

Low-Energy Ionic Collisions at Molecular Solids

Jobin Cyriac,^{†,‡,⊥} T. Pradeep,^{*,†} H. Kang,[§] R. Souda,[∥] and R. G. Cooks^{*,‡}

[†]DST Unit of Nanoscience, Department of Chemistry, Indian Institute of Technology Madras, Chennai 600 036, India

[‡]Department of Chemistry, Purdue University, West Lafayette, Indiana 47907, United States

[§]Department of Chemistry, Seoul National University, Gwanak-gu, Seoul 151-747, Republic of Korea

International Center for Materials Nanoarchitectonics, National Institute for Materials Science, 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan



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1. GENERAL OVERVIEW

The roots of mass spectrometry (MS) can be traced to the early 20th century when in the Cavendish Laboratory at Cambridge University, U.K., J. J. Thomson performed his first experiments using the "parabola spectrograph". F. W. Aston, a student of Thomson's, contributed greatly to the technique with his originality in instrumentation and innovative applications.^{1–3} A contemporary of Aston, Arthur Dempster, at the University of Chicago, Illinois, seeded the technique of MS across the Atlantic Ocean.⁴ The Second World War and the postwar era accelerated innovation in scientific instrumentation, and this affected the pioneers in MS as well. The latter part of the 20th century saw enormous advances in MS. Mass spectrometry is no longer a discipline confined to the basic sciences; it has expanded into many areas of science, engineering, medicine,

Received: October 5, 2011

Published: August 22, 2012





Figure 1. Important processes occurring during ion/surface collisions and the corresponding energy regimes.

agriculture, and quality control and has become a preferred tool for molecular analysis. The subject of this review, low-energy ion/surface interactions, portrays innovations in surface science and preparative methods associated with MS.

Ion-induced ejection of secondary species from a surface was known from J. J. Thomson's "Kanalstrahlen" experiments.⁵ However, Arnot and Milligan's investigation (in 1936) of the secondary ion yield and energy distribution of negative ions induced by colliding positive ions with surfaces is considered as the genesis of MS-based ion/surface experiments.⁶⁻⁸ The method was later termed secondary ion mass spectrometry (SIMS), in which bombardment of kiloelectronvolt (keV) energy primary ion beams at a condensed-phase interface releases charged atomic and molecular species which are then mass analyzed. Early SIMS experiments were used mostly for elemental analysis in a dynamic mode of operation.9 In the 1970s Benninghoven and co-workers showed the use of low-ion dose static SIMS experiments for the essentially nondestructive analysis of molecular surfaces, including organic materials.^{10–13} During the 1980s, SIMS emerged as a major surface molecular and elemental characterization tool as it was able to provide improved surface sensitivity and greater chemical specificity than electron spectroscopies, although it lacked the quantitative performance of the latter.

Subsequently, SIMS was developed to study chemisorption, adsorbate structure, surface reactivity, organic surfaces, and extended to biological samples.^{12,14–16} Now, apart from *static* and dynamic SIMS, other alternatives are available: *imaging* SIMS, where a highly focused ion beam provides chemical imaging with high spatial resolution, and *cluster bombardment* SIMS, in which low-damage cross sections and enhanced ion yields are achieved.^{16–21} At about the same time, surface-induced dissociation (SID) experiments emerged as a

molecular activation tool in MS. In this method, molecular ions collide at a surface (typically in the ion kinetic energy range of 20–200 eV), leading to fragmentation due to internal energy uptake occurring in competition with neutralization.^{22,23} This is a powerful method and is complementary to collisioninduced dissociation (CID), the most common activation technique in tandem mass spectrometry (MS/MS), where the primary ions are activated through gaseous collisions. Recent work by Wysocki and co-workers has shown SID to be the preferred method of structural characterization of protein complexes.²⁴

In the late 1980s, data from SID in conjunction with the already established and rich area of gas-phase ion chemistry led to ion/surface collisions being performed at molecular surfaces rather than at metal surfaces. The activation of ions at these surfaces not only caused effective fragmentation of projectile molecular ions, which of course provides structural information, but also minimized neutralization and facilitated chemical reactions at these surfaces. As a consequence, the ion/surface collision procedure can provide information on the chemical nature of molecular surfaces and can alter them by forming covalent bonds with surface atoms or groups. The activation and reactive processes are fundamentally a hyperthermal energy counterpart of SIMS. The more important processes are designated as chemical sputtering (CS) and a similar process, low-energy sputtering (LES), ion/surface reactions, reactive scattering, reactive landing (RL), and soft landing (SL) (see Figure 1). Scheme 1 represents ion/surface collision events and the resulting product ion mass spectrum due to a number of these processes. Competition between these processes depends on the collision energy and the nature of the collision partners. For example, the elastic collision process of ion soft landing competes with the inelastic process in which the ion dissociates

Scheme 1. Ion/Surface Collision Event and the Resultant Product Ion Mass Spectrum a



^{*a*}The product mass spectrum consists of ions due to various events occurring during ion/surface collision.

upon collision (SID) and also with the several types of reactive collision processes. In CS, surface species are ejected as ions due to charge transfer between the impinging ion and the adsorbate at the surface. In the closely related LES experiment, pre-existing ions are ejected from the surface. As will become evident, these very low energy processes have recently been recognized as increasingly important, with CS proving to be a powerful new tool in the characterization of ice surfaces.

New chemical bonds are formed or broken in ion/surface reactive scattering or reactive collisions. The exchange of atoms or groups of atoms between the projectile ion and the molecular surface and/or charge exchange occur in reactive collisions. It is possible to direct gas phase generated molecular ions or clusters, possessing appropriate chemical functionality, with a few electronvolts of kinetic energy at a surface and to achieve (i) covalent immobilization of mass-selected projectile ions onto the molecular surface (termed RL) or nondestructive deposition of polyatomic ions on a condensed-phase interface (termed SL).

Extreme sensitivity to the outermost atomic layer makes the hyperthermal low-energy ion/surface collision a unique tool for surface analysis and controlled surface modification. From a molecular perspective, the surface phenomena occurring at molecular materials are applicable to gas-liquid interfaces and are important for fundamental understanding of heterogeneous processes occurring at gas-liquid as gas-solid interfaces. This makes hyperthermal or low-energy ion/surface interactions broadly applicable to research in chemistry and physics and a method that encompasses the interface between materials and biology. While the ion/surface scattering method based on elastic scattering has been used to perform elemental and structural analysis of surfaces, the use of reactive ions opens a variety of channels: dissociation of molecular ions, transfer of an atom or molecule, soft landing, ion/surface charge exchange, etc.

Various aspects of hyperthermal energy ion/surface interactions have been reviewed.^{12,22,23,25–37} Reviews devoted to ion/surface collisions at ice surfaces are also available.^{38–40} The goal of this review is to provide the current status of instrumentation and understanding of the processes and applications of ion/surface interactions at various molecular surfaces. We have limited the coverage to molecular surfaces and associated chemical processes occurring during impact of a hyperthermal energy ion. Most of the discussion will be on polyatomic ions. One topic that is excluded is the inelastic ion/ surface collision process, SID, as good overviews on this subject are available.^{41,42} Literature until June 2011 has been considered for this review.

The term "molecular solid" comprises the wide range of molecular materials that may be used in ion/surface collision experiments. Such surfaces include self-assembled monolayers (SAMs; in the text these are abbreviated in terms of their end group functionality), graphitic surfaces, polymers, liquids of low volatility, adsorbed molecules on substrates, etc. Apart from room temperature surfaces, the surfaces of interest include the condensed phases of simple molecules as well, condensed phases that are generally called "ices". All the aforesaid molecular materials are considered as molecular solids in the discussion.

The energy regime that we consider lies in an intermediate range; a realistic lower limit of kinetic energy is $\sim 1 \text{ eV}$, and the higher limit is on the order of a few hundred electronvolts ($\sim 300 \text{ eV}$) (see Figure 1). Primary ion energies of several kiloelectronvolts (1–15 keV), which is used in a typical SIMS experiment, have been considered in the case of condensed molecular solids to allow correlation with the results of CS or other LES experiments.

1.1. Fundamental Principles

Energy transfer in the course of an ion/surface collision can be simplified as

$$E_{\text{total}} = E_{\text{tr}} + E_{\text{int}} + E_{\text{surf}} = E'_{\text{tr}} + E'_{\text{int}} + E'_{\text{surf}}$$

 $(E_{\rm tr} = {\rm translational energy of the incident projectile, <math>E_{\rm int} = {\rm its}$ initial internal energy, $E_{\rm surf} = {\rm initial energy of the surface, E'_{\rm tr} = {\rm translational energy of the product ion, E'_{\rm int} = {\rm internal energy of}$ the ion after surface collision, and $E'_{\rm surf} - E_{\rm surf} = {\rm energy}$ adsorbed by the surface).²⁸ Many physical and chemical processes can occur during the collision event (see Figure 1 and Scheme 1). The occurrence of several elementary processes—elastic, inelastic, and reactive collisions in the lowenergy range—assures a wide scope for this subject.

A series of complex interactions occur in the course of elastic or inelastic collisions. If sufficient energy transfer occurs in a collision cascade, secondary ions and/or neutrals are emitted, and the process is known as sputtering. Measurement of mass distributions of the secondary ions and the observation of associated chemical processes is done in SIMS. No single mechanism aptly accommodates all facts observed in studies of sputtering. Atomic SIMS can be explained by binary atomic sputtering theory, which provides a good physical model and is often used in the analysis of metals, semiconductors, and simple inorganic salts.¹² Ionization adds a considerable complication to this model. In molecular SIMS (studies of molecular surfaces by SIMS), an energetic collision cascade alone is unlikely to eject intact molecules and cannot account for ionization. Therefore, most molecular SIMS models have incorporated a translational or vibrational component into the mechanism.¹² Ion emission is initiated by a momentum transfer process followed by release of translationally and vibrationally excited target components. The translational energy distribution of the sputtered particles is broad and peaks at low energy, well below 10 eV. A fraction of the desorbed species may have sufficient internal energy to fragment in the gas phase, giving mass spectra showing both intact molecular and fragment ions.

SID takes place by transferring a fraction of the ion kinetic energy into internal energy, which in turn controls the ion's

dissociation into various fragment ions.²³ The extent of fragmentation depends upon the total internal energy content of the excited ion and the time scale, which is determined by velocity and the experimental conditions. Typically, the process occurs on the picosecond time scale, and 5-35% of the ion kinetic energy is converted into internal energy. Collisions with neutrals can further modify the ion internal energy of the sputtered ions. The basic processes can be difficult to discern since SID is accompanied by competing reactions at the surface (ion/surface reactions) involving different interaction potentials.²³ Simulations suggest that projectile ions are first excited via impulsive collisions with the surface and inelastically scattered from the surface and that they then dissociate unimolecularly some distance from the surface.⁴³ The initial ion kinetic energy, the nature of the incoming ion, 44,45 the nature of the surface-most often SAMs, the surface roughness,⁴⁶ and the angle of collision⁴⁷ affect the energy transferred.

The internal energy distribution P(E) of the surface excited ions can be estimated by studying the dissociation of "thermometer molecules" such as metal carbonyl radical cations, which have known energetics of fragmentation.^{22,48} In a specific example, the extent of surface activation of $Cr(CO)_6^+$ ions in 70 eV collisions at an H-SAM surface has been calculated. The percentages of energy transferred into internal modes, E_{int} into the surface, \breve{E}_{surf} and as final translational energy, $E_{\rm fr}$ were found to be 9%, 81%, and 10%, respectively.⁴⁹ Modeling based on Rice-Ramsperger-Kassel-Marcus (RRKM) kinetics has been developed for determining the percentage of $T \rightarrow V$ transfer during SID of large molecules such as peptides.⁴⁵ For a singly protonated octapeptide, des-Arg¹-bradykinin, the average energy deposited into the ion was found to increase from H-SAM (10.1%) to LiF (12.0%), diamond (19.2%), and F-SAM (20.5%) mainly due to mass effects. However, the width of the internal energy distribution is controlled by surface stiffness and followed the order H-SAM < F-SAM < LiF < diamond. Collision energy resolved SID of des-Arg¹- and des-Arg⁹-bradykinin shows that there is a sharp transition in fragmentation behavior.⁵⁰ Both ions produce very few SID fragments at low collision energies (15-25 eV), but with increasing collision energy above 30 eV, the number of fragments in the spectrum increases dramatically. This must be due to access to a variety of dissociation pathways. Timeresolved studies support the fact that most of the high-energy fragments are formed directly from the excited precursor ion but could not be attributed to consecutive dissociation of primary fragment ions.⁵⁰

A number of reactive processes such as electron transfer, fragmentation, atom abstraction, oxidation, and RL can occur in low-energy ion/surface collision events. Most often, the relative collision energy of an ion is of the same order of magnitude as chemical bond energies. Hence, the ion/surface interaction is large enough to lead to bond dissociation and to bond formation (which normally requires substantial activation energy). The observed chemical processes are strongly influenced by the chemical nature of the projectile ion as well as the electronic structure and chemical nature of the surface. A brief account of various reactive processes is given below.

1.1.1. Electron Transfer. Several possibilities fall under this heading. Electron transfer that leads to ion neutralization is often the most probable event. The electron is lost from either the adsorbate or the metal surface to which the adsorbate is bound, and the surface gains a charge, while the projectile ion is neutralized. The efficiency of such electron transfer processes is

determined by the difference between the electron affinity of the ion (i.e., its recombination energy) and the work function of the metal surface. Aside from thermochemical factors, the kinetics of electron tunneling also varies strongly with the distance of the closest encounter between the projectile ion and the surface. Fluorocarbon SAMs (F-SAMs) and long chain alkyl SAMs (H-SAMs) are found to reduce the neutralization of projectile cations relative to bare metals. Comparatively high ionization energies and the underlying large distances between the impinging ion and metal surface reduce the neutralization of projectile ions.⁵¹⁻⁵³ A doubly charged molecular ion may undergo charge exchange to form singly charged ions, which can be easily identified and detected.⁵⁴⁻⁵⁶ The singly charged intermediates formed may decompose further. For example, collisions of multiply charged fullerene cations C_{60}^{n+} (n = 1-5)at steel surfaces result only in singly charged scattered ions and dissociation products formed by loss of sequential C2 units.^{32,57} The extent of fragmentation is determined by the collision energy. A possible explanation for this process may be the immediate neutralization of the incoming ions followed by autoionization due to thermally activated electron emission.57

Apart from these simple electron transfer processes, charge inversion may occur by double electron transfer $(M^+ \rightarrow M^-)$ or charge stripping ($M^- \rightarrow M^+$), where the incident positively charged ions are converted into negatively charged ions (and vice versa).⁵⁸ Most charge inversion reactions have been performed in the kiloelectronvolt energy range, mainly because at these energies electron stripping and electron transfer reaction have sufficiently high cross-sections. Projectile ions can lose electrons by charge stripping with liberation of free electrons, and often these reactions are accompanied by dissociation when the nascent product is sufficiently excited. Charge inversion is frequently observed in gas-phase processes^{59,60} and has proven to be of considerable value in the determination of thermochemical properties of gaseous ions.^{61,62} Doubly charged cations derived from benzene and toluene in collisions at highly oriented pyrolitic graphite (HOPG) surfaces were found to produce only singly charged products.^{56,63} An important process in the collisions of dications is evidently single-electron charge transfer between the surface and the projectile with formation of singly charged intermediates which may further decompose to lower mass fragments.⁶⁴

Charge transfer can lead to another important process, closely related to projectile ion neutralization, which is referred to as chemical sputtering (CS). This has great potential value in industrial processing of materials, where it is also referred to as ion-assisted erosion or ion-assisted etching.³⁰ In CS, ions are released as a result of a chemical reaction, not momentum transfer. During the collision event, charge exchange occurs between the surface (surface adsorbate) and the impinging projectile ion, causing ionization of the surface molecules and their release from the surface.⁶⁵ CS is distinct from the momentum transfer events that underlie physical sputtering in kiloelectronvolt collisions. CS may occur with or without further fragmentation depending on the difference in ionization energies (or other appropriate thermochemical properties, e.g., proton affinity) of the projectile and the target. The mass spectrum of the desorbing ionized species carries information on the nature of the outermost layers of the surface.

A study aimed at understanding the formation of sputtered neutrals showed that abundant neutral species released from the surface are due to sputtered adsorbate rather than collisional neutralization of hyperthermal precursor ions.⁶⁶ A fraction of the sputtered molecules and neutralized precursor species will have kinetic energies in the hyperthermal range so that they can be reionized by a second surface collision.⁶⁶

1.1.2. Reactive Collisions. In reactive collisions, the colliding ion beam itself acts as a chemical reagent, forming new bonds with surface groups or abstracting atoms or groups of atoms from the surface. In these processes, thermodynamically favored reactions that lead to the formation of new chemical bonds will be favored. One of the most extensively studied ion/surface reactions is atom or group abstraction from SAMs.^{23,34,52,67–73} Figure 2 shows a good example of ion/



Figure 2. Ion/surface collision spectrum recorded after collision of 30 eV benzene molecular ions at an H-SAM surface. The ion at m/z 91 corresponds to the addition of a methyl group followed by loss of H₂ and that at m/z 65 to further loss of C₂H₂. The peak at m/z 79 is due to a H atom abstraction reaction. The inset shows the collision process and some reaction products. Reprinted from ref 72. Copyright 1993 American Chemical Society.

surface reactions upon 30 eV collisions of benzene radical molecular ions at an H-SAM surface. The peaks at m/z 91, 79, and 65 are due to ion/surface reactions. Many similar examples involve the exchange of atoms or groups of atoms between the ionic projectile and the molecular surface.^{74,75} The abstraction of single hydrogen atoms from hydrocarbon surfaces was observed to occur with impinging radical cations containing heteroatoms, while multiple hydrogen atom abstraction occurs in highly unsaturated ions.^{76,77} The abstraction of whole adsorbate molecules or functional moieties can occur during hyperthermal Cs⁺ reactive scattering at surfaces.^{78–80}

Reactions between incident gas molecules and surfaces are generally classified into two broad types of mechanisms, nonequilibrium Eley–Rideal (ER) and equilibrium Langmuir–Hinshelwood (LH) mechanisms. Most ordinary (nonionic) reactions at the gas–surface interface occur via the LH mechanism in which the reagents are chemisorbed and equilibrated at the surface and the product translational energy is independent of the incident reagent. During the ER process, an incident gaseous ion reacts directly with a surface adsorbate and leaves with a significant fraction of its translational energy. Low-energy ion/surface reactions are believed to proceed in a single scattering event with an estimated interaction time that falls in the nonequilibrium ER regime. For a typical example of the pickup of surface hydrocarbon fragments by naphthalene projectiles, calculations show that the time scale is on the order of 100 fs.⁸¹ Many convincing arguments favoring the ER mechanism in ion/surface reactions have been subsequently reported. Abstractions of O atoms from oxidized Si and Al surfaces by O⁺ and NO⁺ ions and C atoms from a graphite surface by low-energy N⁺ ions strongly support the ER mechanism. $^{82-86}$ Evidence for the ER mechanism in ion/ surface collisions of Cs⁺ with various adsorbate species has been demonstrated theoretically and experimentally.^{87–89} Formation of endohedral fullerenes produced by the collision of Cs⁺ at a fullerene surface suggests that the reaction proceeds through a single collision event.^{90–92} Fragments such as $Cs@C_{50}^+$ or C_{44}^+ can be formed during their flight from the surface via a sequential emission of C2 units either from the endohedral product or from the sputtered fullerene.⁹⁰⁻⁹²

While it seems evident that low-energy ion/surface reactions occur during a single scattering event under nonequilibrium condition, speculations continue on whether the reactions actually occur at the surface or in the gas phase near the surface and so involve the desorbing species.^{93,94} For example, reactive collision processes of Cs⁺ ions were initially considered to occur by the latter mechanism, collisional desorption of the adsorbates followed by Cs⁺-molecule association in the gas phase, when the phenomenon was first observed with chemisorbed species.^{78,95,96} In later experiments with physisorbed molecules, however, a much higher (up to $\sim 100\%$) yield was observed for the abstraction of the adsorbates by Cs⁺,^{80,87,97} and classical molecular dynamics (MD) simulations^{88,98} suggested that this abstraction process actually occurs in a one-step mechanism classified as an ER reaction. It may be possible to view the early experimental observations with chemisorbed molecules also as a direct ER process. Reactive collision events with chemisorbed molecules may belong to a special case of the ER reaction which occurs with low efficiency, because the ion/surface collision geometry and the energy transfer must be very precisely controlled to achieve the collisional desorption of strongly adsorbed species and also the Cs⁺-molecule association reaction.⁸⁸ In the scattering of alkalimetal ions, the effect of ion neutralization at the surface is insignificant. However, when polyatomic organic ions collide with hydrocarbon-covered surfaces, the incident ions can be neutralized during the low-energy collisions (except in the SL case),³³ and protons are often sputtered as a result of these collisions.⁹⁹ For such events, it was proposed that the association reaction occurs between the neutral projectiles and sputtered protons near the surface to form protonated molecular ions (a sputtered ion mechanism).⁹⁹ A few intermediate mechanisms have been proposed that fall between these two extremes.^{100,101}

1.1.3. Soft Landing. At low energies on the order of 10 eV, polyatomic ions can be deposited intact onto surfaces.¹⁰² The process is referred to as SL, in which the intact capture of hyperthermal polyatomic ions at surfaces is achieved. The term SL refers specifically to those deposition events in which the species does not lose its molecular connectivity. In the strictest sense, the ion is not neutralized, but this distinction is often not made. Neutralization can occur by electron or proton transfer to (or from) the adsorbate. The landing species must dissipate

its kinetic energy during impact without breaking covalent bonds. The energy is distributed into vibrational and electronic degrees of freedom of the projectile and the surface. What distinguishes SL from other methods of preparing materials is the unique purity (chemical, isotopic, structural) of the selected projectile and the control that can be exerted over the nature of the deposition process exercised simply through kinetic energy (KE) selection.

One of the most fascinating aspects of the SL process is its charge retention.¹⁰² Properties such as organization, density, and steric constraints of the monolayers in which SL occurs and the orientation of the end groups of the monolayers are critical factors determining the trapping efficiency of the surface and the degree of neutralization experienced by the ions. The charge associated with a soft-landed ion can be preserved for hours or even days in matrices such as SAMs and other functionalized molecular surfaces.^{35,36} The contrast between clean metal surfaces, where image forces capture and neutralize slow ions, and self-assembled monolayers which act as leaky dielectrics precluding charge buildup (and associated repulsion of arriving ions) is that the latter do not provide the option for facile ion/electron recombination that is available at clean metal surfaces. A reviewer has commented that it is not an exaggeration to state that investigating SAM surfaces has enabled a number of breakthroughs in understanding and applications of soft landing. H-SAMs provide relatively soft matrices for collisions resulting in less fragmentation, so favoring SL of labile ions.¹⁰³ The ions are strongly held inside the SAM matrix by electrostatic interactions between the softlanded ions and their induced electric dipoles in the substrate. The ions in a well-protected matrix (such as an F-SAM) can develop a significant potential on an insulating surface.¹⁰⁴ The attractive potential between the ion and the surface, which is a function of distance, determines the efficiency of trapping of ions at the surface. Also it is found that intact SL is more successful with closed-shell rather than open-shell ions due to the ease of neutralization and fragmentation of the latter.^{102,103,105}

Charge retention by soft-landed protonated bradykinin and gramicidin S was followed by examining fragmentation patterns recorded using SIMS spectra to interrogate the surface after SL.¹⁰⁶⁻¹⁰⁹ Multiply protonated peptide ions soft-landed onto F-SAM surfaces retain both doubly and singly protonated peptides, whereas H-SAM surfaces preserve only singly protonated species.^{106,107} Doubly charged species convert to singly charged species on the H-SAM surface. Complete neutralization of the same species was observed on the COOH-SAM surface.^{106,107} Ions are well protected in the F-SAM matrix compared to the H-SAM matrix, presumably due to the larger polarity and polarizability of the former.¹¹⁰ Charge retention decreases in the order F-SAM > H-SAM > COOH-SAM, indicating much increased neutralization efficiency of the hydrophilic COOH-SAM surface relative to the inert H-SAM and F-SAM surfaces. The desorption kinetics of ions and neutral peptide molecules retained on different surfaces support these observations (see Figure 3).¹⁰⁸ In Figure 3, the decrease of doubly protonated signal is attributed to the formation of a singly charged ion by proton exchange $(k = 10^{-2} \text{ min}^{-1})$. By contrast, the singly charged species mainly decays by the thermal desorption pathway ($k = 6 \times 10^{-4} \text{ min}^{-1}$) as proton loss from this ion is very slow ($k = 10^{-5} \text{ min}^{-1}$). In contrast again, the neutral species formed by instantaneous neutralization of the singly protonated ion upon collision with the surface



Figure 3. Kinetic plots obtained for the (a) [gramicidin S + 2H]²⁺ ion, (b) [gramicidin S + H]⁺ ion, and (c) neutral gramicidin S molecules on a surface: experimental data (O) and the results of the kinetic modeling with (solid lines) and without (red dashed lines) the instantaneous charge loss by ions upon collision being taken into account. Reprinted from ref 108. Copyright 2007 American Chemical Society.

shows a linear increase during ion deposition and an almost linear decrease after SL. In another experiment, it was shown that neutralization of a soft-landed $M^{\rm III}({\rm salen})^+$ complex of Mn and Co deposited on F-SAM was very slow compared to that on H-SAM, where it occurs readily.¹¹¹

The second pathway for neutralization, through electron transfer, was observed in the case of SL of such molecular cations as rhodamine B or Jacobsen's catalyst. Metal, semiconductor, and F-SAM surfaces neutralize the ions, as expected, by instantaneous electron transfer, and the insulator surface (SiO₂ and Teflon) retains the charges for several days after SL of the molecular ions. Protonated species could discharge on the metal oxide (e.g., iron oxide) surface by proton transfer.¹¹² It is argued that this proton transfer is coupled with protonated oxide reduction (e.g., Fe³⁺ \rightarrow Fe²⁺) by electron transfer from the conductance band of the bulk metal.

A projectile ion may sometimes undergo RL or dissociative soft landing depending upon its kinetic energy and the nature of the surface. Projectiles that react readily with atoms or functional groups present at the surface will tend to undergo RL rather than simple SL.^{105,112–114} In dissociative landing, the fragments resulting from dissociation of the projectile ion in the course of the surface collision are trapped within the surface rather than being scattered away as in SID. This process may occur with cleavage and elimination of groups and successive recombination of the landed species. For example, rhodamine (B and 6G) undergoes fragment deposition,¹¹⁵ and 1,3divinyltetramethyldisilazane forms an inorganic silicocarbonitride film at collision energies¹¹⁶ above 100 eV. These processes do not necessarily overwhelm simple SL, so for example, the intact deposition of peptide ions onto F-SAM is feasible even at collision energies on the order of 150 eV.110 Because F-SAM surfaces have greater effective mass (interaction with the CF₃ group vs the CH₃ group in an H-SAM), they are more effective at converting laboratory KE into internal energy and hence in

promoting dissociation, both in dissociative SL and in the competitive inelastic collision process of SID.

2. SURFACES FOR ION/SURFACE COLLISIONS

Collisions of simple atomic and diatomic ions at clean metal surfaces have been the subject of a series of experiments since the late 1960s.^{27,117–122} Molecular materials are interesting compared to bare metals since they change the work function, functionality, and energy transfer characteristics of the surface. Well-defined highly ordered surfaces are good choices for fundamental studies. One of the best choices is the SAMs,¹²³ most often alkanethiolate SAMs on gold (Au–SAMs). The relatively low surface energy of the Au–SAMs results in low levels of surface contamination, and these surfaces are stable in ultra-high-vacuum (UHV) conditions.

Most significantly, alterations in the terminal atoms or functional groups in SAMs expose a wide variety of surface species for interaction with the projectile beam. Development of new technologies such as molecular and biodevices using organic thin films is attractive and adds importance to the study of ion/surface collisions at SAMs and other surfaces. SAMs, especially F-SAMs, are ideal choices for SID applications as they have reduced neutralization efficiencies compared to metal surfaces. Scattering from SAM surfaces results in a narrower internal energy distribution of the scattered ions (narrower, for example, than that of Au(111) surfaces), making them excellent for SID experiments.¹²⁴ However, typical SAM surfaces impart less energy to the internal modes of the scattered ions as they represent a more easily deformable target than a metal surface. The energy transfer to the surface is dependent on the masses of both partners in the collision.¹²⁵ Increased translational energy to internal energy $(T \rightarrow V)$ conversion and decreased neutralization of projectile ions occurs at fluorinated surfaces relative to hydrocarbon-terminated surfaces. 45,126-129 F-SAMs are attractive when maximum energy transfer is required as in SID experiments, and it is probable that its more massive terminal group is implicated. Compared to a F-SAM surface, an H-SAM has a lower ionization energy (IE) (13.38 eV for C_3F_8 and 10.94 eV for C_3H_8), which likely facilitates neutralization (the C-H bond energy is 98 kcal/mol in C₂H₆, and the C-F bond energy is high, 130 kcal/mol, in $\tilde{C_2F_6}$.¹³⁰ Increased neutralization might be an advantage in SL (where it avoids charge buildup) but not in SID (where it reduces the fragment ion current).

The ion/surface reaction efficiency varies with the orientation of the atom or group present at the monolayer terminus.¹³¹ Reactive collisions involving fluorine addition to the benzene molecular ion showed even and odd carbon chain alternation ascribed to angular orientation of the terminal CF₃ group relative to the surface plane.⁷³ The intensity of the products of hydrogen and methyl addition to the pyrazine ion upon collisions at an H-SAM also vary for odd versus even chain lengths.¹³¹ This difference can be explained readily by taking fluorine addition to the benzene molecular ion as an example. The intensity of the fluorine abstraction peak is greater for odd-numbered chains than for even-numbered chains. The last fluorine atom of odd-numbered chains extends substantially above the plane defined by the outermost carbon atoms.¹³² However, in even-numbered chains, all three fluorine atoms lie slightly above the plane defined by the outermost carbon atoms. In the former case, the exposed fluorine atom would appear to be relatively accessible to the projectile ion for abstraction.

