-H_2CO_2)^+$ | |

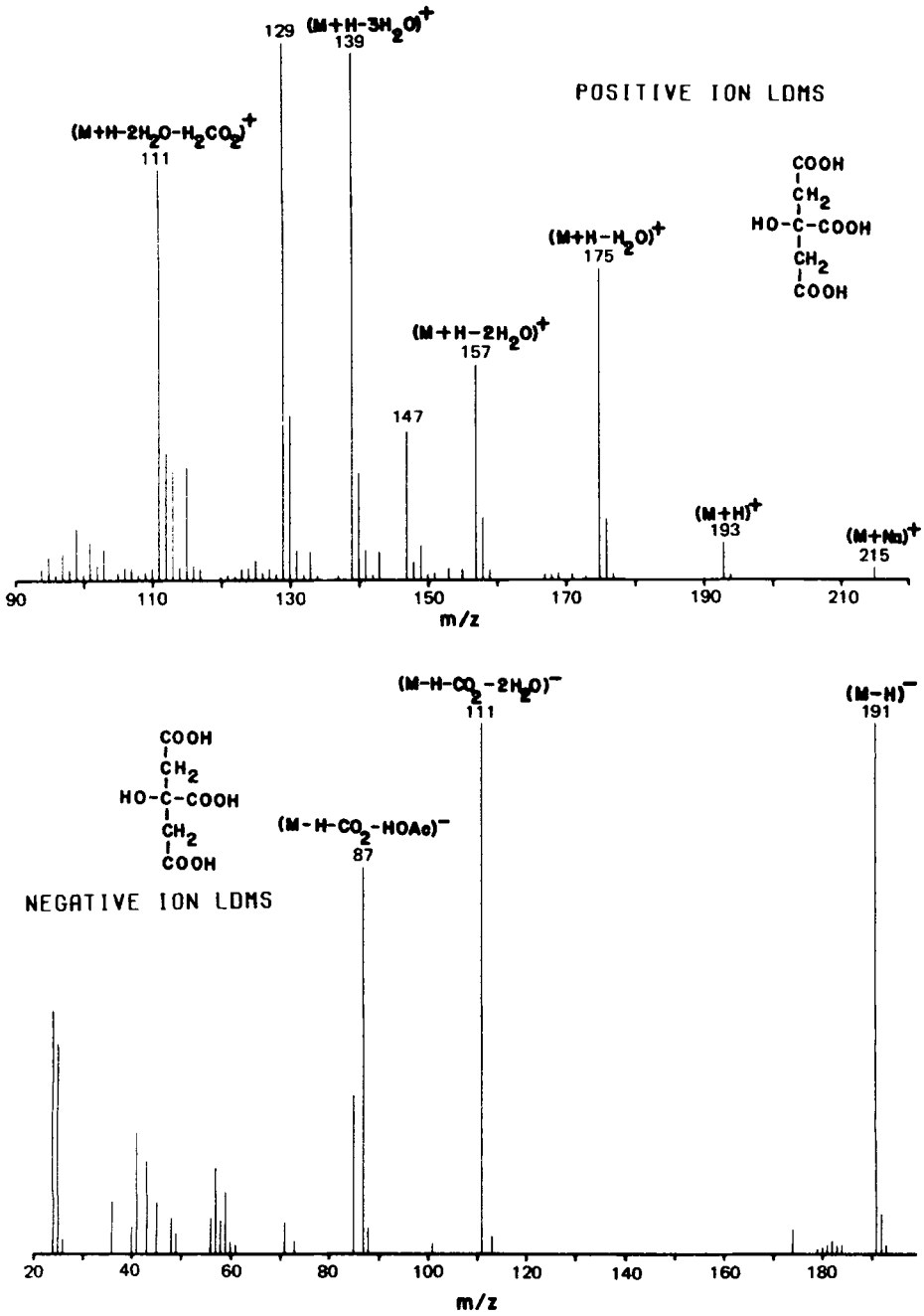



FIG. 2. Laser desorption mass spectra of citric acid. Note abundant $(M-H)^-$ ions and extensive fragmentation of $(M+H)^+$.

acid molecules (Table I). The negative ion mass spectrum (Figure 2) of citric acid was dominated by $(M-H)^-$, m/z 191, and contained abundant fragment ions at m/z 111 and 87. These are rationalized as shown in Table I. Examination of citric acid using negative chemical ionization (NCI) MS/MS and collision induced dissociation (CID) yielded slightly different results, water loss giving rise to the most abundant fragment at m/z 173 and acetic acid loss yielding ions at m/z 131.[14] Neither of these fragment species is observed in the LD mass spectrum, the minor peak between m/z 170 and 180 in Figure 2 being m/z 174. CID did give rise to fragment ions m/z 111, but generation of m/z 87 was not a major dissociation pathway.

