J.Serb.Chem.Soc. 66(11–12)735–752(2001) JSCS–2900 UDC 535.352/.353+537.567:543.51 Review paper

REVIEW

Ion/surface collisions: An alternative to gas-phase collisional activation in mass spectrometry

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(Received 3 September 2001)

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Keywords: mass spectrometry, ion activation, ion fragmentation, ion/surface collisions, internal energy.

1. INTRODUCTION

In order to characterize an ion in mass spectrometry, be it the molecular ion or any of its fragments, it is often necessary to employ an extra stage of analysis, in addition to plotting its normal mass spectrum. In a typical procedure, the ion to be studied is selected by the first analyzer, it then undergoes an activation and fragmentation process, and, finally, the fragmentation products are separated by the second analyzer and registered at the detector. This technique has been named tandem mass spectrometry¹ for obvious reasons: there are two mass analyzers and they work in tandem. Another way of denoting this method is by the acronym MS/MS, which was introduced as a parallel to the GC/MS notation.² Indeed, the two techniques share the same basic principle: the first stage is the separation of one species from the rest – it can be achieved by gas chromatography, in the case of a mixture of compounds, but it can also be effected by a mass analyzer, in the case of a mixture of ions. The MS/MS symbolism seems to be prevailing lately due to the development of mass spectrometers which enable three, four or more stages of analysis; thus, the corresponding tech-

^{*} Dedicated to Professor Dragutin M. Dražić, in appreciation of his many contributions to the advancement of chemical sciences and chemical education; and of his consistent struggle towards a better and dignified university.

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niques can be described as MS/MS/MS, or MS/MS/MS, or, generally, MSⁿ, as cleverly suggested by McLafferty!³

The most extensively used method of ion activation involves collisions of fast ions with neutral gas molecules. In these inelastic collisions, some of the ion's translational energy is converted to its internal energy leading to subsequent fragmentation. This method has been termed collision-induced dissociation (CID) and it represents an indispensable tool in ion structure characterization in mass spectrometry. The CID method involves introduction of a certain amount of gas into the region between two analyzers; for this purpose, instruments are fitted with special, differentially pumped, "collision cells". However, in practice, a number of problems can be encountered in applying the CID method: (i) the amount of internal energy deposited into the ion upon collision may be insufficient for its fragmentation; this is especially true for large ions; (ii) the internal energy deposited into the ion is a function of the collision gas pressure, a parameter difficult to control; (iii) even at fairly high collision gas pressures (e.g., 10⁻⁵ Torr), a large fraction of the ions does not undergo collision with gas molecules, thus rendering the method intrinsically less sensitive; (iv) of the ions that do collide, some experience single and some multiple collisions, which causes problems in interpretation; (v) the introduction of any amount of gas into an instrument under high vacuum seems "unreasonable"; indeed, significant loss of performance, especially resolution, might take place.

These inadequacies motivated constant efforts in the exploration for alternative activation methods. It seems obvious that elimintion of the collision gas should be a desirable goal; the idea was to substitute the gasous target with a solid surface. The first such experiments involved "grazing" ion/surface collisions; however, rather than causing ion activation and dissociation, this procedure resulted in charge transfer reactions.⁴ This approach was then abandoned and it was not until ten years later that a significant breakthrough was reported: using a home-made instrument, Mabud *et al.* demonstrated that low translational energy ions (10–100 eV) can be efficiently fragmented following collision at a metal surface.⁵ In a series of studies that followed, the usefulness of this new technique was convincingly documented; it was named surface-induced dissociation, abbreviated SID, paralleling the acronym CID, used for the corresponding gas-phase activation method, the collision-induced dissociation.

The basic SID phenomenon is fairly simple. The desired ions (the projectiles) are mass-selected by the first analyzer, decelerated to 10–100 eV translational energy and directed towards a solid surface (the target). Upon collision at the target, the projectile ions are activated and reflected from the surface; some of the activated ions undergo fragmentation and their products are subsequently passed through the second mass analyzer and recorded at the detector, yielding the SID spectrum of the projectile ions.