It is also clear that the surface molecular species themselves can undergo ion-beam-induced reactions or fragmentation. Ioninduced processes on H-SAM surfaces appear to lead to dissociation of C–H and C–C bonds in the chain. More than 10 eV of energy can be transferred to the surface in a typical 25 eV collision event, more than enough to break the 2–4 eV bonds of the SAMs.⁵³ Many of the species formed by ion bombardment are likely to spontaneously desorb at 300 K. The threshold incident energy for the release of ionic fragments from surface molecules is typically ~20 eV and was found to be independent of the nature of incident molecular ions derived from furan, pyridine, and thiophene.¹³³

Structurally rigid F-SAM surfaces and flexible perfluoropolyether (PFPE) chains show similar T \rightarrow V conversion efficiencies. The reaction/fragmentation behavior of C₆H₆⁺ at Teflon suggests correlation between this surface and F-SAM surface.¹³⁴ Similar behavior is also observed in the case of perfluorinated Langmuir–Blodgett (LB) films and F-SAM surfaces.¹³⁵ These observations clearly indicate that only the topmost surface layers take part in the hyperthermal energy collision event. Interestingly, experimental observations show quantitative similarities in energy transfer between hydrocarbon and semiconductor Si surfaces.⁴⁸ When the energy is increased (>10 keV Ga⁺ primary ion), formation of Au–S and Au– adsorbate cluster ions starts to occur in the product ion spectra just as occurs in SIMS under kiloelectronvolt conditions.^{136,137}

Ionic liquids, polymer oils, graphitic surfaces, and polymer surfaces are other interesting targets. Room temperature ionic liquids are compatible with UHV conditions. The liquid surfaces have the obvious additional advantage that the surfaces are molecularly flat and are renewed after each collision because of the high mobility of molecules in liquid compared to SAMs. Glycerol-based liquids have been used in SL experiments to preserve the biological activity of the soft-landed proteins.^{138,139} The limitations of using a high-vapor-pressure liquid in highvacuum applications were mitigated by the addition of polyols or sugars.¹⁴⁰

HOPG substrates provide an excellent SL surface for fullerene ions^{141–145} and a good surface for SID in general.¹⁴⁶ Atomic defects such as vacancies and interstitials have been produced at HOPG surfaces by low-energy ion collisions, and these atomic defects are further etched into nanoscopic pits and channels via O₂ oxidation of the surface.^{147,148} HOPG can act as a good hydrophobic surface for condensed molecular solids. Above 120 K, water forms 2D islands as a result of surface diffusion.¹⁴⁹ Another carbonaceous surface, fullerene, produces Cs@C₆₀ or Cs@C₇₀ endohedral fullerene ions upon reactive collision of hyperthermal energy Cs⁺ ions.^{90,92}

Size-selected metal clusters have been soft landed onto HOPG and metal oxide substrates as a result of interest in the chemical reactivity of the deposited clusters.^{150–156} Depending on the kinetic energy of the cluster, they can undergo pinning and implantation on the graphite substrate. Clusters which are stable at room temperature can be created using a higher collision energy (a few hundred to a few thousand electron-volts) using the pinning technique.^{157–159} The clusters can be immobilized on the substrate at the point of landing by creation of a surface defect in the uppermost graphite layer.

Changes in the physicochemical properties of a large number of polymers have been reported when they are modified by ion beams.^{160–162} Hyperthermal fluorocarbon, organosiloxane, and thiophene ions have been used successfully as an alternative to

Table 1	. First-Gen	eration Ior	/Surface	Collision	Instruments

instrument	mass filter (first stage) m	nass analyzer (second stage)	ionization	~year reported	refs
Delaware	FTMS	FTMS	EI, CI, ESI	1997	203
FOM (Amsterdam)	TOF	TOF	photoionization	1994	595
Illinois	Wien filter	Q	EI	1993	76
Innsbruck	BE (reverse geometry)	TOF	EI (Nier type)	1997	261
Marburg I	TOF	TOF	²⁵² Cf plasma	1993	596, 597
Notre Dame	Wien filter	velocity image detector	laser ionization	1992	598
POSTECH I	Wien filter	Q	EI, cold plasma	1990	170, 599
POSTECH II	none	EQ	surface ionization	2001	87, 172
Prague	В	В	EI	1998	68
Princeton	Q	Q	EI	1995	260
Purdue 0	В	Q	EI/CI	1985	171
Purdue I	BE	EQ	EI/CI	1991	167
Purdue II	Qoq	oQ	EI/CI	2002	262
Tokyo	TOF	TOF	laser ionization	1995	243, 600
VCU	Q	Q	EI	1991	168, 169

Table 2. Instrument Descriptions

instrument	layout
Delaware ²⁰³	Ions were focused into the standard dual cell of an FTMS instrument by a lens assembly. The scattered ions recoiled into the source side FTMS cell, where they were trapped and detected by FTMS. A probe potential of +2 V ensured that the fragment ions were injected into the FTMS cell efficiently.
FOM (Amsterdam) ⁵⁹⁵	Ions were accelerated in an electric field and injected into the drift tube of a TOF mass spectrometer. The original gridless reflector was replaced by one with grids in which the collision surface was mounted. The SID fragments were identified on the basis of their flight times in the second stage. The angle defined by the source, the surface, and the detector was about 6°.
Illinois ⁷⁶	Ions were accelerated to ~ 1 keV through a Wien filter, a velocity filter with static crossed magnetic and electric fields for mass selection, bent 3° to remove fast neutrals, and finally refocused and decelerated to the appropriate energy prior to collision with the target. A quadrupole mass spectrometer was used as an analyzer for scattered ions and to conduct TPD experiments.
Innsbruck ²⁶¹	Ions were accelerated to 3 keV by a double-focusing two-sector mass spectrometer of reverse geometry. After passing the exit slit of the mass spectrometer, the ions were refocused at the collision surface by deceleration optics. The surface normal was at 45° with respect to the incident and scattered ion beam. The second mass analyzer was a linear TOF spectrometer, and the scattered ions were extracted by pulsed extraction voltages and detected by a dual microchannel plate.
Marburg I ^{596,597,601}	A modified ²⁵² Cf plasma desorption TOF mass spectrometer was used, with mass selection of the primary ions being achieved by pulsing the deflecting voltage.
Notre Dame ⁵⁹⁸	Ions were accelerated to -200 eV, mass selected using a Wien filter, and decelerated and focused with a Menzinger lens. Scattered ions were collected with a two-dimensional velocity image detector, which was positioned along the surface normal to quantify the number of ions impinging onto its surface.
POSTECH I ^{170,599}	Preaccelerated ions were mass selected through a Wien filter, bent 12° to remove fast neutrals, and decelerated to the required energy (1–300 eV). Ions scattered from the surface were detected using a quadrupole mass spectrometer, and the ion kinetic energy was analyzed with a retarding field analyzer. Surface products were characterized by electron spectroscopy and TPD.
POSTECH II ^{87,172}	Low-energy (5–100 eV) beams of alkali-metal ions were generated from a compact surface ionization source, located close to the target inside a vacuum chamber. A quadrupole mass spectrometer with an axial energy filter was used to analyze the scattered ions. Angle-resolved ion/surface scattering experiments were done using independent rotation of the ion source and the target.
Prague ⁶⁸	Ions were accelerated to 140–300 eV, mass analyzed using a 90° permanent magnet, and decelerated to the required energy. The scattered ions from the surface passed through a detection slit and then accelerated to 1000 eV into a magnetic sector instrument equipped with a Galileo channel multiplier.
Princeton ²⁶⁰	Two quadrupole mass spectrometers were mounted in a custom Conflat flange. One quadrupole served as a mass-selective ion source, and the other quadrupole served as a scattered ion detector.
Purdue 0 ¹⁷¹	Ion beams were accelerated to 6 keV prior to mass analysis by a magnetic sector (B) and then decelerated to ground potential prior to collision at the surface. The surface was placed at 45° to intersect the ion path. A mass analyzing quadrupole was placed at 90° with respect to the incident beam. A 45° energy analyzer placed between the surface and analyzer quadrupole led to a 90° angle between the incident and emerging beams.
Purdue I ¹⁶⁷	The ion beam was focused at the exit slit of the front-end electrostatic analyzer of a double-focusing sector mass spectrometer, and a quadrupole doublet collimated the ion beam onto the surface. The second stage was composed of an EQ combination, electrically floated to provide the required low axial velocity for product ion analysis. See Figure 4 for a schematic of this instrument.
Purdue II ²⁶²	Ions were extracted from the source and transferred into a quadrupole mass filter. The static quadrupole guided the ion beam either to the electron multiplier or to be turned through a 90° angle toward the target surface. The scattered ions were mass analyzed by a quadrupole mass filter and detected by a second electron multiplier.
Tokyo ^{243,600}	Ions were decelerated along a parabolic trajectory by an electric field inside a reflectron and allowed to collide with the surface. Product ions scattered from the surface were accelerated along a parabolic trajectory and then analyzed by a TOF mass spectrometer. The angle between the surface normal and the second flight path could be varied between 0° and 4° by rotating the reflectron.
VCU ^{168,169}	Two quadrupole mass analyzers were placed at 90° to each other with a surface placed to intersect the ion optical path of the two quadrupoles.

plasma processing to grow thin films on polymer surfaces, as will be discussed in section $6.7.^{162-166}$

processes which are very uncommon in liquid-phase water is

Surface composition, phase changes, solvation, transport properties, and chemical reactions have been studied by appropriate ion/surface collision experiments involving condensed molecular solids. The unique behavior of ice surfaces in

fascinating, and this topic is elaborated in sections 7 and 8.

3. INSTRUMENTATION FOR ION/SURFACE COLLISION EXPERIMENTS

The simplest ion/surface collision instrument includes an ion source followed by a mass analyzer to select ions of interest with a desired kinetic energy as the first stage of the instrument, followed by the surface of interest at which collisions leading to excitation or reactions are performed. An analyzer mass spectrometer is used in the second stage to analyze the scattered products/secondary ions. As will be obvious, in the SL experiments the second-stage mass spectrometer may not be necessary. The primary difference between the various instruments that have been built is the choice of ionization methods and the type of mass analyzer. Design considerations include the usual trade-off between resolution and transmission, with both mass and energy resolution being considerations. Not only are there intrinsic factors involved-such as access to particular conditions for particular ion/surface collision processes-but differences in the types of mass and energy analyzers affect transmission, resolution, and data acquisition speed.

The discussion in this section is divided into two parts. The instruments in operation before the year 2002 are considered first-generation instruments and are presented only briefly (see Tables 1 and 2). This choice of time span is made to cover the developments during the past decade in more detail. Good reviews are available on the first-generation instruments.^{23,28,33,34} One cautionary statement: The performance parameters given are actual data for particular systems at the particular time they were reported on. They normally do not represent the best possible performance with the types of instruments selected. Similarly, there have been many advances in ion optics and modeling of devices such as ion funnels since these instruments were described, and the presentation does not attempt to update the original descriptions to reflect the current state of the art.

3.1. First-Generation Instruments

Early hyperthermal ion/surface reactive collision experiments were performed in the BEEQ instrument at Purdue.¹⁶⁷ This was a hybrid sector instrument with a BEEQ (B = magneticsector, E = electric sector, and Q = quadrupole) configuration (referred to as Purdue I in the present review). The BEEQ allowed mass and energy selection of the primary ion beam (using BE) and measurement of the energy and mass (using (EQ) of product ions scattered through selected scattering angles (see Figure 4). A double-focusing sector mass spectrometer was used as the first stage. At the same time, instruments at Virginia Commonwealth University (VCU),^{168,169} Richmond, VA, and at POSTECH,¹⁷⁰ Korea, were also used to perform reactive collisions at surfaces. The VCU instrument based on early Purdue BQ¹⁷¹ and QQ instruments used a simple design with two quadrupole mass analyzers placed 90° to each other. The surface of interest was placed at 45° to the ion optical path of these quadrupoles. The ion beam instrument developed at POSTECH, South Korea (referred to as POSTECH I),¹⁷⁰ used mass- and energyselected beams of reactive ions in the range of 1-300 eV energy, and the scattered ions were detected using a quadrupole mass analyzer. A later instrument, an angle- and energyresolved ion/surface scattering instrument (referred to as POSTECH II), was constructed and utilized to investigate the scattering dynamics of low-energy ions.^{87,172} The instrument was devoted to reactive collision experiments of alkali-metal

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Figure 4. Schematic of the BEEQ instrument at Purdue (Purdue I). The first section of the instrument is a double-focusing (BE) mass spectrometer to select primary ions by mass and kinetic energy and deliver them to the scattering chamber, which accommodates a target and postcollision analyzer (EQ) system. The electrostatic quadrupole doublet and beam steering assembly located between the surface and BE system focus the primary beam onto the target surface. Reprinted with permission from ref 167. Copyright 1992 American Institute of Physics.

ions, particularly Cs^+ , produced from surface ionization sources (see section 7).

3.2. Newer Instruments

Newer generation instruments incorporate various highperformance state-of-the-art components as a result of a large number of innovations in instrumentation and in ionization methods. The major differences between the instruments center on the great variety of mass analyzers, the most common of which are discussed in turn (see Table 3).

Quadrupoles are widely used as mass filters since they provide adequate ion transmission and mass resolution but are compact devices (see Tables 1 and 2). There are at least three newgeneration ion/surface collision instruments which use simple quadrupole mass analyzers in both the mass selection and the mass analysis stages: Arizona I,¹⁷³ Israel Institute of Technology,^{91,92} and IIT Madras^{174,175} instruments belong in this category. The Arizona I and IIT instruments (see Figure 5) adopt more or less the same design as the early VCU instrument.¹⁶⁸ These instruments consist of two quadrupoles arranged in a 90° geometry with the surface positioned at the intersection of the optical paths, producing a collision angle of 45° with respect to the surface normal. The collision energy is controlled by the potential difference between the surface and the ion source, with mass-selected singly charged ions from the first quadrupole colliding with the surface. Excellent energy resolution is reported with the IIT Madras instrument.¹⁷⁶ The measured full width at half-maximum (fwhm) of 1 eV Ar⁺ is ~62%. For 5 and 10 eV it is 10% and 4%, respectively.

Table 3. Newer Instruments

instrument	mass filter (first stage)	mass analyzer (second stage)	ionization methods	refs
Arizona I	Q	Q	EI	173
Arizona II	EB	TOF	FAB, EI	183
Arizona III	Q	TOF	ESI	177
Caltech	BQ	Q	ICP plasma	182
IIT Madras	Q	Q	EI	174
Israel Institute of Technology	Q	Q	Cs ⁺ ion gun	91, 92
Manchester	hQhQh	Q	ESI	178
Marburg II	TOF	TOF	laser ionization	190
PNNL I (also called PNNL SL I)	QQq ICR	ICR	MALDI/ ESI	179, 180
PNNL II	BE	Q	EI	181
Hebrew University, Israel	TOF	TOF	ESI	189
Texas A&M	IM	TOF	MALDI	191, 192
Washington	EB	Q	EI/CI	66



Figure 5. Schematic of the low-energy ion scattering instrument at IIT Madras, India. Q1 is the mass filter, and Q3 is the analyzer quadrupole. The substrate is represented by S, and the collision angle is 45°. Reprinted from ref 175. Copyright 2008 American Chemical Society.

Compared to these instruments, a different configuration is used in the Israel Institute of Technology instrument.^{91,92} The Cs⁺ ion gun and C₆₀ oven are held at 45° relative to the substrate, and the analyzer quadrupole is normal to the surface. The C₆₀ beam source is used to deposit fullerene ions onto the substrate, and a Cs⁺ ion gun is used for subsequent bombardment experiments to study the formation of endohedral fullerenes.

Instruments at Manchester and Arizona (called Arizona III) are composed of a tandem quadrupole mass spectrometer in the first stage.^{177,178} Both systems use modified commercial instruments (Manchester, Quattro I, Micromass; Arizona, QTOF II, Micromass). They therefore provide the advantage

of CID capabilities prior to the surface collision. One major limitation of these instruments is the loss of reflectron functionality when a time-of-flight (TOF) instrument is used as the second-stage mass spectrometer, which results in poor TOF resolution. A schematic of the Arizona III instrument is given in Figure 6. A PNNL (Pacific Northwest National Laboratory, Richland, WA) instrument (PNNL I), used for ion/surface collision studies, is composed of three quadrupoles between the ion source and the electrostatic ion guide components. These quadrupoles are used for collisional focusing (collisional quadrupole, CQ), mass resolution (resolving quadrupole, RQ), and ion accumulation (accumulation quadrupole, AQ).^{179,180} This is a triple-quadrupole arrangement, where the first two quadrupoles serve for mass resolving and accumulation followed by a third quadrupole for collisional relaxation. The resulting ions are then directed to a Fourier transform ion cyclotron resonance (FTICR) cell through an electrostatic ion optical system. The surface is introduced at the rear trapping plate of the ICR cell.

The beam scattering instrument at PNNL (PNNL II) uses a double-focusing sector field mass spectrometer, as in the Purdue I instrument (BEEQ).¹⁸¹ These types of mass analyzers produce stable ion beams that are precisely defined in mass and energy. PNNL II has an energy resolution of 2000-5000 at 1.25 keV compared to 1000 (10% valley) for a 3 keV ion beam for the BEEQ instrument at Purdue. The energy distribution shows a width of 1.7 eV (fwhm) at a lower energy such as 40 eV. The sector instrument at CalTech has a different arrangement: the ions are resolved using a sector magnet followed by a quadrupole doublet for ion deceleration to the desired collision energy.¹⁸² Higher resolution is achieved using a smaller exit slit. A typical energy distribution of 5-10 eV (fwhm) is achieved at a 20-1000 eV beam energy. An interesting design has been adopted for the Arizona II instrument by modifying a commercial instrument.^{173,183} The mass and energy of the precursor ion are selected using a double-focusing sector instrument (JEOL HX 110), and ions enter the TOF analyzer through the exit slit of the sector (see Figure 7). After entering the TOF chamber, the ion beam is focused by a pair of quadrupole lenses. However, this arrangement suffers from decreased mass resolution in the reflectron TOF analyzers when it is operated in the surface collision mode, but it has the convenience of rapid data acquisition. The same kind of commercial instrument is used as the first stage in the Washington instrument for surface neutralization-surface reionization mass spectrometry (so-called "ping-pong" NRMS as opposed to conventional gas-phase neutralization-reionization mass spectrometry) experiments (see Figure 8).⁶⁶ The mass resolution at full ion transmission of the JEOL instrument with all slits fully open is >1000.

Ion/surface interaction provisions can be incorporated into *TOF mass spectrometers*. The first of this kind was a tandem TOF instrument which was adapted for SID by placing a stainless steel surface between two orthogonal TOF regions.¹⁸⁴ The mass range and resolution of this instrument were further enhanced by incorporating an electrostatic reflectron in the second TOF stage.¹⁸⁴ This concept in SID was further pursued and improved by several research groups.^{81,183,185–188} Wysocki and co-workers used a flange-mounted surface immediately after the reflectron by removing the drift tube (used in the linear mode of operation) to convert the commercial matrix-assisted laser desorption ionization (MALDI)-TOF mass spectrometer (Proflex, Bruker Daltonics) for SID applica-



Figure 6. Schematic of the QTOF instrument at Arizona (Arizona III). An SID device was incorporated between the quadrupole analyzer Q1 and the collision cell. The collision cell of the original commercial QTOF instrument has been moved toward the TOF entrance and the hexapole ion guide (Hex₂) removed completely. Reprinted from ref 177. Copyright 2008 American Chemical Society.



Figure 7. Schematic of the in-line JEOL sector time-of-flight instrument at Arizona (Arizona II). Reprinted with permission ref 183. Copyright 2001 Elsevier B.V.



Figure 8. Schematic diagram of the ping-pong NRMS instrument at Washington. Fast neutrals formed at the "ping" surface form ions at the "pong" surface. Reprinted with permission from ref 66. Copyright 2009 Elsevier B.V.

tions.¹⁸⁷ A tandem linear TOF mass spectrometer was used for ion/surface collision studies at Hebrew University, Israel.¹⁸⁹ A primary TOF spectrometer served to prepare mass-selected cluster ion pulses of controlled and well-defined kinetic energy. Mass selection was accomplished using a pulsed ion mirror in the field-free drift region. Similarly, the new instrument at Marburg, (Marburg II) Germany, used TOF mass analyzers in both stages.¹⁹⁰ The ions formed were transferred via the flight tube to the collision chamber. After collision at the surface, the resulting positive ions were accelerated in the electrostatic field of the reflector and reflected in the electrostatic mirror for transfer to the TOF spectrometer. By applying appropriate voltages to the lenses, the kinetic energy of the ions could be adjusted between 0 and 2 keV (nominal) with a resolution of about 100 meV. Impact of the ions at the surface occurred at normal incidence. Similar orthogonal extraction of collisionally cooled ions or fragmentation products from the surface was adopted in other instruments also, notably Texas^{191,192} and Arizona III.¹⁷⁷ In general, TOF mass analyzers have the advantages of high mass/charge range and high efficiency of product ion analysis. A crucial factor in such instrumentation is the time delay between the mass gate and the surface extraction pulses. High mass resolution requires Wiley-McLaren-type focusing to compensate for temporal, spatial, and initial kinetic energy distributions.¹⁹³

Ion mobility spectrometry (IMS) has been used for studies of hyperthermal ion/surface collisions. Combinations such as MALDI-IM-TOF MS^{191,194} and IM-TOF¹⁹² have been successfully implemented. A mobility resolution ($m/\Delta m$, fwhm) of 50–75 was obtained using a special drift cell as compared to a value of 20–30 for a conventional ion mobility (IM) drift cell. To improve the transmission and resolution efficiency, a longer periodic focusing cell¹⁹⁵ (periodic electrostatic ion guide) was used. The electrostatic potential well within the ring electrode of the IM-TOF instrument confines the scattered ions.¹⁹² The IM-TOF instrument utilizes a surface-normal incident angle for performing SID within the TOF extraction source, which helps to overcome the limitation of the small internal energy deposition associated with grazing incident angle in-line instruments.^{168,191}

Use of Fourier transform ion cyclotron resonance mass spectrometry (FTICR MS) for mass analysis has contributed remarkably to studies of gas-phase ion activation processes and subsequent product analysis, especially for large biomolecules, as the tool combines very high resolution and accuracy compared to other mass analyzers.^{196,197} Ion activation through surface collisions in an ICR instrument has been common since

the late 1980s.¹⁹⁸ Use of SID in ICR is considered a useful substitute for conventional ICR activation techniques such as sustained off-resonance irradiation (SORI)¹⁹⁹ collision-induced and infrared multiphoton (IRMPD) dissociation. The SID strategy was found to provide more peptide sequence coverage in FTICR for structural characterization of singly protonated peptide ions.¹⁷⁹ Ion activation by surface collisions can give results similar to those of gas-phase activation, including multiple-collision processes.^{179,200,201} However, hard surfaces such as F-SAMs and diamond give uniquely high internal energy depositions, and at high collision energies (above 30 eV), evidence for shattering of two small peptides has been observed, which results in much better sequence coverage compared to that of slow gaseous collisional activation.²⁰² Two Delaware^{203,204} instruments use FTICR mass analyzers for ion/ surface studies. Also in the PNNL I instrument, the surface is placed flat on the back trapping plate of the ICR cell.^{180,201} The kinetic energy of the ions striking the surface is varied by changing the direct current (dc) offset applied to the ICR cell. A typical ion current of 50-80 pA is achieved using this configuration. The SID fragments are stored in the ICR cell using gated trapping. The collision energy is defined by the difference in the potential applied to AQ and the potential applied to the rear trapping plate and the target surface.

3.3. Instrumentation for Ion Soft Landing

Several instruments have been designed explicitly for SL (Table 4). Recent devices aim at control of ion deposition parameters as well as in situ characterization of the modified surface. The first instrument used to demonstrate the SL phenomena

instrument	mass filter (first stage)	ionization method
EPFL (Switzerland)	Q	sputtering
Georgia Tech	EB	LSIMS
Illinois	Wien filter	EI
Johns Hopkins University	В	laser vaporization
Karlsruhe (Germany) instrument	Q	EI
Keio (Japan)	Q	laser ionization
Max Plank Institute of Polymer Research	EB	MALDI
Max Plank Institute of Solid State Research	Q	ESI
PNNL (Cowin)	Wien filter	plasma ionizer

Table 4.	Soft	Landing	Instruments ^a
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PNNL SL I

PNNL SL II

PNNL SL III

Purdue SL I

Purdue SL II

Purdue SL III

U.K.

Barbara

Washington SL I

Washington SL II

Scripps Research Institute

University of Birmingham,

University of North Texas

University of California, Santa

^aSeveral other cluster SL instruments are described in section 3.3.

QQq-ICR

QQq

QQQ

QQQ

q-LIT

q-RIT

Q

В

EB

TOF

drift tube

ESI

ESI

ESI

EI

ESI

ESI

ESI

ESI

ESI

plasma

sputtering

magnetron

sputter

laser ablation

consisted of a plasma (Colutron) ion source and a Wien velocity filter for mass selection.²⁰⁵ The mass-selected ions were decelerated into a liquid nitrogen (LN_2) cooled copper target using a six-element decelerator.

The BEEQ instrument at Purdue was used for SL in the 1990s.^{102,103,105} The ions were decelerated to 10–20 eV energy and allowed to deposit onto the substrate. Similar sector instruments (magnetic and electrical) for SL were built in Washington²⁰⁶ (referred to as Washington SL I) and at the Georgia Institute of Technology.²⁰⁷ The Washington instrument employed an electrospray ionization (ESI) source, an ion funnel, a multichannel deceleration lens, and a multichannel array collector (see Figure 9).^{206,208} Using this instrument,



Figure 9. Schematic of the SL instrument at Washington (Washington SL I): (A) syringe pump, (B) electrospray needle, (C) glass-lined transfer capillary, (D) funnel lens, (E) octopole, (F) acceleration lens, (G) electrostatic sector with shunts, (H) movable slit mounted on a linear motion feedthrough, (I) Faraday cup ion collector mounted on a linear motion feedthrough, (J) HV-floated Faraday cages. Reprinted from ref 206. Copyright 2005 American Chemical Society.

simultaneous separation and collection of individual compounds in nanomole quantities was demonstrated successfully.²⁰⁶ The configuration of the hybrid instrument at Georgia Tech was EBqQ.²⁰⁷ The electric and magnetic sectors in this instrument were followed by a radio frequency (rf)-only quadrupole (q) collision cell and then finally a mass-analyzing quadrupole (Q). The substrate was fixed immediately after the sectors. A modified sector field tandem mass spectrometer was used at the Max Plank Institute for Polymer Research, Germany, with a custom-built MALDI source (N2 laser 337 nm), for SL experiments.¹⁴² The ions were separated according to their m/z ratio in the first stage of the mass analyzer. A magnetic sector alone (with other ion optics) was used for mass selection in the cluster SL instruments at the University of California, Santa Barbara,²⁰⁹ Institut für Festkörperforschung, Jülich, Germany,²¹⁰ and Johns Hopkins University.²¹¹

Quadrupole mass filters have limitations that quickly become apparent in SL compared to ion/surface collision experiments when interest turns to biological molecules which require a higher mass range and maximum transmission efficiency. To overcome this difficulty, the mass resolution is set to as low as possible to increase the ion current to maximize transmission efficiency. The modified triple-quadrupole instruments at Scripps Research,²¹² the Max-Planck-Institute for Solid State Research, Germany,^{115,213} Karlsruhe, Germany,¹⁴¹ PNNL (PNNL SL II (see Figure 10)),¹⁰⁴ Keio, Japan,²¹⁴ and several size-selected cluster deposition instruments (see later in this section) all use quadrupole mass filters. The Scripps and Max

refs 219–221

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2.06

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236, 237

233, 234



Figure 10. Schematic view of PNNL SL II: (I) ESI source, (II) ion funnel, (III) focusing stage, (IV) ion selection stage, (V) quadrupole bender, (VI) UHV chamber for SL, (VII) surface introduction stage. Some important parts are the (6) 1 mm conductance limit, (7) prefilter, (10) Einzel lenses, (11) gate valve, (12) 2 mm conductance limit, (14) deceleration area, (15) surface, (16) CCD camera, and (17) magnetic translator. Reprinted from ref 104. Copyright 2007 American Chemical Society.

Planck instruments have a similar arrangement: they are constituted by a series of quadrupole mass filters for ion focusing and mass selection. The Max-Planck-Institute for Solid State Research instrument analyzes the ions before SL using a linear TOF mass spectrometer and a retarding grid detector. The SL ion current is in the range of 1-50 pA, and the deposition energy can be varied between 1 and 80 eV. This instrument is equipped with a low-temperature scanning tunneling microscopy (STM) capability,²¹⁵ which has allowed remarkable data to be recorded for landed biomolecules. In the Keio instrument, organometallic clusters produced by laser vaporization are directed onto a surface by a sequence of ion optical elements, a quadrupole deflector, and a quadrupole mass filter.²¹⁴ The cluster cations are deposited onto a LN₂ cooled substrate using a collision energy of 20 ± 10 eV. Both the Keio and Karlsruhe instruments have a comparable total ion

current of ~1 nA and an fwhm of around 2–5 eV. PNNL SL II has a three quadrupole arrangement (see Figure 10).¹⁰⁴ Ions exiting collisional quadrupole (CQ) are mass selected by a resolving quadrupole (RQ) and then isolated from the fast neutrals by a quadrupole deflector. Ion beam currents for peptide SL in the PNNL SL II instruments are 60 pA, but a target placed after RQ could provide a current of 300–500 pA for mass-selected peptide ions.¹⁰⁴ A reflection–absorption infrared spectroscopy (RAIRS) capability has now been added to this instrument.²¹⁶ The latest instrument at PNNL (PNNL SL III) has a similar sequence of quadrupoles.¹⁰⁹ It has two focusing collision quadrupoles and a large 19 mm diameter quadrupole mass filter after the ion funnel interface. An in situ SIMS capability is a special advantage of this instrument.