The differences between the LD and NCI/MS/MS results can be interpreted to suggest formation of m/z 87 during laser irradiation by condensed phase processes, rather than by dissociation of gas phase ions prior to their acceleration into the TOF drift tube. The rate of any particular fragmentation process increases with internal energy of the parent ion.[16] Hence, if fragment ions in the LD mass spectrum arise by dissociation of $(M-H)^-$, their presence or absence will give a relative measure of internal excitations accessed by laser irradiation. M/z 173 and 131 appear following CID of citric acid quasimolecular anion. They are not present in the LD

mass spectrum and suggest that LD accesses lower internal energies than does CID. Since CID accesses internal excitations of the order of 10 eV,[17] optimum conditions for laser desorption must generate ions having average internal energies well below this value. Because m/z 87 is not generated by CID, its genesis in LD is ascribed to decomposition prior to ionization rather than gas phase reaction. Ions at masses below $(M+H)^+$ and $(M-H)^-$ can also be rationalized as products of thermal decomposition, since it is not possible to distinguish such processes from unimolecular processes occuring before acceleration.

The presence of abundant fragments $C_2^-$ and $C_2H^-$ in the negative ion mass spectrum and the extensive fragmentation observed in the positive ion mass spectrum further suggest that sample decomposition occurs during LD. It is noteworthy that $C_nH_m^-$ cluster ions are generated by laser pyrolysis of carbon containing materials. This suggests that pyrolysis also occurs in the LD experiments discussed here. One description of the laser desorption process postulates the existence of zones of differing internal energy in the irradiated volume. If this is true, a single laser pulse could generate molecular species in low energy regions, and products of decomposition and pyrolysis in high energy regions. This is precisely the experimental result. Thus the hypothesis of regions of both high and low internal

energy in the irradiated microvolume accounts for the observed emission of both quasimolecular species and fragments resulting from extensive thermal decomposition of parent molecules. It is interesting that some spectra show dominant contributions from quasimolecular ions and pyrolysis products, the low abundance of fragment ions suggesting that in some excited microvolumes intermediate energy ranges are not sampled.[18]

A characteristic of the LD results for acids is the relative stability of $(M-H)^-$ to dissociation as compared to $(M+H)^+$. Thus fragile acids yield negative ion LD spectra having $(M-H)^-$ as either the base peak or a very intense peak and few fragment ions, while positive ion spectra contain larger numbers of fragments, some of which dominate the protonated molecule. This is analogous to the behavior of acids in positive and negative CI.[14] The results obtained for benzilic, gallic, and pyromellitic acid underscore the usefullness of negative ion LD mass spectra of acidic compounds.

Laser desorption of benzilic and pyromellitic acids, for example, showed water loss from the protonated molecules as the largest detectable positive ion (Figures 3 and 4). This is not surprising when one considers that loss of water from protonated benzilic acid could generate acylium ions 1 while protonated pyromellitic acid could undergo facile dehydration to generate the protonated monoanhydride 2.

