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Surface-induced dissociation of acetone cations from self-assembled monolayer surface of fluorinated alkyl thiol on Au (1 1 1) substrate at low collision energies

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In honor of Professor Helmut Schwarz.

Abstract

We have studied the dissociation of acetone molecular cations to acetyl cations following collision with a monolayer surface of fluorinated alkyl thiol (FC_{12}) self-assembled on Au (1 1 1) substrate at 13, 25.2 and 49.6 eV kinetic energies. Three energetically distinct dissociation processes contribute to total dissociation in this energy range. At all energies there is a common dissociation pathway involving loss of nearly all of the parent ion's kinetic energy in the collision process. Fragment ions resulting from this dissociation mechanism are scattered over a wide range of angles. The second pathway, observed at 25.2 and 49.6 eV kinetic energy is delayed dissociation of collisionally excited acetone cations after only a small fraction of the ion's kinetic energy is lost in the collision process. Fragment ions resulting from this unique dynamics feature are scattered close to the surface parallel. These dissociations take place after the excited ions have passed through the collision region and the energy analyzer and prior to their entering the mass analyzer. At 49.6 eV kinetic energy, a small intensity fragment ion peak appears at intermediate kinetic energy spectra between the low energy loss and the highly inelastic scattering peaks.

Keywords: Ion-surface collisions; Surface-induced dissociation; Inelastic scattering; Energy transfer; Acetone cations

1. Introduction

Recent dynamics studies [1–3] of the surface-induced dissociation (SID) of small polyatomic ions performed in our laboratory have revealed unexpected and dynamically different features of ion excitation/dissociation and scattering of fragment ions. Some of these features are analogous to features reported by Herman and coworkers [4–7] in their studies of small polyatomic ions. Many of these characteristics were found to be quite different for different systems. For example, we observed three peaks in the energy distributions of fragment ions from collision of ~50 eV benzene and ethanol molecular cations whose intensity distributions exhibited quite different angular distributions. Common features for both these ions were the presence of two peaks; one corresponding to the loss of nearly all of the primary ion's kinetic energy and the other corresponding to very

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small amount of kinetic energy loss (quasi-elastic). An intermediate energy loss process appears at energies around 50 eV. Most of the energy lost in these highly inelastic processes is dissipated in the surface and only a modest fraction is converted into internal modes of the ions.

These SID results clearly demonstrated that the dynamics of ion activation and subsequent dissociations in ion-surface collisions is not as simple as inferred from early experimental studies [8–12] where only the fragment ion intensities were measured at a fixed angle with a large acceptance angle detector. Further, theoretical simulations of the kinetics of SID reactions [13] have thus far not considered the dynamics of these processes. It is obvious from the energy- and angle-resolved studies that energy transfer in the collision step proceeds via several different interaction processes and that the energy transferred into internal modes of the ions is only a fraction of the total energy lost by the ion. It is also evident that trajectory simulations which are in good agreement with kinetics studies should be revised to incorporate new dynamics information.

For ethanol cations we observed a uniquely different dissociation process in which the dissociation of a substantial fraction of the excited ions was delayed by several microseconds after collision of the primary ion with the surface. Fragment ions resulting from this dissociation process were scattered very close to the surface parallel, just as the undissociated primary ions. Accordingly we described this dynamics feature as “skittering” of the ions along the surface after the momentum exchanging collision which redirects their velocity vector. This dynamics feature is accompanied by a quasi-elastic scattering peak of the ethanol cation which also skitters along the surface and has kinetic energy loss identical, within experimental error, to that for the fragment ions. Since there are no known long-lived electronically excited states of ethanol cations, we suggested that this dissociation process is preceded by a rearrangement to a lower energy structure below the threshold for dissociation and that this results from the multiple weak encounters of the ion with the regular surface of the self-assembled monolayer (SAM) on Au (1 1 1). This state is not reached and therefore not observed for other kinds of excitation followed by unimolecular decay. This exploration of a lower energy well on the potential surface for the ion is expected to cause the dissociation rate to rise more slowly than for isolated ions and can rationalize the observed molecular ion component and slow decay of excited ethanol cations [2].

Our dynamics studies of the SID of several cations have supported earlier suggestions that only the end group, atom or a fraction of the chain of the self-assembled monolayer (SAM) surface molecule participates effectively in the collisional energy transfer process. RRKM [14,15] modeling of experimental data from SID of small peptides with the same SAM surface on a FTMS reached similar conclusions [10,11]. These studies also estimated internal energy transfer distributions in dissociating ions that were in good agreement with available literature values. It must however be pointed out that RRKM modeling assumes that internal energy is fully randomized before the unimolecular decay of the excited ions and ions dissociate from a single potential energy surface. Dynamics experiments also support the inference that the bulk surface also contributes to SID. The fact that several peaks are present in the energy distributions of the fragment ions is a clear indication that SID is more complex than was concluded from primary and fragment ion intensity measurements alone.