The Purdue SL I instrument is a modified commercial triplequadrupole instrument.²¹⁷ A movable surface was added immediately behind the detector without further mechanical changes being made to the instrument. The surface was floated, and additional voltages were applied to the final lens of the third quadrupole. The voltages applied to the conversion dynode and the electron multiplier are adjustable to pass ions through the detector housing to the surface.²¹⁷

The ICR ion/surface collision instrument at PNNL (PNNL I) is now mostly used for SL purposes (so it is referred to as PNNL SL I when used for SL).^{180,218} The energy distribution peaks around 14 eV with an fwhm of ~5 eV. This instrument was able to provide a 1–30 pA SL ion current for peptides, and in situ SIMS with ICR detection has been added.¹⁰⁸

A number of state-of-the-art cluster deposition instruments have been built for size-selected cluster science. The list is long, but some representative instruments are the Heiz instrument^{224–226} and those located at EPFL, Switzerland,^{219–221} the University of Utah, Salt Lake City,²²² the Technische Universität Darmstadt, Germany,²²³ and the Universidad Autónoma de Nuevo León, Mexico.²²⁷ The listed instruments use quadrupoles in the mass selection stage. Separation is achieved using a differential mobility analyzer (DMA) at AIST, Japan,^{228,229} and Keio University, Japan,²³⁰ and using a drift tube at the University of North Texas.²³¹ Fairly uniform size clusters were prepared using these instruments. The use of mobility separation avoids complex instrumentation, and the



Figure 11. Size-selected cluster deposition instrument at the University of Birmingham, U.K. The instrument is equipped with a magnetron gas condensation cluster source (a) and a lateral time-of-flight mass filter: (b) adjustable-diameter nozzle, (c) skimmers, (d) high-voltage lens, (e) Einzel lens, (f) x-y deflector plates for spatial control of the cluster beam, (g, h) Einzel lenses. Reprinted with permission from ref 235. Copyright 2007 Elsevier B.V.

experiments can be performed at relatively high pressures. A distinct mass selection method, based on the TOF principle, was adopted for size-selected cluster deposition at the University of Birmingham, U.K.²³²⁻²³⁵ The ion beam is displaced laterally by accelerating a portion of it perpendicular to its original direction by a pulsed electric field, letting it drift for some time. and then stopping the perpendicular movement by a pulsed electric field in the opposite direction. The magnitude of the displacement is related to the magnitude and timing of the high-voltage pulse as well as the ion mass. In this way, one can select a small range from the mass distribution of the beam. An instrument using this technique is shown in Figure 11. It allows selection of the size of the ionized particle from atoms to nanoparticles ($\sim 1-70000$ in m/z). The reported mass resolution was $m/\Delta m \approx 25$, with a transmission of about 50% for a given size independent of mass. The deposition rate using this instrument was about 0.1 monolayer (ML) of Ag atoms/min.

Another type of mass analyzer used in SL instruments is the *ion trap*, viz., the two-dimensional linear ion trap (LIT) and closely related but geometrically simple rectilinear ion trap (RIT). Both of these ion trap instruments were fabricated at Purdue.^{236–238} The first one (LIT, referred to as Purdue SL II) was derived from a commercial Thermo LTQ mass spectrometer. Application of appropriate dc potentials to the electrodes enables the LIT to be used for either radial ion ejection for mass analyzer by using an rf field that lies in the x-y plane of the analyzer. The landing surface is positioned after the LIT's back end cap. The Purdue SL III uses a homebuilt RIT mass analyzer instead of a commercial LIT (see Figure 12).^{238,239} The ease of RIT fabrication makes it an



Figure 12. Schematic of the RIT-based SL instrument at Purdue (Purdue SL III) showing the bent square quadrupole and RIT (a) and SL chamber and reaction chamber (b). Reprinted with permission from ref 239. Copyright 2009 Elsevier B.V.

attractive alternative to the LIT, although with some compromise on mass resolution.²⁴⁰ The RIT is comparable in structure to a simple LIT. The instrument also has a 90° bent square quadrupole ion guide which filters fast neutrals and can also be operated as an independent and continuous mass filter for mass selection. During SL, axial ejection is employed, and to record mass spectra, the alternative radial ejection mode is used. This instrument has in situ SIMS surface analysis capabilities as well as in situ Raman analysis.^{239,619} The RIT acts in an additional role as the mass analyzer during SIMS analysis of the sputtered ions being directed into it. The LIT/ RIT is advantageous for SL experiments in various ways: the device ejects ions at low kinetic energy, which is desirable for

SL, and the instrument can operate in a pulsed mode with a cycle time for ion accumulation chosen to optimize SL efficiency.

One of the important performance criteria of SL instrumentation is the ion yield. Ingenious designs can provide a non-mass-selected ion current of more than 1 nA, with 500 pA in the mass-selected mode.^{104,141,214,239} In other cases yields of ~5%²⁴¹ are obtained under optimized conditions; otherwise, a 2% yield is generally achieved.¹¹³ The Washington SL II was built solely for high ion yields (at the surface) without a mass analyzer.^{241,242} These authors have reported a ~2 nA ion current during SL of ions derived from biomolecules.

3.4. Ionization Methods

The choice of the ionization method is dictated largely by the process of interest, the nature of the ions to be produced, and the design of the instrument (see Tables 1 and 2). The widely used ionization methods for ion/surface collision experiments in their early stages of development were electron ionization (EI), chemical ionization (CI), and laser-induced ionization. Later, the significance of complex ions which cannot be generated by these conventional vapor-phase methods led to the use of ESI and laser desorption ionization (LDI). Some groups have studied negatively charged ions in ion/surface collision experiments,^{185,189,243,244} although most studies deal with positive ions.

The stability of the ion current and the relatively small kinetic energy spread are the main advantages of EI even though the requirement of sample volatility and extensive fragmentation during ionization precludes the use of EI to generate many interesting projectile ions. The average energy spread (fwhm) of these sources is typically less than 2 eV with an ion current in the low nanoampere range. A distinct type of EI source was implemented in the PNNL (Cowin and coworkers) instrument which used a high-pressure nozzle ionizer with an expanding supersonic jet of gas crossing an electron beam (~100 eV) from a nearby filament to generate high ion beam currents with low energy spreads.²⁴⁵

ESI offers the ability to generate intact molecular ions of nonvolatile organic compounds, especially biomolecules; hence, it can be effective in both analytical and preparative mass spectrometry.²⁴⁶ The simple sample format, mostly aqueous solutions, and compatibility with the accessible mass range of TOF and linear ion traps are additional advantages of this ionization methodology. It is known that proteins or even enzymes can be successfully ionized by ESI, sometimes retaining at least temporarily the native structure and viability.²⁴⁷ The retention of peptide structure²⁴⁸ and enzymatic activity²³⁶ after SL has been verified. The efficiency of ion formation and transfer through the atmospheric interface are limitations of ESI, which can be overcome by using optical systems such as ion funnels in the atmospheric pressure interface.^{104,238}

Desorption ionization methods are often used for SL.^{142,179,192} In the case of size-selected metal cluster SL, high-energy sputtering/vaporization methods are widely used and ions are generated from the corresponding bulk metals.²⁴⁹ Melting points of metals and the kinetic energy of the produced clusters are the decisive factors in these sources. The list of other ion sources includes the magnetron sputter source,^{250–253} (high-power) laser vaporization,^{209,224,231,254–256} the gas condensation cluster source,^{234,257} and sputtering sources.^{221,258,259}



Figure 13. Comparison of the sandwich cluster SL experiment using two different substrates: (a) Au and (b) C_{18} -SAM. Temperature-dependent variation of the V(benzene)₂ cluster after deposition of (a) 5.0×10^{14} ions onto gold and (b) 2.0×10^{14} ions onto C_{18} -SAM at 180 K as monitored using IRAS. Reprinted from ref 275. Copyright 2006 American Chemical Society.

3.5. Some Ion Transfer Optics

Ion optics are essential to achieve beams of the desired kinetic energy and cross-sectional shape. The choice of ion optics depends on the type of mass analyzer used, especially the acceleration or deceleration optics near the surface. For example, quadrupole mass filters work best at low axial ion energies, and the ion beam leaving the mass filter is not spatially focused. Simple Einzel lens assemblies can be used to control the beam geometry in such cases, 173,174,243,260 sometimes along with deceleration optics,²⁶¹ but a situation where the ions are passed through sectors at high kinetic energy and then decelerated near the surface requires the use of a multielement deceleration lens system that is located immediately in front of the target.^{66,68,167} A few ion optical elements which have special applicability in ion/surface instruments are discussed below. Statements on the performance of these elements are based on their use in a low-energy ion/surface collision instrument. This should not be considered as representing the best current performance or general performance of the component in a commercial instrument.

3.5.1. Static Quadrupole Bending Lens. This module is also called a "quadrupole deflector" and is composed of four round electrodes (sometimes 90° quarter sections of a cylinder) where opposite electrodes are electrically connected. By selecting appropriate potentials on these electrodes, depending on the kinetic energy of the ions, the system can act as a quadrupole bending lens. Compared to ion bending through a small angle using an ion deflector, 245,260 this type of system sometimes has a lower ion transmission efficiency, but it turns ions through 90° with adequate sensitivity and ease of operation. Apart from preventing fast neutrals or ions of opposite polarity from reaching the surface, the instrument footprint can be reduced. Several instruments, Purdue II,²⁶² PNNL SL I and II,^{104,180} Keio, Japan,²¹⁴ Karlsruhe,¹⁴¹ and Université de Lausanne, Switzerland,²²⁴ take advantage of this 90° bending lens (see Figure 10 for an instrument with a quadrupole bending lens). The University of Lyon, France,²⁶³

cluster depositon instrument uses the deflector alone for size selection.

3.5.2. Octapole/Hexapole Ion Guide. Commonly used rf-only multipole ion guides of the quadrupole,²³⁷ hexapole,¹⁷⁸ and octapole^{214,262} types are frequently used in ion/surface collision instruments. These guides generate an actual or effective potential minimum radially along the axis which produces a narrow ion beam.²⁶⁴ The flatter (pseudo)potential well in the octapole ion guide provides a higher transmission efficiency than does a hexapole ion guide, and neither ion guide shows the strong mass discrimination effects on transmission seen in quadrupoles due to node formation.²⁶² This fine spatial tuning is important when ionization is done using an external ESI ion source because the ion beam from the inlet system is spread due to mutual ion repulsion and collisions with residual air and solvent molecules. An alternative design of an octapole ion guide has been proposed.²⁶⁵ In this arrangement eight truncated cone-shaped rods are arranged in a conical geometry. This device allows focusing of Ni_{20}^{+} clusters into a 2 mm diameter spot compared to a 9 mm diameter spot when a normal octapole is used in SL experiments.²⁶⁵

3.5.3. Ion Funnel. The multipole ion guides described above have limited utility in the atmospheric interface or in the higher vacuum pressure region. Ion funnels are the right choice for such situations. An ion funnel is a series of cylindrical ring electrodes of progressively smaller internal diameter which is used for collisional focusing at elevated pressures.²⁶⁶ The coapplication of rf (opposite polarity on adjacent electrodes) and dc electric fields focuses the ions efficiently and transmits them from a higher to a lower pressure region.²⁶⁷ This effectively focuses ions by reversing the Coulombically driven ion cloud expansion and transmits them through a relatively small exit aperture.^{267,268}In a typical design, the first plate has a \sim 20 mm aperture while the last plate has a 2 mm aperture through which the ion funnel delivers ions into the vacuum system ion optics.^{104,180} An advantage of this protocol, which is relevant to SL, is the gentle desolvation of protein and other biological ions and their entry into the vacuum region without



Figure 14. SFM topographical images of HOPG after SL modification (a, d) and STM images (b, c). The surfaces shown in (a)–(c) were modified using $C_{42}H_{18}$, and that shown in (d) was modified using $C_{96}H_{30}$. Polycrystalline structures composed of different domains are visible in (b), and the resulting lamellar orientation is marked. Two different types of phases (1, 2) are distinguishable from the image given in (c). Reprinted with permission from ref 142. Copyright 2006 Macmillan Publishers Ltd.

the noncovalent interactions that maintain the highly ordered structure being affected.^{104,238,242,269}

4. POSTCOLLISION SURFACE ANALYSIS

Postcollision surface analysis is essential in understanding the consequences of ion/surface collisions. In situ analysis capabilities provide potential advantages over ex situ methods by rapid characterization and elimination of possible contamination. The selection of ex situ techniques for detection is sometimes appropriate, but one should always be aware of the effect of exposure to the ambient atmosphere on the modified surface. Several experiments have followed ion/surface interactions by using in situ chemical sputtering (CS) (e.g., with $60-70 \text{ eV} \text{ Xe}^+$ or CF_3^+)^{74,270-272} and SIMS.^{106,109,207,216,218,238,239,273,274} Some important analysis methods are now discussed briefly.

The products of RL and SL can be characterized by spectroscopic methods, particularly reflection absorption infrared spectroscopy (RAIRS or IRRAS/IRAS) or surfaceenhanced Raman spectroscopy (SERS), as an alternative to MS methods. The presence and position of amide I and amide II bands originating from peptide bonds can be directly correlated to the secondary structure of the peptide.^{216,248} These studies demonstrated that SL can be used to prepare peptides on substrates in stable conformations that do not exist in solution and that covalent linkage of the peptide to the surface is feasible using appropriate SAMs.^{114,207,216,248,273} The efficiencies of SL of V(benzene)₂ sandwich clusters onto bare gold and C_{18} -SAM surfaces were compared using IRAS experiments.^{214,275} The SAM substrate permits a higher SL efficiency than the Au surface. As shown in Figure 13, the four bands observed for each substrate, 747 cm⁻¹, C–H out-of-plane bending, 956 cm⁻¹, symmetric ring-breathing mode, 988 cm⁻¹, C-H in-plane bending mode, and 1418 cm⁻¹, asymmetric C-C stretching mode, are in good agreement with the infrared data for a neutral V(benzene)₂ complex in an Ar matrix.²⁷⁶ The two bands at 956 and 988 cm^{-1} start to appear when approximately 1.0×10^{14} cations have been deposited onto the bare Au substrate (area $\sim 4 \text{ mm}^2$), and an additional two bands appear at 747 and 1418 cm⁻¹ when the deposition number increases above 4.0×10^{14} ions. In contrast, with a C₁₈-SAM substrate, these four bands can be clearly observed at much lower deposition numbers (i.e., <1.0 \times 10¹⁴). The cluster cations lose their charge during SL and adsorb as neutrals with the intact native sandwich structure.²⁷⁵ In another study,

esterification in the course of deposition of benzoyl cations on an HO-SAM was confirmed by ex situ RAIRS, demonstrating C–O bond formation. 272

SERS^{277,278} is a promising analysis method for characterizing surface modifications by SL. The detection limits can easily be in the submonolayer coverage regime with a 10^5-10^6 enhancement observed for soft-landed rhodamine and crystal violet.^{279,280} The bonding of surface metal atoms to the softlanded crystal violet species was found to be by π coordination.²⁸⁰ SERS was utilized for characterizing softlanded nucleosides cytidine and 2'-deoxycytidine, which even lack a chromophore for resonant excitation.²⁸⁰ This was a landmark study in which a spectroscopic method (other than MS) was used to characterize soft-landed biomolecules. SERS has been used to understand the structure of silicon (Si_{4,6,7})²⁸¹ and small carbon (C_{1,2,4})²⁸² clusters prepared by size-selected SL. The data suggest that Si₄ is a planar rhombus, Si₆ is a distorted octahedron ,and Si₇ is a pentagonal bipyramid.²⁸¹

Temperature-programmed desorption (TPD) is helpful in providing insights into ion/surface interactions. For example, SL of V(benzene)₂ sandwich clusters and subsequent TPD gave additional information on the interaction between SAMs and soft-landed ions.^{214,275} TPD analysis shows that the threshold for vaporization gradually increases with the chain length of the SAM, demonstrating that the soft-landed clusters are more strongly trapped by longer chain SAMs. Desorption temperatures of the clusters on all the SAM substrates are higher than that for the bare Au substrate. TPD and temperature-programmed reaction (TPR) are often used to test the catalytic reactivity of metal clusters prepared by SL of size-selected clusters.^{151,152,209} In the case of "ices", TPD is often chosen for post ion/surface interaction investigations.^{245,283}

Hyperthermal energy ion-induced modifications of surfaces, including organic thin film growth, creation of mixed interface layers from ions, ambient neutrals, and/or surface atoms, and attachment of specific chemical functionalities, are being used in various technological processes.^{116,284,285} The morphology of soft-landed hydrocarbons $C_{42}H_{18}$ and $C_{96}H_{30}$ was investigated in air at room temperature by scanning force microscopy (SFM) and scanning tunneling microscopy (STM) (see Figure 14).^{142,286} These giant molecules exhibit a nearly homogeneous surface, characterized by several HOPG steps with sharp edges (marked with a black arrow in Figure 14) after SL. STM shows that the molecular packing occurs in layers consisting of stacks of single molecules packed "edge on". The tilt angle is larger for

Table 5. Polyatomic Ion/Surface Collisions

projectile ion (M ⁺)	surface	products	refs
$C_6 D_6^{+\bullet} / C_6 H_6^{+\bullet}$	H-SAM	$[M + H/D]^+, [M + CH_3 - H_2(HD/D_2)]^+$	52, 68, 72, 134, 169, 260, 306
	F-SAM	$[M + F - H]^+$, $[M + F - H_2]^+$, $[M + CF_3 - H]^+$, $[M + CF_3 - H_2]^+$	72, 134, 135
	HO-SAM	$[M + CH_2OH - H_2O]^+$ (a possible reaction product)	52
$C_4H_4N_2^{+\bullet}$ (pyrazine)	H-SAM	$M + H^{+}/M + CH_{3}^{+}$	67, 77
	D-SAM	$M + D^{+}/M + CD_{3}^{+}$	67, 77
	HD-SAM	deuterated and hydrogenated C_2 adducts; $[M + C_2H_5 - H_2]^+$, no mixed C_2 species	77
C ₄ H ₄ N ₂ ^{+•} (pyridazine)	hydrocarbon	$[M + H]^+$	260
C₅H₅N ^{+•} (pyridine)	C ₅ D ₅ N	$M + H^{+}$, $C_5D_5NH^{+}$, $C_5H_4N^{+}$	76, 308
$C_{5}H_{5}N^{+\bullet}$	1,4-benzenedimethanethiol on Au(111)	$M + C_1 - C_8$ hydrocarbon	309
	1,4-benzenedimethanethiol on Ag(111)	$M + C_1 - C_4$ hydrocarbon	309
$C_5H_5N^{+\bullet}$	HO-SAM	$M + H^+$	310
$C_5H_5N^{+\bullet}$	CH ₃ CH ₂ O-SAM	$M + H^+$	310
	CH ₃ O-SAM	$M + H^+$	310
$C_5D_5N^{+\bullet}$	H-SAM	$M + H^+$	66, 133, 602
M ^{+•} (naphthalene, phenanthrene)	hydrocarbon	$\mathbf{M} + \mathbf{C}_{1-6}\mathbf{H}_n^+$	81
HC_2N^+	H-SAM	$M + (1-4)H^+$	25, 77
OCNCO ⁺ and OCNCS ⁺	F-SAM	transhalogenation products	361
CD ₃ SOCD ₃ ⁺	H-SAM/hydrocarbon	$M + H^+$	134
CD ₃ SOCD ₃ ⁺	COOH-SAM (LB film)	$M + H^+$	135
pyrene ⁺	HD-SAM	$M + C_2 H_y$ and $M + C_2 D_y$	77
$CH_{n}^{+}, C_{2}H_{m}^{+}$	hydrocarbon-adsorbed HOPG	$C_2H_3^+/C_3H_3^+$	316, 317, 319
CH ₃ ⁺	InP	formation of a carbon film	313
$C_3H_4^{+\bullet}$	F-SAM	$\mathrm{CH}_{n}\mathrm{F}^{+}\ (n=1,\ 2)$	321
$C_3 H_n^{+\bullet} (n = 6, 8)$	HOPG	$M + H^+$	146
$CH_{n}^{+}(n=0-4)$	F-SAM	CF^+ , $C_2HF_2^+$ and $C_3F_3^+$	311
$C_2 H_n^+$ (<i>n</i> = 2, 4)	HOPG	$M + H^+$, $M + CH_3 - H_2^+$	317
$C_7 H_6^{2+}$	hydrocarbon	$C_7 H_7^+$	56
CH ₃ I ^{+●}	F-SAM	IF ^{+•}	315
$CH_2Br_2^{+\bullet}$	F-SAM	CH_2F^+ , $CHBrF^+$, CF_2Br^+	271
CCl ₃ ⁺	F-SAM	CF ₂ Cl ⁺ (surface reaction)	217
•CH ₂ OCH ₂ ⁺	F-SAM	CH ₂ F ⁺ and FCH ₂ OCH ₂ ⁺	75
CH ₃ COCH ₃ ^{+•}	hydrocarbon	CH ₂ OH ⁺ and (CH ₃ COCH ₃)H ⁺	322, 323
	H-SAM	$M + H^{+}, M + CH_{3}^{+}$	602
$(CH_3COCH_3)_n^+$	hydrocarbon	$(CH_3COCH_3)_nH^+$, $(CH_3COCH_3)_nCH_3CO^+$	324, 325, 603
$C_2H_5OH^+/C_2D_5OD^+$	H-SAM/COOH-SAM	$M + H^{+}$	129, 169
HCOOH ⁺	hydrocarbon	$HC(OH)_{2}^{+}$	329, 330
CF ⁺ , CF ₂ ⁺	Si, SiO ₂	CF _n accumulation	313
CF ₃ ⁺	polymer	fluorinating the surface	162, 165, 421, 422
$C_{3}F_{5}^{+}$	polymer	fluorocarbon thin film formation	162, 165, 190, 421, 422, 424
NH3 ⁺	hydrocarbon surface	$M + H^+$	190

 $C_{96}H_{30}$ compared to $C_{42}H_{18}$. In a different study, plasmagenerated endohedral fullerene clusters were soft landed onto HOPG, and the resulting cluster-covered samples were transferred into a variable-temperature STM instrument under UHV conditions.^{143–145} Successive STM measurements revealed that La@ C_{60} could be mobile on an HOPG surface.¹⁴³

There are several other techniques used in postcollision surface analysis, and detailed descriptions are not made here. They include SIMS,²⁰⁷ contact angle measurements,²⁸⁷ desorption electrospray ionization (DESI),²³⁸ ESI,^{208,236,237} fluorescence,^{113,241} inductively coupled plasma mass spectrometry (ICP MS),²⁰⁷ MALDI,¹⁴² Raman spectroscopy,^{288,289} scanning electron microscopy (SEM),^{242,290} scanning/atomic force microscopy (SFM/AFM),^{164,231,280,291–296} scanning tunneling microscopy (STM),^{209,219,258,297} transmission elec-

tron microscopy (TEM),^{234,255,298,299} thermal desorption spectroscopy (TDS),¹⁴¹ TOF SIMS imaging,^{74,300} TOF SIMS,^{104,115,218,273} thermal energy atom scattering (TEAS),²²⁰ near-edge X-ray absorption fine structure (NEXAFS) spectroscopy,^{285,301} grazing incidence small-angle X-ray scattering (GISAXS),¹⁵¹ photoluminescence,^{115,166} ultraviolet photoelectron spectroscopy (UPS),^{226,285,291} X-ray absorption fine structure (XAFS) spectroscopy,³⁰² X-ray photoelectron spectroscopy (XPS),^{153,155,288,293,294,301,303,304} electron energy loss spectroscopy (EELS),²²⁶ Auger spectroscopy,²⁵¹ and quartz crystal microbalance (QCM) measurements.³⁰⁵

The next sections are focused on surface reactions and modifications performed using hyperthermal energy ions.

5. POLYATOMIC ION/SURFACE COLLISIONS

Early reports of polyatomic ion/surface reactions in the hyperthermal energy regime concerned ionic collisions with adsorbed hydrocarbons or H-SAMs.^{25,54,67,169} Abstraction of a hydrogen atom is the usual reaction when an organic radical cation impinges on a hydrocarbon surface. Abstraction of up to four hydrogen atoms or a methyl group is also observed. A brief description of these and other polyatomic ion/surface collision events is given below (see Table 5).

5.1. Aromatic Hydrocarbon lons

Benzene molecular ion $(C_6H_6^{+\bullet})$ collisions at H-SAM and F-SAM surfaces showed peaks corresponding to H, CH₃, F, and CF₃ additions followed by H and H₂ loss from the adducts.^{72,93} $C_6H_6^{+\bullet}$ abstracts a methyl group from H-SAM, but the product ion readily loses H₂ (see Figure 2) to form $C_7H_7^{+,169,306}$ Alternately, another thermodynamically favorable route to form $C_7H_7^{+\bullet}$ is the reaction between the sputtered $C_3H_5^{+\bullet}$ from the hydrocarbon surface and the neutralized benzene with elimination of C_2H_4 .⁹³ Sputtered protons are observed in the mass spectra, suggesting that the formation of protonated molecules occurs via a proton transfer mechanism.²⁶⁰ The product ion due to $C_6H_6^{+\bullet}$ collisions shows a strong inelastic scattering feature, with a maximum in translational energy distribution at 2–6 eV for a collision energy of ~28 eV and a maximum in angular distribution at angles of 70–75°, much lower than the specular angle (90°).⁶⁸

The relative concentrations of CH₃ groups in mixed CH₃and OH-terminated SAMs could be linked to the extent of methyl abstraction by impinging benzene molecular ions.⁵² Fragmentation and neutralization observed for benzene molecular ions increases as the percentage of OH groups present on the surface increases.⁵² This increased efficiency of the mixed monolayers with the higher fraction of OH was attributed either to the small effective mass increase in the terminal group $(CH_3 \rightarrow OH)$ or to the differences in the interaction potentials between the projectile ion and the different surfaces. From Figure 15, it is evident that the relative abundance of the low-mass fragments is enhanced as the percentage of OH is increased, suggesting an increase in the internal energy transfer to the benzene projectile ion. Comparison of scattered ion intensities upon benzene molecular ion collisions at various hydrocarbon SAMs indicates that the neutralization of the ion beam that occurs for each SAM film is not a result of the presence of defect sites but is dependent on the length of the carbon chain. Unusual reaction products have been observed for the ion C₆H₅⁺ derived from benzene when it is subjected to collision with a COOH-SAM surface pretreated with an ammonium salt to convert the terminal group to the ammonium salt.³⁰⁷ Product ions $C_6H_5CH_2^+$ and $C_6H_5CH_2CH_2^+$ were observed in the scattered ion mass spectra as a result of C-C bond formation during collision.

Compared to the benzene cation, the pyridine molecular ion $(C_5H_5N^+)$ undergoes efficient pickup reactions upon surface collisions. Collision of $C_5H_5N^+$ at Ag(111) covered by C_5D_5N leads to the formation of $C_5H_5NH^+$ and $C_5D_5NH^+$ in similar yields.^{76,308} Both the projectile and the sputtered adsorbate abstract hydrogen to give these thermochemically favored product ions. It is interesting to note that no M^+ ($C_5H_5N^+$) radical cations survive the collision with the surface, even when the adsorbed pyridine coverage is varied from nominally zero to 1.1 ML. Two contributing factors control these effects: the



Figure 15. Product ion spectra that result from a 30 eV collision of a benzene molecular ion with a surface containing various proportions of H- and HO-SAMs: (a) 100% $C_{12}/0\%$ $C_{11}OH$, (b) 50% $C_{12}/50\%$ $C_{11}OH$, (c) 25% $C_{12}/75\%$ $C_{11}OH$, (d) unsymmetrical disulfide (C_{12} – S–S– $C_{11}OH$). Note that the relative abundance of the fragment ions is enhanced with an increase in the OH concentration (%). Reprinted from ref 52. Copyright 2003 American Chemical Society.

relative thermodynamic instability of M^+ and the ability of the surface to neutralize or protonate the projectile ions to form the stable MH^+ species. It is suggested that neutral C_5H_5NH species are not formed in the ion/surface collision process even though the C_5H_5NH radical is stable.⁶⁶

Reactive collisions of $C_5H_5N^+$ have been used in differentiating the adsorbate geometries on two different metal surfaces. 1,4-Benzenedimethanethiol chemisorbs on Au(111) and Ag(111) surfaces in two distinct geometries.³⁰⁹ At a 50 eV collision energy, $C_5H_5N^+$ picks up hydrogen to a major degree, as well as C_1 to C_8 hydrocarbon groups, from the adsorbate molecule from the 1,4-benzenedimethanethiol monolayer assembled on Au, whereas the monolayer on Ag allows abstraction of only a small portion of the molecule, C_1 to C_4 with a significantly different intensity pattern. The mass spectra show distinctive features associated with these two different substrates (Figure 16). For different isomeric oxygenated adsorbates, hydrogen atom abstraction by the $C_5H_5N^+$ ion was found to be favored at CH_3CH_2O - and CH_3O -terminated surfaces relative to the HO-terminated surface.³¹⁰

Pyrazine molecular ions $(C_4H_4N_2^+)$ have been the subject of many studies and have been shown to be able to pick up hydrogen atoms, methyl radicals, and groups containing multiple carbon atoms^{67,77} (see Scheme 2). Data from isotopically mixed surfaces show that the carbon units originate from a single chain and are transferred as intact alkyl groups.⁷⁷ Ionized polycyclic aromatic hydrocarbons (PAHs) are

relatively difficult to fragment in SID, but they undergo ion/



Figure 16. Product ion mass spectra due to collision of 50 eV $C_{s}H_{s}N^{+}$ ions at 1,4-BDMT on a Au surface (a) and a Ag surface (b). Note the difference in pickup of hydrocarbon fragments from the two surfaces. Reprinted from ref 309. Copyright 1999 American Chemical Society.





^aAdapted from ref 67. Copyright 1991 American Chemical Society.

surface reactions, picking up units with multiple carbon atoms from the adsorbed hydrocarbons. Attachment of $C_1H_n-C_6H_n$ to naphthalene, phenanthrene, or pyrene ions has been observed.^{77,81} The multiple carbon units are likely to be derived from ion/surface reactions via a single chain as suggested by reaction at an isotopically labeled mixed SAM surface. Multiple-H abstraction from a single alkyl chain was observed, though it requires breaking of multiple bonds for each H to be added. For example, HC_2N^+ , a highly unsaturated ion derived from CH_3CN , abstracts up to four hydrogen atoms from a hydrocarbon-covered stainless steel surface.^{25,77} The removal of hydrogens from adjacent carbons on the same chain might result in the formation of a double bond, an entropically more favorable process than removal of hydrogen from the two terminal carbons.