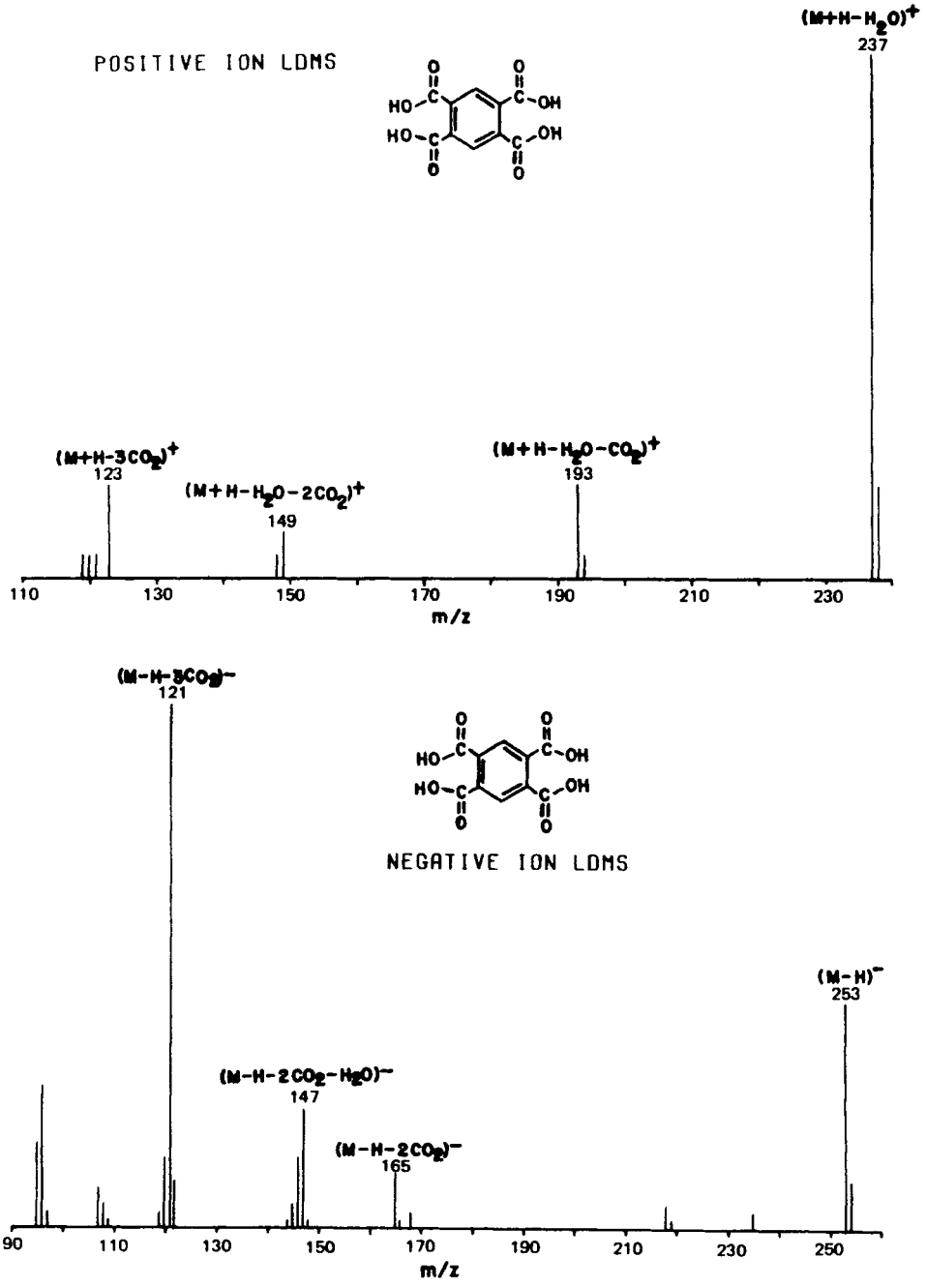



FIG. 3. Laser desorption mass spectra of pyromellitic acid. Note $(M-H)^-$ while the largest positive ion observed is $(M+H-H_2O)^+$.

