

Surface induced dissociation for tandem time-of-flight mass spectrometry*

Evan R. Williams¹, Liling Fang and Richard N. Zare

Department of Chemistry, Stanford University, Stanford, CA 94305-5080 (USA)

(First received 15 July 1992; in final form 21 September 1992)

Abstract

We have investigated surface induced dissociation (SID) in a reflectron time-of-flight (TOF) mass spectrometer using an "in-line" collision device in the reflectron mirror. Ions are created by multiphoton ionization, mass selected by pulsed deflection, and impinge on the collision device with collision energy that can be raised from 0 to 2.6 keV. The present apparatus achieves unit mass resolution at m/z 200 for the precursor ion selection and a product ion mass resolution of 70 at m/z 100. We find that high internal excitation of ions results for collision energies in excess of 150 eV, as determined from the fragmentation of phenanthrene molecular ions, $(C_{14}H_{10})^+$. The SID process is shown to cause efficient ion dissociation; for example, the sum of the abundance of all daughter ions, relative to the initial parent ion abundance of 4-methylanisole, $(C_8H_{10}O)^+$, is 0.15 ± 0.03 at a collision energy of 30 eV. In addition to SID, we observe sputtering of hydrocarbon molecules on the collision device surface as well as reaction with these adsorbate species. Thus, SID appears to be an attractive technique for TOF tandem mass spectrometry, particularly for the dissociation of large singly-charged ions.

Keywords: surface induced dissociation; time-of-flight; multiphoton ionization.

Introduction

Time-of-flight mass spectrometry (TOF-MS) [1–6] has numerous advantages for the analysis of large molecules including high sensitivity, moderately high resolution, and virtually unlimited mass range. In combination with matrix-assisted laser desorption (LD) [1–4], singly charged ions in the hundreds of thousands of daltons molecular weight range can be produced and detected with mass measuring accuracy of 0.01% [4]. The multi-channel detection capability of TOF-MS makes possible the measurement of a complete mass

spectrum from a single laser shot, and greatly enhances sensitivity for such pulsed measurements. In reflectron instruments, resolutions of several thousand are readily achieved [5,6]. For ions that are spatially or energetically well defined, resolution up to 28 000 at m/z 867 [5] has been demonstrated.

"Soft" ionization techniques, such as matrix-assisted LD and electrospray ionization, produce primarily molecular ions with almost no fragmentation. When soft ionization is employed in TOF-MS, this combination gives molecular weight but almost no structural information. To elucidate structure, a powerful method is tandem mass spectrometry (MS–MS) [7] in which ions are mass selected, dissociated, and the resulting ion fragments are analyzed. Collisionally activated dissociation (CAD) [7–9], the most common form

Correspondence to: R.N. Zare, Department of Chemistry, Stanford University, Stanford, CA 94305-5080, USA.

*Dedicated to Professor Wade L. Fite.

¹Present Address: Department of Chemistry, University of California, Berkeley, CA 94720, USA.

of MS–MS, is relatively ineffective at producing structurally useful fragmentation from singly charged ions above m/z 3500, such as those formed by matrix-assisted LD. This has been attributed to both an increasing number of degrees of freedom [8], as well as inefficient energy transfer in the collisional process itself caused by decreasing center-of-mass (COM) collision energy [9] with increasing ion mass.

Surface induced dissociation (SID) [10–14,16] pioneered by Cooks and co-workers, has several advantages for dissociating large ions. By replacing the collision partner with a solid surface, the COM collision energy comes to a first approximation, independent of mass, and is determined by the kinetic energy of the incoming ion. Thus, higher internal energy deposition is accessible to larger ions with this technique. Approximately 10–15% of ion translational energy is converted into internal energy for collisions up to 120 eV [10,11]. For ions that are reflected from the surface, the interaction time with the surface is short ($< 10^{-11}$ s), so that ion isomerization during the collision event is unlikely. In contrast, ion isomerization can occur during the multiple collision conditions commonly used in low-energy CAD. SID has been adapted to a variety of instruments, including hybrids [12,13], tandem quadrupole [14], Wien filters [15], TOF [16–22], ion trap [23], Fourier-transform [24,25] and four-sector mass spectrometers [26]. Structurally useful information from the dissociation of peptide ions has been reported [13,24,26], with extensive fragmentation observed for singly-charged ions as large as bovine insulin molecular ions (m/z 5734) [18].