Surface-induced dissociation is just one of a number of phenomena that can take place upon ion/surface encounter. It is the one mostly studied and utilized; however, other processes were also observed and reported.

- Some of the ions undergo reactive collisions with the surface: the incoming ions pick-up one or more atoms from the surface and are reflected and detected as new,



Fig. 1. Types of processes which occur when projectile ions of tens of eV collision energy impact upon solid surfaces. In the last two processes, A represents an atom or group originating from the surface.

larger species. Through a variety of mechanisms, atoms like hydrogen or fluorine, or polyatomic species, like hydrocarbon groups, can be abstracted from the surface.⁶

– Processes were observed and studied in which the surface molecules react with the incoming ions forming new compounds. This phenomenon, referred to as surface modification, constitutes a potentially important method for obtaining tailored surfaces.^{7,8}

– Another process that can take place is chemical sputtering. This process is initiated by charge exchange between the projectile and the surface molecules. The ionized surface molecule can fragment and those fragment ions will also be registered in the reflected ion spectrum.^{9,10} These sputtered ions are obviously characteristic of the surface and can be used in studies of the surface composition or other characteristics.¹¹

 Doubly charged ions undergo partial charge exchange upon collision with the surface and are reflected and detected as singly charged ions.¹²

A schematic representation of some of these processes is shown in Fig. 1. Indeed, once the ion/surface interaction was examined in some more detail, a very rich chemistry was revealed, as documented in several reviews. $^{13-15}$

2. INSTRUMENTATION

The first successful surface-induced dissociation experiments were performed at Purdue University using the home-made hybrid instrument shown in Fig. 2. Ions are generated in an electron impact source, accelerated through a series of lenses, and mass analyzed by the magnetic analyzer. The mass selected ions are decelerated prior to col-



Fig. 2. Schematic representation of the first instrument for surface-induced dissociation studies. It had a BQ configuration and was constructed at Purdue University.

lision at the solid surface. The fragmentation products are extracted with another series of lenses, mass analyzed by a quadrupole and recorded at the detector. The collision energy is controlled by the potential difference between the source and the grounded target; a range between 10 and 100 eV energy is typically used, but lower and higher values have also been employed.

The above instrument is representative of one of the main types of SID instruments, those in which the collision occurs between the analyzers in a beam-type tandem mass spectrometer. It is a hybrid instrument, due to the fact that the two analyzers are of different type, one being a magnet (B) and the other a quadrupole (Q); thus, it is refered to as a BQ configuration. In addition ty hybrids, tandem quadrupoles^{16,17} and tandem time-of-flight (TOF) instruments have been successfully applied.¹⁸

In order to avoid having to re-orient two analyzers of a mass spectrometer at large angles (typically 45 degrees), the ion beam can be directed so as to achieve large angle scattering while maintaining the normal in-line ion optical design. A variety of beam deflection devices have been tested, but the SID performance of such instruments is generally inferior.^{19–22}

A completely different approach to studies of ion/surface interaction had to be used with instruments such as Fourier transform ion cyclotron resonance (FTICR)^{23,24} or quadrupole ion traps.²⁵ These instruments possess a single mass analyzer in which both the steps of mass analysis and ion/surface collision must take place. In these instruments, the ions are directed toward the instrument walls for collision. In time-of-flight instruments, collisions occur with a surface placed within the reflector electrode assembly.²⁶



Fig. 3. Schematic representation of the ultra-high vacuum, four analyzer instrument for ion/surface collision studies. It has a BEEQ configuration.

Following several years of experience in ion/surface interaction experiments, the Purdue group designed and built a new sophisticated mass spectrometer specifically dedicated to ion/surface collision studies (Fig. 3).²⁷ Ions are produced in an electron impact ion source, accelerated through 2 keV and the desired ion is selected by the combined action of a magnetic sector and an electrostatic analyzer. This arrangement enables mass selection at high resolution. The resulting beam is decelerated and focused onto the target, mounted on a rotatable sample stage at the center of the main scattering chamber, held at a pressure of $\approx 4 \times 10^{-9}$ Torr. Following collision, the product ions are extracted into a post-collision analyzer consisting of an electric sector and a quadrupole mass filter; this assembly can be rotated around the scattering center during instrument operation thus enabling angular studies to be carried out.^{28,29}