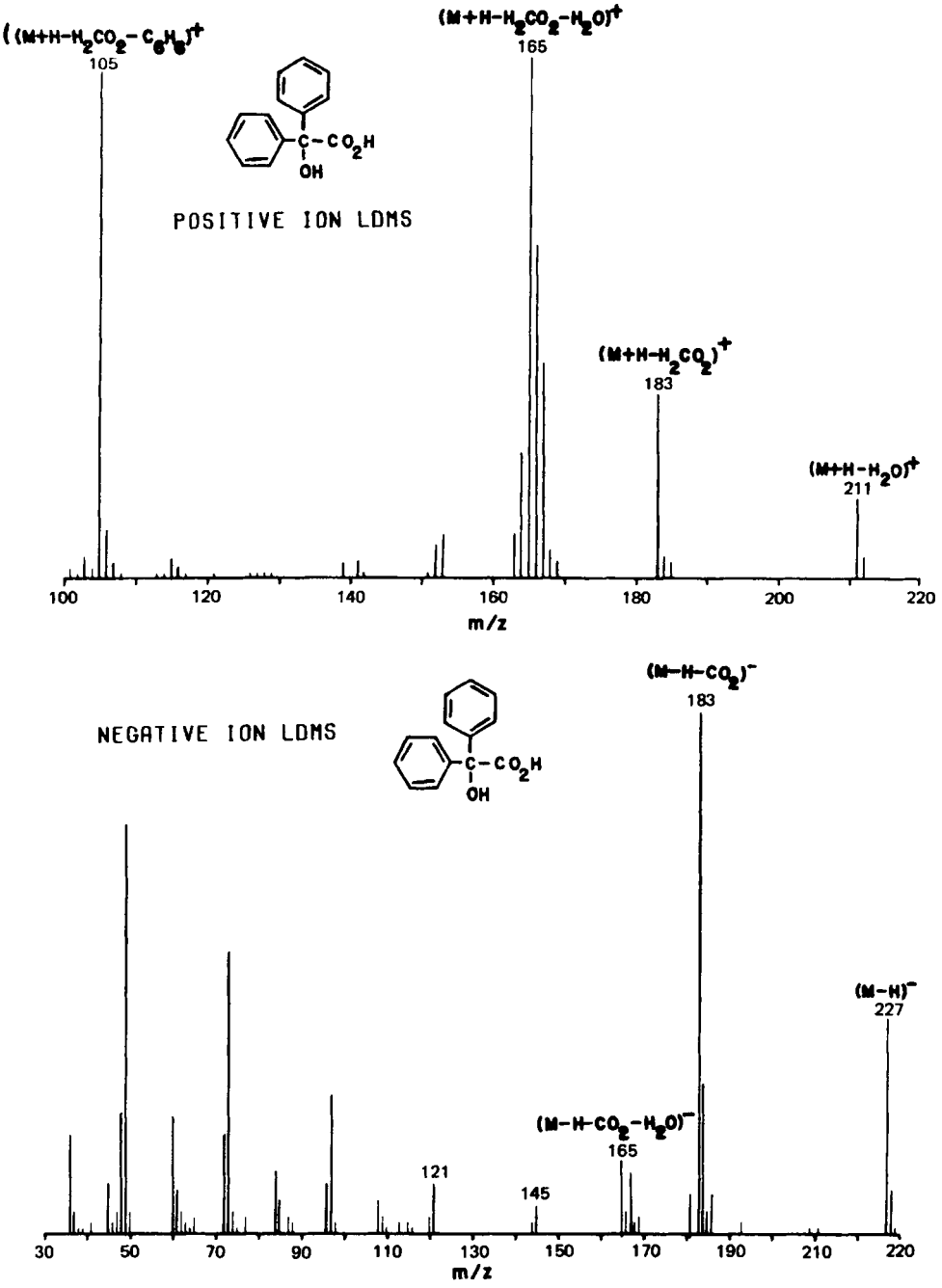
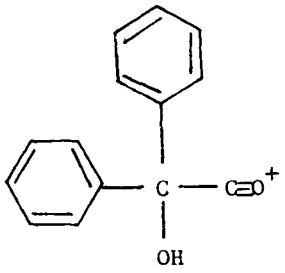



FIG. 4. Laser desorption mass spectra of benzilic acid. Note abundant $(M-H)^-$ ions. Note also that both spectra show ions at m/z 165 and 183, and the negative ion spectrum contains $C_nH^-$ ions (see text).



