Cationization by Alkali Ion Attachment in Laser Desorption Mass Spectrometry

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The formation of quasimolecular ions by alkali ion attachment in laser desorption mass spectrometry has been investigated by using a CW CO_2 laser. For molecules such as sucrose the desorption of preformed ions could be excluded. Evidence is presented for the ionization by alkali ion attachment in the gas phase. Quasimolecular ions of organic salts were found to result from cationization reactions in the gas phase and from surface reactions. Very fast cation exchange reactions have been discovered for salts and acids impinging on alkali ion emitting surfaces.

Introduction

The effect of the emission of quasimolecular ions from organic sample layers upon laser irradiation is used in laser desorption mass spectrometry (LD MS) [1–21] for the analysis of thermally labile compounds. The simple mass spectra obtained from well-known thermally labile compounds such as organic salts, oligosaccharides, peptides and nucleotides demonstrate the potentialities of this ionization method for molecular weight determination. Typically $[M+H]^+$ or $[M+\text{Alkali}]^+$ ions are formed with high relative abundance.

This phenomenon of laser induced formation of quasimolecular ions has been observed with pulsed lasers in a broad frequency range from the IR to the UV, at irradiances of about 10^5 to 10^9 W cm^{-2} and at pulse durations between some ns and 100 µs [16]. Even CW lasers of low power densities ($\geqq 10$ W cm^{-2}) have been successfully applied. The sample preparation, the energy deposition from the laser, the wave length and other parameters affect the appearance of mass spectra. The experimental results presented so far allow the conclusion to be drawn that lower power densities ($\leqq 10^6$ W cm^{-2}) and photon energies < 1 eV are in favour of the formation of abundant quasimolecular ions such as $[M+\text{Alkali}]^+$ and $[M-H]^-$ ions. $[M+H]^+$ ions are less frequently observed, mostly with nitrogen or phosphor containing compounds. Typically no $M^{+\cdot}$ molecular ions are formed. The $[M-H]^-$ ions are generated from acidic compounds. They are also abundant in the LD mass spectra of the corresponding salts. The alkali ions in the $[M+\text{Alkali}]^+$ quasimolecular ions result either from alkali salts added to the sample, from impurities or from contaminations of the substrate material with alkali metals.

Alkali ion attachment is the most important ionization mechanism for molecular weight determination of large organic molecules because $[M+\text{Alkali}]^+$ ions are particularly stable with respect to monomolecular decompositions [22, 23]. Accordingly the elucidation of the mechanisms by which $[M+\text{Alkali}]^+$ ions are formed is of main interest in LD mass spectrometry.

Since cationization by alkali ion attachment is observed at all laser frequencies this phenomenon can be attributed to a secondary effect of the irradiation i.e. to a heating of the sample and/or substrate. This conclusion is obvious for LD with IR lasers of lower power densities. Applying CW CO_2 lasers any ionization mechanism should arise from thermal effects. The previous observation of a long lasting emission of cations from quaternary salts [7] which gave rise to speculations on nonthermal effects in LD proved to result from a pure thermal evaporation of these salts [24].

The present paper is concerned with the origin of the $[M+\text{Alkali}]^+$ quasimolecular ions. In discussing the formation of these ions it is important to differentiate between salts and polar nonionic compounds because different reaction mechanisms may contribute to the production of ions. For polar nonionic molecules such as sucrose the following reactions have to be considered:

1. Thermal evaporation of preformed $[M+\text{Alkali}]^+$ ions. Polar molecules are capable to solvate alkali ions. However, the feasibility of a thermal evaporation of ions is questionable since

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this mechanism competes with the evaporation of neutral molecules and the recombination of the positive alkali ions with the negative counterions in the layer. Even a recombination of ions with the substrate surface has to be considered. Therefore a high rate of sample evaporation should be a prerequisite for the thermal evaporation of preformed ions. The desorption of quasimolecular ions at temperatures above the threshold of a thermionic emission of free alkali ions should be impossible because organic molecules cannot withstand these temperatures (> 900 K).