Schey et al. [16] first demonstrated that SID could be effected in TOF-MS using two linear TOF instruments in a 90° geometry, with collisions occurring on a surface at 45° . Extensive fragmentation of anthracene, forming primarily fragments containing one through three carbons could be effected with 200 eV collisions, demonstrating the high internal energy deposition accessible with this technique. Subsequent work [17] using a reflectron geometry to detect the SID ions resulted in a

product ion resolution of ≈ 100 at m/z 51, a factor of 10 improvement over linear TOF detection.

We [18,19], as well as Whetten and co-workers [20–22], have independently developed a method for SID in a reflectron TOF mass spectrometer. Mass-selected precursor ions are made to undergo collisions with a solid surface placed in the reflectron mirror; the resulting product ions are subsequently extracted and mass selectively detected based on their flight times to the detector. Whetten and co-workers have used this method to study the impact of cluster ions with surfaces [20–22]. Negligible SID product ions were observed for C_{60}^+ and C_{70}^+ for any collision energy [20]. In contrast, extensive fragmentation for naphthalene molecular ions, $(C_{10}H_8^+)$ [20], and $Na_nF_{n-1}^+$ clusters up to $n = 30$ (m/z 1241) were observed [21]. We have demonstrated the use of this method for studying decomposition of large singly charged peptides [18] and reactions of polycyclic aromatic hydrocarbon ions with surface-adsorbed species [19]. In our studies, an “in-line” collision device is used which has the advantage that little modification to the spectrometer is required, and collection of conventional mass spectra is not adversely affected. Here, we describe in more detail SID in our reflectron tandem TOF mass spectrometer for SID, and demonstrate its performance.

Experimental

A reflectron TOF mass spectrometer (R.M. Jordan Co.) was modified to include a stainless steel collision surface, mounted on a linear motion feedthrough at the end of the reflectron mirror (Fig. 1). For measuring conventional mass spectra, the surface was aligned with the last reflectron plate, and the same potentials were applied to both plates. Ions are deflected toward the detector using a continuous ≈ 120 V potential on a plate prior to the pulsed ion deflection chamber. This provides a $\approx 3^\circ$ deflection of the ion beam so that ions will strike the detector upon reflection. For SID, the collision surface was inserted into the reflectron; optimum sensitivity and resolution was obtained when the

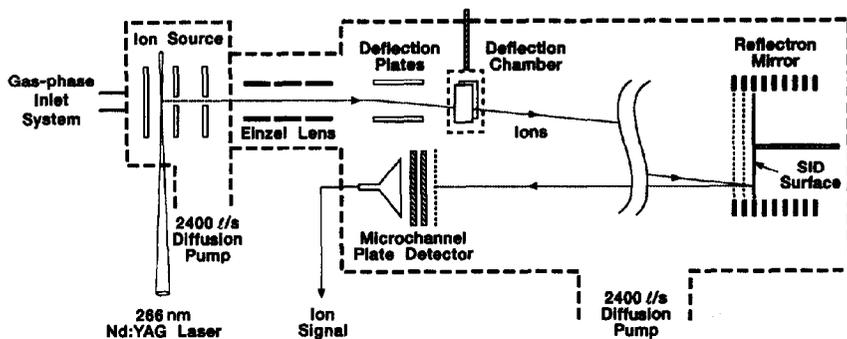


Fig. 1. Schematic of the tandem TOF mass spectrometer for SID.

surface was aligned with the third plate in the reflectron. Ions are made to undergo collisions with the surface by reducing the potential on the surface to below that of the ion acceleration energy with the collision energy given by the difference between these two values. Acceleration energies of between 2.0 and 2.6 kV were used. Comparable spectra were obtained within this energy range. Below 1.5 kV, the SID ion signal was reduced, presumably because of reduced collection efficiency of these ions. Plates 1 and 2 in the reflectron were covered with 82% transmittance stainless steel mesh, and both plates were maintained at ground potential. For measuring SID spectra, approximately twice the deflection voltage (≈ 250 V) used for measuring conventional mass spectra was found to be optimum. This is consistent with an ion deflection angle of 6° .

Precursor ions were selected by deflecting all other ions away from their usual flight path by using a pulsed electric field perpendicular to the ion flight path. For this, a deflection chamber with an entrance of $2.5\text{ cm} \times 1.9\text{ cm} \times 1.9\text{ cm}$ was constructed (Fig. 2); stainless steel mesh (82% transmittance) over the entrance and exit were used to reduce the effective electric field, induced by the pulse, on ions outside the chamber. An ion deflection angle of 2° is sufficient to collide ions into the first grounded plate of the reflectron, and could be obtained in this geometry using ≈ 100 V pulses

(R.M. Jordan Co. pulser; 0–400 V max., 10 ns rise time) applied to an L-shaped electrode in the deflection chamber. Note that this deflection is perpendicular to that necessary for ions to strike the detector (*vide supra*). The chamber was attached to a linear motion feedthrough making it easily retractable for measuring conventional mass spectra.