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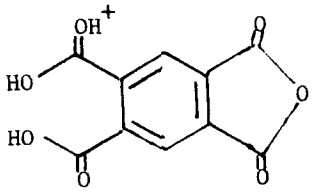

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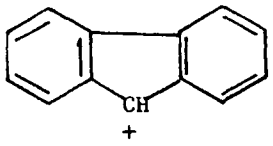
Further fragmentation of $(M+H-H_2O)^+$ from benzilic acid by CO loss would generate m/z 183, which may have the protonated diphenylketone structure, a suggestion that could explain the high relative abundance of this fragment. The species detected at m/z 165 and 105 can be rationalized as $(M+H-H_2CO_2-H_2O)^+$ and $(M+H-H_2CO_2-C_6H_6)^+$, respectively (Table II). The large abundance of m/z 165 suggests that it is a stable ionic species, and since consecutive losses of water and formic acid from the protonated molecule necessitate loss of at least one aromatic hydrogen, m/z 165 generated during LD of benzilic acid may have the structure of the $(M-1)^+$ ion from fluorene (3). Hydrogen atom loss from fluorene



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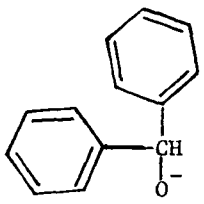

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TABLE II

| Pyromellitic acid | | | |
|---|---|---|---|
| m/z | | m/z | |
| 237 | $(M+H-H_2O)^+$ | 253 | $(M-H)^-$ |
| 193 | $(M+H-H_2O-CO_2)^+$ | 235 | $(M-H-H_2O)^-$ |
| 149 | $(M+H-H_2O-2CO_2)^+$ | 165 | $(M-H-2CO_2)^-$ |
| 123 | $(M+H-3CO_2)^+$ | 147 | $(M-H-2CO_2-H_2O)^-$ |
| | | 121 | $(M-H-3CO_2)^-$ |

| Benzilic acid | | | |
|---|---|---|---|
| m/z | | m/z | |
| 211 | $(M+H-H_2O)^+$ | 227 | $(M-H)^-$ |
| 183 | $(M+H-H_2CO_2)^+$ | 183 | $(M-H-CO_2)^-$ |
| 165 | $(M+H-H_2CO_2-H_2O)^+$ | 165 | $(M-H-CO_2-H_2O)^-$ |
| 153 | $(M+H-H_2CO_2-CH_2O)^+$ | 145 | $C_{12}H^-$ |
| 105 | $(M+H-H_2CO_2-C_6H_6)^+$ | 121 | $C_{10}H^-$ |
| | | 108 | $C_9^-$ |
| | | 97 | $C_8H^-$ |

| Gallic acid | | | |
|---|---|---|---|
| m/z | | m/z | |
| 171 | $(M+H)^+$ | 169 | $(M-H)^-$ |
| 170 | $M^{+\cdot}$ | 125 | $(M-H-CO_2^-)$ |
| 153 | $(M+H-H_2O)^+$ | 96 | $(M-H-CO_2-HCO)^{\cdot}$ |

molecular ion gives rise to a peak nearly equal in abundance to $M^{+\cdot}$,[19] illustrating the stability of these species to further dissociation on a microsecond time scale. The major ions below $(M+H-H_2O)^+$ in the LD mass spectrum of pyromellitic acid can be rationalized as consecutive decarboxylations of $(M+H-H_2O)^+$ to give m/z 193 and 149, and as three decarboxylations of $(M+H)^+$ to give m/z 123 (Table II).

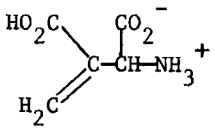
In contrast to these results, the negative ion LD mass spectra of both benzilic acid and pyromellitic acid contain $(M-H)^-$ as an abundant ion (Figures 3 and 4). For pyromellitic acid the base peak corresponds to the triply decarboxylated anion, with other reactions giving rise to ions at m/z 147 and 165 (Table II). It is striking that loss of a single $CO_2$ molecule, which would generate ions at m/z 209, was not observed. Loss of $CO_2$ did account for the major fragment observed in the negative ion mass spectrum of benzilic acid, m/z 183. The dominance of this latter species could be explained as the formation of alkoxide anions 4. Further decomposition of m/z 183 by water loss would yield ions observed at m/z 165. It is noteworthy that laser desorption of this compound gave both positive and negative ions at m/z 165, suggesting that $(M-H)^{\pm}$ ions from fluorene may constitute especially stable species for both positive and negative ions.