2. Ionization via reactions of molecules with alkali ions in the gas phase. Organic molecules and alkali ions desorbed from surfaces at different temperatures may combine in the gas phase. Such a mechanism has been proposed by P. G. Kistemaker et al. [25] to explain the observed delayed emission of $[M+K]^+$ ions in some LD experiments applying a CW CO_2 laser. In these experiments the $[M+K]^+$ ions could not be detected prior to the onset of the K^+ emission and the onset of evaporation of neutral molecules. Evidence for a gas phase ionization mechanism has recently been obtained by these authors [26] and is also reported in the present paper. It has to be added that the appearance of $[M+Ag]^+$ ions of sucrose in the gas phase upon irradiation of a sample layer by short laser pulses of 10^8 W cm^{-2} [17, 27] also points to an ionization mechanism where M and Ag^+ combine in the gas phase close to the surface because the temperatures required for the release of Ag^+ from the substrate are by far too high to leave organic molecules intact. For disaccharides there is sufficient experimental evidence of thermal evaporation of intact molecules under appropriate conditions of chemical ionization [28].

3. Cationization of molecules supplied from the gas phase or via surface diffusion on alkali ion donating surfaces. This mode of surface ionization has been observed for molecules impinging from the gas phase onto electrically charged surfaces of ionic conductors [22, 29]. However, the feasibility of this reaction for uncharged surfaces at high temperatures still needs to be investigated.

With alkali salts of some acids it was found that $[M+\text{Alkali}]^+$ ions are formed by decomposition of clustered neutral salt molecules on surfaces having temperatures above 1300 K [30]. This mechanism should also contribute to the formation of quasimolecular ions of salts in LD MS.

The following results are reported for conditions of LD MS where the ion emission is induced by heating of the sample and/or the substrate. Most experiments were performed with sucrose and sodium acetate by using a CW CO_2 laser of low power density. For sucrose which is widely used to probe surface dependent ionization techniques the question of the existence of a direct thermal emission of preformed ions was of main interest.

Experimental

The experimental arrangement used in this study is schematically shown in Figure 1. The quadrupole mass spectrometer (Extranuclear Lab.) is coupled to a multichannel analyser (Wenzel Elektronik) for accumulation of spectra. In general $2k$ channels were used for one mass spectrum. The minimum scanning time for a spectrum (at low resolution) was 10^{-2} s.

A self constructed CW CO_2 laser was used. Most experiments were performed with an unfocused beam at 10,6 μm and without using a grating system for wave length selection. The power density of the unfocused beam was about 200 W cm^{-2} and the beam diameter about 4 mm. Focusing was possible by a Ge lens ($f = 128$ mm).

The samples were deposited on an indirectly electrically heatable stainless steel sheet or on a directly heatable 10 μm W wire placed above the metal sheet. Both were electrically and mechanically connected with a pushrod system (diameter 28 mm) allowing a rapid replacement of the sample via a vacuum lock system. The position of the pushrod with respect to the ion optics of the quadrupole filter could be adjusted by micromanipulators.

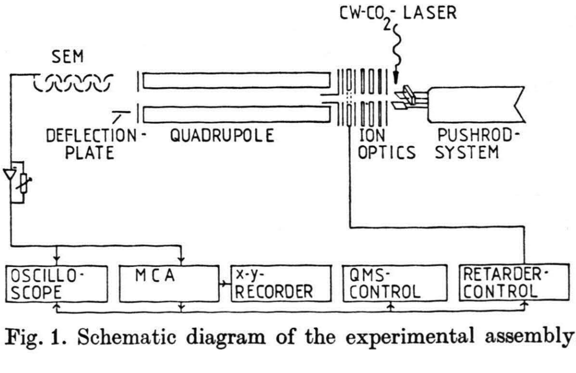

Fig. 1. Schematic diagram of the experimental assembly.

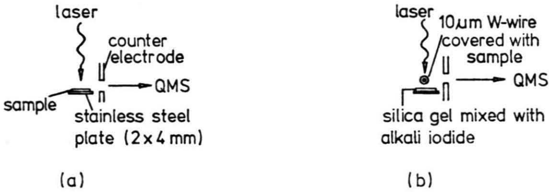

Fig. 2. Experimental set-ups of the ion source. In most experiments the W wire and the metal plate in (b) are electrically connected and at 20 V (for exceptions see Figs. 3 and 4). The counter electrode is at 0 V. The W wire and the metal plate are electrically heatable.

The different set-ups of the ion source as used in this study are shown in Figure 2. In general the samples were deposited from aqueous solution. The alkali ion emitter was prepared by mixing silica gel and alkali iodides at a volume ratio of about 1 : 1.

In most experiments the ion emitter was at $+20$ V and the 2–3 mm distant counter electrode at 0 V. A retardation electrode with two gold meshes placed in front of the quadrupole was used for energy analysis of the emitted ions. The retardation curves were obtained by measuring the transmitted ion current as function of the voltage difference between emitter and retardation electrode.