Sample was introduced through a heated inlet

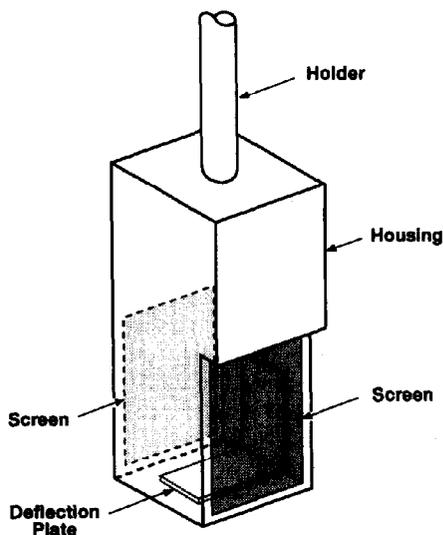


Fig. 2. Schematic of the ion deflection chamber used for precursor ion selection.

system to maintain a source pressure between 4×10^{-7} and 5×10^{-6} Torr. The main flight chamber is differentially pumped through a 0.64 cm diameter orifice; under these conditions, the pressure in this region was between 2×10^{-8} and 3×10^{-7} Torr. Liquid samples were degassed by using several freeze–pump–thaw cycles. Ions were produced by multiphoton ionization (MPI) using 266 nm photons generated from a Nd:YAG laser (Continuum Model 661-30) and focused with a 25 cm focal length fused silica cylindrical lens (Optics for Research). Laser power between 10^6 and 10^8 W cm $^{-2}$ was used.

Ion signals were amplified using both a $10 \times$ pre-amplifier (EG&G Ortec Model 9301) connected directly to the microchannel plate feedthrough and an EG&G Ortec 474 timing filter amplifier. Spectra were recorded using a 200 MHz transient recorder and fast signal averager (dsp, Technology, Inc., Model Nos. 2301, 5300, 4300, 4101 and 6001) and transferred to a personal computer for subsequent analysis.

Results and discussion

Mass selection

The ability to mass select individual ions for MS–MS is of key importance in determining ion structural information from an individual component of interest when ions of more than one m/z value are present, e.g. ion fragmentation of a single component or multiple components in a mixture. In TOF-MS, pulsed deflection can be used to select individual ions based on an ion's mass-dependent flight time to the deflector. To demonstrate the performance of our system, ions from Br-naphthalene, produced using 266 nm MPI, were accelerated and detected in our reflectron TOF instrument. The molecular ion region, shown in Fig. 3 (solid line), consists of four principal ions, $^{12}\text{C}_{10}\text{H}_7^{79}\text{Br}^+$ (m/z 206), $^{12}\text{C}_9^{13}\text{C}_1\text{H}_7^{79}\text{Br}^+$ (m/z 207), $^{12}\text{C}_{10}\text{H}_7^{81}\text{Br}^+$ (m/z 208), and $^{12}\text{C}_9^{13}\text{C}_1\text{H}_7^{81}\text{Br}^+$ (m/z 209). Using pulsed deflection to isolate ions with $m/z \geq 208$, complete removal of m/z 206, and sub-

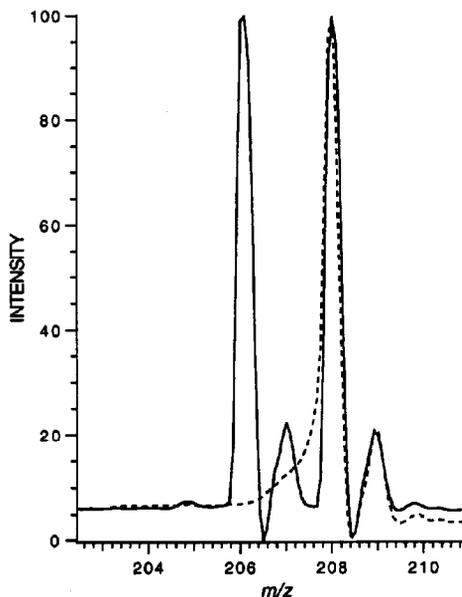


Fig. 3. Molecular ion region of Br-naphthalene (266 nm MPI) with (---) and without (—) pulsed ion deflection of ions of $m/z \leq 207$.

stantial removal of m/z 207 ($> 50\%$) is possible, leaving the $^{12}\text{C}_{10}\text{H}_7^{81}\text{Br}^+$ and $^{12}\text{C}_9^{13}\text{C}_1\text{H}_7^{81}\text{Br}^+$ ions to pass unaffected (Fig. 3, dashed line). Thus, approximately unit mass resolution at m/z 200 is obtained. This mass selection process itself produces no loss in sensitivity or resolution for the selected ions, although the presence of two screens on the deflection chamber lens reduces the total ion signal by approximately 65% [27].