It is instructive to note the appearance of $\bar{C}_n$ and $C_nH^-$ ions in Figure 3, as these indicate the use of excessive

laser power density resulting in pyrolysis and cluster ion formation. We have observed this as a general phenomenon in laser desorption of organic compounds. The pattern observed here for $C_n^-$ and $C_nH^-$ ions in which clusters with n=even dominate those with n=odd is seen consistently. This generalization is illustrated by the fact that $C_{11}$ species are not detectable, even though $C_{12}^-$ and $C_{12}H^-$ are observed.

Gallic acid yielded results similar to those of benzilic acid and pyromellitic acid in that water loss from $(M+H)^+$ gave rise to the most abundant positive ion, while $(M-H)^-$ comprised the base peak in the negative ion mass spectrum (Table II, Figure 5). Decarboxylation of deprotonated gallic acid gave rise to an abundant fragment at m/z 125 in the negative ion LD mass spectrum.

In the course of our laser desorption studies the acid 5 was also investigated.[20] Although of only moderate molecular weight (MW 145),



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it has proved difficult to derivatize, a factor that has forestalled obtaining its mass spectrum using conventional

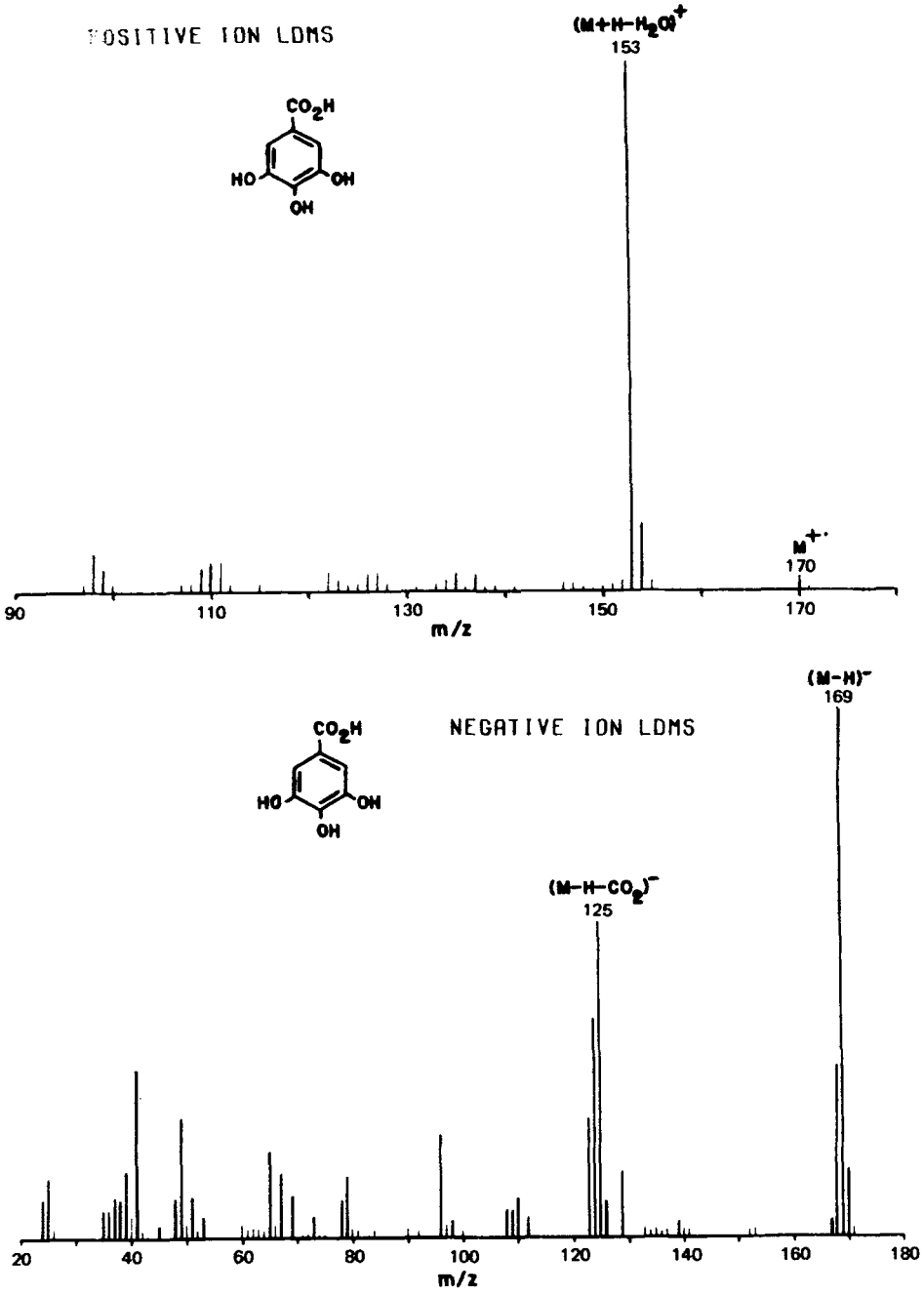