Results and Discussion

Sucrose

A purely thermal desorption of $[M+Na]^+$ ions has been reported for a mixture of a crown ether with NaI [31]. The $[M+Na]^+$ ions are observed at temperatures below the onset of a thermionic emission of Na^+ thus excluding any gas phase ionization by ion molecule reactions. This thermal phenomenon can be ascribed to the high stability of the $[M+Na]^+$ complex and to a rather low coulomb binding energy between the alkali and halogen ions.

Electrical heating of a mixture of sucrose and NaI did not result in the desorption of $[M+Na]^+$ ions [31]. Provided such a mechanism exists at higher rates of sample evaporation the $[M+Na]^+$ ions should be detectable in the gas phase prior to the appearance of Na^+ ions [32].

In a first series of experiments we have investigated the relative onset of the emission of $[M+\text{Alkali}]^+$ ions to the emission of alkali ions (Na^+, Li^+) upon laser irradiation of rather thick sample layers. The thickness of the layer deposited on the foil (see Fig. 2a) was about 1 mm and the laser power density about $200\ \text{W cm}^{-2}$. Since sucrose absorbs the IR laser light high rates of sample evaporation are achieved independent of the substrate temperature.

The results of a large number of experiments are as follows:

1. The ion emission starts delayed after a considerable loss of sample material. The time-lag between the onset of the laser irradiation and the appearance of ions was between about 0,1 to several seconds depending on the experimental conditions. The time-lag was longest for a clean metal sheet and became significantly shorter for a strongly absorbing substrate.
2. No $[M+Na]^+$ or $[M+Li]^+$ ions have ever been observed to preceed the onset of cation emission with the detection time resolution of 10 ms. In some experiments the alkali ions were detected first.
3. During the $[M+\text{Alkali}]^+$ ion emission part of the substrate surface or (carbonized) sample layer was at temperatures far above the onset of a thermionic alkali ion emission (>1100 K) as could be controlled through a viewing window of the vacuum chamber.

These results almost exclude a thermal evaporation mechanism for the $[M+\text{Alkali}]^+$ ions and point to a dependence of the quasimolecular ion emission on the presence of alkali ion emitting hot surfaces. This conclusion is supported by experiments in which a small amount of sample (some µg of sucrose $+$NaI) was deposited on a polished nonabsorbing metal sheet. Under these conditions no ion emission could be discovered in spite of a high evaporation rate of sucrose.

Strong evidence for a gas phase ionization mechanism via ionmolecule reaction without any contribution from a direct evaporation of preformed quasimolecular ions was obtained from a further series of experiment: In these experiments the arrangement of Fig. 2b was used in which the sample covering the wire was placed above an alkali ion emitting surface. The alkali ion emitter was composed of a mixture of alkali halide and silica gel. Laser irradiation of both the sucrose sample and the silica gel caused the evaporation of the sample in an alkali ion beam emitted from the silica gel.

The temperature of the alkali ion emitter was above 1300 K. For a rather small amount of pure sucrose (about 5 ng) abundant quasimolecular and fragment ions were obtained. The ions are exclusively formed by the attachment of alkali ions (K^+, Na^+, Li^+) emitted from the silica gel. The same result was obtained for a sucrose/NaI 1 : 1 sample mixture (5 ng) placed in a K^+ ion beam. $[M + K]^+$ ions,

$$[C_6H_{10}O_5 + K]^+, \quad [C_6H_{12}O_6 + K]^+$$

and $[C_{12}H_{20}O_{10} + K]^+$ ions could be detected but no $[M + Na]^+$ ions.

It is obvious that these ions cannot arise from a direct evaporation mechanism. They may be formed either by ion molecule reactions in the gas phase or by alkali ion attachment to molecules impinging on the heated silica gel surface. A contribution of the latter surface ionization mechanism could be excluded by a comparison of the energy distribution of the $[M + K]^+$ ions with that of the K^+ ions applying a different voltage to the wire covered by the sample (+ 30 V) and to the K^+ ion emitter (+ 60 V). In Fig. 3 the integral energy distributions of both ions are displayed. They have been obtained by scanning the potential of a retardation electrode placed in front of the mass filter between 0 and 60 V. The displacement of the retardation curves reveals a different place of origin for both ions. Most of the $[M + K]^+$ ions are formed near the wire surface (at 30 V).