A potential of 100 V was found to sufficiently deflect ions so that no signal for these ions was observed. Increasing this potential to 400 V, the maximum possible with our current electronics, improved the resolution of our mass selection, and was used for all experiments. The resolution of ion selection is expected to increase with $\text{mass}^{1/2}$; at a given acceleration energy, larger ions travel more slowly and can be separated more efficiently. Thus, even higher resolution should be obtainable for larger ions. Our current resolution is limited by the

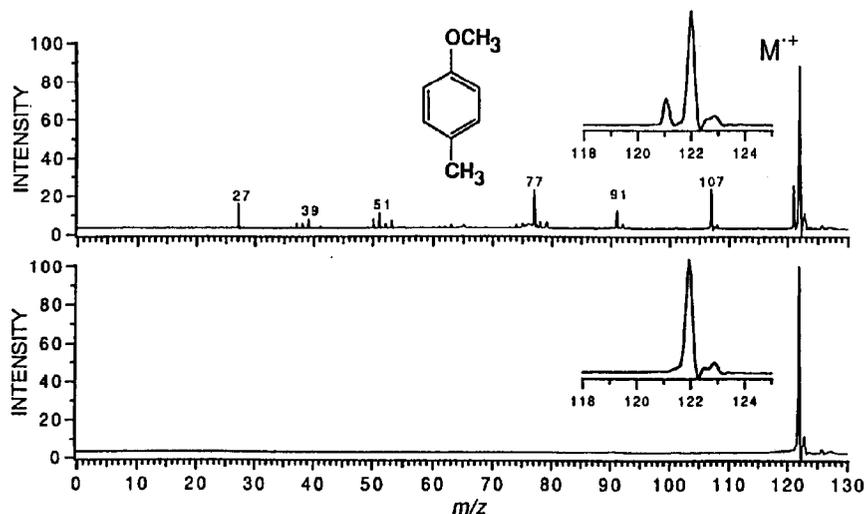


Fig. 4. 266 nm MPI spectrum of 4-methylanisole ($C_8H_{10}O$) with (bottom) and without (top) pulsed ion selection of the molecular ion. The insets show expansion of the molecular ion region.

speed (V/t) of our deflection pulse. Ultimately, the resolution of this method is determined by the initial spread in ion kinetic energies from the source. In all our experiments, mass selection was accomplished by removing lower mass ions. The selection of a single m/z value could be obtained by using two voltage pulses with a notch to pass a single m/z value ion of interest. We are modifying our pulse electronics to do this.

SID

Mass-selected ions can be made to undergo collision with the solid surface in the reflectron by reducing the potential on the surface to below that of the ion kinetic energy. Collision energy is then given by the difference in these potentials. Figures 4-6 illustrate the results of SID for the 4-methylanisole molecular ion ($C_8H_{10}O^+$). A high power 266 nm MPI spectrum of 4-methylanisole is shown in Fig. 4 (top); pulsed deflection effectively isolates the $C_8H_{10}O^+$ ion from its fragments (Fig. 4, bottom). The results of 30 and 50 eV collisions of

these ions with the surface are shown in Fig. 5. Such spectra can be produced for multiple collision energies. A plot of selected ion intensity versus laboratory collision energy, also called a breakdown curve, is shown in Fig. 6. As has been demonstrated by Hayward et al. [28], such breakdown curves can be useful in distinguishing isomers that show similar SID spectra over a limited range of collision energies.