FIG. 5. Laser desorption mass spectra of gallic acid. Note dominance by the quasimolecular anion, m/z 169. The positive ion results show water loss as the base peak.

ion sources. Laser desorption generates abundant quasimolecular ions of this acid without derivatization, results that are characteristic for LD of organic salts.[1,8] The LD mass spectra (Figure 6, Table III) reveal features similar to those described above. Cationized, $(M+Na)^+$, m/z 168, and protonated, m/z 146, molecules are emitted at high intensity, and formic acid loss can account for the most abundant positive ion fragment m/z 100. Other ions characteristic of the compound include $(M+H-H_2O)^+$, m/z 128, $(M+H-H_2O-NH_3)^+$, m/z 111, and loss of both water and $CO_2$, m/z 84. Ions m/z

TABLE III

$H_2CC(CO_2H)CH(CO_2^-)NH_3^+$

| m/z | | m/z | |
|---|---|---|---|
| 168 | $(M+Na)^+$ | 144 | $(M-H)^-$ |
| 146 | $(M+H)^+$ | 100 | $(M-H-CO_2)^-$ |
| 128 | $(M+H-H_2O-NH)^+$ | 74 | $(M-H-CO_2-C_2H_2)^-$ |
| 111 | $(M+H-H_2O-NH_3)^+$ | 71 | $(M-H-CO_2-CH_2NH)^-$ |
| 100 | $(M+H-H_2CO_2)^+$ | 66 | $C_2OCN^-$ |
| 84 | $(M+H-H_2O-CO_2)^+$ | 56 | $(M-H-2CO_2)^-$ |
| 71 | $(M+H-H_2CO_2-CH_2NH)^+$ | 50 | $C_3N^-$ |
| 56 | $(M+H-H_2CO_2-CO_2)^+$ | 42 | $OCN^-$ |
| 30 | $CH_2NH_2^+$ | 26 | $CN^-$ |
| 18 | $NH_4^+$ | | |