The above results clearly show that for conditions of lower irradiances there is no contribution of a direct thermal desorption of preformed ions from electrolytic solutions. The same conclusion has been derived from a comparison of the rate of diffusion and recombination of solvated ions with the rate of evaporation of solvent molecules [32]. Even above 10^6 W cm^{-2} a thermal desorption of quasimolecular ions is not probable provided electronic excitation and plasma formation is avoided.

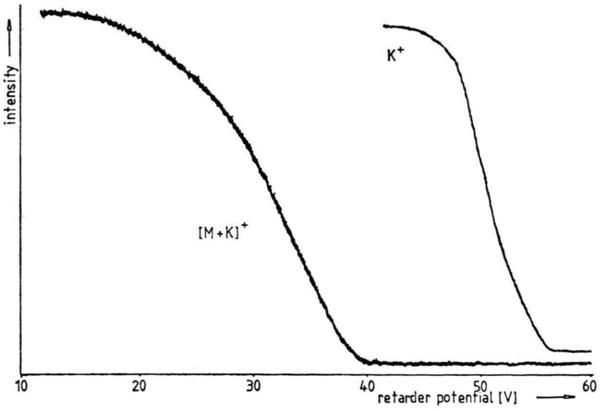

Fig. 3. Retardation curves of the K^+ and $[M + K]^+$ sucrose ion. The experimental arrangement is shown in Fig. 1 and 2b. The W wire was at 30 V, the K^+ emitter at 60 V and the extraction electrode at 0 V.

In view of this result it is obvious that the $[M + \text{Alkali}]^+$ ions of glucose and adenosin observed in former thermal desorption experiments [31] are formed by ion molecule reactions in the gas phase. The different behaviour of the crown ether results from the strong complexation of the Na^+ ion as mentioned above forming stable $[(M + Na)^+I^-]$ salt molecules which have been discovered in the gas phase [32].

Recent experiments of Hardin and Vestal [20] point to a different mechanism of ion generation in which $[M + \text{Alkali}]^+$ ions are formed via decomposition of desorbed clusters in the gas phase. The above experiments do not support such a mechanism even a sputtering of small particles of the sample material has been observed under various conditions of laser and electrical heating of samples. The sputtering of small clusters may be favoured by a larger amount of solvent still present in addition to a less or non-absorbing sample layer on a rapidly heated target.

The question as to the difference between electrical heating and laser heating arises. Applying electrical heating instead of laser heating for the evaporation of sucrose and for the emission of K^+ ions (Fig. 2b) mass spectra of sucrose have been obtained which are mostly free of fragment ions. In particular no

$$[C_6H_{10}O_5 + K]^+ \quad \text{and} \quad [C_6H_{12}O_6 + K]^+$$

fragment ions have been detected in agreement with recent results of van der Peyl et al. [26]. However, these ions are always observed if the evaporation of sucrose is performed by CO_2-laser irradiation i.e. if the sample layer is deposited on a non-absorbing metal substrate surface. For an absorbing substrate such as silica gel and an optically thin sucrose layer similar spectra are obtained as with electrical heating of the sample. The effect of wave length on the fragmentation of absorbing sample molecules has been discovered before [7] and was investigated in more detail. However, a discussion of the results is outside the scope of this paper.

Acids and Salts

In addition to sucrose, stachyose etc. the ionization by alkali ion attachment in the gas phase has been performed with acids such as acetic acid, citric acid, stearic acid and arginine. To this end the samples were evaporated from the electrically heated W wire exposed to a K^+ ion emitter as shown in Figure 2b. Again the different energy distribution of the K^+ and $[M + K]^+$ ions revealed a gas phase reaction. This is shown for sodium stearate in Figure 4.

Applying the same ionization technique to sodium acetate (CH_3CO_2Na) three types of quasimolecular ions are observed: $CH_3CO_2Na_2^+$, $(CH_3CO_2Na)_nK^+$ with $n = 1, 2, 3, 4$ and $CH_3CO_2K_2^+$ (Figure 5). They point to different ion formation processes: 1. The formation of the $CH_3CO_2Na_2^+$ ions can be attributed to the decomposition of dimers or higher clusters on the K^+ ion emitting hot silica gel surface [30]. It was found that this ion forming reaction gives rise to a more abundant ion signal with heated metal than with silica gel surfaces. 2. Gas phase ion molecule reactions lead to the formation of the $(CH_3CO_2Na)_nK^+$ ions. A very small contribution to the signal intensity from an attachment of K^+ ions on the silica gel surface is probable but could not yet be established. 3. The formation of the $CH_3CO_2K_2^+$ ions obviously involves alkali ion exchange reactions on the K^+ emitting surface prior to the ionization by K^+ attachment on the surface or in the gas phase.