5.2. Aliphatic Hydrocarbon lons

We now discuss the reactions observed with short-chain hydrocarbon reagent ions (see Table 5). Collision of methane ions, CH_n (n = 0-4) with an F-SAM surface produces fluorine-

containing scattered ions, including CF⁺, C₂HF₂⁺, and C₃F₃⁺.³¹¹ Among these product ions, formation of CF⁺ was found to be a favorable ion/surface reaction. Formation of ¹²CF⁺ and ¹³CF⁺ products in equal abundance at higher collision energies (≥ 60 eV), when a ¹³C-labeled methane ion was used as the projectile ion, indicates that the mechanism involves formation of a symmetrical fluoronium collision complex; $F^{13}C-F^+-{}^{12}CF$. On a metal surface, CH₃⁺ deposits as an intact methyl group below 3 eV,312 and above 30 eV formation of covalently bound hydrocarbon films on metal surfaces and carbon films on InP was observed.^{312,313} Collisions of CF_3^+ ions at hydrocarboncovered surfaces generate various fluorohydrocarbons.³¹⁴ The iodomethane ion (CH_3I^+) colliding at an F-SAM surface produces IF⁺ as a major product.³¹⁵ IF⁺ is formed through initial fragmentation of CH₃I⁺ at the surface to produce atomic iodine followed by the addition of F from the surface to yield IF^{+•}. The corresponding Br-containing ions are much less reactive, and the chloro analogues are virtually unreactive. This may be because CH₃I reaction did not involve charge exchange, or it may be due to the fact that formation of IF⁺ is less endothermic than BrF⁺ and ClF⁺.³¹⁵ However, when CH₂Br₂⁺ ions were allowed to collide with an F-SAM surface, F was abstracted from the surface as verified by the products CH₂F⁺, CHBrF⁺, and CF₂Br⁺,²⁷¹ while the CCl_3^+ ion at 70 eV collision was effective in transhalogenation of an F-SAM surface.²¹⁷

Herman and co-workers have done a series of experiments with small hydrocarbon (C_1-C_3) projectile ions at collision energies of <50 eV.^{146,316-319} The reaction products observed due to the collision of small hydrocarbon ions CH_n^+ and $C_2H_m^+$ and their D isotopic variants on HOPG surfaces at room temperature showed hydrogen atom transfer and carbon chain buildup reaction.^{316,317,319} The actual reactions occur between adsorbed hydrocarbons and projectile ions. Subsequent dissociation of the reaction products occurs in addition to fragmentation of the projectile ions. These reaction products disappeared when the HOPG surface was heated to 600 °C as the adsorbed hydrocarbon layer was removed by heating and elastic scattering became dominant. It was found that the hydrogen abstraction reactions and subsequent fragmentations of $C_2D_4^+$ at hydrophobic H-diamond and hydrophilic Odiamond surfaces were very similar.³¹⁹ The collision of C_3H_n (*n* = 2-8) ions and their deuterated analogues could not execute carbon chain buildup reactions at room temperature.¹⁴⁶ However, the radical cations $C_3H_8^+$ and $C_3H_6^+$ showed fragmentation and products of H atom transfer between the projectile ion and adsorbed hydrocarbon on the surface. The even-electron ions $C_{2}H_{7}^{+}$ and $C_{2}H_{5}^{+}$ showed only fragmentation of the incident projectile ions, consistent with thermochemical expectations. These experiments demonstrated that the inelasticity of surface collisions of smaller projectile ions was lower than that with larger polyatomic ions. Surface C-H and C-C bond cleavages have been observed with the *t*- $C_4H_9^+$ ion (an even-electron ion) at H-SAM surfaces, but abstraction reactions were absent, which is consistent with the result for even-electron C₃ ions.^{133,146} When the hydrocarbon cation and dication $C_7 H_m^{-1+/2+}$ (m = 6, 7, 8) generated from toluene were subjected to SID at an HOPG surface, the observed products were singly charged species due to direct dissociation of the projectiles and hydrogen abstraction products as well as dissociation of the surface-induced species, but no C adducts were observed. 56,320 C₃H₄⁺ ions derived from isomeric allene and propyne molecular ions collide with F-SAM surfaces and fragment as well as generate CH_nF^+ (n = 1, 2)

surface reaction products.³²¹ A plot of CH_3^+/CH_2^+ abundance ratio versus collision energy for propyne and allene reveals the isomeric differences.³²¹

5.3. Simple Organic Ions

Several ions derived from simple organic molecules have been used as projectile ions in surface collisions (see Table 5). The collisional interaction of the acetone molecular ion, $CH_3COCH_3^+$, at hydrocarbon surfaces produces the hydrogen atom abstraction product $(CH_3COCH_3)H^+$ and its unimolecular decay fragment $CH_2OH^{+322,323}$ (see Scheme 3a). In

Scheme 3. (a) Decay Path of the Protonated Ion $(CH_3COCH_3)H^{+\bullet}$ and (b) Reaction between the Distonic Ion and F-SAM Surface Which Involves C–F Bond Cleavage and Formation of a New Bond betweeen the F Atom and the Reagent Ion and Subsequent Loss of Formaldehyde^{*a*}

(a)



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the case of other acetone-derived projectile ions, the product ions include the stoichiometric cluster ions $(CH_3COCH_3)_n^+$, the hydrogen atom pickup reaction product $(CH_3COCH_3)_nH^+$, and the acetylated ion series $(CH_3COCH_3)_nCH_3CO^+$.^{32,324,325} Interaction of various molecular cluster ions of acetone, acetonitrile, and ethanol with hydrocarbon-covered steel

surfaces shows simple dissociation, intracluster ion-molecule reaction, and hydrogen atom transfer from the surface.³²⁶⁻³²⁸ The DMSO- d_6 molecular ion picks up hydrogen atoms exclusively from the surface.^{134,135} The formic acid molecular ion produces protonated species and fragments in a reactive collision process.³²⁹ Both the undissociated protonated formic acid and the dissociation product CHO⁺ appear in the mass spectra.³³⁰ The preferential formation of CHO⁺ suggests that the protonated species exists as HC(OH)₂⁺.

The distonic ion³³¹ •CH₂OCH₂⁺ derived from 1,3-dioxalane after collision with an F-SAM surface undergoes F atom abstraction to yield CH₂F⁺ and FCH₂OCH₂⁺.⁷⁵ The presence of the product ion FCH₂OCH₂⁺ implies a free radical abstraction reaction (see Scheme 3b). This radical-driven chemistry is confirmed using closed-shell methoxymethyl cation CH₃OCH₂⁺ and another homologous distonic ion, •C₂H₄OCH₂⁺, at the F-SAM surface, which further indicates that the radical site plays an important role in the activation of highly inert C–F bonds.^{75,332,333} The surface collision processes are useful in characterizing aspects of the chemical nature of the ion and of the surface. Although a variety of reactions and fragmentations occur, they are readily rationalized as being constrained by well-known considerations of gas-phase organic ion reactivity and thermochemical stability.

5.4. Organic Reactions at Surfaces

Ion/surface collisions are enriched by the occurrence of a variety of organic reactions occurring in the surface-bound species (see Table 6). Hyperthermal energy collisions of $C_6H_5CO^+$ and $C_6H_5CH_2^+$ projectile ions at HO-SAM surfaces cause esterification and ether formation, respectively.²⁷² Esterification proceeds through collision of the benzoyl cation at the HO-SAM with simultaneous loss of a proton from the surface (see Figure 17b, inset). The IR bands at 1724 and 1284 cm⁻¹, corresponding to C=O and C-O stretching, respectively, agree with the formation of a benzoate-terminated

ion (M ⁺)	surface	products	comments	refs
$C_6H_5CO^+$	HO-SAM	C–O bond formation at the surface	reactive landing	272
$C_6H_5CH_2^+$	HO-SAM	C–O bond formation at the surface	reactive landing	272
$C_6H_5^+$	NH4 ⁺ COO ⁻ -SAM	C–C bond formation reaction (Kolbe reaction)		307
$C_4 S_4^{+}$	α -terthiophene (gas phase) and Si(100)	polythiophene formation on the substrate		288, 289
$C_4 S_4^+$	<i>p</i> -terphenyl (gas phase) and Si(100)	polyphenyl formation on the surface		285, 288, 290
$C_4 S_4^{+}$	gas-phase 2-methoxy-5-[(2'-ethylhexyl)oxy]- 1,4-bis(4',4"-distyrylbenzene)	poly(phenylenevinylene) film		291
OH^+	polystyrene	C-OH bond formation at the surface	C—OR, C=O, and COOH functionalities due to further oxidation of C—OH bonds	313, 334
H^{+}	dotriacontane, docosanoic acid	cross-linking reaction at the surface	selective cleavage of a C–H bond	294
H^{+}	poly(<i>trans</i> -isoprene)	cross-linking reaction at the surface	selective cleavage of a C–H bond	293, 294
H^+	acrylic acid oligomer	poly(acrylic acid)	cross-linking	340
H^+	H-SAM	C–C bond formation with thiol chain		343, 344
NH^{+}	polystyrene	C–NH ₂ , C–NHR at the surface		334
O ⁺	H-SAM/F-SAM	C–C bond break	abstraction product OH ⁻ /OF ⁻ , chemical sputtering products	347



Figure 17. RAIR spectra of the HO-SAM surface modified using benzoyl cation collisions and pure HO-SAM (a). Product ion mass spectrum upon collision of CF_3^+ (at 70 eV) with the HO-SAM surface after reaction with the $C_6H_5CO^+$ ion at 15 eV for 2 h (b). This figure was compiled from Figures 1 and 4 of ref 272. Copyright 2002 American Chemical Society.

SAM surface. Comparison of RAIR spectra before and after benzoyl cation modification is made in Figure 17a. The HO-SAM does not show any C=O and C–O features, but the SAM surface modified using ion collisions shows features comparable to those of a surface prepared by a chemical reaction route which contains 22% benzoate-terminated molecules. The occurrence of the surface reaction was further confirmed by CF_3^+ chemical sputtering (Figure 17b). In another study, a direct chemical conversion by interfacial Kolbe reaction at a COOH-SAM made it possible to prepare an arylterminated surface.³⁰⁷ Similar C–C bond formation was also found at lower energy (~10 eV) in the case of other ions such as $C_6H_5^+$ and $BrC_6H_4^+$ (see reaction 1). Additional evidence of

$$ClC_{6}H_{4}^{+} + \text{OOCCH}_{2}(CH_{2})_{9} - S - Au$$

$$\rightarrow ClC_{6}H_{4} - CH_{2}(CH_{2})_{9} - S - Au + CO_{2}$$
(1)

C–C bond formation is found in the reactive scattering of $C_6H_5^+$ at higher collision energy (>20 eV), which produced $C_6H_5CH_2^{+.307}$ Addition of functional groups such as OH or NH₂ to the polymer surface (e.g., polystyrene) was demonstrated successfully using mass-selected hyperthermal energy OH⁺ or NH⁺ ions.³³⁴

5.4.1. Surface Polymerization by Ion-Assisted Depo-sition. Using hyperthermal ion beams, Hanley and co-workers

generated polymer thin films on various surfaces by gas-phase deposition of monomeric units. This approach is known as surface polymerization by ion-assisted deposition (SPIAD).^{288,289} Polythiophene growth on a Si(100) substrate by SPIAD was performed by combining thiophene ion $(C_4S_4^+)$ deposition with simultaneous dosing of oligomeric α terthiophene vapor.^{288,289} Similarly, the preparation of polyphenyl films occurred when mass-selected polyatomic thiophene ions and p-terphenyl neutrals were used.^{285,288,290} Addition of the neutral oligomeric species allows fast film growth and permits the production of a much wider range of film type than that available by direct polyatomic ion deposition. Successful formation of polythiophene, 288,289 polyphenyl,^{288,290} and thin films of phenylenevinylene,²⁹¹ thiophene,¹⁶⁴ and titanylphthalocyanine³³⁵ was accomplished using SPIAD. The morphology of the film formed by ioninduced polymerization could be controlled by selecting an appropriate ion energy and ion:neutral ratio. Polymerization was found to be optimized at a 200 eV ion energy and over a narrow set of ion:neutral (e.g., 1:150) ratios.^{288,336} A high neutral flux favored surface polymerization as the dosed neutral will otherwise eventually desorb and the remaining adsorbate will be sputtered by the incoming ions. However, very high energy ions lead to excessive sputtering and so might overwhelm the polymerization event. The reaction appears to proceed via a cationic polymerization mechanism. The carbon

atom of the incident ion has enough kinetic energy to abstract hydrogen from an adjacent terthiophene molecule or directly add to terthiophene. 336,337

Interesting electronic properties have been found in SPIAD films. They display more electron delocalization, narrower band gaps, and reduced barriers to hole injection compared with their evaporated film counterparts.^{291,338,339} SPIAD experiments attempted with acetylene ions and titanylphthalocyanine (TiOPc) showed the formation of TiOPc dimers, bound face to face, although the overall phthalocyanine ring structure otherwise remained intact.³³⁵

5.4.2. Cross-Linking Reactions. A similar hyperthermal approach to the cross-linking of adsorbed organic molecules to form a polymer thin film was developed using low-energy proton collisions.^{294,340} The conversion of $T \rightarrow V$ during a 10 eV H⁺ collision resulted in preferential cleavage of C-H bonds, leaving inact C-X or O-H bonds. The activated molecules created cross-links to form a polymeric film with the same chemical functionalities as the precursor molecules. The validity of this approach was previously suggested theoretically.²⁹⁴ Polymerization, cross-linking, and intact thin film formation have been found in the case of dotriacontane, docosanoic acid, poly(acrylic acid) oligomer, polystyrene, and polyiso-prene.^{293,294,340,341} Cross-linking of polyisoprene or polystyrene to form cross-linked network films is found to proceed through a slightly different mechanism. The role of hyperthermal energy protons, in such cases, is to cleave C-H bonds, allowing the carbon radicals so created to initiate a polymerization chain reaction of the isoprene C=C bonds.²⁹³ This is different from the case of dotriacontane saturated hydrocarbon in which an excess fluence is required for the cleavage of more C-H bonds before enough C-C cross-linked bonds can be formed to yield a polymeric film. The effect of cross-linking extended 2 mm into the area not subjected to proton bombardment in the case of polyisoprene. The AFM images of virgin film and protonirradiated film given in Figure 18 clearly indicate the growth of



Figure 18. AFM images showing the surface morphology of (a) a virgin poly(*trans*-isoprene) film, (b) the same virgin film after 5 min of immersion in hexane, (c) the same film after irradiation with 10 eV H⁺ ions at a fluence of 2×10^{16} cm⁻², and (d) the irradiated film after 5 min of immersion in hexane. Reprinted with permission from ref 293. Copyright 2006 The Royal Society of Chemistry.

dendritic structures. Cross-linking of poly(acrylic acid) oligomer with 100% retention of COOH shows the selectivity and performance of kinematically driven synthesis of cross-linked molecular films.³⁴⁰ The thicknesses of the polymer film before and after irradiation using hyperthermal protons were identical, confirming that the proton bombardment caused neither sputtering nor material loss during C–C cleavage. On the other hand, an increase in kinetic energy of the proton to 100 eV causes severe molecular damage, resulting in etching of the film.³⁴¹ The cross-linking chemistry has been applied successfully to induce interchain cross-linkage in deposited multiwalled carbon nanotubes (MWCNTs), leading to higher mechanical strength.³⁴²

Collisions of protons can preferentially cleave C–H bonds and induce cross-linking of H-SAM surfaces themselves.^{343,344} Perturbation due to C–C bond formation in the cross-linking reaction adds bond strain to the SAM chain that weakens the Au–S bond. Some molecules are lost, and some diffuse through the surface and aggregate to form nanoclusters.³⁴³ Formation of large clusters is favored by a high proton beam energy and fluence.³⁴⁴ In spite of this, atomic hydrogen collisions on thiol-SAMs can cleave the thiolate bond directly when the length of the chain is small (<12), but hydrogen atom abstraction and consequent cross-linking reactions will be dominant for longer chain thiols.^{345,346} It is found that hyperthermal O⁺ can abstract hydrogen atoms from the H-SAM surface and break C–C bonds in both the hydrocarbon and fluorocarbon SAM chains.^{347,348}

5.5. Reactions of Metal-Containing lons

As in the case of polyatomic organic ion projectiles, information on the nature of surface groups or atoms is accessible by abstraction reactions using metal-containing ions (see Table 7). The ion/surface reactions observed with $W(CO)_6^+$ and $Cr(CO)_6^+$ at different surfaces clearly display "pickup" reactions.^{349–351} With fluorinated surfaces, in addition to metal fluorides, more complex species are formed which retain one or more carbon atoms or carbonyl groups. At collision energies above 30 eV, the product ion spectra after the collision of $W(CO)_6^+$ at poly(tetrafluoroethylene) (PTFE) contain ions of general formula WF_m (m = 1-5) and $W(CO)_n F_m$ (n = 1, 2; m = 1, 2^{71,349} The peak due to chemical sputtering (CS) of the surface was abundant at higher collision energies. Gas-phase ion/molecule reactions between $W(CO)_6$ and single fluorocarbon chains support the occurrence of multiple-F abstraction over simple F atom extraction, a thermodynamically favored result.71,3

A series of experiments has been conducted using ferrocene-SAMs. When a ferrocene-SAM was subjected to collisions of the projectile ion $Cr(CO)_{n}^{+}$ (n = 0, 2, 6), desorption of the cyclopentadienyl (Cp) moiety was observed as $Cr(C_5H_5)^{+.350}$ Product ions spectra contained both $Fe(C_{s}H_{s})^{+}$ and Cr- $(C_5H_5)^+$ when Cr^+ was used as the impinging ion. The latter product shows that the Cr⁺ ion was able to pick up the Cp group from the surface. Formation of $Cr(C_5H_5)^+$ persisted even when the projectile ion was replaced by $Cr(CO)_6^+$ or $Cr(CO)_{2}^{+}$, while the new product $Cr(C_{5}H_{5})CO^{+}$ was seen in low abundance. Other metal carbonyls, those of Fe, Mo, and W, fail to form the corresponding cyclopentadienyl adduct. 350 The suggested mechanism for this ion/surface reaction is through the formation of a double-decker sandwich structure such as $(CO)_{r}Cr + (Cp)Fe(Cp)$ -surface. Besides these reactions, the ferrocene ion did not undergo reactive scattering when it was

projectile ion (M ⁺)	surface	products	refs
W(CO) ₆ ⁺	Teflon/F-SAM	WF _m ($m = 1-5$), W(CO) _n F _m ($n = 1, 2; m = 1, 2$)	71, 349
$Cr(CO)_{n}^{+}$ (<i>n</i> = 0, 2, 6)	ferrocene-SAM	$Cr(C_5H_5)^+$	350
$Cr(CO)_{n}^{+}$ (<i>n</i> = 0, 2, 6)	F-SAM	CrF^+ , CrF_2^+ , $Cr(CO)F^+$	71
$Mo(CO)_n^+$ (<i>n</i> = 0, 2, 3, 6)	F-SAM	MoF_n^+ (<i>n</i> = 1-4), $MoCF_n^+$ (<i>n</i> = 1-3)	71
$W(CO)_n^+$ (<i>n</i> = 0, 3, 6)	F-SAM	WF_n^+ (<i>n</i> = 1–5), W(CO) _x F _y ⁺ , WCF _m ⁺	71
$Fe(Cp)_{n}^{+}(n=0-2)$	F-SAM	FeF_{n}^{+} (<i>n</i> = 1, 2), FeCpF^{+}	71
$\mathrm{TiCl}_{n}^{+} (n = 0 - 4)$	F-SAM	$Ti(Cl)_x F_y^+$	71
$Ni(Cp)_2^+$	F-SAM	$\operatorname{NiH}_{2}^{+}$, $\operatorname{Ni}(\operatorname{Cp})\operatorname{H}_{2}^{+}$	355
M^+ (M = Al, Bi, Mo, Cr, W, Sb, Te, Re)	F-SAM	M + F_n^+ ; multiple-F abstraction efficiency, $Re^+ > W^+ > Mo^+ > Cr^+$	135, 355-357
$(CH_3)_2SiNCS^+$, $(CH_3)_2SiNCO^+$, $Si(NCO)_n^+$	F-SAM	MF^{+}, MF_{2}^{+}	270, 361
$\operatorname{SiCl}_n^+ (n = 0 - 4)$	F-SAM	MF^+	355
SiCl ₃ ⁺	HO-SAM	SiCl ₂ OH ⁺	310
SiCl ₃ ⁺	CH ₃ O-SAM	SiCl ₂ OCH ₃ ⁺	310
SiCl ₃ ⁺	CH ₃ CH ₂ O-SAM	SiCl ₂ CH ₃ ⁺ , SiCl ₂ CH ₂ CH ₃ ⁺	310
$Si(CH_3)_3^+$	HO-SAM	Si-O bond formation at the surface	300, 363
$BBr_n^+ (n = 0-2)$	F-SAM	BF ⁺ , BF ₂ ⁺ , BBrF ⁺	130
$BBr_n^+ (n = 0-2)$	H-SAM	BH_2^+ , BBrH, BBrCH ₃ ⁺ , no BH^+	130

Table 7. Reactions of Metal-Containing Ions

used as the projectile ion at hydrocarbon surfaces,⁴⁸ even though ferrocene undergoes SID at both hydrocarbon and metal surfaces.^{71,353} However, Fe- or Ti-containing ions derived from the corresponding Cp derivative exhibit F abstraction reactions from fluorinated surfaces, while CS products were completely absent.⁷¹ This absence supports the suggestion that the sole mechanism for the process is oxidative addition in the course of a single collision event without electron transfer being involved. Protonated aminoferrocene and (alkylamino)ferrocenes were used for RL modification of carboxy-functionalized multiwalled carbon nanotubes (MWCNTs) to develop improved electrochemical transducers.³⁵⁴

Mild activation of nickelocene molecular ions, Ni(Cp)₂⁺, at an F-SAM surface leads to an interesting concerted hydrogen rearrangement reaction yielding NiH₂⁺ ions.³⁵⁵ The mechanism for this reaction is likely not the direct insertion of Ni⁺ into H₂. The hydrogen abstraction is likely to be concerted with Cp ring fusion to produce $C_{10}H_8$. Collision activation could excite one of the lower vibrational modes of the nickelocenium ion by internal energy transfer, leading to Cp ring fusion and simultaneous transfer of two hydrogens to Ni⁺ to form NiH₂⁺ and $C_{10}H_8$ or NiH₂ and $C_{10}H_8^{+.355}$ Ferrocenium and cobaltocenium ions failed to produce the corresponding hydrides in similar experiments.

Addition of multiple F atoms was observed for Al⁺, Bi⁺, Mo⁺, Cr⁺, W⁺, Sb⁺, Te⁺, and Re⁺ projectiles when a perfluorinated surface was the target.^{70,71,135,356,357} Associated processes such as F substitution reactions at the surface and CS of surfacederived ions were also observed. Multiple-F abstraction (up to 5) was abundant in many cases (see Figure 19). The reactivity of the ions toward F abstraction was observed to follow the order $Re^+ > W^+ > Mo^+ > Cr^+$.³⁵⁷ The multiple-F abstraction efficiency was pronounced for Re⁺, W⁺, and Mo⁺ ions. Fluorine addition to a metal ion colliding with an LB film was investigated by using Mo⁺ and Cr⁺ ions as projectiles.¹³⁵ The proposed mechanism of multiple-F additions appears to involve the second $-CF_2$ - groups on the fluoroalkanethiol chain.^{71,135} The extent of reaction is likely dependent on the penetration of the atomic metal ion to a depth so as to reach at least the first CF₂ unit below the terminal CF₃ group.⁷¹ The energy released in the course of a C=C bond formation (the result of multiple-F atom abstraction from the terminal CF_3CF_2 - group) helps to



Figure 19. Reactive collisions of $W^{+\bullet}$ at an F-SAM surface at various incident energies. The collision energies and the ion/surface reaction products are indicated. Reprinted with permission from ref 357. Copyright 1999 John Wiley and Sons Ltd.

drive the endothermic $M^+ \rightarrow MF_n^+$ process. The reaction occurs in the course of a single scattering event at the surface rather than involving deposition of reactant at the surface and product release in a subsequent collision.³⁵⁷ Simulations show that incident ions (10–60 eV) could easily penetrate the first two to three carbon atoms of a C₆ surface.¹²⁴ Abstraction of

two F atoms is favored thermochemically by 53 kcal/mol when both F atoms originate from the same alkyl chain.⁷⁰

It is possible that the metal ion must adopt an electronic structure with available unpaired electrons to undergo atom abstraction during collision. Re⁺ has a large number of unpaired electrons $(5s^25p^65d^56s^1)$ compared to other metal ions, and this is probably the reason behind its high reactivity toward F abstraction and its ability to cleave C–C bonds readily.³⁵⁷ C–C bond activation and subsequent fluorocarbon (C_mF_n (m = 1, 2; n = 1–5)) abstraction, excluding C_xF_y formation due to CS, was found mainly with W⁺ and Re⁺ as projectiles.

Well-defined TiC thin films have been formed on the HOPG surface upon collision of Ti⁺, TiCl⁺, and TiCl₃⁺ at higher collision energies (>100 eV).³⁵⁸ Primarily SID and dissociative scattering species were observed when the collision energy was below 100 eV, but F abstraction by these projectile ions was observed from fluorocarbon surfaces.⁷¹ From these investigations of various metal ion projectiles, predictions of abstraction reactions require consideration of such factors as the availability of the vacant orbitals, the degree of orbital overlap between the projectile and the surface species, thermochemistry, the electronic structure of the ions, and the geometry of the reactants at the surface. A detailed study of polyatomic ions (mostly Cl compounds) derived from group IIIA, IVA, VA, VIA, and VIIA element collisions at F-SAM surfaces presented by Cooks and co-workers⁷⁰ shows that all ions undergo CS and complex ion/surface reactions. Generally, it was found that polyatomic ions derived from these compounds were less reactive than the corresponding atomic projectiles.

5.6. Some Miscellaneous Ions

The ion $Si(CH_3)_3^+$ has been used as a thermometer to achieve an understanding of energy transfer during ion/surface interaction at various surfaces.^{124,359,360} The dimethylsilyl pseudo-halogen species (CH₃)₂SiNCS⁺, (CH₃)₂SiNCO⁺, and $Si(NCO)_n^+$ undergo ion/surface reactions leading to the abstraction of one and two F atoms from the F-SAM surface together with SID processes.^{270,361} The silyl-containing species are much more reactive than carbonyl pseudo-halogen derived ions. A rich variety of reaction products appears in the product ion spectra. They range from simple SiF^+ species due to collisions of Si^+ or $SiCl_n^+$ projectile ions⁷⁰ at fluorinated surfaces to pseudo-halogen exchange products. The ions SiF⁺ and SiH_2F^+ are the dominant species among the reaction products of dimethylsilyl pseudo-halogens.³⁶¹ Silyl ions with fewer NCO groups appear to be more reactive in F atom transfer reactions.²⁷⁰ The dimethylsilyl group was retained in projectile ions undergoing ion/surface reactions at low collision energies, suggesting that transhalogenation, namely, F-for-NCS substitution, may occur between the surface and the projectile. Hence, the halogen or pseudo-halogen transfer reactions can be exploited to introduce functional groups NCS, NCO, CH₃, and $Si(CH_3)_2$ in the F-SAM surfaces.³⁶¹ The operating mechanism is thought to be based on Lewis acid-base reactions at the surface rather than redox or electron transfer chemistry. However, thermochemical considerations show that F abstraction may involve the unpaired electrons in the outermost orbitals of the projectile ion.270

Collisions (<15 eV) of the silylium cations $SiCl_3^+$ and $Si(CH_3)_3^+$ at various SAM surfaces resulted in covalent modification of the surface and dissociative ion/surface reactions.^{300,362} Silyl cations, including $Si(CH_3)_3^+$, $Si(CD_3)_3^+$,

Si $(OCH_3)_3^+$, Si $(C_2H_5)_3^+$, Si $(CH_3)_2C_6H_5^+$, and Si $(CH_3)_2F^+$, have been used to modify HO-SAM surfaces at low collision energies.^{300,363} Scattered ion mass spectra recorded using 70 eV CF_3^+ projectile ions serve to characterize the modified surface. Comparison of this CS spectrum with that of an authentic chemically prepared trimethylsilyl ether SAM is made in Figure 20. The notable difference between these two scattering spectra



Figure 20. Scattered ion mass spectra due to the collision of CF_3^+ ions at 70 eV with (a) an HO-SAM surface modified using 15 eV Si $(CH_3)_3^+$ ion and (b) a trimethyl silyl ether SAM surface prepared by a chemical route. Reprinted from ref 300. Copyright 2002 American Chemical Society.

was the existence of OH features for the surface modified via reactive collisions. It is clear that all the surface groups have not reacted in the course of the ion/surface collision. Further characterization with XPS or re-examination after washing with simple solvents confirmed covalent bond formation between the projectile ion and the surface.³⁰⁰ Other trivalent silyl-containing projectiles were also found to be capable of surface modification by group or atom transfer ion/surface reactions.^{300,362,363}

We have seen that the extent of ion/surface collision reaction depends on the structure of the adsorbate. This fact can be used to obtain specific information on its chemical composition. An example is the reaction of $SiCl_3^+$ at isomeric surfaces, bearing functional groups such as HO-, CH₃O-, and CH₃CH₂O-.³¹⁰ The distinctive product formation provides qualitative information about the nature of the isomeric surfaces. Scattering of SiCl₃⁺ ion at 60 eV collision yields dissociative ion/surface reaction products, e.g., SiCl₂OH⁺ and SiCl₂OCH₃⁺, from the HO-terminated and CH₃O-terminated surfaces, respectively. By contrast, for the CH₃CH₂O- surface, products were observed that contain alkyl groups derived from the surface such as $SiCl_2CH_3^+$ and $SiCl_2C_2H_5^+$, but none of them contained the O atom from the surface. A second example is the differentiation of isomeric chlorobenzyl mercaptan (CBM) monolayer surfaces by the reaction of Cr⁺ and Cr-containing projectile ions.³⁵¹ The abundant reaction product at ~80 eV, C₇H₆SCr⁺, is formed after ion/surface reaction and subsequent elimination of HCl: this species was prominent in the case of 4-CBM but not for the 2-CBM surface. By contrast, the peak due to $C_7H_5Cr^+$ was intense for the 2-CBM surface.