3. SURFACE-INDUCED DISSOCIATION

As an example of a typical SID spectrum, consider the one of the molecular ion of *p*-methylphenetole (m/z 136) obtained at two different collision energies (Fig. 4).³⁰ The upper spectrum was obtained at 15 eV collision energy; it shows a single fragmentation of the molecular ion. When the collision energy was increased to 30 eV, a dramatic change in the appearance of the SID spectrum was observed. The molecular ion was practically absent, while several fragment ions were registered in high abundance. The observation that the base peak in this spectrum belongs to the m/z 29 ion (C₂H₅⁺), a product of high energy requirement, points to the fact that a significant amount of internal energy had been deposited into the projectile upon collision. Indeed, the fragmentation behaviour is a sensitive function of the internal energy of the ion, which itself is determined by the collision energy, which is in turn controlled by the potential difference between the ion source and the target. In view of the fact that the collision energy in



Fig. 4. SID spectrum of the molecular ion of p-methylphenetole (m/z 136) obtained at a) 15 eV, and b) 30 eV collision energy.

gas-phase collision processes (CID) is determined by the collision gas pressure, which is a parameter much more difficult to control, the advantage of SID versus CID in this respect can be noted.

One of the biggest problems in CID experiments arises from the fact that very stable or very large ions are difficult to fragment since insuficient internal energy is transferred to them in collisions with gaseous targets.³¹ This behaviour can be rationalized by recognizing that the internal energy is distributed between the many degrees of freedom (thus many bonds) in large molecules, so that not enough energy can be accumulated in any one of the bonds, resulting in no fragmentation. Collisions of ions with solid surfaces, *i.e.*, SID, were shown to enable much larger internal energy depositions, making SID supperior to CID in studies of "tough to fragment" compounds, such as polynuclear aromatic hydrocarbons.^{32,33} As a case in point, consider the behaviour of the molecular ion of pyrene, $C_{16}H_{10}^+$, a very stable species, notoriously difficult to fragment. As shown by



Fig. 5. Comparison between the efficiency of SID (upper spectra) and CID (lower spectra) for the fragmentation of the molecular ion of pyrene $C_{16}H_{10}^+$.

the lower three spectra in Fig. 5, collisions with argon gas at 50 and 100 eV collision energy do not yield any fragments; at 200 eV, fragmentation is evident, but the molecular ion $(m/z \ 202)$ is the only dominant feature. When the pyrene molecular ion is subjected to collisions at a stainless steel surface (the three upper spectra in Fig. 5), a dramatic difference is observed: at 50 eV collision energy, fragmentation is already evident; at 100 eV,



Fig. 6. SID spectrum of the doubly-protonated molecular ion of melittin (molecular weight 2845) obtained upon 110 eV collisions at a fluorinated SAM surface. (The letter designations, such as y, a and b, follow the nomenclature suggested by Roepstorff and Fohlman, *J. Biomed. Mass Spectrom.* **11** (1984) 601).

abundant fragments down to C_2 are formed; finally, at 200 eV collision energy, neither the molecular ion, nor any of the higher mass fragments are present in the SID spectrum, which is now dominated by the low mass fragments.³³

Considerable interest of mass spectroscopists has been centered around activation and fragmentation of peptides with the aim to use collision induced dissociation in the gas phase as an alternative to sequencing by the well established Edman degradation technique.^{34–36} Cooks et al. were the first to report fragmentation of peptides by surface induced dissociation;³⁷ that approach was subsequently adopted by several research groups.^{22,24,38–40} In particular, Wysocki and coworkers have demonstrated the efficient use of SID for studies on large biomolecules, such as peptides and proteins.^{41,42} The molecular ions of peptides are shown to fragment extensively upon collision at solid surfaces, thus enabling the determination of the amino acid sequence. As an example, the 110 eV collision energy spectrum of the doubly charged molecular ion of melittin (molecular weight 2845) is shown in Fig. 6. This polypeptide consists of 26 amino acids and the main features in the SID spectrum shown are due to partial neutralization of the doubly-charged $(M+2H)^{2+}$ ions to yield (M+H)⁺ ions, which then undergo extensive fragmentation, yielding substantial sequence information.⁴² Based on the success of those early experiments, SID has become increasingly popular as a method for peptide analysis, as illustrated by a number of recent impressive reports.43-46