For 4-methylanisole, the relatively low energy processes, loss of 1CH_3 and 1OCH_3 to produce $C_7H_7O^+$ (m/z 107), and $C_7H_7^+$ (m/z 91) ions, have maximum intensities at 15 and 30 eV, respectively (Fig. 6). The high energy process for formation of CH_3^+ (m/z 15) continues to increase with collision energies > 140 eV. Product ion resolution of 65 (FWHM) at m/z 109 is obtained. Reducing the distance between the floated collision surface and the grounded extraction screened plate (Fig. 2), and increasing the absolute potential of the source and collision plate, both of which increase the extraction fields, were found to improve resolution. A further improvement in resolution should be obtainable by applying a voltage pulse on the surface a

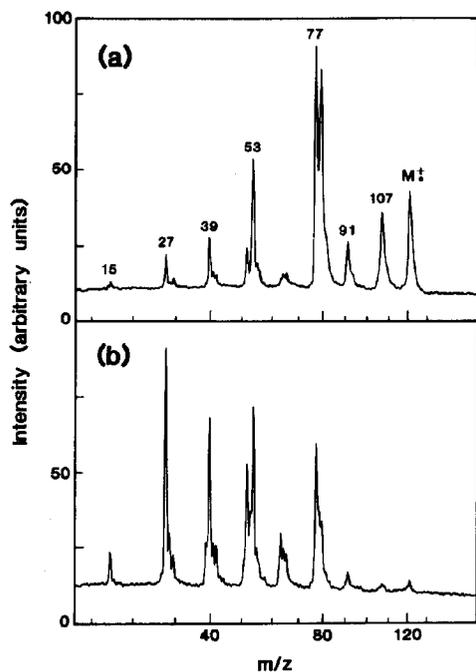


Fig. 5. SID spectra of the molecular ion of 4-methylanisole, $C_8H_{10}O^+$, at 30 (a) and 50 eV (b) collision energies.

short time after the precursor ion collides with the surface. Thus, ions that have lower kinetic energy, and have not traveled far from the surface, would receive an added acceleration to compensate for their lower initial kinetic energy. This is analogous to pulsed extraction techniques [29] used to improve source resolution. We are currently testing this procedure.

Energy deposition

Higher energy collisions can produce extensive ion dissociation, even in very stable ions. One such class of ions are molecular ions of polycyclic aromatic hydrocarbons (PAHs). These ions have been extensively characterized with a variety of MS-MS dissociation techniques [30]. The results of colliding molecular ions of phenanthrene, $C_{14}H_{10}^+$, with our surface with 80, 120, and 180 eV energy are shown in Fig. 7. With collisions below 150 eV, the principal dissociation is loss of acetylene (appearance potential ≈ 16 eV [31]) which is ≈ 8 eV above the ionization energy, and indicates substantial internal energy deposition at these collision energies. We are unable to resolve loss of H^+ and H_2 , expected fragmentation pathways (appearance potential ≈ 16.0 and ≈ 16.5 eV respectively [31])

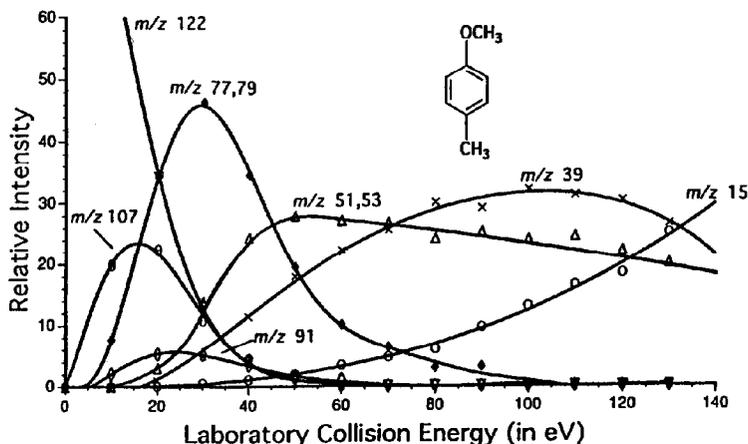


Fig. 6. SID breakdown curve for the 4-methylanisole molecular ion, $C_8H_{10}O^+$.