Among other interesting projectiles, BBr_n^+ (n = 0-2) ions undergo ion/surface reactions with F-SAM and H-SAM surfaces, yielding various, unique abstraction products.¹³⁰ Bare

Table 8. Soft Landing Phenomena

Review

projectile ion/derived from	substrate	comments	refs
$C_{s}H_{1s}OSi_{2}^{+}$	F-SAM		102
$C_5H_{14}OSi_2Cl^+$	F-SAM		102
(CH ₃) ₂ SiNCS ⁺	F-SAM		102, 217
ClCH ₂ (CH ₃)SiOSi(CH ₃) ₂ ⁺	F-SAM	dissociative SL	105, 217
$C_3H_{10}OSi_2Cl^+$	F-SAM		102, 105
2,4,6-triphenylpyrylium cation	F-SAM	dissociative SL	217
N,N -dimethyl- p -toluidine, $(M - 1)^+$	H-SAM		103
N,N-dimethyl- <i>p</i> -toluidine, $(M - 1)^+$	F-SAM	"harder" compared to H-SAM	103
<i>m</i> -(trifluoromethyl)benzoyl ion	F-SAM	L	103
trypsin	Au/glycerol@Au/plasma-treated metal	retained biological activity	113, 236
lysozyme	Au/glycerol@Au	retained biological activity	113, 138, 236
streptavidin	plasma-treated metal		113
hyaluronan	steel	reactive landing	242, 379
insulin	Au		236
apomyoglobin	Au		236
DNA (160-mer ds-DNA)	nitrocellulose membrane	retained biological activity	369
bovine serum albumin (BSA)	HOPG	preferential landing onto the step edges of the substrate	213
serine	Au	serine octamer formation, chiral enrichment	371
peptide Ac-A15K	NHS-SAM	reactive landing, α -helical conformation	248, 375
cyclic peptide c-RGDfK	NHS-SAM	higher reactive landing efficiency compared to that of the linear peptide	114, 273
linear peptide GRGDSPK	NHS-SAM		273
gramicidin S + 2H ⁺	F-SAM		216
dodecanediamine + H ⁺	NHS-SAM/COF-SAM	reactive landing (amide bond formation)	216
microperoxidase-11	Au	intact deposition	376, 377
virus (rice yellow mottle, tobacco mosaic, etc.)		retained their respective structure	212, 380
$M(benzene)_2^+$ (M = Ti, Sc, Cr)	H-SAM, COOH-SAM, F-SAM	retains the sandwich structure, compounds produced in a molecular beam by laser evaporation	275, 383 -387
$V_n(benzene)_{n+1}^+$	H-SAM	retains the multidecker structure	214, 382, 383
<i>cis</i> -bis(isothiocyanato)bis(2,2'-bipyridyl-4,4'- dicarboxylato)ruthenium(II)	$TiO_2(110)$		301
mixed VO(Salen)H ⁺ and Ni(Salen)H ⁺	F-SAM	redox reaction at the surface	274
$M^{III}(salen)^+$ (M = Co, Mn)	H-SAM, F-SAM	charge retention on F-SAM, neutralization on H-SAM	111
Jacobsen's catalyst	Si, SiO ₂ , Au, SAM		238, 239
aminoferrocenes	COOH-MWCNTs	reactive landing	354
$Tu(bpy)_{3}^{2+}/Tu(bpy)_{2}^{2+}$	HO-SAMs	reactive landing	109, 391
Zr ^{IV} – <i>n</i> -propoxide	steel	reactive landing	393
rhodamine B/6G cation	Si, SiO ₂ , Au, SAMs	charge retention on insulator substrate; above 100 eV, fragment deposition	115, 239
crown ether with alkali-metal halides	Cu(100)	crown ether alkali-metal complex adsorbed flat on the surface	215
¹¹¹ In (isotope atom)	Cu	radioactive isotope separation	604-606
Ag_n^+ (<i>n</i> = 1,17,19)	Pt(111)	size-selected deposition	219
Ag ₃ ⁺	Al_2O_3	propylene epoxidation	400
Ag_{309}^{+} , Ag_{561}^{+}	C ₆₀ ML or BL on Au/graphite	diffusion experiments	296, 443
Ag ₁₋₃	T1O ₂		607
Au_{6-10}	alumina	partial oxidation of propene	402
Au ₁₋₄	titania	CO oxidation	151
Au_n^+ (<i>n</i> = 500–1000)	HOPG		417
Au ₈	HOPG	oxidation and reduction of the clusters	153
Au ₁₋₈	$11O_2(110)$	intact size-selected clusters	297
Au ₁₇	graphite	immobilization of a protein molecule	406
Au ₂₀	MgO	CO oxidation	152
Pt_{8-10}	porous anodized alumina	oxidative dehydrogenation of propane reaction	156
Pt clusters (2–3 nm)		self-organization	298
Pd_n^{-} (<i>n</i> = 1, 2, 3, 4, 7, 10, 16, 20, 250)	$TiO_2(110)$	CO oxidation	155
Pd_{8-12} , Pd_{15-18}	amorphous alumina	oxidative decomposition of methanol	254
Al ₁₇	HO-SAM		408
IN1 ₃₀	MgO, Mg	CO dissociation	154

Table 8. continued

projectile ion/derived from	substrate	comments	refs
C ⁺	Si(100), Ni(111), Ta, W, Au	C films, diamond-like structure	26
$C_n^+ (50 \le n < 60, \text{ even } n)$	HOPG		141, 292, 415, 416
$C_{58}H_n^+$ (<i>n</i> = 0–8)	HOPG		141
$\begin{array}{c} C_{42}H_{18}{}^{+}, \ C_{60}H_{24}{}^{+}, \ C_{60}H_{24}S_{3}{}^{+}, \ C_{96}H_{30}{}^{+}, \\ C_{222}H_{42}{}^{+} \end{array}$	HOPG	formation of graphene segments	142, 418 -420
$C_{80}H_{52}, C_{200}H_{132}, C_{320}H_{212}$	steel		420
La@C ₆₀ ⁺ , Ce@C ₆₀ ⁺	HOPG		143
$Ce@C_n^+$ (<i>n</i> = 36, 44, 50)	HOPG		144
$Si_2NC_8H_{19}^+$	Si	above 100 eV energy, Si–C–N-like film formation	116
Cs ⁺	thin ice films	mobility of ions through water ice	444, 445, 448
$D_{3}O^{+}/H_{3}O^{+}$	thin ice (H ₂ O) films	mobility of ions through ice	444, 445
$D_{3}O^{+}/H_{3}O^{+}$	<i>n</i> -hexane/3-methylpentane/ methylcyclohexane		283, 450
D_3O^+	hydrocarbon—water—hydrocarbon sandwich structure		449



Figure 21. (A) Photograph (in blue light) of a microarray of four proteins soft-landed onto a Au substrate. Each spot is 1 mm in radius. (B) ESI mass spectrum of a mixture of 2.5 μ g mL⁻¹ cytochrome *c* (molecular mass 12 360 Da), 2.5 μ g mL⁻¹ lysozyme (molecular mass 14 316 Da), 2.5 μ g mL⁻¹ insulin (molecular mass 5734 Da), and 2.5 μ g mL⁻¹ apomyoglobin (molecular mass 16 951 Da) in methanol/water (1:1) used for soft landing. The ions of the 9 charge state of cytochrome *c* (*m*/*z* 1359), 11 charge state of lysozyme (*m*/*z* 1301), 4 charge state of insulin (*m*/*z* 1398), and 15 charge state of apomyoblobin (*m*/*z* 1135) were selected for ion SL on the basis of a window of 5 *m*/*z* units. The nominal charge landed for each protein was on the order of 10⁻⁶ C. Mass spectra of the soft-landed proteins after the spots were rinsed: (C) insulin, (D) lysozyme, (E) apomyoglobin, and (F) cytochrome *c*. Reprinted with permission from ref 236. Copyright 2003 American Association for the Advancement of Science.

 B^+ ions react with the F-SAM surface, giving rise to BF_2^+ at collision energies of 25-100 eV and BF⁺ at collision energies above 50 eV. The lower onset energy of BF_2^+ suggests multiple abstraction in a single step with accompanying C-C bond formation either within a chain (to give C=C) or between chains (to give C-C). As a result of the transhalogenation reaction, in the case of BBr⁺ projectile ions, the abstraction product was BBrF⁺. For the BBr₂⁺ ion, the F-adduct was absent but the transhalogenation product BBrF⁺ appears to be the major product. However, when these projectile ions were used to examine an H-SAM surface, there were no odd-electron ions, e.g., BH⁺, but other reaction products such as BH₂⁺, BBrH⁺, and BBrCH₃⁺ were present in the product ion spectra. The disparity between the H-SAM surface and the F-SAM surface can be explained in terms of the difference between their ionization energies, bond energies, and chain flexibility.¹³⁰

Pseudo-halogen-containing ions such as OCNCO⁺ and OCNCS⁺ are normally considered as "hard ions" in the SID process but are subject to transhalogenation reactions as in the case of BBr_n⁺ projectile ions.³⁶¹ Evidence of reactions of an isothiocyanate group between the ion and surface, abstraction of -F or $-CF_3$, and combination of bond forming and dissociations has been reported.³⁶¹ Some of the product ions are FCO⁺, FCS⁺, SF⁺, NCSF⁺, CNCSH⁺, and CF₂NCS⁺. The projectile OCNCS⁺ was found to be more reactive than OCNCO⁺, and both ions modify the F-SAM surface by leaving CO, CS, or NCS groups on the surface. State-selected NH₃⁺ ions undergo a simple H atom pickup reaction and dissociation at an ammonia-adsorbed indium tin oxide (ITO) surface.¹⁹⁰

6. SOFT LANDING AND RELATED PHENOMENA

The separation of materials by the mass analysis and collection of atomic ions was an important component of the Manhattan project. *Calutron*, a type of magnetic mass spectrometer, was used to separate every atom of ²³⁵U used for the production of the first atomic bomb.^{364,365} Much later work showed that, under appropriate conditions, SL is an effective method of separation and collection of molecular ions in high purity. In contrast to atomic ion collection, low collision energies must be employed. The option to explore the chemistry of highly pure reactant species is a distinguishing characteristic of SL experiments. The experiment has potential value in materials science, microelectronics, nanotechnology, biology, catalysis, and fundamental studies of ion/surface collision phenomena. We have described various instruments used for ion SL (section 3.3). See Table 8 for some important systems prepared by the ion SL method.

The concept of SL with polyatomic ions was explored by Cooks and co-workers in 1976,²⁰⁵ but did not receive much attention until the 1990s.^{102,205} An early SL experiment was the deposition of cationized organics formed after desorption ionization and landing onto a second surface.³⁶⁶ The process was demonstrated with the ions derived from trimethylsilyl isothiocynate, hexamethyldisiloxane, 1,3-bis(chloromethyl)-tetramethyldisiloxane, *N,N*-dimethyl-*p*-toluidine, and *m*-(trifluoromethyl)benzoyl chloride, which were soft landed onto F-SAM or H-SAM surfaces.^{102,103,105,217} The projectile ions were trapped in the SAMs and released during subsequent CS experiments as intact ions.²¹⁷ Some degree of dissociation accompanying SL was also observed.²¹⁷ For smaller organic ions, the H-SAM surface shows differences in SL efficiency compared to the F-SAM surface.¹⁰³ In this context, the H-SAM surfaces act as "softer" surfaces and provide fewer fragments,

just as is the case in the SID process.^{45,126,127} The charge on the surface can be retained even after its exposure to laboratory air.^{218,239} In many situations projectiles which react readily with atoms or groups present at the surface undergo RL.¹⁰⁴

The following paragraphs discuss some applications of SL.

6.1. Separation and Protein Array Formation

Protein chips in the array format are used for the analysis of protein function as well as for drug target identification.^{367,368} Techniques based on SL should have a clear advantage in ability to separate protein species with a small mass difference, although they will be limited in the amounts of sample that can be generated. A preliminary experiment performed on a mixture of four proteins, cytochrome c, lysozyme, insulin, and apomyoglobin, achieved separation based on mass, and each protein was deposited at a different position on a surface using a target positioning system. A photograph of the resulting microarray is shown in Figure 21A. The landed proteins were rinsed off the surface individually using a methanol/water mixture and analyzed by ESI MS. Panels C-F of Figure 21 show the ESI spectra resulting from analysis of the rinsed solutions for each spot. These spectra contain only multiply charged ions of the corresponding protein and show no evidence of fragmentation or cross-contamination. In another experiment, Turecek and co-workers simultaneously separated five peptides from a mixture and deposited the pure compounds onto an array collector.²⁰⁸ Isolated components were found in nanomole quantities. A DNA fragment (160-mer ds-DNA) soft-landed onto a nitrocellulose membrane surface was recovered and subjected successfully to enzymatic polymerase chain reaction (PCR) amplification.³⁶⁹ SL deposition of bovine serum albumin (BSA) on an HOPG surface preferentially decorated the step edges of the substrate.²¹³ It was found that BSA assembles into two-dimensional fractal aggregates.

The amino acid serine is known to form homochiral octameric clusters in mass spectrometric ionization processes. This chiral enrichment has been studied in connection with homochirogenesis and the prebiotic conditions needed for the origin of (homochiral) life.³⁷⁰ ESI or sonic-spray ionization was used to generate protonated homochiral octamers of serine.³⁷¹ Chiral enrichment was then confirmed by SL of mass-selected protonated serine octamers. SL has also been applied for the isolation of polymeric components from a mixture. For example, monodispersed synthetic polymer from a polydisperse polymer was isolated by SL.³⁷²

6.2. Peptide Immobilization by Soft Landing

RL of proteins or peptides is a solvent-free method to immobilize biological functionality onto surfaces. Efficient covalent linkage of peptide ions to *N*-hydroxysuccinimidyl ester terminated alkanethiol (NHS-SAM) has been demonstrated.^{114,216,248,273} The primary amino groups present in the lysine side chain of the peptide or protein react with the NHS-SAM by forming amide bonds. RAIRS measurements confirm the amide bond and show that ~60% of the maximum coverage was obtained in an experiment lasting 2 h. Conformationally pure peptides could be immobilized using RL depending on the nature of the surface. The singly protonated peptide Ac-A15K, a model system that preserves its α -helical structure in the gas phase,³⁷³ was successfully transferred onto a SAM surface without losing its helical conformation.²⁴⁸ As expected, on the H-SAM surface, Ac-A15K underwent SL whereas, on NHS-SAM, it experienced RL by forming an amide bond. Compared to the normal electrospray deposition experiment, where the peptide was dominated by the β -sheet conformation, SL of the Ac-A15K peptide shows sharp amide I and II bands in infrared reflection absorption spectra. The positions of the amide I band at 1666 cm⁻¹ and the broad amide A band at 3307 cm⁻¹ suggest that Ac-A15K exists in a pure α -helical conformation (see Figure 22).^{114,374} By comparison, the cyclic peptide c-



Figure 22. IRRAS spectra of the Ac-A15K layer on an H-SAM surface prepared by electrospray deposition (blue) and SL (red). The H-SAM background has been substracted from both spectra. Reprinted with permission from ref 114. Copyright 2008 John Wiley and Sons Inc.

RGDfK, which lacks an N-terminal group, showed higher RL efficiency compared to the linear peptide GRGDSPK, which contains an N-terminal group.^{114,273} RL efficiency of peptides or proteins decreases at higher collision energy (>100 eV), and most likely the reaction occurs during the collision event and hence is optimum over a defined range of collision energies.²⁷³ Properties of the substrate have a strong effect on the conformations of soft-landed peptide ions. Deposition of the α -helical [Ac-A₁₅K + H]⁺ onto H-SAMs immobilizes both the α - and 3₁₀-helical conformations.³⁷⁵ By contrast, a significant fraction of Ac-A₁₅K molecules were present as the β -sheet conformation on the F-SAMs and COOH-SAMs.

It has been shown that microperoxidase-11 (MP-11) exists in different conformations on a Au substrate depending on the charge state. MP-11 is a model compound which exhibits reversible electrochemistry of the heme Fe^{II}/Fe^{III} couple.^{376,377} The redox properties of soft-landed proteins with a selected charge state were investigated using cyclic voltammetry (CV).^{376,377} Large shifts of the E^0 value for the triply charged protein were attributed to its unfolded conformation and hence its better attachment to the Au electrode surface due to the higher availability of amino groups.³⁷⁶ The lower value of the reorganization energy as well as of the electron transfer kinetic constant calculated for the unfolded conformation supports this hypothesis. Covalent immobilization of MP-11 onto MWCNT electrodes was achieved using RL.³⁷⁸ The immobilization does not seem to induce large conformational changes or denaturation of the soft-landed enzyme.

6.3. Retention of Biological Activity

Biological activity appears sometimes to be preserved during ESI, subsequent MS analysis, and SL when especially gentle (nondenaturing) conditions are used. Two enzymes, trypsin and lysozyme, separated and soft-landed on different substrates were tested for biological activity.^{113,236} The activity of trypsin (soft-landed on Au surface) was tested by digesting cytochrome c on the surface.²³⁶ Characteristic tryptic fragments of

cyctochrome *c* were confirmed by MALDI MS. Lysozyme, an antibacterial molecule that enzymatically degrades polysaccharide components found on the cell walls of bacteria, was found to be enzymatically active after SL onto a gold substrate or into a liquid surface containing glycerol.^{138,236} The activity of lysozyme was tested with hexa-*N*-acetylchitohexaose substrate.

On plasma-treated metal surfaces, soft-landed trypsin was found to form two layers.¹¹³ The bottom layer was chemically bonded to the surface due to RL at the metal oxide surface, but the upper layer was loosely bound and could be washed away without loss of functionality.¹¹³ Molecules remaining attached to the metal oxide surface showed about 50-60% biological activity. The calculated average fraction of trypsin molecules that survived the collision without loss of enzymatic activity was 84%. In another example, the SEM images of a soft-landed polysaccharide, hyaluronan, displayed its characteristic ability to prevent platelets from adhering to the stainless steel surfaces.^{242,379} Reactively landed hyaluronan preserves the protective properties of the surface against blood platelet activation even after washing with polar solvents.³⁷⁹ It has also been shown that rice yellow mottle virus and tobacco mosaic virus retain their respective spherical and rodlike ultrastructure after ESI and subsequent mass-selected deposition.^{212,380}

6.4. Soft Landing of Organometallics

Compounds that are difficult to synthesize by solution-phase chemistry, such as some organometallic complexes, could in principle be generated by gas-phase reactions and then SL onto surfaces without structural change. Several examples of SL of gas-phase-generated metal—benzene or metal—salen complexes have been reported.^{214,381} Nakajima and co-workers prepared a series of metal—benzene complex/cluster ions by gas-phase synthesis and subsequently soft-landed them onto various substrates. V(benzene)₂⁺ and multidecker sandwich cluster ions of general formula V_n (benzene)_{n+1} were generated in a molecular beam by laser evaporation. The sandwich-like structure was preserved after SL.^{214,382,383} Similarly, other metal sandwich compounds, M(benzene)₂ (M = Ti, Sc, Cr), were synthesized in the gas phase and captured on various SAM substrates at room temperature.^{275,287,383–387} RAIRS confirmed that clusters soft-landed into a low-temperature Ar matrix or onto a SAM surface at room temperature retain the sandwich structure.

The gas-phase-generated multidecker V_2 (benzene)₃ complex nondissociatively soft-lands onto a room temperature 1octadecanethiol SAM substrate at kinetic energies of <50 eV (see Figure 23).³⁸³ TPD results suggest that these ions undergo dissociation to V(benzene)₂ and V_2 (benzene)₂ during landing and are trapped on the SAM substrate.383 The landed complexes were neutralized, even on F-SAM, due to charge transfer from the SAM substrate, but their native sandwich structures remained intact. The high activation energy for desorption determined using TPD suggests that the deposited metal-benzene clusters are strongly trapped inside the alkyl chains of the SAM.³⁸⁷ The threshold desorption temperature of V-benzene sandwich clusters on a C₁₆ hydrocarbon SAM-Si(111) substrate was 30 K higher than that of an oxidized Si surface (~210 K),²⁸⁷ but this desorption temperature was much lower than that on a C_{16} hydrocarbon SAM-Au(111) surface (~290 K).²⁷⁵ SAMs prepared on silicon are less ordered and less densely packed in comparison to the well-ordered Au-SAMs, making them a less effective trapping substrate.³⁸⁸ Since the projectile ion kinetic energy was ~ 20 eV, the ion could



Figure 23. RAIR (IRAS) spectrum of the V_2 (benzene)₃ complex on a C_{18} -SAM, with calculated IR absorption spectra for singlet and triplet states. Reprinted from ref 383. Copyright 2007 American Chemical Society.

penetrate into the SAM matrix, which was manifested by the high desorption barrier (rather than a lower value of <100 kJ/ mol, which corresponds to interaction between the methyl surface and the ion).³⁸⁹ In the case of the COOH-SAM, the hydrogen-bonding groups near the terminus create a rigid network structure. Soft-landed complexes could not penetrate into the SAM matrix but were adsorbed onto its surface.^{386,390} The desorption temperature of the soft-landed complex from the C₁₀F-SAM surface increased to ~320 K.³⁸⁴ This difference is evidently the result of an increase in enthalpy of transition corresponding to the rotator phase of the supporting SAM matrix as a consequence of the fluorination of its molecular chains.

Another interesting difference between the F-SAM and the H-SAM surfaces in the SL of organometallic compounds was found in orientation differences. The entrapped clusters are highly oriented on the H-SAM surface with their molecular axess tilted $70-80^{\circ}$ from the surface normal.^{275,385} The $Cr(benzene)_2$ complexes embedded in the $C_{10}F$ -SAM matrix were oriented with their molecular axes perpendicular to the surface plane, and the complexes on the surface orient with their molecular axes slanted to the surface plane.³⁸⁴ Such preferences in orientation in the F-SAM are probably due to a repulsive interaction between the π -cloud of the capping benzene rings of the complex and the outmost CF₃ group and side chain C-F groups of the fluorocarbon axes of the F-SAM matrix. The situation in the H-SAM surface was attributed to the attractive CH- π interaction between the capping benzene rings of the cluster and the lateral methylene groups of the alkanethiolates.²⁷⁵ On the COOH-SAM surface, the Cr-(benzene)₂ complex prefers to orient its molecular axes along the surface normal direction rather than in the surface plane, presumably due to chemical interactions between the benzene ring of the complex and the carbonyl groups at the SAM surface.386

Reactive undercoordinated metal complexes generated in the gas phase and subsequently immobilized at SAM surfaces showed what could be catalytic activity toward gaseous reagents.^{109,391} Ru(bpy)₂²⁺ generated in the gas phase by CID of the corresponding Ru(bpy)₃²⁺ and then reactively landed onto COOH-SAMs were subsequently exposed to O₂ and C₂H₄. The results suggested that the immobilized complex

forms an oxidized complex upon exposure to O_2 followed by deoxygenation in the presence of C_2H_4 .

A thermal atmospheric ionization method, APTDI (atmospheric-pressure thermal desorption ionization),³⁹² can provide a unique route to generate mixed-metal clusters. Ionization mixtures of V^{IV}O(salen), Ni^{II}(salen), and Co^{II}(salen) (salen = N,N'-ethylenebis(salicylimine)) yielded mixed-metal cluster ions.³⁸¹ Normal ESI spectra of the same organometallic compounds were noticeably more complex than the APTDI mass spectra. The oligomers generated by APTDI potentially have higher reactivity than single-metal clusters and could be successfully transferred to an interface via SL. The reactivity was evident by the redox chemistry seen in the CID of Co-VO and Ni-VO mixed clusters. Evidence of the presence of reactive organometallic complexes on surfaces was obtained after selective deposition of metal-salen complexes onto F-SAM substrates. The $V^VO(salen)^+$ and $[Ni^{II}(salen) + H]^+$ complexes were generated by ESI and mass-selected before being deposited onto the F-SAM. A time dependence study after ion deposition showed loss of O from V^VO(salen)⁺, forming $V^{III}(\mbox{salen})^{\scriptscriptstyle +},$ over a four-day period, indicating a slow interfacial reduction process.²⁷⁴ Both reduction and oxidation on the surface were observed, as seen in the loss of O from VO(salen) and loss of 4H from $VO(salen)_2^+$. The regeneration of V^VO(salen)⁺ upon exposure to molecular oxygen and its subsequent reduction to V^{III}(salen)⁺ in vacuum completes the catalytic cycle of O₂ reduction by the immobilized vanadiumsalen species. Comparison of the soft-landed M^{III}(salen)⁺ complexes of Co and Mn shows the presence of protonated Co^{III}(salen) features in the SIMS spectra.¹¹¹ This was likely due to the facile reduction of the complex in the SIMS plume.

RL of Zr^{IV}-1-propoxide was found to produce a zirconium oxide coating on a stainless steel substrate which can be used for selective phosphopeptide capture and subsequent analysis by desorption ionization, specifically by MALDI.³⁹³ The modified surface was found to be efficient in enriching, by a factor of 20-90, singly phosphorylated peptides in midfemtomole amounts for both synthetic peptide mixtures and a tryptic digest of α -casein.³⁹³ Similarly, RL on various surfaces showed that zirconia was superior to titania followed by hafnia in terms of phospopeptide enrichment efficiency.³⁹⁴ The functionality of the N3 dye cis-bis(isothiocyanato)bis(2,2'-bipyridyl-4,4'dicarboxylato)ruthenium(II) has been successfully transferred onto the $TiO_2(110)$ surface by SL.³⁰¹ The carboxyl groups of a biisonicotinic acid ligand deprotonate so that its O atoms bind to Ti atoms of the substrate, and one of the thiocynate groups binds via a S atom to an O atom of the substrate.³⁰¹

6.5. Preparation of Catalytic Surfaces

Supported subnanometer-sized metal clusters possess distinct catalytic reactivity that is not observed in their bulk analogues. Preparation of size-selected metal clusters with optimum monodispersity allows study of their size effect under catalytically realistic conditions. Several groups have prepared size-selected metal clusters of Ag, Au, Pt, and Pd by SL and investigated their catalytic activity. Some interesting chemistry is described below.

For a number of years it has been known that Ag clusters could be soft landed onto a substrate, ^{219,221} and several aspects of such clusters have been studied. ^{209,220,221,234,258,259,295,395–399} Size-selected Ag₃ clusters and Au nanoparticles (3.5 nm, formed by the aggregation of the trimers) on an alumina support can catalyze propylene epoxidation. ⁴⁰⁰ Only a

negligible amount of $\rm CO_2$ formation was observed, which is the main problem in Ag bulk metal catalysis of the same reaction. The reaction proceeded with high yields at lower temperatures. Density functional theory (DFT) calculations support the expectation that oxidized silver trimers should be more active and selective for epoxidation compared to the bulk metal surface because of the open-shell nature of their electronic structure.⁴⁰⁰

Au clusters prepared by SL were used for catalytic oxidation of CO, propene, and other substrates.^{151–153,226,255,297,401–405} Au_{6–10} clusters soft-landed onto an unconventional alumina support were active in the partial oxidation of propene.⁴⁰² Surprisingly, alumina-supported Au clusters (Au_n/Al₂O₃) were active in the presence of water vapor instead of hydrogen, which is essential to maintain the hydroxyl equilibrium at the surface.⁴⁰² Conventionally, titania is considered to be crucial for the production of •OH/•OOH radicals, which are believed to be needed for the promotion of the partial oxidation step on Au/TiO₂. The deposited Au provides unique binding sites for immobilization of protein, and the minimal contact reduces the risk of protein denaturing.^{235,406}

Naked Pt clusters are ideal model systems for fundamental catalysis investigations.^{156,255,298,299} Oxidative dehydrogenation of propane catalyzed by size-selected Pt₈₋₁₀ clusters deposited on a high-area surface was 40-100 times more active than that on a normal Pt catalytic surface.¹⁵⁶ Moreover, the clusters were highly selective toward the formation of propylene over other products. From quantum chemical calculations, it was suggested that the highly selective activity may be due to the undercoordination of Pt in the cluster state.¹⁵⁶ The deposited Pt clusters were encapsulated by a reduced titania layer in a high-temperature (~1100 K) annealing process, resulting in a passive state of "strong metal support interaction" (SMSI) with very low catalytic activity,⁴⁰⁷ but it was found that a sputter annealing procedure transfers the Pt clusters on $TiO_2(110)$ from their inert SMSI state into a catalytically active one for CO oxidation.¹⁵⁰ In this procedure, the sample is sputtered with Ar⁺ ions at room temperature and then annealed at the same temperature. In Figure 24, CO₂ production at the surface is shown as a function of the sample temperature when CO and O2 reactants were pulsed alternatively onto the sample. The CO₂ production after the sputter-annealing treatment indicated that Pt nanoclusters on $TiO_2(110)$ were transferred from their inert SMSI state to a catalytically active and thermally stable form.150

The catalytic activity of size-selected Pd clusters has been studied in detail.^{226,254} A wide range of clusters of Pd (Pd_n (n = 1-25)) were deposited on a rutile TiO₂(110) surface, and the electronic structure dependence of reactivity was explored.¹⁵⁵ The reactivities of these clusters for CO oxidation were compared. The changes in electronic structure, determined by XPS, revealed that the Pd 3d binding energy varied non-monotonically with the cluster size. It is evident from the comparison of CO oxidation that the activity increased for Pd₂ and decreased slowly on going to the Pd₇ cluster. The activity increased again in a monotonic fashion before dropping again at Pd₂₅. The low activity correlated with a higher than expected Pd 3d binding energy, which was attributed to a particularly stable valence electronic structure.

Preparation and physicochemical investigations of sizedselected clusters derived from various other metals have been reported: Al,⁴⁰⁸ Cu,^{231,252} Si,²²⁸ W,⁴⁰⁹ Ni,^{154,229,410,411} Ru,²⁵⁰



Figure 24. (a) Vanishingly small CO_2 production (red-orange) obtained on the SMSI sample displayed in the left inset upon dosing alternating pulses of O_2 (blue) and CO (green) as shown in the right inset as a function of the sample temperature and time (heating rate 1 K/s, pulse frequency 0.1 Hz). (b) High CO_2 production obtained on the sample displayed in the left inset (same preparation as in panel a), followed by Ar ion sputtering at room temperature and annealing at 1100 K for 1 h. Red and orange colors refer to the CO_2 production synchronized with CO and O_2 pulses, respectively. Reprinted from ref 150. Copyright 2011 American Chemical Society.

 ${\rm Mo_4S_{6'}}^{251}$ ${\rm Mo_n/(MoO_3)_{nv}}^{211}$ Met-Cars, 412 and various bimetallic clusters. 223,263,413

Although the results show potential value in catalysis, the challenging task of scaling up the production of size-selected clusters at surfaces for use as industrial nanocatalysts remains to be accomplished. DFT calculations predict high CO oxidation activity for ligand-protected subnanometer-sized Au clusters.⁴¹⁴ This may open up the use of ESI as an ionization source for cluster ion production. Use of high-current SL experiments could also scale up the production step considerably.

6.6. Nanopatterning

The SL approach is useful in producing ordered structures of organic macromolecules on surfaces. For example, in contrast to chemical extraction, a wide range of small endohedral fullerenes (e.g., $La@C_n$, $Ce@C_n$) are available by deposition of mass-selected cluster beams.^{143–145} A simple way to prepare alkali-metal fullerides could be to deposit a small amount of alkali metal on top of a well-defined solid C_n film at room temperature.⁴¹⁵ Subsequently, the alkali-metal atoms will diffuse into and penetrate the interstitial sites of the C_n lattice.