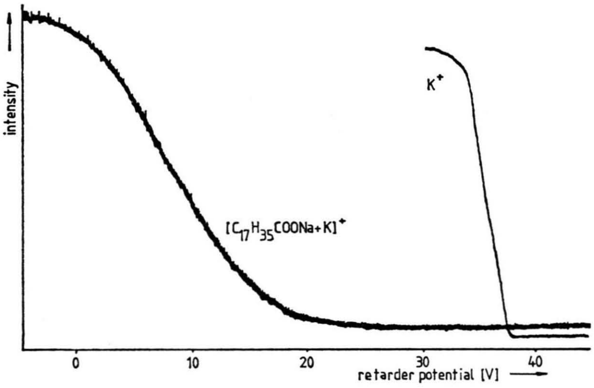

Fig. 4. Retardation curves of the K^+ ion and $[M + K]^+$ ion of sodium stearate. The W wire covered by the sample was at 20 V, the K^+ emitter at 40 V and the extraction electrode at 0 V (Figure 2b).

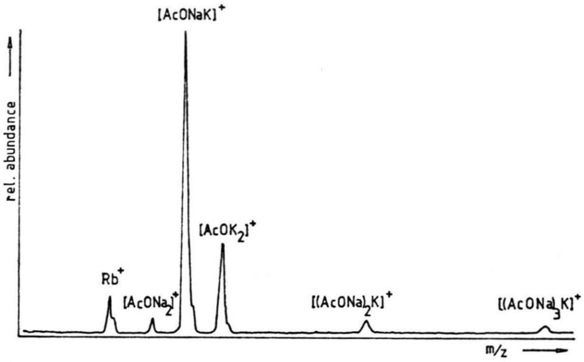

Fig. 5. Quadrupole mass spectrum of sodium acetate (AcONa) obtained by evaporation of the sample onto a K^+ ion emitting silica gel surface. The experimental set-up is that of Figure 2b. The evaporation of AcONa was performed by electrical heating of the W wire.

Similar products of alkali ion exchange reactions have been observed with various salts including $CH_3CO_2N(C_4H_9)_4$. Evidence for H, K exchange reactions on the silica gel/KI surface was derived from the spectra of acids such as acetic acid and arginine which exhibit weak peaks due to $[M - H + 2K]^+$ ions.

In these experiments the temperature of the K^+ emitter was always above 1100 K. For surface reactions leaving organic molecules intact these temperatures are surprisingly high. It may be concluded that the exchange reactions are extremely fast proceeding without thermal accomodation of the molecules, most probably within less than one ns. The subsequent ionization by alkali ion attachment may be a surface or a gas phase reaction. It was not yet possible to differentiate between both contributions.

The various quasimolecular ions of salts are also observed in LD mass spectra where the sample was deposited directly on the silica gel/KI surface without using a solvent. Under these conditions diffusion of molecules from surface areas of low to those of high temperatures may become important for the decomposition or attachment reactions. Further experiments are needed to elucidate the different ion formation processes in LD of salts.

Conclusion

At lower laser power densities polar molecules such as sucrose are ionized by attachment of alkali ions in the gas phase. The contribution of a direct thermal evaporation of preformed ions from electrolytic solution could be excluded. There is also no evidence for the formation of quasimolecular ions by surface reactions.

In the case of salts quasimolecular ions are formed by ion molecule reactions in the gas phase and by heterogeneous reactions on alkali ion emitting surfaces. A direct evaporation of ions has been observed with some complex salts but not yet with quasimolecular ions of alkali salts of acids.

The formation of quasimolecular ions by LD (in the pulse and CW mode) should be mainly the effect of a rapid heating of the substrate resulting in the emission of alkali ions and the evaporation of sample molecules at the same time and with a minimum spatial separation between the thermionic emission of the alkali ions at high temperatures and the sample evaporation at low temperatures. The development of such a temperature gradient along the sample may be favoured by carbonization of part of the sample layer.

A wave length dependence of fragment ion formation is observed for thick layers of sample molecules only provided the laser radiation is absorbed by the sample molecules.

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