In another line of development, interest has been directed towards developing the SID methodology for use on Fourier transform ion cyclotron resonance^{47–50} and time-of-flight mass spectrometers.^{51–54} Simultaneously, extension of mass spectrometry to the analysis of high molecular weight materials, such as biopolymers, has been made possible through the development of "soft" ionization methods, such as electrospray ionization (ESI)⁵⁵ and matrix-assisted laser desorption ionization (MALDI).⁵⁶ These ionization methods have been used in a variety of SID applications with great success.^{57–59}

4. SOLID SURFACES

At the early stages of SID development, the significance of the nature of the solid surface was not fully recognized. The first experiments employed a stainless steel surface; attempts to evaluate the effect of changing the surface by substituting the stainless steel target with silver or platinum failed to bring about any significant differences in the SID spectra. Further experiments included GaAs, graphite and silicon targets and they all gave similar results, pointing to the essentially passive role of the solid surface in the SID process.⁶⁰ These observations were rationalized by the fact that inadequate vacuum conditions existed in the target region, *i.e.*, 5×10^{-5} Torr; under these conditions, all targets are covered with a layer of adsorbate, which was shown to be of hydrocarbon nature and to originate from the pump oil. This was further born out by the presence of an (M+1) peak in most SID spectra obtained upon collision at metal surfaces, irrespective of the nature of the metal. These peaks were shown to be due to products of ion/surface reactive collisions in which the incoming ion M⁺ reacts with the hydrocarbon adsorbed at the surface, picks up a hydrogen atom, then leaves as the $(M+1)^+$ ion; these processes have been studied and reported in detail.⁶



Fig. 7. Schematic representation of functionalized self-assembled monolayer (SAM) surfaces. Y represents the terminal functional group attached to the alkyl chain. In the CF_3 terminating surface, all but the bottom two carbon atoms have been fluorinated.

An entirely different type of target are the self-assembled monolayer (SAM) surfaces, which were first employed in SID experiments in 1991.^{61,62*} These surfaces consist of alkanethiol monolayers adsorbed on gold mirrors evaporated onto silicon wafers.⁶³ The monolayers exhibit a known packing of the alkyl chains that causes the terminal functional groups to be held at the outer surface of the monolayer.^{64,65} Consequently, by appropriate choice of the terminal functional group, it is possible to obtain targets with different characteristics. Some of the SAM surfaces that have been used in SID experiments are schematically shown in Fig. 7. The alkanethiol chains are typically 10–15 carbon atoms long; Y represents the terminal functional group which is responsible for the target behaviour.

Of all the SAM surfaces tested, the one which terminates with a CF_3 group has been shown to exhibit the best characteristics.^{66–68} In this surface, all but the bottom two carbon atoms are fluorinated – thus, this surface is usually referred to as a "fluorinated surface". The most important feature in SID applications is the ability of fluorinated surfaces to effect the largest translational to internal energy conversion, thus enabling most extensive fragmentation of the projectile ions. This point is illustrated with a couple of examples below.

60 eV collisions of the pyrene molecular ion $C_{16}H_{10}^+$ with an OH terminating surface result in very limited fragmentation; the SID spectrum is dominated by the intact molecular ion, while groups of ions at C_{14} and C_{12} appear at low abundance (Fig. 8a). Under the same experimental conditions, but using a fluorinated surface, the molecular ion of pyrene shows extensive fragmentation down to C_2 fragment ions (Fig. 8b).⁶⁶

Another example is provided by the notoriously stable fullerene molecular ion. In fact, the doubly charged fullerene ion C_{60}^{2+} was the object of study.⁶⁹ Upon collisions of this dication at 250 eV collision energy at a CH₃ group terminating SAM surface (Fig. 9a), only partial neutralization of the projectile takes place resulting in the C_{60}^{+} peak; the collision does not result in sufficient internal energy deposition to the projectile to cause its frag-

^{*} It is interesting to note that two groups, one at Purdue University and the other at Virginia Commonwealth University, independently introduced SAM surfaces as targets in SID experiments. When that was realized, it was decided to publish both papers simultaneously in the same journal, back to back! A nice example of scientific interaction, correctness and good will.