Besides fullerene derivatives, pure fullerenes containing fewer carbon atoms have been prepared in the gas phase and soft landed. The C_n^+ (50 $\leq n < 60$; *n* is even) ions, generated by EI of C_{60} and deposited at < 6 eV, produce a product with substantially higher thermal stability than a pure C_{60} thin film.^{141,292,415,416} C_n thin film formation on HOPG surfaces proceeds initially via 2D islands followed by 3D pyramid-like structures at higher coverage on the basis of the Volmer–Weber scenario.^{415,416} Higher primary kinetic energies favor the formation of smaller and less dendritic islands.²⁹² Soft-landed C_{58}^+ ions easily undergo reaction with residual gases to generate hydride derivatives $C_{58}H_n$ (n = 0-8).¹⁴¹ In another study, formation of amorphous carbon films was observed when neutral C clusters were deposited on a surface.³⁰² Earlier

it was shown that the deposition of C^+ ion beams at hyperthermal energy onto metal surfaces forms diamond-like structures.²⁶ ESI of Au colloids or Au clusters onto HOPG was found to form three-dimensional agglomerates on the surface.^{213,417} These three-dimensional structures are between 250 and 640 nm in diameter and 3 and 17 nm in height and were preferentially formed at the step edges of the HOPG surfaces. The growth mechanism again follows the Volmer–Weber model, which implies a stronger interaction between the deposited particles than between the particles and the substrate.

The recent interest in graphene, due to its unique charge transfer properties, motivates grafting of surfaces with such materials. Poor solubility in common organic solvents prevents the use of surface-coating techniques. Nano-graphene segments, in other words, PAHs such as $C_{42}H_{18}$, $C_{60}H_{24}$, $C_{60}H_{24}S_{3}$, C₉₆H₃₀, C₂₂₂H₄₂, and polyphenylene-dendronized perylenes (PDPs) and several of their derivatives, were generated by laser desorption and successfully soft landed, at energies of ~35 eV, onto the HOPG substrate.^{142,418–420} The self-organization observed for C_{42} and C_{96} soft-landed films shows lamellar structure domains of two coexisting "edge-on" phases due to $\pi-\pi$ stacking of the deposited molecules¹⁴² (see Figure 14 for an STM image of the soft-landed species). Large conjugated molecules containing extensively delocalized π orbitals leading to strong π - stacking and thus improved charge transport and increased charge density are ideal for electronic applications.⁴¹⁹ The dimensions of these structures range from a few nanometers to a few tens of nanometers with stacked molecule tilt angles of 18° . In the case of C₆₀ and C₂₂₂₁ SL leads to the formation of two-dimensional polycrystalline molecular domains that may not be exactly edge-on phase packed.⁴¹⁸ Such self-organization is absent when other widely adopted methods of surface coating are used. The graphene segments neither fragment nor lose their structural characteristics during the deposition process. MALDI-TOF spectra of thin films formed by deposition of nano-graphene segments show the corresponding molecular ion peaks, Figure 25. The series of ions generated from PDPs C₈₀H₅₂, C₂₀₀H₁₃₂, and C₃₂₀H₂₁₂ and its derivatives show that SL can be successful at impact energies below 180 eV, without causing fragmentation.⁴²⁰ The yield of soft-landed material reaches its maximum value when the kinetic energy of the projectile ion lies between 50 and 100 eV.420

When crown ethers were electrosprayed together with salts of selected alkali-metal cations (H⁺, Na⁺, or Cs⁺), the resultant host–guest complexes underwent successful SL.²¹⁵ Conventional sublimation processes failed to produce such complexes at the surface. In situ low-temperature (~43 K) STM images showed intact SL with crown ethers adsorbed flat on a Cu(100) substrate with an ion placed centrally within the cavity (Figure 26). This example shows that SL is a versatile surface functionalization method with molecular host–guest complexes.

6.7. Fluorinated Surfaces

Organofluorine ions have been used as efficient sputtering agents in several technologically important surface modifications. 162,163,165,284,421,422 Hyperthermal energy $C_nF_m^+$ ions have been used commonly as etching or modification agents for metal, semiconductor, or polymer surfaces. 284,313,423 Chemical modification of the surface is strongly dependent on the ion kinetic energy and the structure of the precursor fluorocarbon ions. The deposition of fluorocarbon ions on polymer surfaces



Figure 25. MALDI-TOF MS spectra of thin layers of deposited (A) $C_{60}H_{24}$, (B) $C_{60}H_{24}S_3$, and (C) $C_{222}H_{42}$. Insets: enlarged spectra of the respective molecular peaks, with simulated signals (bars) corresponding to the natural isotopic mass distribution of the individual molecules. Reprinted with permission from ref 418. Copyright 2009 John Wiley and Sons, Inc.



Figure 26. Top row: geometry of the DB24C8 complex at the Cu(100) surface (DB24C8–Cs⁺, $-Na^+$, and $-H^+$). Middle row: simulated STM images according to the above structures. Bottom row: magnified STM topographs of single complexes. Reprinted from ref 215. Copyright 2010 American Chemical Society.

is a highly flexible method for nanostructure film growth or preparation of chemical gradient surfaces with a high level of

control over the process.^{164,165,284,424} C₃F₅⁺ ions are more effective in growing fluorocarbon thin films on the surface, but CF_3^+ was successful in fluorinating polymer sub-strates.^{162,165,421,422} The reaction might proceed through covalently bound polyatomic precursors or fragments that can react and become incorporated within the surface materials rather than merely donating F atoms.¹⁶² The reaction channels may proceed in a different way at different collision energies; for 2-3 eV collisions, CF⁺ or CF₂⁺ ions are simply deposited at the Si surface, but formation of CF_2^+ and CF_3^+ was observed when the incident energy exceeded 20 eV due to impact dissociation and reaction.³¹³ No fluorocarbon species was observed at 100 eV; instead silicon carbide was formed.³¹³ Simple deposition of $C_3F_5^+$ and thiophene ions at hyperthermal energy generates thin film nanostructures on H-Si(100) with control over morphology by varying the ion energy and ion structure.¹⁶⁴ Another choice of F-containing ion for surface modification was SF_5^+ , ⁴²⁵ which was found to induce fluorination by grafting reactive F atoms formed upon dissociation.¹⁶¹ At higher collision energy, in the kiloelectronvolt range, SF_5^+ bombardment is widely used for depth profiling experiments on polymer surfaces.^{426,427} Other ions used for surface modification include SO_3^+ and the organosilane ion $Si_2O(CH_3)_5^{+.161,163,424}$

6.8. Ambient Ion Soft Landing and Electrospray Deposition

Ion SL experiments can be performed under ambient conditions. In a typical example, ions generated by ESI are passed through a heated metal drying tube, and dry ions of selected polarity are deposited onto a substrate.^{428–430} The dry ions are used as reagent ions in heterogeneous ion/surface reactions or for surface patterning. Unlike vacuum SL, mass selection is not used in such an experiment, but the ionization conditions and reagents are optimized to provide the desired projectile ion. When the experiment is performed at atmospheric pressure (or reduced pressure) without mass selection or optimization for single-ion formation, it is sometimes termed atmospheric pressure ion deposition or electrospray deposition.^{431–440} This method has been employed to prepare arrays or patterns of nanostructures, nanotubes, fullerenes, etc.^{434,435,437,441,442} These are viable methods for the formation of nanostructure or thin films of functional materials, but they lack the molecular specificity of mass-selected ion soft-landing experiments.

6.9. Other Uses of Soft Landing

The use of the SL method in molecular separation and immobilization and in surface patterning has so far been discussed. The highly controlled and well-defined experimental conditions in SL can be utilized for several types of fundamental studies which are difficult to perform otherwise. One such example is the investigation of the mechanism of penetration of nanoparticles into thin films. A monolayer of C₆₀ prepared on a Au support cannot be a good barrier for Ag₃₀₉⁺ clusters. These clusters easily diffuse through C_{60} monolayers in a few hours.⁴⁴³ Such penetration does not occur through multilayers of C₆₀ supported on a Au surface or a monolayer of C₆₀ on graphite. Simple diffusion does not explain the penetration of nanoparticles through thin films or nanoscopic barriers.^{296,443} Attractive forces between the metal and metallic particles are involved. Au clusters (~350 atoms) soft-landed onto an H-SAM on a Au subtrate were found to diffuse through the ML and localize at the Au-S interface.²⁹⁵ This happened as a result of cluster implantation in the SAM followed by molecular reorganization.

It is often difficult to measure ion mobility in condensed molecular solids, but SL of ions directly onto an absorbate can overcome many errors associated with these studies. A measure of the mobility of ions in water ice can be obtained by making Kelvin probe measurements. 444,445 SL of hydronium (D_3O^{\ast}) ions onto ice films creates a potential difference across the ice film which was monitored using a Kelvin probe as a function of temperature.⁴⁴⁴ First, D_3O^+ and Cs^+ ions were soft landed (~1 eV) on amorphous water ice at 30 K. Upon increasing the temperature, a sharp drop in voltage occurred near 50 K, a temperature much lower than its glass transition temperature of 135 K.446,447 This is attributed to a dielectric response due to reorientation of dipoles of the amorphous ice film. Interestingly, SL studies show that neither Cs^+ nor H_3O^+ ions can move from the ice film surface to the interior at higher temperatures.^{445,448} These observations will be discussed in section 7.2. In a similar setup, hydronium ions were found to migrate across epitaxially grown micelle-like films of hydrocarbon/water/hydrocarbon sandwich structures (temperature range 90–150 K).⁴⁴⁹ The motion of hydronium and $\hat{C}s^+$ ions through simple hydrocarbon films, viz., n-hexane, 3-methylpentane, and methylcyclohexane, was also investigated.^{283,450} The ions were found to migrate through the amorphous version of these films as expected, and very limited diffusion was observed through crystalline films.²⁸³

7. COLLISIONS AT CONDENSED MOLECULAR SOLIDS

This section of the review is devoted to studies of low-energy ion collisions at condensed molecular solids or "ices" formed from various molecules such as water, ammonia, methane, carbon dioxide, hydrocarbons, etc. Puzzles ranging from the origin of ${\rm life}^{451,452}$ to ozone depletion 453 propel interest in the chemistry and physics of ice surfaces. From a standpoint of physical chemistry, an ice surface has properties much different from those of liquid water or even bulk ice. Upon the phase transition from liquid to solid, the rate of reagent diffusion is reduced by several orders of magnitude. The rates of reactions are much slower at the temperature of ice. With such drastic changes, the occurrence of chemical reactions with appreciable speeds might be considered doubtful, and this expectation is generally valid in bulk ice. At the surface of ice, however, reactions may occur even at very low temperatures, sometimes at such appreciable speeds that they affect the global environment. Ice surfaces can be used as a testing ground for the investigation of water-molecule interactions, solvation phenomena, and processes in two-dimensional environments.^{38,40}

7.1. Reactive Scattering and Sputtering

For the study of ice surfaces, the projectile ion is typically used as a probe rather than as a means of modifying the surfaces. Monoatomic projectile ions such as Cs^+ and noble gas ions have been widely used.^{38,174} In particular, reactive scattering of Cs^+ has been extensively used in recent investigations of reactions at ice surfaces.^{38,39} In the original publications, the term "reactive ion scattering (RIS)" is used, but the term "reactive scattering" is used in the current review. In certain cases, ice surfaces contain pre-existing ions such as those produced by the ionization of electrolytes. These pre-existing ions can be detected by means of low-energy sputtering (LES).⁴⁵⁴ Ion desorption from surfaces can also occur by

Table 9. Hyperthermal Energy Collisions at Condensed Molecular Solids

method (projectile ion)	system	aim/observations	refs
reactive scattering and LES (Cs ⁺)	H_2O-D_2O	rate and activation energy of self-diffusion and H/D exchange of water	462, 476, 479, 496
	H ₃ O ⁺ -water ice	affinity of protons for the ice surface and proton transfer mechanism	478-480
	$H_{3}O^{+}-H_{2}O-D_{2}O$	hydronium ion-mediated proton transfer at the ice surface	495
	$OH^H_2O-D_2O$	hydroxide ion-mediated proton transfer at the ice surface	497
	HCl–water ice	molecular and ionized states of HCl on ice	457, 477
	Na-water ice	hydrolysis of Na	484
	H ₃ O ⁺ -NH ₃ -water ice	incomplete proton transfer from H_3O^+ to NH_3 on the ice surface	454, 458
	H_3O^+ -amine-water ice	proton transfer efficiency on ice is reversed from the order of amine basicity	502
	CO ₂ -Na-water ice	CO ₂ hydrolysis is not facilitated by a hydroxide ion	463
	NO ₂ -water ice	NO ₂ hydrolysis produces nitrous acid	465
	SO ₂ -water ice	SO ₂ hydrolysis occurs through various intermediates	511
	C ₂ H ₄ -HCl-water ice	electrophilic addition reaction mechanism at the condensed molecular surface	466
	ethanol/2-methylpropan-2-ol—water ice	$S_{\rm N} 1$ and $S_{\rm N} 2$ mechanisms at the condensed molecular surface	505
	NH ₃ -water ice and UV irradiation	ammonium ion formation	608
	CH ₃ NH ₂ -water ice and UV irradiation	protonated methylamine formation	483
	$CH_3NH_2-CO_2$ -water ice and UV irradiation	glycine and carbamic acid formation	464
	NaX-water ice (X = F, Cl, Br)	surface/bulk segregation and transport properties of electrolyte ions	472-474
reactive scattering (Cs ⁺)	CO and CO_2 on $Pt(111)$	mechanism of Cs ⁺ reactive ion scattering	89
	Ar, Kr, Xe, and N ₂ on Pt(111)	adsorbate mass effect on the reactive ion scattering cross-section	609
	C_2H_4 on Pt(111)	dehydrogenation mechanism of ethylene to ethylidyne	459, 610
	C ₂ D ₄ and H on Pt(111)	ethylidene intermediate in H/D exchange reaction with ethylene	80, 610
reactive scattering (H ⁺)	water ice and alcohol	H ₂ ⁺ formation	469
CS (Ar ⁺)	water ice-chloromethanes (CCl ₄ , CHCl ₃ , CH ₂ Cl ₂)	except CCl ₄ , others undergo diffusive mixing	174
	water ice-simple carboxylic acids	structural reorganization on the ice film	175
	water ice	micropore collapse in the top layers of the ice film	176
	water ice-butanol		494

means of the charge exchange processes of CS.^{174,175} Table 9 lists ice systems investigated using hyperthermal energy ions.

The Cs⁺ reactive scattering was first discovered on a Si surface with chemisorbed water molecules: Cs⁺ ions scattered from the surface picked up water molecules to form Cs⁺-water complexes.^{78,95,96} Since then, such processes have been examined on various surfaces and molecular adsorbate systems, including ice films,^{79,80,87,89,97,454–466} and the mechanism has been investigated theoretically.^{88,98,467,468} These studies clearly suggest that reactive scattering occurs via an ER-type abstraction mechanism, discussed in section 1.1.2. Figure 27 illustrates the reactive scattering mechanism with four representative snapshots of a Cs⁺ scattering trajectory in a classical MD simulation.^{39,88} The abstraction reaction is driven by the ion-dipole attraction force between the Cs⁺ ion and an adsorbate molecule. The impinging projectile first releases part of its initial energy to the surface (Figure 27b) even without direct collision with the adsorbate. Subsequently, the projectile pulls the adsorbate gently away from the surface in its outgoing trajectory (parts c and d of Figures 27 in sequence), leading to the formation of a Cs⁺-molecule complex. The velocity of the outgoing Cs⁺ must be slow enough to accommodate the inertia of the adsorbate.^{88,98} As a result, adsorbates of low mass and small binding energy are efficiently abstracted. A heavier projectile like Cs⁺ transfers more energy to the target surface, and its lower velocity in the outgoing trajectory enhances the efficiency of reactive scattering events.⁹⁵ Detailed aspects of Cs⁺



Figure 27. Illustration of the reactive scattering mechanism of a Cs^+ ion in four snapshots of a scattering trajectory from a Pt(111) surface: (a) initial positions before impact, (b) impact of the Cs^+ and energy release to the surface, (c) Cs^+ pulling the adsorbate away in its outgoing trajectory, (d) slow outgoing Cs^+ dragging the adsorbate along and forming a Cs^+ -molecule association product. Reprinted with permission from ref 88. Copyright 2004 John Wiley and Sons, Inc.

reactive scattering and its application for surface analysis have been reviewed. $^{\rm 39}$

Figure 28 shows an example of reactive collision mass spectra, which were obtained on a D_2O ice film exposed first to



Figure 28. Cs⁺ reactive scattering and LES spectra monitoring the H_3O^+ - NH_3 reaction on ice. The D₂O film [3–4 bilayers (BLs), 1 BL = 1.1×10^{15} water molecules cm⁻²] was exposed first to 0.5 L of HCl to generate hydronium ions and then to NH₃ at varying exposures: (a) 0.02 L, (b) 0.3 L, (c) 0.7 L. The sample temperature was 100 K. The Cs⁺ collision energy was 30 eV. Reprinted with permission from ref 454. Copyright 2001 John Wiley and Sons, Inc.

0.5 L of HCl gas and then to varying amounts of NH₃ gas at 140 K.⁴⁵⁴ The spectra show peaks at higher masses than Cs⁺ (m/z 133), viz., CsNH₃⁺ at m/z 150, Cs(D₂O)_n⁺ (n = 1, 2) at m/z 153 and 173, and CsHCl⁺ at m/z 168, indicating the presence of the corresponding molecules on the surface. The intensities of H/D-exchanged species represent their original concentrations on the surface, because H/D isotopic scrambling does not occur during the ion/surface collision time ($<1 \times 10^{-12}$ s).

The conversion efficiency of a neutral adsorbate (X) into a gaseous ion (CsX^+) ranges from $\sim 10^{-4}$ for chemisorbed species to ~ 0.1 for physisorbed small molecules. Typical product ion signal intensities for ice film surfaces are much stronger than those for chemisorbed species. Also, it is worthwhile to point out that reactive collisions of Cs^+ are ineffective for detecting large molecules such as polymers or long-chain SAM molecules.⁴⁶¹

The mass spectra in Figure 28 also show LES signals corresponding to pre-existing ions on the surface. The hydronium ions seen are produced by the spontaneous ionization of HCl on the ice surface, and they undergo proton transfer reactions with NH₃ to generate ammonium ions. The spectra show characteristic H/D isotopomers of each species produced by H/D exchange reactions with D₂O molecules. The LES signals due to preformed hydronium and ammonium ions exhibited sputtering thresholds at Cs⁺ impact energies of 17 and 19 eV, respectively.⁴⁵⁴ On the other hand, on pure H₂O and NH₃ surfaces, these ions were emitted only above ~60 eV

due to their formation during secondary ion emission.⁴⁵⁴ It was also found that ultra-low-energy (a few electronvolts) collision of H⁺ with the ice surface can produce $H_2^{+.469}$ The reaction proceeds more efficiently on amorphous solid water than crystalline water, reflecting differences in the surface concentration of dangling O–H bonds. Simple alkanols also behave in the same manner. The combined occurrence of reactive scattering and LES provides a powerful means to probe both neutral molecules and ions on surfaces and, therefore, to follow reactions on ice surfaces such as the ionization of electrolytes and acid–base reactions, which are described below.

7.2. Surface Composition and Structure

Impurities in ice become concentrated in the quasi-liquid layers in the surface and at grain boundary regions due to the "freeze concentration effect", and this has important consequences for atmospheric reactions on ice surfaces.⁴⁷⁰ However, there appear to be numerous exceptions to this general trend, where the surface segregation behavior of the dissolving species and their bulk solubility are determined by thermodynamic factors specific to individual chemical species. A good example is the formation of stable bulk phases of clathrate hydrates.⁴⁷¹ Chemical specificity in the segregation phenomena can be studied by monitoring the surface populations of the dissolving species during the slow annealing of ice samples. Kang and co-workers⁴⁷²⁻⁴⁷⁴ examined these propensities in Na⁺ and halide ions at the surface and in the interior of ice films. They ionized NaF, NaCl, and NaBr molecules on ice films by the vapor deposition of the salts, and the variation in the surface population of the ions was monitored as a function of the ice temperature for 100-140 K by using LES. As shown in Figure 29, the LES intensities of Na^+ and F^- ions decrease with an increase in temperature above ~120 K, whereas the Cl⁻ and Br⁻ intensities remain unchanged.^{473,474} The results indicate that Na⁺ and F⁻ ions migrate from the ice surface to the interior at the elevated temperatures. The migration process is driven



Figure 29. Surface populations of Na⁺ (\Box), F⁻ (\blacktriangle), Cl⁻ (\diamondsuit), and Br⁻ (\odot) ions as a function of the ice film temperature measured from LES intensities of the ions. NaF, NaCl, and NaBr were deposited for a coverage of 0.8 ML for each salt on a D₂O ice film grown at 130 K. The LES signals were measured at the indicated temperatures of salt adsorption. The LES intensities are shown on the normalized scale with the intensity at 100–105 K as a reference. The Cs⁺ beam energy was 35 eV. The figure is drawn on the basis of the data in refs 473 and 474.

by the ion solvation energy, and it requires that surface water molecules have enough mobility to facilitate ion passage at temperatures above 120 K. It is worth noting that such a segregation behavior for ice agrees with the negative adsorption energy of these ions at water surfaces predicted by the Gibbs surface tension equation and MD simulations.⁴⁷⁵

An interesting property of hydronium ions observed in recent studies is that they preferentially reside at the surface of ice rather than in its interior. Evidence of this property has come from a variety of experimental observations over the past decade.^{445,476–482} The adsorption and ionization of HCl on an ice film promotes H/D exchange on the surface.⁴⁷⁶ However, vertical proton transfer to the film interior is inefficient. Continuous exposure of HCl gas on the ice film led to saturation in the hydronium ion population at the surface, and the amount of HCl uptake required for this saturation was independent of the thickness of the ice film.⁴⁷⁷ These observations suggest that protons stay at the ice surface and hardly migrate to the interior. This behavior can be attributed either to the active trapping of protons at the surface or to the lack of proton mobility to the ice interior.^{478,479}

The observation of asymmetric transport of protons at an ice surface and in its interior led to the conclusion that protons have a thermodynamic propensity to reside at the ice surface.^{478,479} The surface preference of the proton allows reinterpretation of the results for the H_3O^+ SL experiment conducted by Cowin et al.,⁴⁴⁵ who showed that H_3O^+ ions deposited onto an ice film surface remained on the surface over a wide range of temperatures (section 6.9). This observation was initially interpreted to indicate the immobility of protons through the ice films.⁴⁴⁵ However, the thermodynamic affinity of a proton for the ice surface and the proton's known mobility in the interior suggest an alternative explanation of the observation consistent with the well-known proton transport mechanism in ice and the observations of related experi-ments.^{471,476-479,481} More recently, the ice systems used in the H_3O^+ SL experiment were re-examined by careful control experiments, ^{482,483} confirming the asymmetric transport behavior of protons.

The properties of hydroxide ions were also studied. Hydrolysis of Na atoms on an ice surface produced Na⁺ and hydroxide ions at the surface.⁴⁸⁴ The LES intensity of hydroxide ions increased as the temperature was raised from 95 to 135 K. The result showed that hydroxide ions have a tendency to float on the ice surface, similar to hydronium ions. The LES intensity of Na⁺ ions shows that these ions migrated to the ice interior, in agreement with the observation of the ion segregation experiments with sodium halide salts mentioned above.^{473,474}

Studies of the dissolution behavior of alkali-metal ions at liquid water surfaces show that polarizable ions such as large halide anions (Br⁻ and I⁻) have a propensity to reside at the surface, whereas F⁻ and Na⁺ avoid surface residence.⁴⁷⁵ These trends agree nicely with the observations made for the ice systems.^{473,474} For the cases of hydronium and hydroxide ions, their interfacial distributions for liquid water are a controversial issue in current investigations of the subject. Various experimental methods (vibrational sum-frequency generation spectroscopy, ζ potentials, and gas bubbles) and theoretical calculations report different results regarding whether water surfaces are acidic or basic relative to the interior.^{481,485}

A chemical sputtering method with hyperthermal noble gas ions has been used to probe the structural changes of condensed molecular solid surfaces.¹⁷⁵ It is known that carboxylic acids can exist either in a chainlike crystalline form or as dimers in the solid state, depending upon the preparation temperature.⁴⁸⁶⁻⁴⁸⁸ When acetic acid is vapor-deposited onto a metal surface at 110 K, it exists in a dimeric amorphous form, but on a thin ice film, it exists as a chainlike crystalline phase at the same temperature. These two forms of acetic acid were distinguished by detecting the selective emission of acetic acid molecular cation from the amorphous phase using 30 eV Ar⁺ collisions.¹⁷⁵ The crystalline form did not produce the molecular cation in the sputtering spectra; instead the formation of the CH₃CO⁺ fragment was the characteristic signature of this structure. Formic acid followed a behavior similar to that of acetic acid, but propionic acid suppressed the formation of the molecular cation in the CS spectra since it existed as dimers in its crystalline form also.

Hyperthermal projectiles do not closely approach the core of individual surface atoms, but are reflected at a larger distance from the surface so they feel the surface as a relatively flat structure.⁴⁶⁷ For this reason, hyperthermal ion scattering may not be an atomistic structural probe of a surface. However, it can be used to monitor changes in the ensemble-averaged structure of surfaces. Cyriac and Pradeep¹⁷⁶ observed that the scattering of ultra-low-energy (~1 eV) Ar⁺ ions is sensitive to the surface morphology of ice films. The Ar⁺ scattering intensity from an amorphous solid water film increased by a factor of 2 as the temperature increased from 110 to 125 K (Figure 30). Such a change was absent in the case of crystalline



Figure 30. Scattering intensity variation of 1 eV Ar⁺ collisions at bare copper (\bigcirc), 50 ML of ASW(H₂O) (\square), 50 ML of ASW(D₂O) (\blacksquare), and 50 ML of crystalline ice (H₂O) (\bullet). The continuous gray line shows an approximate representation of the overall behavior of ASW. Inset: typical Ar⁺ scattering mass spectra of 50 ML of ASW for three different temperatures and averaged for 50 scans. The collision energy was 1 eV. Reprinted from ref 176. Copyright 2008 American Chemical Society.

ice films and for other condensed molecular solids. The Ar⁺ intensity dropped around ~160 K due to water desorption and then subsequently increased as the bare copper surface was exposed. These results suggest that an amorphous ice film undergoes a structural transformation at 110–125 K, which is below the onset temperature of the glass transition (136)

K)^{489,490} and well below the appearance of quasi-liquid layers.⁴⁹¹ The observed structural change may involve the collapse of micropores in the top layers of the ice surface.

7.3. Transport Properties

Several unique reaction properties found at an ice surface compared to its liquid-phase counterpart are intimately related to the difference in molecular mobility in the two phases. Selfdiffusion at ice surfaces has been studied by measuring the kinetics of the diffusional mixing of H₂O and D₂O molecules at the surface.⁴⁶² In this study, a thin H₂O ice film was prepared and then covered with a fractional layer of D_2O . The diffusion of water molecules in the top one to two molecular layers of the surface gradually changed the relative populations of H₂O and D₂O in the outermost layer and was monitored as a function of time by reactive scattering. The study indicated that the interlayer diffusion in the surface took several seconds at 140 K and about 1 h at 100 K. Temperature-dependent kinetic measurements yielded a self-diffusion activation energy (E_a^s) of 14 \pm 2 kJ mol^{-1}. In comparison, the self-diffusion activation energy in bulk ice (E_a^{bulk}) was measured to be $71 \pm 4 \text{ kJ mol}^{-1}$ in laser-induced thermal desorption experiments.⁴⁹² These studies show that surface diffusion occurs significantly faster than bulk diffusion in the temperature regime of 100-140 K, and the gap between the two diffusion rates widens exponentially as the temperature decreases due to the large difference in the activation energies.⁴⁰ This illustrates that, if reactions of ice occur at low temperatures, they will occur preferentially at the surface where molecules have a much higher mobility, rather than in the interior.

The diffusion of chloromethane molecules $(CCl_4, CHCl_3, CH_2Cl_2, and CH_3Cl)$ through ice films has been studied by the CS method.¹⁷⁴ To show the sensitivity of CS, the CS spectra at two different temperatures (125 and 130 K) from a system prepared by depositing 50 ML of CHCl₃ followed by 250 ML of H₂O at 110 K are shown in Figure 31. The CHCl₃ concentration increases at the surface with increasing temperature. The study showed that, except for CCl₄, other



Figure 31. Intensities of the $CHCl_2^+$ and $CHCl_3^+$ peaks are increased due to the change in concentration of $CHCl_3$ on the surface with increasing temperature. The projectile ion is 30 eV Ar⁺, and the system is 50 ML of $CHCl_3@250$ ML of ASW. With the temperature rise from 125 K (lower trace) to 130 K (upper trace), more $CHCl_3$ diffuses through ice overlayers. Reprinted from ref 174. Copyright 2007 American Chemical Society.

chloromethanes investigated, viz., CHCl₃ and CH₂Cl₂, underwent diffusive mixing with amorphous solid water (ASW) in the temperature range of 100-150 K.¹⁷⁴ CCl₄ was not able to diffuse through more than four overlayers of ASW. The hydrogen bond network of the ASW film restricted the transport of CCl₄ molecules. Other molecular solids, D₂O and CH₃OH, also acted as barriers to diffusive mixing of CCl₄. The interaction energy between chloromethanes and water in the solid state was in the order $CCl_4 < CHCl_3 < CH_2Cl_2 < CH_3Cl_1$ which is the reverse order of the liquid-phase interactions.⁴ Considering that the overall interaction between chloromethanes and water is based on the atomic charge of chlorine and its molecular polarizability, replacement of a Cl atom by a H atom can have a significant effect on diffusivity in ice. Using Ar⁺ sputtering, it was found that 1-butanol undergoes diffusive mixing with water ice.⁴⁹⁴ Even after deposition of 1000 ML of ASW over solid 1-butanol, both species are observed on the surface. By contrast, water is not seen when 1-butanol is deposited over ASW. The results suggest that long-chain alcohols may act as barriers to H₂O diffusion because of their hydrophobic nature.