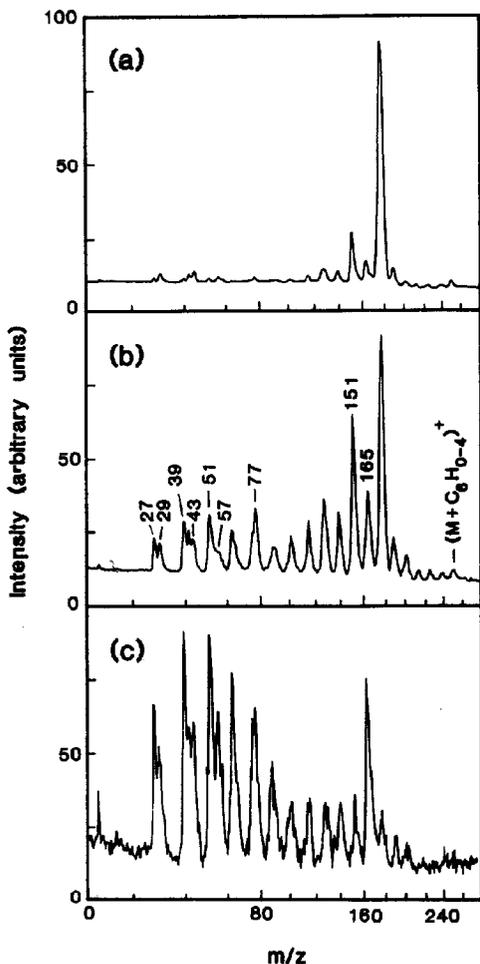


Fig. 7. SID spectra of the molecular ion of phenanthrene, $C_{14}H_{10}^+$, with 80 (a), 120 (b) and 180 eV (c) collision energies.

from undissociated molecular ions, although their presence is indicated by broadening in this peak.

Comparable fragmentation was reported for molecular ions of anthracene in the 90° TOF-SID studies of Schey et al. [17]. It has been shown that these two $C_{14}H_{10}$ isomers isomerize to a common structure prior to dissociation [30], and thus show indistinguishable MS-MS spectra. With 80 eV col-

lisions of phenanthrene molecular ions, we find even more extensive dissociation than obtained by Schey et al. at 100 eV, consistent with a higher internal energy deposition with our $\approx 84^\circ$ collisions. This difference could also be caused by a more efficient angular collection of product ions (*vide infra*). In comparing our results, one caveat is that the internal energy of our precursor ions formed by 266 nm MPI may be different than those formed by electron impact used by Cooks. Since the lowest dissociation energy is approximately 8 eV above the ionization potential, a large spread of molecular ion internal energies is possible upon ionization. Surprisingly, we find that our SID spectra did not change appreciably with ionization laser power, from threshold, where only molecular ions were observed, to where extensive fragmentation was produced. However, this could be the result of a substantially lower cross-section for absorption of a third photon ($3 \times 4.6 = 13.8$ eV, maximum) than that of a fourth photon which deposits sufficient energy ($4 \times 4.6 = 18.4$ eV, maximum) to produce dissociation.

Sputtering and surface reactions

In addition to SID product ions, we also observe ions produced by both sputtering [32] and reactions with surface-adsorbed species [33]. Sputtered ions, as indicated by m/z 29, 43, and 57 ($C_2H_5^+$, $C_3H_7^+$ and $C_4H_9^+$, respectively) in Fig. 7, occur with collision energies above ≈ 50 eV. These ions are the only ions observed in the spectrum with collision energies > 500 eV. Ion reactions with surface adsorbates, to produce carbon attached species up to $(M + C_nH_n)^+$ ($n = 0-4$), have been observed for both naphthalene and phenanthrene molecular ions [19]. Such time-resolved measurements could be used to study the kinetics of these surface reactions. We are unable to resolve attachment of a single hydrogen atom (commonly observed for odd electron ions with high proton affinity [33]), even for the molecular ion of aniline, $C_6H_7N^+$, the smallest ion we have tried to date.

Kinetic energy loss

Maximum sensitivity for detection of SID product ions is obtained using a deflection potential of ≈ 250 V, approximately twice that used when the reflectron is operated without collisions. Thus, under conditions of maximum signal, ions are striking the lower portion of the collision surface which is directly in line with the microchannel plate detector. This indicates that ions lose the majority of their parallel energy upon collision with the surface. By comparing our experimentally measured flight times to calculated values [34], we find a substantial portion of the ion's kinetic energy perpendicular to the surface is lost as well. For example, with 40 eV collisions, the centroid of the molecular ion peak of 4-methylanisole corresponds to ions that bounce off the surface with ≈ 14 eV of kinetic energy normal to the surface. Under these conditions, the 90 ns peak width (FWHM) corresponds to a kinetic energy distribution of 40 eV. Similar average recoil energies have been measured by Cooks and co-workers who recently showed that 25 eV *n*-butylbenzene molecular ions that dissociated upon colliding with a ferrocenyl-terminated self assembled monolayer surface initially rebounded with ≈ 10 eV of kinetic energy [34]. Large energy losses have also been reported by Beck et al. [20] for kinetic energy perpendicular to the surface.