Fig. 8. SID spectra of the molecular ion of pyrene $(C_{16}H_{10}^+)$ obtained upon 60 eV collisions at a) OH terminating SAM surface, and b) CF₃ terminating (fluorinated) SAM surface.

mentation. However, when this surface is substituted with a fluorinated surface (all other conditions remaining unchanged), a dramatic difference in behaviour is observed (Fig. 9b). The projectile C_{60}^{2+} fragments by consecutive losses of C_2 mass units to give C_{58}^{2+} , C_{56}^{2+} , C_{54}^{2+} , *etc.*; in parallel to this, some C_{60}^{2+} ions undergo charge exchange with the surface to form C_{60}^{+} , which subsequently also fragments by loss of C_2 neutral fragments resulting in the C_{58}^{+} , C_{56}^{+} , C_{54}^{+} , *etc.* series of peaks.

From these and a number of related studies,^{44,47,50,70,71} it was concluded that fluorinated SAM surfaces represent the best targets for surface-induced dissociation; in particular, collisions at these surfaces are "hard", they enable very large translational to internal energy conversions; some authors have described them as "brick walls", in contrast to some of the other SAM surfaces, which behave like "soft mattresses".⁷² Based on a large number of experimental data, it was determined that some 11–13 % of the projectile translation energy is converted into its internal energy upon collision at (hydrocarbon adsorbate covered) metal surfaces.¹⁶ This conversion efficiency is similar for most types of SAM surfaces;



Fig. 9. Charge exchange and fragmentation of the doubly-charged molecular ion of fullerene upon 250 eV collisions at a) CH₃ terminating SAM surface, and b) CF₃ terminating (fluorinated) SAM surface.

however, a typical conversion of 19–20 % was reported in most studies employing fluorinated SAM surfaces.^{66–68,73} In addition to those typical values, about which there is a general consensus, some exceptionally high conversion efficiencies were also claimed, such as 28 % for the benzene molecular ion colliding at a fluorinated surface,⁷⁴ and up to 35 % for alkali-halide clusters impacting on a silicon surface.⁷⁵ It should be noted that fluorinated surfaces remain clean inside the mass spectrometer, *i.e.*, no hydrocarbon deposits are formed; consequently, collisions at these surfaces do not result in the formation of (M+H)⁺ adduct ions.^{*} In other words, fluorinated SAM surfaces are non-sticky, they behave like teflon, to which they do indeed resemble!

While SAM surfaces provide many advantages for the study of fundamental aspects of SID, more readily accessible surfaces would be of great interest for analytical studies. A commercial liquid, fluorinated polyether Krytox, $F[CF(CF_3)CF_2O]_{27(ave)}CF_2CF_3$, has been shown to exhibit excellent characteristics.⁷⁶ Krytox has a very low vapour pressure and can be applied as a thick layer (microns) on a support. In most experiments, SID spectra obtained upon collisions at a Krytox surface were remarkably similar to those obtained with fluorinated SAM surfaces.⁷⁷

^{*} While no hydrogen pick-up is observed from fluorinated SAM surfaces, collisions of ions at those surfaces can result in the pick-up of one or more fluorine atoms (Ref. 66)

5. ISOMERIC ION DISTINCTION

One of the usual testing procedures for any new ion activation and fragmentation method is the examination of its capabilities to distinguish between isomeric ion structures. Surface induced dissociation has been successfully applied to a number of tough isomer problems, well known to mass spectrometrists. As examples of the potential of SID in that area, a few studies are summarized below.