Proton mobility is a fundamental and important property in the physics and chemistry of ice. As discussed in section 7.2, there is a general consensus that a proton is mobile in ice at elevated temperatures.^{478,479,481} Also, a proton tends to reside at the surface of ice where it is stabilized.^{478-480,482} The hyperthermal energy ion probe offers a tool to pursue the proton transfer behavior by looking into the H/D isotopomers of water molecules and hydronium ions at ice surfaces generated by proton-induced H/D exchange reactions.^{478,479} Below 120 K, at which the rotational and diffusional motions of water molecules are frozen, a proton hopping relay (Grötthuss mechanism) is the only possible mechanism of proton transfer in ice. This is evidenced by the LES detection of H_3O^+ at the surface of the H₂O/proton/D₂O film and also by the absence of D-substituted hydronium ions at the surface. Protons can move only across a limited distance by this mechanism, but nevertheless, this makes protons a unique mobile species in low-temperature ices, whereas water molecules and other foreign species are virtually frozen in position. Upon the activation of molecular rotations which occurs at temperatures above 125 K, the hop-and-turn process starts to occur involving the coupling of proton hopping and water molecule reorientation. All these proton transport processes can occur below the onset temperature (130 K) of water molecule diffusion near the ice surface, indicating that proton transfer can occur more easily than water self-diffusion.⁴

Proton transfer along the surface of ice was examined through the measurement of the H/D exchange kinetics of surface H₂O and D₂O molecules in the presence of excess protons generated from HCl ionization.^{476,495} Protons were transferred from hydronium ions mostly to the adjacent water molecules when the surface temperature was low (70 K), but the rate and propagation range of the proton transfer increased as the temperature increased above 90 K.⁴⁹⁶ This finding shows that the proton transfer process at an ice surface is thermally activated, and there exists an energy barrier of substantial magnitude (10 ± 3 kJ mol⁻¹) for the proton transfer.⁴⁹⁶ This is in agreement with the thermodynamic affinity of protons for ice surfaces, a conclusion derived from independent observations for the surface segregation of protons (section 7.2).^{478–480,482}

On a pure ice film surface in the absence of externally added protons, the H/D exchange reaction occurs slowly compared

to that observed on the proton-rich ice surface.⁴⁹⁵ The activation energy of the reaction was also higher ($17 \pm 4 \text{ kJ} \text{ mol}^{-1}$) on the pure ice surface. This is because H/D exchange on this surface requires the formation of ion pairs (H_3O^+ and OH^-) which require thermal energy in addition to the occurrence of proton transfers.

Similar experiments performed with excess hydroxide ions on ice films⁴⁹⁷ showed that hydroxide ions, like hydronium ions, mediate proton transfer at an ice surface and promote the H/D exchange of water molecules. The Arrhenius activation energy of $9.4 \pm 2.0 \text{ kJ mol}^{-1}$ was estimated for the proton transfer mediated by hydroxide ions, which is comparable in magnitude to the activation energy for the hydronium ion-mediated proton transfer. These studies indicate that proton transfer at an ice surface involves a substantial energy barrier, regardless of whether the process is mediated by hydroxide ion.

7.4. Acid–Base Chemistry

Available spectroscopic tools to investigate acid—base chemistry at ice surfaces are few, for example, IR spectroscopy,^{498–500} metastable impact electron spectroscopy (MIES),⁵⁰¹ and the hyperthermal ion beam techniques described in this review. Acid—base reactions are important in ice surface chemistry because they are intimately related to two important properties of ice surfaces discussed in the previous sections: (i) thermodynamic affinity of protons and hydroxide ions for ice surfaces and (ii) unique mobility of protons in ice.

The simplest and most extensively studied example of an acid–base reaction on ice is the ionization of strong protic acids.⁴⁹⁸ Experiments performed using a hyperthermal energy Cs^+ ion probe shows that HCl partially ionizes to hydronium and chloride ions on ice films at temperatures below 120 K and that undissociated HCl also exists.^{457,477} The presence of an undissociated HCl molecule on the surface was evident from the CsHCl⁺ signal, while hydronium ions (HD₂O⁺ and D₃O⁺) and hydrated clusters (HD₄O₂⁺ and D₅O₂⁺) represented the ionized form.⁴⁵⁷ The results indicate that, although HCl is a strong acid which ionizes completely in an aqueous solution, it acts as a weak acid on ice surfaces at low temperatures, and the degree of ionization varies with the temperature and morphology of the ice surface.

As a model case of acid-base reactions involving proton transfer on ice, Park et al.454,458,502 conducted detailed investigations of the reactions between the hydronium ion and amine molecules, including NH₃. For example, the hydronium ion-ammonia system was prepared by doping a D_2O ice film with HCl followed by dosing with NH₃ gas. The ratio of proton donors to acceptor was changed by varying the NH₃ concentration. Reactive scattering spectra given in Figure 28 show the donor and acceptor species present on the surface at varying concentrations of NH₃.⁴⁵⁴ The absence of NH₃ molecules on the surface indicates that proton transfer from hydronium ion to ammonia is complete. At a high coverage of NH_3 (spectrum b), however, the $CsNH_3^+$ signal shows that a substantial portion of NH3 remains unconsumed despite the coexistence of D₃O⁺. In fact, all donor and acceptor species of the reaction $(NH_3, NH_3D^+, D_2O_1 \text{ and } D_3O^+)$ coexist even beyond the equivalence point of the titration. This shows that the acid-base reaction does not reach a true equilibrium on the ice surface due to incomplete proton transfer, in contrast with its complete occurrence in an aqueous solution at room temperature.

The extent of proton transfer was evaluated by measuring the reaction quotient (Q) of the reaction, defined by $Q = [H_2O][BH^+]/[H_3O^+][B]$, where B is an amine, as a function of amine exposure. As Figure 32 shows, the Q value on an ice



Figure 32. Reaction quotient (*Q*) for proton transfer from hydronium ion to $NH_3(\bullet)$, $CH_3NH_2(\Box)$, and $(CH_3)_2NH(\bullet)$ measured as a function of amine exposure on an ice surface. The surface hydronium ions were produced by adding 0.3 L of HCl onto the ice film at 60 K and then warming it to 140 K. The donor and acceptor populations were measured from the corresponding LES and RIS signals. Reprinted with permission from ref 502. Copyright 2007 John Wiley and Sons, Inc.

surface is much smaller than the equilibrium constant of the same reaction in the gas phase or in an aqueous solution, and Q decreases with increasing amine exposure. The relative proton transfer efficiency by various amines deduced from these results follows the order NH₃ > (CH₃)NH₂ \approx (CH₃)₂NH,⁵⁰² but this is opposite the trend in intrinsic basicity of amines or their basicity in aqueous solutions. Thermochemical analysis suggests that incomplete solvation of reactant and product species at the ice surface reduces the proton transfer efficiency and reverses the order of the proton-accepting abilities of amines.

The hydronium ions formed by UV irradiation of ice transfer protons to methylamine molecules adsorbed on the film surface to form methylammonium ions (CH₃NH₃⁺), and the proton transfer occurs via a tunneling mechanism (hopping relay) at low temperature (50–130 K).⁴⁸³ The methylammonium ion was stable at the ice surface, in contrast with its spontaneous deprotonation to a neutral methylamine molecule in aqueous solution. Later, the study was extended to ammonium ion (NH₄⁺), which was formed through UV photolysis of an NH₃–H₂O ice mixture.⁵⁰³ The IR spectrum of NH₄⁺ suggests the possibility that it is formed in interstellar ice particles and contributes to the 6.85 μ m band discovered in the astronomical observations of dense molecular clouds using an infrared telescope.⁵⁰⁴

7.5. Chemical Reactions

Reactions between hydrogen halide and the alcohols ethanol and 2-methylpropan-2-ol are well-known to follow $S_N 2$ and $S_N 1$ pathways, respectively, in the liquid phase. The intermediate states of these reactions are protonated alcohols and carbocations, which exist only for transient times and rapidly convert to alkyl halides. However, these $S_N 1$ and $S_N 2$ intermediates are stabilized when the corresponding reactions occur on solid alcohol films at a low temperature.⁵⁰⁵ Specifically, HBr reacts with the ethanol surface, exclusively producing protonated ethanol species. The reaction between HBr and 2-methylpropan-2-ol resulted in protonated 2-methylpropan-2-ol and the *tert*-butyl cation in 20% and 78% yields, respectively. Importantly, alkyl bromides, which are the final products of the reactions in liquid solvents, were hardly detected on the molecular films. This indicates that the reactions on the frozen films are kinetically controlled, in contrast with the thermodynamically controlled reactions in the liquid phase. The kinetic barriers on the cold molecular surfaces stabilize the ionic intermediates (protonated alcohols and *tert*-butyl cation) and effectively block the completion of the S_N1 and S_N2 reaction pathways by impeding the diffusive encounter between the halide ion and the alcohol counterion.⁵⁰⁵

In an analogous study, the electrophilic addition reaction of ethene with HCl was investigated on frozen molecular films.⁴⁶⁶ The acid-catalyzed electrophilic addition reactions of alkenes are believed to occur through alkyl cation intermediates, but primary alkyl cations such as an ethyl cation have never been identified using spectroscopy, even for reactions in superacids.⁵⁰⁶ On a water ice film, the reaction of ethene with HCl initially produced the π complex of HCl and ethene at temperatures below about 93 K.466 LES was used to detect a $C_2H_5^+$ signal on the surface at temperatures of 80-100 K, which indicated the formation and kinetic stabilization of an ethyl cation-like species. This species dissociated into ethene and hydronium and chloride ions at high temperatures, but it did not complete the final step on the potential surface to produce ethyl chloride. The ethyl cation-like species was not formed in the reaction of ethene with hydronium ion or when the reaction of ethene with HCl occurred on a frozen ethene film, indicating that the ethyl cation-like species was formed via direct proton transfer from molecular HCl to ethene in water solvating environments. The study shows evidence that the reaction involves an intermediate species that has an ethyl-like structure with ionic character, but it remains uncertain whether this species is actually an ethyl cation or a structure intermediate between the HCl-ethene π complex and its ionized state.

Inorganic reactions studied on ice films to date include the hydrolysis of alkali-metal atoms^{484,507–509} and the reactions of simple oxide gases, viz., $\rm CO_2$,⁴⁶³ $\rm NO_2$,⁴⁶⁵ and $\rm SO_2$.⁵¹¹ Na⁺ and OH⁻ ions, produced by hydrolysis of Na, were efficiently solvated by water molecules at all temperatures investigated, whereas the sodium hydroxide molecule was found to solvate only at high temperatures.⁴⁸⁴ The OH⁻ ions tend to reside at the film surface, whereas Na⁺ ions migrate to the film interior. The adsorbed Na atoms completely reacted away without forming neutral Na clusters on the surface when the Na coverage was lower than 1 ML. These observations were complementary to the results of the TOF SIMS and metastable impact electron spectroscopy (MIES) studies of Na hydrolysis on ice films obtained under the conditions of lower temperature (15–100 K) and higher Na coverage (>1 ML) (section 8.6).^{507–509}

Reactions of acidic oxide gases at the surfaces of snow and ice particles are important to atmospheric chemistry and environmental sciences.⁵¹⁰ While CO₂ gas is unreactive to the ice films regardless of the presence or absence of excess hydroxide ions on the surfaces,⁴⁶³ SO₂⁵¹¹ and NO₂⁴⁶⁵ readily react with the ice surface to produce various chemical species even at low temperatures (80–150 K). Figure 33 shows spectra due to reactive scattering and LES from a D₂O ice film on which SO₂



Figure 33. (a) RIS mass spectrum obtained from a D_2O ice film exposed to SO_2 gas. (b) LES spectrum of negative ions. The ice film (4 BL thickness) was exposed to 0.2 L of SO_2 at 80 K, and the RIS and LES measurements were made at 140 K. The RIS signals at masses above m/z = 190 amu/charge were magnified by the factors indicated. (c) Temperature-programmed RIS and LES measurements for the signals of interest detected on the surface exposed to SO_2 at 80 K. The RIS yield on the left ordinate iss defined as the ratio of the RIS product to the Cs⁺ signal intensity (CsX⁺:Cs⁺). The temperature ramping rate was 1 K s⁻¹. Data were taken from Figures 1 and 2 of ref 511. Copyright 2009 American Chemical Society.

is absorbed at 140 K. Spectrum a shows that SO₂ adsorption produces signals of $CsSO_2^+$ (m/z 197), $CsDSO_2^+$ (m/z 199), and $Cs(D_2O)(SO_2)^+$ (m/z 217) in reactive scattering experiments. The $CsSO_2^+$ and $Cs(D_2O)(SO_2)^+$ signals indicate the presence of molecular SO₂ adsorbates. Spectrum b shows the negative ion LES signals from the surface, which include OD⁻ (m/z 18), SO_2^- (m/z 64), DSO_2^- (m/z 66), and DSO_3^- (m/z 82). The spectra show that SO₂ is transformed into various molecular anions by hydrolysis on the surface.

When the ice film with SO₂ adsorbates was warmed slowly from 80 to 150 K, the signals of various SO₂-related species appeared and disappeared at different temperatures (see Figure 33c).⁵¹¹ The results indicate that physisorbed SO₂ species (detected as $CsSO_2^+$) sharply decrease during the temperature increase from 100 to 140 K. In the narrow temperature range of 130–150 K, DSO₂ (detected as $CsDSO_2^+$), DSO_2^- , and $DSO_3^$ intensities grow at the expense of the decreasing SO_2^- intensity, indicating the conversion of SO_2^- to these species. Combined hyperthermal energy ion collision and TPD experiments indicate that the reaction of SO_2 on deuterated ice produces three types of surface species: a solvated SO_2 species with a partial negative charge, a DSO_2 species, and an anionic $DSO_3^$ like species.

Table 10. SIMS Data for Condensed Molecular Solids

primary ion (keV range)	system (15–200 K)	some sputtered species	aim/observations	refs
Au ⁺	water ice	$(H_2O)_nH^+$, $(H_2O)_n^+$, $(H_2O)_{n-1}OH^+$	intensity of $(H_2O)_n^+ > (H_2O)_nH^+ \sim (H_2O)_{n-1}OH^+$	517
Au_3^+	water ice	$(H_2O)_nH^+$, $(H_2O)_n^+$, $(H_2O)_{n-1}OH^+$	intensity of $(H_2O)_nH^+ > (H_2O)_n^+$, when $n < 20$	517
Au_3^+, C_{60}^+	water ice	$(H_2O)_nH^+$, $(H_2O)_n^+$, $(H_2O)_{n-1}OH^+$	$10^4~{\rm increase}$ in yield compared to that of ${\rm Au^+}$	517
Au_3^+, C_{60}^+	water ice	$(H_2O)_nOH^-$	less than 10 times compared to that of positive ions	517
Au_3^+, C_{60}^+	water ice		depth profiling	591-593
C_{60}^{+}	water ice	$(H_2O)_nH^+, (H_2O)_n^+$	intensity of $(H_2O)_n H^+ > (H_2O)_n^+$, when $n < 20$	517
C_{60}^{+}	trehalose film		molecular depth profiling	520, 587
	histamine—ice		molecular depth profiling	589, 590
Ar ⁺ /C ₆₀ ⁺ / Ga ⁺	MX–water (MX = LiCl, KI, NaI, NaCl, etc.)	$((H_2O)_n M^{\pm} (M = Li^+, Na^+, K^+, Cs^+ \text{ or } F^-, Cl^-, I^-)$	cation water clusters > anion water clusters	563, 564
He ⁺ /Ar ⁺	CF ₄ @Pt(111)	$CF_{x}^{+}(x=0-3), F^{+}$		615
He ⁺	water ice	H^+ , H_3O^+ , $Ni(H_2O)^+$	existence of quasi-liquid form and dewetting at 160 K	530, 534
	CF ₄ -D ₂ O	efficient production of $(D_2O)D^+$ ions	$2 \mbox{ orders of magnitude higher than that of a pure D_2O\mbox{ film}$	568
	methanol–D ₂ O	$(CH_3OH)H^+$, $(CH_3OH)D^+$, $(CH_3OD)D^+$	complete intermixing above 136 K, hydrophilic hydration above 120 K, H/D exchange above 140 K, determined T_g of methanol	515, 530, 558, 565
	ethanol $-D_2O$	$(C_2H_5OH)H^+$, $(C_2H_5OH)D^+$, $(C_2H_5OD)D^+$, CH_2OH^+	complete intermixing above 140 K	566
	acetic acid $-D_2O$	$(CH_3COOH)H$, (CH_3COOH) D ⁺ , $(CH_3COOD)D^+$, CH_3CO^+	complete intermixing above 150 K, determined T_g of acetic acid	487
	methylamine $-D_2O$	$(CH_3NH_2)H$, $(CH_3NH_2)D$, $CH_2ND_2^+$ CH^+ CH^+ other common	complete intermixing above 140 K	569
	$methane - D_2 O$	CH_5 , C_2H_3 , other common ions		508
	$CO = D_2 O$	$D^{+}, D_{3}O^{+}, C^{+}, O^{+}, CO^{+}, C_{3}O_{2}^{+}$	complete intermixing at 15 K	010 572 (1(
	$CD_2 - D_2O$ CD_3OD – methylamine	$(CH_3NH_2)H^+, CH_2ND_2^+, (CH_3NH_2)D^+$	no complete intermixing at 15 K, determined T_g of CO ₂ of 50 K complete intermixing above 125 K	573, 616 567
	HCOOH-D ₂ O ice	$(D_2O)H^+$, $(D_2O)D^+$, (HCOOH) H^+	HCOOH stays mainly on the surface due to hydrophilic hydration, determined $T_{\rm g}$ of HCOOH	516, 572, 581
	$C_3H_7OH-D_2O$ ice	$C_2H_3^+$, $(D_2O)D^+$, etc.	hydrophilic hydration at 100–145 K, hydrophobic hydration at > 145 K	516
	C_6H_{14} / C_6F_{14} -D ₂ O ice	CH_3^+ , $C_2H_3^+$, CF^+ , CF_3^+ , etc.	dissolve into the bulk due to hydrophobic hydration	516
	C ₈ H ₁₈ -water ice	$C_2H_3^+$, $(D_2O)D^+$, etc.	hydrophobic hydration, incorporate into the bulk at <120 K	557
	C ₈ H ₁₈ -CH ₃ OH	$C_2H_3^+$, (CD ₃ OD)D ⁺ , etc.	stays on the surface until 135 K	557
	pyridine $-D_2O$	$(C_{5}H_{5}N)H^{+}, (C_{5}H_{5}N)D^{+}, C_{4}H_{n}^{+}, C_{3}H_{n}N^{+}, etc.$	D ₂ O dissolves in pyridine film above 110 K, pyridine stays on D ₂ O film until 180 K	559
	benzene–D ₂ O	$C_{3}H_{3}^{+}, C_{4}H_{n}^{+}, C_{6}H_{n}^{+}, \text{ etc.}$	benzene dissolves in D ₂ O film above 120 K by hydrophobic hydration, benzene stays on D ₂ O film	559
	butane-methanol	$C_2H_3', CD_3', etc.$	butane is incorporated into methanol below 70 K	535
	NH ₃ -HCl@water ice	NH_4^+ , CI , OH , etc.	hydration of NH_4Cl above 100 K	560
	NU – UCOOU–water ice	H_4 , CI, OH, etc.	hydration of NH_4Cl and HCl above 40 K	501
	LiX-water (X = Cl. Br. I)	Li ⁺ . X ⁻	above 140 K solubility increases at 160 K, evidence of deeply supercooled water	509, 538,
	NaCl-water	Na^+ Cl^-	Na ⁺ ion hydrated preferentially at low temperatures	539, 541 542
	LiI-ethanol	$(C_{a}H_{a}OH)Li^{+}$, $(LiI)Li^{+}$, etc.	LiL incorporated into the bulk	546
	CCl ₂ F ₂	$CClF_{2}^{+}, CCl_{2}F^{+}, CF^{+}, F^{+}$	crystallization and dewetting at 57 K	617
	<i>n</i> -hexane	$C_{m}H_{m}^{+}$ (m = 1-6)	glass transition at 110 K, dewetting at 130 K	537
	ethylbenzene	-m n (··································	intermixing at \sim 80 K, glass transition at \sim 118 K	618
	water, ethanol, etc. on p-Si (100)		onset of self-diffusion temperature	552-554
	Xe-water ice		Xe hydrated in the bulk of water up to 165 K	540
	D ₂ O-hexane	$C_2H_3^+$	dewetting at 165 K due to glass-liquid transition	532
	D ₂ O-dipalmitoyl- <i>sn</i> -glycero-3- phosphocholine	$C_2H_3^+$, NCH ₃ ⁺ , etc.	hydrophobic water adsorption starts at 133 K	574, 575
	D ₂ O– bis[trifluoromethanesulfon- yl]imide ([emim][Tf ₂ N])	$[\text{emim}]^+$, $C_2H_5^+$, CF_3^+ , $[Tf_2N]^-$, F^- , etc.	phase transition in water ice identified	576
	$[emim][Tf_2N]$	$[\text{emim}]^+$, $C_2H_5^+$,	crystallization at 200–220 K	536

Table 10. continued

primary ion (keV range)	system (15–200 K)	some sputtered species	aim/observations	refs
	D ₂ O-CH ₃ NH ₂	$(CH_3NH_2) H^+, CH_2ND_2^+, (CH_3NH_2)D^+$	H/D exchange reaction above 140 K	567
	CD ₃ OD-CH ₃ NH ₂	$(CH_3NH_2)H^+$, $CH_2ND_2^+$, $(CH_3NH_2)D^+$	H/D exchange reaction above 125 K	567
Ar ⁺	Cl_2 / Cl_2O / $ClONO_2$ -water ice	Cl ₁₋₅ ⁺ , Cl ₁₋₅ ⁺ , HOCl ⁻ , NO ⁺ , H ₂ NO ₃ ⁺ , water clusters, etc.	above 120 K, Cl ₂ undergoes reaction with ice surface to form HOCl, water, and HCl	569, 570, 583
	ClONO ₂ -HCl-water ice	Cl ₁₋₃ ⁻ , H ₂ OCl ⁻ , NO ₂ ⁻ , NO ₃ ⁻	formation of nitric acid at the surface	570
	Co-depositing SO_3-H_2O	$(H_2SO_4)H^+$, $(H_2SO_4)H_2O^+$, $(H_2SO_4)(H_2O)_{1-2}H^+$	formation of sulfuric acid monohydrate and tetrahydrate	582



Figure 34. Positive ion SIMS spectrum of water ice using Au^+ primary ions. Three series of cluster ions, $(H_2O)_n^+$, $(H_2O)_nH^+$, and $(H_2O)_{n-1}OH^+$, were observed; the first one is the most intense. Reprinted from ref 517. Copyright 2010 American Chemical Society.

The study of hydrolysis of NO_2 on ice films shows that NO_2 adsorbs molecularly on the ice surface at 90 K.⁴⁶⁵ Upon heating the surface to 140 K, NO_2 adsorbates are readily converted into nitrous acid (HONO) on the surface. The implication of this

observation for the atmospheric chemistry of NO_2 is that nitrous acid gas will be formed by the heterogeneous hydrolysis of NO_2 on condensed ice surfaces even during the night

without the absorption of sunlight, which is in accordance with field observations.

The examples shown above demonstrate that ice surfaces can be used to take a "frozen snapshot" of a reaction and to capture the reaction intermediates. Characterization of reaction intermediates trapped on the ice surface using ion scattering and sputtering methods reveals important clues for the reaction mechanism. Such investigations may also be useful for understanding the corresponding reactions at gas/liquid interfaces.

8. SIMS ANALYSIS OF CONDENSED MOLECULAR SOLIDS

Although organic SIMS was an active area of research in the 1980s, the literature available on SIMS or fast atom bombardment (FAB) analysis of frozen molecular materials is mainly due to Michl and co-workers.^{512–514} More recently, SIMS has become a valued tool in low-temperature studies (see Table 10). Sputtered species and their yields from condensed-phase molecular solids provide molecular information as well as the composition for a specific chemical environment. These aspects are important in fundamental understanding related to upper atmospheric chemistry. Inclusion of temperature-programming capabilities in TOF SIMS, viz., temperature-programmed (TP) TOF SIMS, is a remarkable development in the analysis of condensed molecular solids.^{515,516} It provides unique information on compositional changes/reactions with respect to temperature. A notable number of such investigations have been carried out by Souda and co-workers.

The use of cluster ion SIMS provides higher ion yields without significant chemical damage of condensed molecular solids. In some cases, yields were 10^4 times higher compared to that of an atomic ion source. ^{517,518} For example, Au₃⁺ or C₆₀⁺ is better than Au⁺ primary ions for generating protonated clusters. ⁵¹⁹ The yield was equivalent to ~1830 molecules per C₆₀⁺ collision at 15 keV, while these numbers were ~1200 and 94 for Au₃⁺ ion and atomic Au⁺ ion projectiles, respectively. It is suggested that the C₆₀⁺ sputter yield is about 3000 amu/keV for organic or ice films and 800 amu/keV for metallic targets. ⁵²⁰

Protonated water clusters, $(H_2O)_nH^+$, and normal water cluster ions, $(H_2O)_n^+$ (*n* up to several tens), are abundant in the sputtering spectra of pure water ice films. See Figure 34 for the positive ion spectrum of an untreated water ice film at ~100 K by 15 keV Au^+ bombardment. Clusters with up to n = 50 have been observed.⁵¹⁷ The protonated form of the water clusters is formed predominantly with cluster ion sources C_{60}^+ and Au_3^+ when the value of *n* is lower than 20.^{517,519} The increased density of surface protons leads to high yields of protonated species. The case is reversed, i.e., water cluster radical ions are abundant compared to the protonated form, when n is larger. Some long-range damage to the crystal structure as a result of sputtering explains the low abundance of protonated water clusters.^{SY7} Negatively charged water clusters, (H₂O)_nOH⁻ were also observed by both atomic and cluster primary ions, ⁵¹⁷ but the yield is far smaller (~10 times) compared to that of its positive counterpart. Dosing HCl onto an ice film doubles the yield of protonated water clusters.⁵²¹ It was found that the yield of protonated water clusters is reduced significantly in the presence of adenine and alanine.⁵¹⁹ This suggests a suppression effect, with the biomolecules taking up some of the available protons that form $(H_2O)H^+$ in the pure water ice.⁵¹⁸ In the case of solid methane, cluster ions $C_n H_x^+$ up to n = 20 are desorbed by low-energy He⁺ ion bombardment.⁵²²

MD simulation and experimental results on the nature of the neutrals ejected; solid C₆H₆ surfaces using atomic projectiles Ar⁺ and H_2^+ suggest that more than one mechanism operates.⁵²³⁻⁵²⁵ At submonolayer coverages of benzene molecules deposited on $Ag\{111\}$ surfaces, the kinetic energy of the ejected neutrals usually ranges from 0.25 to 1.00 eV, and these are ejected as a consequence of collisions with substrate particles.⁵²³ For multilayer coverage, the energy of the neutrals shows more of a thermal nature. A peak corresponding to extremely low kinetic energy (0.04 eV) becomes dominant. The thermal emission may be due to exothermic chemical reaction of fragments formed in a molecular collision cascade of C₆H₆ molecules. Another aspect to be considered in SIMS analysis of condensed molecular solids is the surface charge. These materials may behave similarly to insulator surfaces and charge up, but there is limited support for this so far. It is shown that the charge pattern generated using a primary ion source on frozen (T < 188 K) ionic liquid [emim][EtSO₄] was stable and could be viewed in a negative ion map of the surface.526

8.1. Phase Changes

It is believed that a glass transition (T_{α}) of ice occurs at 136 K_{r}^{490} but there are several who claim the T_{σ} value of water be assigned as 165 K on the basis of an unusually small endotherm in the heat capacity in comparison to the $T_{\rm g}$ scaled heat capacity between water and other inorganic glasses.^{527,528} The glass transition and crystallization of ASW films can be explored on the basis of molecular diffusion, the change in film morphology, and hydration/dehydration via interactions with another molecule. All of these characteristics are accessible by TP TOF SIMS measurements. The intermixing of isotopically labeled water molecules ($H_2^{16}O$ and $H_2^{18}O$) occurs at ~136 K, which is followed by a film morphology change at 160-165 K. These phenomena are ascribable to liquid properties.⁵²⁹ Note that these transition temperatures correspond to the conventional and reassigned $T_{\rm g}$ values of water. The methanol-water ice system has been used to probe changes occurring in the water ice film. The surface segregation of embedded methanol appears in secondary ions at the conventional $T_{\rm g}$ of 136 K.⁵³⁰ Ion intensities from the binary films prepared by deposition of 25 ML of H₂O on 25 ML of CD₃OD at 15 K are given in Figure 35a. From the figure it is clear that the H_3O^+ ion intensity dropped at 136 K whereas sputtered CD₃⁺ ions from methanol increased. The penetration of methanol though water overalyers can be connected to the emergence of a liquidlike phase. The observation of $(CH_3OD)D^+$ from CH_3OH (1) ML)/D₂O (50 ML) at 136 K suggests that the transition occurred along with isotope (H/D) exchange.⁵³¹ H/D exchange was induced above the glass transition (136 K) due to the translational diffusion of water molecules. Another system used to explore the phase changes in solid water was hexane-water ice.⁵³² In contrast to methanol, n-hexane incorporated in the bulk of an amorphous water film is immobilized at the conventional T_g (136 K) despite the occurrence of translational diffusion of water molecules. The molecules are released immediately before the film morphology change at 160 K. Changes in the structure of hydrogen-bonded cages of water are thought to be responsible for this behavior. At the conventional $T_{g'}$ translational diffusion of water occurs without the cage structure being changed.

Similarly, the T_g of methanol has been studied using CD₃OD and water.⁵³⁰ The transition at 80 K was due to molecular



Figure 35. (a) Temperature-programmed TOF SIMS intensities of CD_3^+ ions sputtered from the film of 25 ML of H_2O grown on top of 25 ML of CD_3OD . The inset shows the TPD spectra of CD_3OD , CD_3OH , and OH from H_2O from the same film. The intensities of H_3O^+ ions sputtered from the 1 ML of H_2O molecules adsorbed on the 50 ML CD_3OD film are given in (b). The intensities are compared for the films prepared at 15 K (porous-amorphous film), heated at 120 K (amorphous film), heated at 120 K (dewetting film), and heated at 120 K for 30 min (crystalline film). This figure is reprinted with permission from Figures 2 and 3 of ref 530. Copyright 2004 American Physical Society.

diffusion, and it could be assigned to the onset of a glass transition of the vapor-deposited methanol film. The deviation from the calorimetric $T_{\rm g}$ value of 103 K reflects the difference in structure or density between the vapor-deposited and liquid-quenched glasses. Figure 35b shows the evolution of the H₃O⁺ ion peak from a system prepared by depositing 1 ML of H₂O on a 50 ML CD₃OD film. Various films—porous-amorphous, amorphous, dewetting, and crystalline—were compared by monitoring the sputtered hydronium ion intensity. It is clear that the water molecule disappears from the porous amorphous methanol film below 100 K while it survives the amorphous film until 115 K. It can be inferred that long-range translational diffusion of methanol occurred at these temperatures.