Dissociation efficiency

For small organic molecules, we find the dissociation efficiency [36] ranges from 7 to 15%, which compares favorably to the 2–12% range reported in hybrid instruments [10]. The efficiency for dissociating very stable ions, such as the molecular ions of PAHs was low; a maximum efficiency for phenanthrene of 7% with 120 eV collisions was obtained. In contrast, 4-methylanisole had a maximum dissociation efficiency of $15 \pm 3\%$, which was obtained with only 30 eV collisions.

Preliminary results obtained with larger peptide ions formed by laser desorption from a continuous-

flow ice matrix [37] indicate SID efficiency around 30% for these even-electron ions. This is likely caused by a lower cross-section for neutralization at the surface. This also indicates that neutralization rather than SID product ion collection efficiency is the major loss of ion signal for SID of smaller, odd-electron ions. Recent results using collisions on self-assembled monolayers appear particularly promising for reducing ion neutralization [38,39].

Conclusions

By using an in-line collision device in a reflectron TOF mass spectrometer, SID can be readily implemented with no loss of performance for measuring simple mass spectra. Precursor ion selection with unit mass resolution at m/z 200 is made possible with pulsed deflection; resolution for SID product ions is ≈ 70 at m/z 100. With this experimental configuration, a substantial portion of SID product ions are collected; we find an SID efficiency [36] of 7–15% for ions below m/z 300. High internal energy deposition has been demonstrated, making SID in TOF-MS a promising method for obtaining ion structural information. This feature is anticipated to be most significant for large ions, such as those formed by matrix-assisted laser desorption.

Acknowledgments

The authors would like to thank Glenn Jones, Jr., and Stacy Shane for experimental assistance and/or helpful advice. Financial support for this research was generously provided by Beckman Instruments, Inc., the National Science Foundation through a postdoctoral fellowship for ERW (Grant No. CHE-8907477), and Continuum Electrooptics (Santa Clara, CA) through the loan of a Nd : YAG laser used in these experiments.

References

- 1 M. Karas and F. Hillenkamp, *Anal. Chem.*, 60 (1988) 2299.