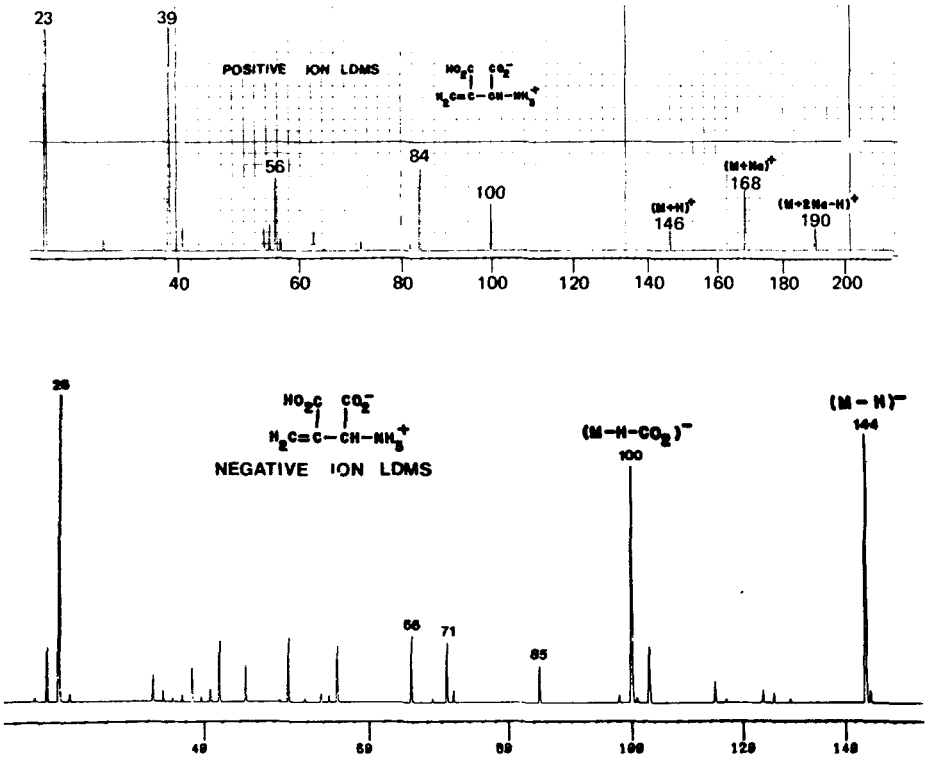


FIG. 6. Laser desorption mass spectra of $H_2C$ $C(CO_2H)CH(NH_3^+)CO_2^-$. Note quasimolecular ions and characteristic fragments generated by laser irradiation.

71 can arise by loss of formic acid and methyleneimine and loss of both formic acid and $CO_2$ could yield m/z 56. Ions at m/z 30 and 18 correspond to $CH_2NH_2^+$ and $NH_4^+$ and are typical low mass fragments of amines. The negative ion LD mass spectrum illustrates emission of abundant $(M-H)^-$ ions, m/z 144, and decarboxylation to give m/z 100. Additional fragment species occur at m/z 74, 71, and 56 (Table III), and

can also be rationalized as losses of stable neutral molecules. These laser desorption results can be compared with mass spectra of biologically important amino acids obtained by SIMS,[21] another ionization method that has proved successful in the analysis of organic salts. Ion bombardment gives rise to similar results in that abundant $(M+H)^+$ and $(M-H)^-$ ions and cationized molecules are emitted from metal supported amino acids.

It is interesting that protonated as well as cationized molecules were generated by LD of hippuric and citric acids and of the amino acid discussed above. This is unusual in that cationized species and not $(M+H)^+$ are normally observed in LD[1-7,22] and warrants comment. Three forms of the amino acid, the zwitterion, the protonated molecule and the deprotonated molecule, can exist in the solid. As a result, $(M+H)^+$ in this case can arise by emission of protonated molecular species present in the solid. Similar results have been reported for other organic salts.[1,8] Neither citric nor hippuric acids are expected to form zwitterions, and $(M+H)^+$ formation requires an alternative explanation.

Recent thermal desorption experiments have shown that $(M+C)^+$ ions, C = alkali cation, can be generated by purely thermal means.[23] Laser desorption chemical ionization results have been interpreted to suggest that LD operates by thermal desorption of alkali ions and neutrals, coincident

with or followed by ion attachment.[22] In the LDCI experiments, $(M+H)^+$ ions were not produced by laser irradiation. Their observation for hippuric and citric acid can be explained by protonation in a laser induced zone of high pressure. This zone might resemble the plasma in a CI source. It is almost certainly not a true plasma in that temperatures of several thousand Kelvin are not compatible with survival of abundant quasimolecular ions. These results provide additional evidence that LD is not a purely thermal process.[1]



## CONCLUSIONS

Laser desorption mass spectra of a variety of organic acids illustrate that the protonated, deprotonated and cationized molecules are generated. Ions appearing in the mass spectrum can be explained as products of thermal decomposition prior to ionization or as fragments of quasimolecular ions. Nevertheless, fragment ions can be rationalized by loss of stable neutrals from quasimolecular ions. Water loss and decarboxylation dominate the observed dissociations and are precisely those observed using CI/MS/MS. Detection of negative ions is advantageous for acidic compounds since higher quasimolecular ion and lower fragment ion abundances are observed compared to positive ions. Evidence for laser induced decomposition prior to ionization and for pyrolysis in the laser focus was observed. Comparison of laser desorption

results with those obtained using collision induced dissociation suggests that in LD some portions of the sample are excited to relatively low internal energies and experience limited fragmentation while others attain high internal energies and decompose to cluster species. The generation of protonated molecules in LD suggests that proton transfer reactions can occur in regions of high sample pressures generated by laser irradiation.

## ACKNOWLEDGEMENTS

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