The structure of the $C_5H_6^+$ ion obtained from different precursors represents one such intriguing problem. SID spectra at 25 eV collision energy were obtained for $C_5H_6^+$ ions generated from six different precursors and are shown in Fig. 10.⁷⁸ The spectra exhibit distinguishing characteristics which can be rationalized in terms of mix-



Fig. 10. SID spectra of $C_5H_6^+$ (*m*/*z* 66) ions generated from a) phenol, b) aniline, c) norbornadiene, d) thiophenol, e) cyclopentadiene, and f) 2-methylenebicyclo[2.2.1]heptane, obtained upon 25 eV collisions at a stainless steel surface.



Fig. 11. SID spectra of $(C_2H_4O)^+$ (*m/z* 44) ions generated from a) acetaldehyde, b) ethylene oxide, c) butyraldehyde, d) 1,3-dioxolane, and e) pyruvic acid, obtained upon 25 eV collisions at a stainless steel surface.



tures of cyclic and acyclic structures. From the fact that the SID spectrum of the phenol-derived $C_5H_6^+$ ion (Fig. 10a) is characterized by a lower relative abundance of the parent ion (*m*/*z* 66) and by extensive fragmentation (*m*/*z* 40 is the base peak), it was inferred that phenol yields predominantly cyclic $C_5H_6^+$ ions. In going from **a** to **f**, the spectra change in a fashion which suggests an increasing contribution of the cyclic form: more dominant molecular ion and less fragmentation.

In another test of ion structure characterization by SID, mass-selected C₂H₄O⁺ ions derived from six precursors were subjected to 25 eV collisions at a stainless steel surface.⁷⁹ Five of those daughter spectra are shown in Fig. 11 and they exhibit more pronounced differences than those observed in gas-phase collision-induced dissociation. The possible structures \mathbf{a} - \mathbf{g} (Scheme 1) have been discussed in detail and assignments were made in terms of either "pure" structures, or mixtures of structures. It was concluded that ions generated from acetaldehyde and butyraldehyde represent the ketonic and enolic species **a** and **b**, respectively. Ethylene carbonate yields structure **d**, while pyruvic acid gives an ionized carbene f. Ions from ethylene oxide and 1,3-dioxolane yield identical SID spectra, which are very similar to the spectrum of ethylene carbonate (not shown). While the cyclic ion c in not excluded, ring opening of ethylene oxide is argued to occur and to involve C-C rather than C-O bond cleavage, giving structure d rather than e. Either prior to, or more probably, upon activation, rearrangements occur to give the ionized carbene f and/or the ylide g. The abundant ion at m/z 29 in the SID spectra of ethylene oxide and 1,3-dioxolane strongly suggests the participation of structure g. It should be noted that $(M+H)^+$ ions appear in the SID spectra of all isomers, but in greatly varying abundance. This ion is due to pick-up of a hydrogen atom from the hydrocarbon adsorbate present at the stainless steel surface, a process already discussed. Fragmentation of this ion yields products at m/z 27 and m/z 19; these features, not present in the corresponding CID spectra, add an extra dimension to the SID spectra which facilitates isomer differentation.

An interesting case of isomer differentiation was reported by Hayakawa *et al.*⁸⁰ The object of their study were two $C_3H_4^+$ isomeric ions, allene and propyne. Their electron impact mass spectra are identical, their CID spectra show some minor differences

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in the abundance of a few extremely weak peaks. SID spectra were shown to be able to distinguish between the two isomers, however, not at all collision energies! Namely, at 24 eV collision energy, the SID spectra are identical; at 55 eV, they exhibit significant differences, again pointing to the fact that SID spectra are a sensitive function of internal energy deposited into the projectile upon collision.

A recent example of SID application as a tool for isomer identification is provided in a *cis/trans* differentiation study of dinuclear platinum complexes, which represent novel antitumor agents of clinical interest. In particular, *cis*- and *trans*-[{Pt(NH₃)₂Cl}₂µ-NH₂(CH₂)_nNH₂]²⁺ ions, where n = 4 and 6, have been studied by electrospray ionization (ESI) and SID. ESI provides projectile ions with sufficiently low internal energy to prevent fragmentation in the source, while SID provides an internal energy deposition with a narrow energy distribution. With this combination, differences in the energy-dependent fragmentation pathways can be detected, which allow the observation of differences due to the *trans* effect of the chloride in the dinuclear complexes.⁸¹