- 2 B. Spengler, D. Kirsch, R. Kaufmann, M. Karas, F. Hillenkamp and U. Giessmann, *Rapid. Commun. Mass Spectrom.*, 4 (1990) 301.
- 3 R.C. Beavis and B.T. Chait, *Rapid. Commun. Mass Spectrom.*, 3 (1989) 233.
- 4 R.C. Beavis and B.T. Chait, *Anal. Chem.*, 62 (1990) 1836.
- 5 R. Grix, R. Kutscher, G. Li, U. Gruner and H. Wollnik, *Rapid. Commun. Mass Spectrom.*, 2 (1988) 83.
- 6 (a) B.A. Mamyrin, V.I. Karataev, D.V. Shmikk and V.A. Zagulin, *Sov. Phys. JETP*, 37 (1973) 45.
(b) V.I. Karataev, B.A. Mamyrin and D.V. Shmikk, *Sov. Phys. Tech. Phys.*, 16 (1972) 1177.
- 7 (a) F.W. McLafferty, (Ed.), *Tandem Mass Spectrometry*, Wiley, New York, 1983.
(b) K.L. Busch, G.L. Glish and S.A. McLuckey, *Mass Spectrometry/Mass Spectrometry*, VCH, Deerfield, FL, 1988.
- 8 M.M. Sheil and P.J. Derrick, *Org. Mass Spectrom.*, 23 (1988) 429.
- 9 D.L. Bricker and D.H. Russell, *J. Am. Chem. Soc.*, 108 (1986) 6174.
- 10 R.G. Cooks, T. Ast and Md.A. Mabud, *Int. J. Mass Spectrom. Ion Processes*, 100 (1990) 209 (and references cited therein).
- 11 M.J. DeKrey, H.I. Kenttämaa, V.H. Wysocki and R.G. Cooks, *Org. Mass Spectrom.*, 21 (1986) 193.
- 12 M.A. Mabud, M.J. DeKrey and R.G. Cooks, *Int. J. Mass Spectrom. Ion Processes*, 67 (1985) 285.
- 13 M.E. Bier, J.C. Schwartz, K.L. Schey and R.G. Cooks, *Int. J. Mass Spectrom. Ion Processes*, 103 (1990) 1.
- 14 M.E. Bier, J.W. Amy, R.G. Cooks, J.E.P. Syka, P. Ceja and G. Stafford, *Int. J. Mass Spectrom. Ion Processes*, 77 (1987) 31.
- 15 W. Aberth, *Anal. Chem.*, 62 (1990) 609.
- 16 K.L. Schey, R.G. Cooks, A. Kraft, R. Grix and H. Wollnik, *Int. J. Mass Spectrom. Ion Processes*, 94 (1989) 1.
- 17 K. Schey, R.G. Cooks, R. Grix and H. Wollnik, *Int. J. Mass Spectrom. Ion Processes*, 77 (1987) 49.
- 18 E.R. Williams, G.C. Jones, Jr., L. Fang and R.N. Zare, *CZE Using Tandem Time-of-Flight Mass Spectrometry*, Proc. 39th ASMS Conference on Mass Spectrometry and Allied Topics, Nashville, TN, May 19-24, 1991, pp. 1273-1274.
- 19 E.R. Williams, G.C. Jones, Jr., L. Fang, R.N. Zare, B.J. Garrison and D.W. Brenner, *J. Am. Chem. Soc.*, 114 (1992) 207.
- 20 R.D. Beck, P. St. John, M.M. Alvarez, F. Diederich and R.L. Whetten, *J. Phys. Chem.*, 95 (1991) 8402.
- 21 R.D. Beck, P. St. John, M.L. Homer and R.L. Whetten, *Science*, 253 (1991) 879.
- 22 R.D. Beck, P. St. John, M.L. Homer and R.L. Whetten, *Chem. Phys. Lett.*, 187 (1991) 122.
- 23 S.A. Lammert and R.G. Cooks, *J. Am. Soc. Mass Spectrom.*, 2 (1991) 487.
- 24 E.R. Williams, K.D. Henry, F.W. McLafferty, J. Shabanowitz and J. Hunt, *J. Am. Soc. Mass Spectrom.*, 1 (1990) 413.
- 25 C.I. Ijames and C.L. Wilkens, *Anal. Chem.*, 62 (1990) 1295.
- 26 A.D. Wright, D. Despreyroux, K.R. Jennings, S. Evans and A. Riddoch, *Org. Mass Spectrom.*, 27 (1992) 525.
- 27 The transmittance of the screens are 82% so that the expected signal loss past two screens is $(0.82)^2 = 67\%$, close to the 65% actually observed.
- 28 M.J. Hayward, Md.A. Mabud and R.G. Cooks, *J. Am. Chem. Soc.*, 110 (1988) 1343.
- 29 (a) W.C. Wiley and I.H. McLaren, *Rev. Sci. Instrum.*, 26 (1955) 1150.
(b) E.D. Erickson, G.E. Yefchak, C.G. Enke and J.F. Holland, *Int. J. Mass Spectrom. Ion Processes*, 97 (1990) 87.
- 30 S.J. Pachuta, H.I. Kenttämaa, T.M. Sack, R.L. Cerny, K.B. Tomer, M.L. Gross, R.R. Pachuta and R.G. Cooks, *J. Am. Chem. Soc.*, 110 (1988) 657.
- 31 H.M. Rosenstock, K. Draxl, B.W. Steiner and J.T. Heron, *J. Phys. Chem. Ref. Data*, 6 (suppl. 1) (1977).
- 32 M. Vincenti and R.G. Cooks, *Org. Mass Spectrom.*, 23 (1988) 317.
- 33 T. Ast, Md.A. Mabud and R.G. Cooks, *Int. J. Mass Spectrom. Ion Processes*, 82 (1988) 131.
- 34 Calculations performed using MacSimion, version 1.1, D. McGilvery and R. Morrison, Centre for High-Resolution Spectroscopy and Opto-Electronic Technology, Montech Pty. Ltd., Monash University, Wellington Rd, Clayton, Vic. 3168, Australia.
- 35 B.E. Winger, H.-J. Lane, S.R. Horing, R.K. Julian, Jr., S.A. Lammert, D.E. Riederer, Jr. and R.G. Cooks, *Rev. Sci. Instrum.* 1992, in press.
- 36 SID dissociation efficiency is defined as the sum of SID product ion abundance at a given collision energy divided by the total ion abundance of the undissociated precursor. The latter value is obtained by raising the potential on the surface to slightly above the kinetic energy of the ions so that no collisions occur.
- 37 E.R. Williams, G.C. Jones, Jr., L. Fang and R.N. Zare, in W.G. Golden (Ed.), *Applied Spectroscopy in Material Science II*, Proc. SPIE 1636, 1992, pp. 172-181.
- 38 B.E. Winger, R.K. Julian, Jr., R.G. Cooks and C.E.D. Chidsey, *J. Am. Chem. Soc.*, 113 (1991) 8967.
- 39 V.H. Wysocki, J.L. Jones and J.-M. Ding, *J. Am. Chem. Soc.*, 113 (1991) 8969.