In addition to water, there are many molecular solids which exhibit no apparent glass transition in calorimetric studies. Typical examples are *n*-alkanes. However, TP TOF SIMS analysis of *n*-pentane films revealed the occurrence of translational diffusion prior to crystallization at 80 K.⁵³³ Therefore, a liquidlike phase is expected to be created immediately before crystallization. Interestingly, the *n*-pentane films form droplets after crystallization, the dewetting temperature depending on the initial film thickness. This phenomenon is explainable as premelting of crystallites. In the case of *n*butane, crystallization occurs around 60 K, but a liquidlike phase is observed at temperatures higher than 80 K along with the solid–solid phase transition.⁵³³ Liquid–crystallite coexistence occurred for water⁵³⁴ and methanol⁵³⁵ as well. The former is attributed to quasi-liquid formed during the phase transition of crystalline ice ($I_c \rightarrow I_h$). The uptake of water molecules deposited on a crystalline methanol film at 120 K (see Figure 35b) might also be an indication of liquid–crystallite coexistence. Crystallization of the room temperature ionic liquid 1-ethyl-3-methylimidazolium bis-[trifluoromethanesulfonyl]imide ([emim][Tf₂N]) occurs in the temperature range of 200–220 K as evidenced from the increased yield of the sputtered [emim]⁺ ion.⁵³⁶

A metastable extension of normal liquid water is termed "deeply supercooled water", but its presence is still under debate. 527,528,537,543 The uptake of electrolytes into the bulk of glassy or crystalline water films is expected to be suppressed, and hence, one can explore the formation of deeply supercooled water from the interaction between the thin films of ASW and alkali-metal halides (e.g., LiCl, LiBr, NaCl, etc.). $^{509,538-542}$ A metastable extension of normal liquid water with molecules having long-range translational diffusion exists above the $T_{\rm g}$ (136 K) and before crystallization. 543 The formation of the alkali-metal halide solution could be attributed to the presence of supercooled liquid water. Using the TP TOF SIMS analysis, it was found that such a supercooled solution exists around 160–165 K. $^{538-542}$

In the case of glassy water, the presence of two distinct phases is confirmed experimentally, which is known as polyamorphism.⁵⁴⁴ Therefore, it is likely that ASW transforms to a low-density liquid (LDL) phase above its T_g (136 K), followed by another liquid phase, high-density liquid (HDL) or supercooled liquid, immediately before crystallization. LDL is considered to be an "ultraviscous liquid" as reflected by the poor solubility of the electrolyte. The liquid-liquid transition (LDL \rightarrow HDL) occurred at ~160 K as manifested by a drastic change in the solubility of the electrolyte (see Figure 36).^{538,540,541} This phenomenon can also be explained in terms of the strong-to-fragile liquid transition.^{534,545} Strong liquid (LDL) might be formed as a precursor state of the glassliquid transition; fragile liquid (supercooled liquid water) is expected to be formed just before crystallization. The conventional T_g of water (136 K) corresponds to the strong liquid, resulting in the unusually small endotherm.⁴⁹⁰ Accurate measurement of the T_g of water (formation of supercooled liquid) can be hindered in calorimetric studies because of the huge crystallization exotherm. Very little is known about the nature of the quasi-liquid coexisting with crystallites. It might be distinct from both LDL and supercooled liquid as inferred from its strong structural correlation to crystals.⁵

Analysis of interactions of LiI and ethanol films showed the existence of at least two liquids, as in the case of water, in the deeply supercooled region.⁵⁴⁶ The viscous one was formed around $T_{\rm g}$ (97 K), where the adsorbed LiI is incorporated into the ethanol bulk. The formation of a supercooled ethanol solution occurred at 130 K. For pure ethanol, a liquidlike phase (quasi-liquid) is likely to coexist with crystallites until film evaporation, which is reflected in the continuous changes in the film morphology. The successive formation of viscous and fluidized liquid has also been observed for vapor-deposited toluene.⁵⁴⁵ These changes are inferred from the occurrence of molecular self-diffusion and dewetting, respectively, at 105 and 117 K. The presence of two liquids (strong and fragile liquids)⁵⁴⁵ explains decoupling between diffusivity and fluidity in the deeply supercooled region.⁵⁴⁷



Figure 36. Intensities of the Li⁺ ions sputtered from 1 ML of (a) LiCl and (b) LiI that are deposited on a 200 ML ASW film, together with those of the proton from the H_2O molecules, as a function of temperature. The Li⁺ intensities are unchanged at 135 K, but they are decreased abruptly at around 160 K because of diffusion of the LiCl and LiI species into the bulk. Reprinted with permission from ref 539. Copyright 2007 American Institute of Physics.

It is expected that the $T_{\rm g}$ of thin films will be reduced relative to the bulk $T_{\rm g}$ value because of the nanoconfinement effect,^{548,549} resembling the reduction of the melting point for nanoconfined crystallites.⁵⁵⁰ The influence of substrates and the free surface on the $T_{\rm g}$ of thin ASW films has been investigated. Self-diffusion and film morphology changes of water monolayers were observed at 120 K when water was deposited on hydrophobic substrates such as quenched ionic liquid and graphite.¹⁴⁹ This phenomenon was induced by surface diffusion of water molecules and instability of the interface structure. The hydrophobicity of graphite influences the dewetting behavior of water films up to 20 ML,⁵⁵¹ but no indications of the nanoconfinement effects are recognized when the molecules are deposited on a Ni(111) substrate because an immobilized layer (a "dead layer") is formed at the interface.

The surface mobility of condensed molecular solids has been investigated using a porous Si substrate.^{552–554} It is found that self-diffusion of water, ethanol, and 3-methylpentane in the topmost layer of thin films commences at temperatures of ca. 110, 85, and 50 K, respectively, which are considerably lower than the corresponding T_g values in the bulk.⁵⁵³ This phenomenon can be explained as the formation of 2D liquids on the free surface. Therefore, the nanoconfinement effect on reduction of the thin films' T_g originates from the interplay between surface and volume diffusions having apparently different onset temperatures, but it can be quenched by the formation of a dead layer at the interface. The surface mobility of water appears to be unaffected by hydrogen bonds with substrates,⁵⁵³ suggesting that molecules move cooperatively via the formation of intermolecular hydrogen bonds, but the molecules incorporated in pores might be entrapped individually at higher coordination sites by hydrogen bonds.⁵⁵⁴ For the monolayer of methanol and ethanol, the molecules tend to hop independently on the surface without formation of the 2D liquid because hydrogen bonds with the substrate prevail over intermolecular interactions.^{553,554}

8.2. Solvation (Hydration)

The ASW films deposited at temperatures below 120 K have a low density, characterized by a porous structure.^{176,555,556} It is found that polar molecules such as HCOOH and C₃H₇OH stay on the surface of ASW, while nonpolar ones such as C_6H_{14} C_6F_{14} , and C_8H_{18} are preferentially incorporated into the bulk.^{516,532,557} The difference between hydrophilic and hydrophobic hydration is the reason for this behavior. Polar molecules form hydrogen bonds with water and hence stay on the surface by facing the hydrophobic end group toward the primary ions. This situation was reflected in the reduced intensities of protons sputtered from the dangling hydroxyl bond. In the case of methanol, hydrophilic hydration occurred above 120 K followed by complete H/D exchange above 140 K.^{515,558} The nonpolar solutes were completely incorporated in the D_2O layer even below 100 K.⁵¹⁶ The molecules are entrapped at a higher coordination site and are confined in the bulk by pore collapse. The occurrence of the hydrophobic hydration in the bulk is inferred from a sharp TPD peak of confined molecules at 160-165 K along with the phase transition of water. In contrast, methanol embedded in the water film segregates to the surface around a conventional T_{σ} of 136 K along with the self-diffusion of water. 530 The adsorbed benzene molecules on the D₂O ice were incorporated into the bulk, but pyridine was hydrated in part on the surface at a temperature around 150 K.559

Ammonia deposited on acidic water (acidified using HCl) was converted to NH_4Cl , and the hydration of NH_4Cl starts above 100 K and is completed above 140 K.⁵⁶⁰ HCl adsorbed onto basic water (prepared by dissolving NH_3) results in hydrated HCl and the reaction product NH_4Cl above 40 K.⁵⁶¹ When HCl was deposited on a pure ice film, the ionic hydrate formed dissolved in the D₂O layer above 140 K, but some of it remained on the surface until the desorption temperature of D₂O. There also exist neutral hydrates of HCl,⁴⁵⁴ which are readily incorporated into the thin layer bulk of D₂O at temperatures well below 140 K.⁵⁶²

The solubility of the alkali-metal halides, viz., LiCl, LiBr, LiI, and NaCl, in water increased rapidly at 160 K due to the appearance of the supercooled liquid water.^{538,539,542} In the framework of polyamorphism, two distinct liquid phases exist in the deeply supercooled water region.⁵⁴⁴ They were characterized by solubility differences of LiCl in water in comparison with LiCl.^{538,540} The ultraviscous liquid (LDL) formed at $T_g = 136$ K hydrates LiCl and LiI molecularly, but they tend to stay on the surface because of amphiphilicity of the molecules.⁵³⁹ They are incorporated into the bulk at 160–165 K because cations and anions are hydrated separately by supercooled liquid (see Figure 36). The formation of aqueous LiI and LiCl solutions at 165 K is confirmed using TP TOF SIMS and RAIRS.^{539,541}

The emission of alkali-metal/halogen water cluster ions show differences with respect to their hydration.^{563,564} Cationic water clusters, $M^+(H_2O)_n$ (M = Li, Na, K, Cs), are more efficiently formed compared to anionic ones; $M^-(H_2O)_n$ (M = F, Cl, I).



Figure 37. TOF SIMS signal from the hydrophilic and hydrophobic surfaces of the lipid DPPC film and the SiO₂/Si(100) surface exposed to a water partial pressure of 1×10^{-7} mbar as a function of the substrate temperature. The hydrophobic DPPC lipid film is represented by the C₂H₃⁺ sputter fragment, the hydrophilic film by NCH₃⁺, SiO₂ by Si⁺, and the adsorbed water by D⁺. Reprinted from ref 574. Copyright 2006 American Chemical Society.

Ar⁺ and C_{60}^{+} were used as primary ions in these cases. These experimental results were further supported by MD simulations.^{563,564} The disparity in ion emission was explained by differences in solvation structure. Complex formation readily takes place due to cation–water (through oxygen) interactions which destroy the hydrogen bonding in water, allowing the cluster to eject more easily, but anions do not disrupt the hydrogen bonding and are well trapped inside the ice matrix.

8.3. Intermixing

Intermixing of (heavy) water with molecules such as methanol, 515,530,565 ethanol, 566 acetic acid, 487 methylamine, 567 and methane has been investigated with combined TPD and TP TOF SIMS. For simple methanol–water systems (Figure 35a) 530 the intensity change of CD_3^+ and H_3O^+ at 136 K is the clear indication of intermixing. For binary films in the ethanol–heavy water system, complete intermixing occurred above 140 K, due to the enhanced mobility of water molecules, where all ethanol molecules form hydrogen bonds with heavy water. 566 The intermixing induced at 120 K in this case was due to increased mobility of the ethanol molecules, but it was incomplete at the molecular level as evidenced by the absence of H/D exchange. These two situations can be differentiated easily by looking at the evolution curves of CH_2OH^+ and $(C_2H_5OH)H^+$ ions relative CH_2OD^+ and $(C_2H_5OH)D^+.{}^{566}$

Changes in functionality may change the solubility of molecules by altering the interaction parameters. The CH₃NH₂ molecule adsorbed on the D₂O surface undergoes a complete H/D exchange without intermixing above 140 K,⁵⁶⁷ but CH₃NH₂ undergoes H/D exchange with CD₃OD after intermixing at a lower temperature of ~125 K because these molecules can interact with each other via both their hydrophilic and hydrophobic end groups. Another system, a CH₃COOH–D₂O binary film, experienced intermixing at 130–140 K.⁴⁸⁷ Complete mixing was observed when D₂O was deposited on thin films of methane and fluoromethane at 15 K.⁵⁶⁸ A pure D₂O film could not be formed on the 20 ML methane film at a coverage up to ca. 100 ML. It is also found that heavy water undergoes complete intermixing with CO but not with CO₂ at 15 K.⁴⁸⁷ For the same reason, it was found that

 D_2O molecules form nanoclusters over CO_2 films as they cannot penetrate effectively through solid CO_2 .⁴⁸⁷ Systems containing Cl and water show minimum interactions in the temperature range of 90–100 K.⁵⁶⁹ A distinct layer of chlorine, with negligible interaction, was formed on solid H_2O in the temperature window of 90–100 K, but reaction occurs at higher temperatures.⁵⁶⁹ Chlorine nitrate forms a filmlike structure on water ice with a degree of polarization and desorbs simply at 130 K without undergoing any reaction.⁵⁷⁰

8.4. Dewetting

The morphological change of thin films is associated not only with the glass-liquid transition but also with crystallization as discussed in section 8.1. When crystalline ice is grown on metal surfaces such as Pt(111) or Pd(111), it favors the formation of 3D grains even at 45 ML of coverage despite the hydrophilicity of these metal substrates and their excellent lattice matching to crystalline ice.⁵⁷¹ The nonwetting growth of crystalline ice is ascribable to the properties of supercooled liquid and quasiliquid, respectively, formed before and after crystallization^{530,534} because dewetting is characteristic of the liquidlike phase induced by surface tension rather than crystallization itself.⁵³² In fact, the adsorbed methanol or other polar molecules significantly quench the dewetting of crystalline water ice by reducing the surface tension of liquidlike layers coexisting with crystallites. 516,565 When water is adsorbed as a monolayer on a hydrophobic substrate, such as graphite and ionic liquids, dewetting occurs in the sub- T_g region (120 K) because surface diffusion dominates instead of volume diffusion.¹⁴⁹

The dewetting temperature of HCOOH and CH₃COOH films was found to be 150 K.^{487,572} For ethanol films, dewetting occurs along with crystallization at 130 K,⁵⁴⁶ where the morphology change of the crystalline film continues at higher temperature and is attributable to the coexistence of a liquidlike phase or premelting. Similar dewetting behavior is observed for crystalline methanol films under isothermal conditions at 120 K.⁵³⁵ When CO₂ molecules are deposited on an ASW film, translational diffusion commences at 50 K, leading to dewetting of the monolayer CO₂ above 60 K.⁵⁷³ For *n*-pentane films, dewetting was observed after crystallization because of

premelting.⁵³³ Thus, crystallites derived from nanometer-sized thin films are so small that their properties tend to be governed by the quasi-liquid layer formed on the crystallite surface or grain boundaries.

8.5. Molecular Interactions

Water-lipid interactions were studied by taking the lipid dipalmitoyl-sn-glycero-3-phosphocholine (DPPC) film as a model compound.^{574,575} Two different orientations of DPPC are possible when it is adsorbed on a substrate. Either the nonpolar fatty acid chain (hydrophobic DPPC) or the polar phosphoric acid ester group (hydrophilic DPPC) can face the vacuum interface. The hydrophobic DPPC direction was monitored by choosing the $C_2H_3^+$ ion. The hydrophilic surface and adsorbed water were examined by selecting NCH₃⁺ and D⁺ sputtered fragments, respectively. Corresponding curves obtained when DPPC was adsorbed on a SiO₂/Si(100) substrate in the temperature range of 15-170 K are given in Figure 37. The onset of water adsorption on the hydrophobic surface was observed at 106 K, approximately 30 K lower than that of the hydrophilic surface, 133 K. The different onset temperatures could be explained in terms of the longer lifetime of the adsorption precursor on the hydrophilic surface due to van der Waals interactions between the lipid polar headgroup and water.

Using thin films of room temperature ionic liquids, matrix effects on secondary ion emission have been discussed.^{576–578} The substrate effects on the kinetics of crystallization and fusion have also been investigated on the basis of temperature evolutions of sputtered secondary ion yields.⁵⁷⁶ The crystallinity of thin [emim][Tf₂N] films is lower on the Ni(111) substrate than on the substrate of highly oriented pyrolytic graphite (HOPG) because the crystalline molecular alignment is disturbed by the interaction with Ni(111) at the interface. The crystal-like ordering of the [emim][Tf₂N] monolayer tends to be retained at temperatures even higher than the bulk melting point on the HOPG substrate. The surface segregation study of cations and anions in binary mixtures of some room temperature ionic liquids revealed that larger and more polarizable ions tend to occupy the topmost surface layer.⁵⁷⁹

8.6. Chemical Reactions

Collision-induced proton transfer is a common process in ion/ surface collisions in the low-energy regime, but a totally different proton transfer reaction (H/D exchange) can be induced thermally in a binary molecular solid system (see section 8.3 also). Earlier, such exchange reactions in ice bulk had been studied by FTIR spectroscopy.⁵⁸⁰ These reactions can be effectively monitored by SIMS. The proton transfer reaction in the water ice system is basically induced by the translational diffusion of molecules, whereas additional routes such as rotation of hydronium ions can also occur (in acidic ice).^{531,561}

For the HCl–water ice system, HCl undergoes proton exchange reactions above 120 K, which was noticeably lower than the onset temperatures for the methanol and NH₄Cl system.⁵⁶² The presence of thermally activated ionic H⁺–Cl⁻ pairs explains the H/D exchange at lower temperatures. The hydrated HCl and NH₄Cl molecules undergo almost complete H/D exchange above 140 and 170 K, respectively.^{560,562} When pure NH₃ was adsorbed on water, the H/D exchange reaction occurred rapidly and completely at 140 K.⁵⁸¹ Similar onset temperatures for H/D exchange were reported between NH₃ and HCOOH.⁵⁸¹ NH₄HCO₂ appeared as a reaction product above 60 K when NH₃ and HCOOH were codeposited at lower temperatures.⁵⁸¹ CH_3NH_2 molecules undergo thermally activated H/D exchange above 140 and 125 K when adsorbed on D₂O and CD₃OD layers, respectively.⁵⁶⁷

The reaction of NH₃ molecules adsorbed on the HCl–water ice film showed a considerable difference compared with that of the pure HCl film.⁵⁶¹ The extent of NH₄Cl formation increased above 40 K for NH₃ molecules adsorbed on pure HCl. This reaction temperature was shifted to 120 K for NH₃ adsorbed on the HCl–water ice system since strongly hydrating water molecules prevent direct contact between NH₃ molecules and Cl^- ions, but for the reverse case, i.e., when HCl was adsorbed on the NH₃–water ice system, the reaction (NH₄Cl formation) again occurred at 40 K. This establishes that NH₃ molecules are more weakly hydrated than HCl molecules.^{531,561}

Hydrolysis of an alkali metal is an interesting fundamental exothermic reaction which occurs efficiently at room temperature. The Na hydrolysis reaction occurred even at 13 K, but the reaction rate was very small until 100 K because the NaOH layer formed acted as a spacer layer to prevent the reaction between the pure water film and the metallic Na overlayer.^{507,509}

Formation of sulfuric acid hydrates was observed when H₂O and SO₃ gas were deposited in various compositions.⁵⁸² Among the chlorine-containing species, interaction of Cl₂ with the ice surface was negligible in the temperature range of 90-100 K.569 ClONO₂ shows some degree of polarization and interaction with water, whereas Cl₂O undergoes hydrogen-bond-like interactions with water. At about 120-130 K, Cl₂ undergoes reaction with an ice surface to form HOCl (hypochlorous acid), water, and solvated HCl.⁵⁶⁹ The possible reaction pathways suggested in the corresponding reference correspond to reaction 2. Over the same temperature range, Cl₂O produced only HOCl and H₂O upon reaction with water (reaction 3).⁵⁶⁹ ClONO₂ desorbs from the pure water ice surface above 130 K without leaving any signs of reaction, 570,583 but it reacts rapidly with HCl at the ice surface. The reaction starts with the production of H₃O⁺ and Cl⁻ ions upon contact between HCl and ice. Then it proceeds via the release of Cl_2 by the reaction between Cl^- and Cl^+ (from $ClONO_2$), which results in the formation of nitric acid at the surface (reaction 4).

$$Cl_2 + 2H_2O \rightarrow HOCl + H_3O^+ + Cl^-$$
 (2)

$$Cl_2O + nH_2O \rightarrow 2HOCl + (n-1)H_2O$$
(3)

$$\begin{aligned} & \text{HCl}_{(g)} + n\text{H}_{2}\text{O}_{(s)} \\ & \rightarrow \text{H}_{3}\text{O}^{+} + \text{Cl}^{-} + (n-1)\text{H}_{2}\text{O}_{(s)} \\ & \text{Cl}^{+}-\text{ONO}_{2}^{-} + \text{H}_{3}\text{O}^{+} + \text{Cl}^{-} \\ & \rightarrow \text{Cl}_{2(g)} + \text{HNO}_{3(s)} + \text{H}_{2}\text{O}_{(s)} \end{aligned} \right\}$$

$$(4)$$

8.7. Understanding SIMS as Relevant to Biological Analysis

One of the common sample preparation methods in biological SIMS is cryofixation, where the sample is frozen at liquid nitrogen temperature. Hence, water ice is a natural matrix in the analysis of biological samples, and several groups have been interested in the effect of the ice matrix on secondary ion formation. Winograd and co-workers^{16,18} and Vickerman and co-workers^{584,585} performed a noted number of experiments on frozen samples. Ice can act as an alternative source of protons.⁵¹⁹ Protonated molecular ion yields for frozen analytes have been found to be enhanced ~2 times compared to a room

temperature sample.⁵⁸⁶ Sometimes the presence of salt suppresses the ion signal in normal SIMS analysis, but this effect has been found to be reduced when the sample is frozen.⁵⁸⁶ Moreover, the addition of simple salts into an ice matrix may generate preformed ions.^{564,586}

It was found that cluster ion projectiles, especially C_{60}^+ , are effective in sputter depth profiling of organic molecules. ^{519,520,587,588} In one of the experiments with histamine in an ice matrix, it was shown that signals related to both the ice and histamine are about 2 orders of magnitude higher for 20 keV C_{60}^+ projectiles than for 15 keV Ga⁺ impact. ^{589,590} Combined experimental and MD simulation studies on pure ice films showed an enhanced sputter yield and reduced ion escape depth for cluster ion projectiles. ^{591–594} Snapshot pictures of the collision event obtained from MD simulations are given in Figure 38 for the projectiles of Au₃ and C_{60}^+ in 1, 3,



Figure 38. Snapshots of atom positions for Au_3^+ and C_{60}^+ bombardment of a 25 Å film of ice (red) on Ag (light blue). The incident angle for the impinging primary ions was 40° with a 15 keV incident energy. Reprinted with permission from ref 591. Copyright 2006 American Physical Society.

and 5 ps. Most of the water molecules near the impact point are removed from the Ag substrate in the course of collision with both projectiles. There can be very little damage accumulation during cluster ion bombardment for weakly binding molecular surfaces such as ice since the energy deposition region is confined and these projectiles are efficient in removing almost all materials close to the surface compared to their atomic ion counterparts.⁵⁹¹

9. SUMMARY AND PERSPECTIVES

Low-energy ionic collisions result in diverse ion/surface interaction phenomena. The ultrahigh purity of the probe beam, flexibility in selecting the ion and its kinetic energy, and the ensuing process control are unique advantages in these experiments. The range of ions used varies from simple organic cations to complex proteins. The chemical reactivity of projectile ions is highlighted only at low kinetic energy. Also, kinetic energy can be used to control the reaction paths or to create new channels in the hyperthermal energy regime, which is inaccessible by a heating method. The extent to which a particular process occurs depends on a variety of factors, among which the chemical nature of the surface and of the impinging ion are most important. Specificity of a chemical reaction with spatial control provides a promising method of chemically specific surface modifications. This feature could make a contribution in the nano- or microelectronics industry. Use of soft landing for preparation of compounds and of catalytically active surfaces is encouraging, but improved yields are needed. Better instrumentation with higher throughput could solve this problem.

Central aspects of the chemistry involved in ion/surface collision events are associated with transformations of surface molecules and projectile ions. Details on these events are emerging in several cases. Time-resolved studies may help in this regard. Most of the studies look at only mass, with changes in ion kinetic energy and internal energy states not being studied. Relaxation by thermal, electron, and photon emission upon collision has not been the subject of study using lowenergy ion impact. Such surface processes need additional measurements. Ab initio MD simultations of molecular ion impact at molecular solids have been performed in a number of important cases and are increasingly useful.

Ion impact at molecular solids of astrochemical relevance is an emerging area. The implications of this research to the chemical atmosphere of Jovian planets and interstellar objects need attention. Although thermal energies are far too low in space, ions impacting charged interstellar dust particles will also be accelerated by Coulombic interactions. Chemical reactivity of solids, existing as liquids and gases at normal temperatures will likely produce several surprises. Besides the implications in the origins of biological compounds that are precursors to living systems, the role of ionic collisions at ice surfaces has evident environmental implications. Associated processes at many molecular solids will be studied purely as a result of chemical curiosity.

Phase changes of molecular solids, which have so far been probed by macroscopic observables, are now accessible microscopically on the basis of static SIMS. A large advantage of this approach lies in its applicability to the effects of a free surface and a substrate interface with an extremely high sensitivity. Molecules in nanoconfined geometries are ubiquitous; their properties are expected to be distinct from those of bulk materials. For example, nanoconfined water interacting with macromolecules and biomembranes plays a decisive role in living cells, where the mobility of water molecules changes with the distance from the interface. A study of biomolecular interaction might be enabled by utilizing static SIMS in terms of hydrophilic and hydrophobic hydrations at the molecular level. However, the effects of the chemical environment on the ionization probability (matrix effects) are still poorly understood. A deeper understanding of ionization mechanisms during low-energy molecular collisions at the surface might open a new application field of SIMS and related techniques.

From the perspective of surface analysis, low-energy ion collision methods (RIS, SIMS, CS, etc.) extend extreme sensitivity and offer a means to identify and characterize molecules and functional groups on surfaces. Such capabilities are found in few other surface spectroscopic methods. In the

From the recent literature, it is clear that significant efforts are being made toward several of the aforementioned aspects, and breakthroughs are expected in the coming years.

AUTHOR INFORMATION

Corresponding Author

*E-mail: pradeep@iitm.ac.in (T.P.); cooks@purdue.edu (R.G.C.).

Present Address

¹Indian Institute of Space Science and Technology, Thiruvananthapuram 695 547, India.

Notes

The authors declare no competing financial interest.

Biographies



Jobin Cyriac was born in Kerala, India, and received his Master's degree from the Mahatma Gandhi University, Kerala. He received his Ph.D. degree from the Indian Institute of Technology (IIT) Madras under the guidance of Prof. T. Pradeep. His Ph.D. research was on low-energy ion scattering at molecular solids, and he developed a spectrometer for such studies. He is currently a postdoctoral fellow with Prof. R. G. Cooks at Aston Labs for Mass Spectrometry, Purdue University. He is interested in exploring various applications of ion/ surface collision phenomena and is keen on developing instrumentation for such studies.



T. Pradeep earned his Ph.D. from the Indian Institute of Science in 1991 and had postdoctoral training at the Lawrence Berkeley Laboratory, University of California, Berkeley, and Purdue University, West Lafayette, IN. He joined IIT Madras in December 1993, where he leads a research group on molecular materials and surfaces. He has held visiting positions at several universities and institutes in Asia and Europe. His research interests are in nanomaterials, molecular surfaces, monolayers, ion/surface collisions, clusters, spectroscopy, electronic structure, and instrumentation. He is committed to finding affordable solutions for drinking water for the poor. One of his technologies has been commercialized. He is the author of the introductory textbook *Nano: The Essentials* (McGraw-Hill) and is one of the authors of the monograph *Nanofluids* (Wiley-Interscience). He is a Fellow of the Indian Academy of Sciences. His other interests include education, popularization of science, and development of advanced teaching aids.



H. Kang received his B.Sc. from Seoul National University (SNU) and a Ph.D. in Physical Chemistry from the California Institute of Technology for his study of gas-phase ion chemistry in 1980–1985. After working on low-energy ion/surface interactions at the University of Houston as a postdoctoral fellow, he joined the chemistry faculty of POSTECH. There he studied reactive ion/surface collisions and developed a surface analysis method based on Cs⁺ reactive scattering. In 2001 he moved to SNU, where he leads a surface science research group and the Center for Space-Time Molecular Dynamics. His current research interest includes ice surface properties, heterogeneous reactions in the atmosphere and interstellar clouds, surface reaction dynamics, and nanoscopic investigation of electrochemical interfaces.



R. Souda was born in 1957 in Nagoya, Japan. He earned his B.S. and M.S. degrees in Physics from Nagoya University. He received his Ph.D. from the University of Tokyo in 1986. He has been at the National Institute for Research in Inorganic Materials (now the National Institute for Materials Science) since 1982. He is currently a Senior Researcher at the National Institute for Materials Science. His research interests are ion beam analysis of solid surfaces and ion/surface charge exchange mechanisms during low-energy ion and electron impacts. His current interest includes molecular-level understanding of the glass–

liquid transition and phase transition of thin films using secondary ion mass spectrometry.



R. G. Cooks received Ph.D. degrees from the University of Natal (now KwaZulu-Natal) and Cambridge University. His interests involve construction of mass spectrometers and their use in fundamental studies and applications. Early in his career, he worked on energy partitioning during metastable ion fragmentation and contributed to the concept and implementation of tandem mass spectrometry and to desorption ionization, especially matrix-based methods. His interest in minimizing sample workup and avoiding chromatography contributed to the development of the ambient ionization methods, including desorption electrospray ionization (DESI). Applications of this method in tissue imaging, forensics, and pharmaceutics are in progress. These same interests also led to the construction of miniature ion trap mass spectrometers and their application to problems of trace chemical detection. His interests in the fundamentals of ion chemistry include inelastic ion/surface collisions, chemical sputtering, and ion soft landing. R. G. Cooks is a past President of the American Society for Mass Spectrometry and the International Mass Spectrometry Society and a Life Member of the British, Chinese, and Indian mass spectrometry societies.

ACKNOWLEDGMENTS

We acknowledge funding from the Department of Science and Technology, Government of India (T.P.), the National Research Foundation of the Korean government (MEST), Grant 2007-0056333 (H.K.), the Japan Society for the Promotion of Science through a Grant-in-Aid for Scientific Research (C), 22540339 (R.S.), the Separations and Analysis Program, Office of Basic Energy Sciences, U.S. Department of Energy, Grant DE-FG02-06ER15807, and the National Science Foundation, Grant CHE NSF 0848650 (R.G.C.). J.C. thanks T.P. and R.G.C. for their guidance and support. We acknowledge assistance from Gautam Sharma.

ABBREVIATIONS

AQ	accumulation quadrupole
ASW	amorphous solid water
CI	crystalline ice
CID	collision-induced dissociation
CQ	collisional quadrupole
CS	chemical sputtering
HDL	high-density liquid
HOPG	highly oriented pyrolitic graphite
LDL	low-density liquid
LES	low-energy sputtering
MS	mass spectrometry

RAIRS/IRAS	reflection-absorption infrared spectroscopy/
	infrared reflection-absorption spectroscopy
RIS	reactive ion scattering/reactive scattering
RL	reactive landing
RQ	resolving quadrupole
SAMs	self-assembled monolayers
SID	surface-induced dissociation
SL	soft landing
SPIAD	surface polymerization by ion-assisted deposi-
	tion

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