6. CONCLUSION

Surface-induced dissociation has already been proven to be a valuable new technique, especially in ion structural characterization. In this respect, it serves as a complementary method to the technique of gas-phase collision-induced dissociation, an older technique that has been universally employed as a means of ion activation, fragmentation and characterization. While it is not argued that SID will replace CID as a general method, it has certainly exhibited some characteristics that constitute distinct advantages over CID. In particular, SID (i) provides good control over collision energy; (ii) large amounts of internal energy can be transferred to the ion, causing extensive fragmentation of hard to dissociate compounds; (iii) a relatively narrow range of internal energies is transferred, leading to a simplification in the fragmentation behaviour; (iv) ion-surface reactive collisions occur simultaneously with dissociation and provide an alternative means of compound identification; (v) replacing the collision gas with a solid surface eliminates the concern over vacuum deterioration in the instrument, which is always important, but crucial for techniques like Fourier transform ion cyclotron resonance mass spectrometry.

On the instrumentation side, much progress has been made. The first instruments were, naturally, all home made. It was encouraging to witness the proliferation of the number of instruments modified for SID applications, as well as their diversification. Successful development of different in-line collision devices made the modification of standard commercial instruments easier.

The first SID instruments involved mainly magnetic and quadrupole mass analyzers; further developments have expanded the scope of SID studies through the use of FTICR, ion traps, and, most recently, time-of-flight instruments. In particular, TOF instruments, coupled with electrospray ionization, represent a powerful tool for SID application to studies of very large molecules.

SUMMARY

AST

Collisions of ions at solid surfaces result in a number of phenomena, of which surface–induced dissociation (SID) is the most important. SID has been shown to be a viable alternative to collision-induced dissociation (CID) in the gas phase as a method for ion activation and fragmentation in mass spectrometry. In particular, SID exhibits the following major characteristics (i) it enables efficient translational to internal energy conversion, which makes possible the fragmentation of very large compounds, such as biomolecules, (ii) the collision energy is easily controlled by controlling the voltage difference between the ion source and the target, (iii) ion/surface reactive collisions occur simultaneously with dissociation, which provides an additional aid in structure characterization, (iv) the elimination of collision gas eliminates the danger of loss of instrument performance (*e.g.*, resolution). Instrumentation, solid targets and applications of surface-induced dissociation are reviewed.

ИЗВОД

СУДАРИ ЈОНА СА ЧВРСТИМ ПОВРШИНАМА: АЛТЕРНАТИВА АКТИВАЦИЈИ СУДАРИМА ЈОНА У ГАСОВИТОЈ ФАЗИ У МАСЕНОЈ СПЕКТРОМЕТРИЈИ

ТЕОДОР АСТ

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Приликом судара јона ниске кинетичке енергије (10-100 eV) са чврстим површинама у масеној спектрометрији, догађа се низ процеса, од којих је најзначајнији активација и фрагментација јона. Ова метода активације позната је под скраћеницом SID (од енглеског: surface-induced dissociation). Јон који се испитује (пројектил) одваја се од осталих јона у првом масеном анализатору; затим се успорава до жељене брзине (односно кинетичке енергије) којом се судара са чврстом површином (метом). У судару долази до побуђивања јона и његове фрагментације, а продукти се раздвајају проласком кроз други масени анализатор и региструју на детектору. У односу на класичну методу активације и фрагментације јона у масеној спектометрији, тј. сударима јона са неутралним молекулима у гасовитој фази (collision-induced dissociation - CID), SID има неколико кључних предности (i) енергију судара могуће је лако контролисати регулисањем напонске разлике између извора и мете; (ii) сударом се пројектилу преноси знатно више унутрашње енергије него код CID методе, што омогућава фрагментацију веома великих молекула (напр. пептида и протеина); (iii) с обзиром да нема уношења сударног гаса у инструмент, не постоји опасност од деградирања перформанси инструмента (напр. резолуције). Приказани су различити инструментални системи, разне врсте мета, као и примери примене SID методе.

(Примљено 3. септембра 2001)

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