The most important parameter for SID is the partitioning of ion’s kinetic energy into internal excitation of the ion and the surface and into recoil of the ion on collision with the surface, as given below:

$$E_{\text{coll}} = E_{\text{int}} + E_{\text{surf}} + E_{\text{kin}} \quad (1)$$

if the ion fragments, the kinetic energy of the excited ion is further partitioned into the kinetic energy of the ionic and neutral fragments in proportion to their masses. Thus by measuring the kinetic energy of the fragment ions we can calculate the kinetic energy of the dissociating primary ion (by multiplying it by the mass ratio, $M_{\text{primary}}/M_{\text{fragment}}$). However, there are no a priori knowledge or rules for the partitioning

of kinetic energy into internal modes of the ion and neutral colliders. Many studies have suggested that a very large fraction of the ion's kinetic energy is transferred into internal modes of the SAM surface. For the type of SAM surface utilized in this research several experiments have suggested that approximately 20% of the ion kinetic energy is converted into internal energy [4,7,9,10]. For 50 eV ions, the kinetic energy of recoiling ions typically accounts for less than 10% of the ion energy, demonstrating that E_{surf} is the principal energy sink [1–7].

It has been suggested that excitation of projectile ions in ion-surface collisions proceeds via vibrational excitation mainly by deformation of both the projectile ion and the surface especially when modified surfaces are used [16–18]. However, the presence of several energetically and spatially distinct processes in the energy spectra of fragment ions lead us to believe that excitation is a more complex process.

To improve our understanding of SID phenomena we have extended our SID dynamics studies to acetone cations whose dissociation dynamics from gaseous collisions has been thoroughly studied. It is no exaggeration to state that the gas phase collision-induced dissociation (CID) dynamics of this molecular cation is better understood than any other system [19–21]. It is well documented that acetone cations in the A state have a long lifetime, of the order of several milliseconds [22,23]. Collisions mix these isolated states with interconversion of translational energy and electronic energy. Accordingly one objective of our SID dynamics study was to search for similar features in surface scattering. We report here our experimental results of the SID of acetone cations at low energies and analyze their consistency with earlier observations of CID and SID dynamics.

CID of acetone cations to acetyl cations (threshold energy 0.7 eV) was suggested to be non-statistical at high (kilo-volt) energies [24]. This was supported by our earlier crossed-beam studies at collision energies below 5 eV energy in the center-of-mass (CM) frame it was found that collisions induce a non-adiabatic transition from the electronically excited A state to the ground state with prompt dissociation on the ground state surface and the release of 2.2 eV into kinetic energy of recoil of the fragment ion and neutral. This superelastic peak disappeared when the electron energy for ionization was reduced to just above the ionization energy. The dynamics studies of its CID as a function of energy showed that energy transfer into internal modes of the acetone cations increased with the CM collision energy, reaching a maximum ∼6 eV, but the dynamics features remained the same, a single peak at non-zero scattering angles.

SID of acetone cations has been studied earlier by Worgotter and coworkers [25,26] and Kane et al. [27], however, those studies were limited to integrated fragment ion abundances and surface-induced reactions with the H-containing surface material, especially the formation of CH_2OH^+ fragment ions. Worgotter et al. estimated higher conversion of translational energy into internal energy on collision and speculated that higher abundance of these ions in their SID spectrum might reflect the presence of acetone cations in the long-lived excited A state in the ion source. We have used fluorinated SAM surface instead of hydrocarbons surfaces in earlier studies and did not observe CH_2OH^+ ions resulting from H-abstraction ion-molecule reactions of acetone cations with the surface.

2. Experimental

The instrument used for present studies has been described in detail elsewhere [28] and only salient features are given here. Primary molecular cations of acetone are formed by ∼70 eV energy electrons and accelerated to ∼1250 eV for mass and energy analysis by a double focusing reverse geometry mass spectrometer (JEOL-GCmate). The mass and energy selected ion beam is transferred into a collision chamber through a 2-mm aperture and decelerated to a lower kinetic energy by a series of cylindrical tube lenses. The ion beam is collimated by a 2-mm aperture and collides with a surface at a fixed angle set to 45° with respect to the surface normal in the experiments reported here. Scattered primary ions

and fragment ions are energy analyzed by a 160° spherical sector energy analyzer, mass analyzed by a quadrupole mass filter and detected by a channel electron multiplier operating in pulse counting mode. The energy analyzer, quadrupole mass filter and the detector are rotated with respect to the collision center to measure energy and intensity distributions of secondary ions as a function of scattering angle.

The collision region, surface, last lens element and the first entrance aperture to the energy analyzer are all maintained at the same potential to minimize field penetration effects which would interfere with their apparent angular scattering distributions. The energy analyzer and quadrupole mass filter are floated at higher potentials using the ion source voltage as reference to decrease ion kinetic energy and increase both energy and mass resolution of the second stage analyzer. The primary ion beam at ∼50 eV energy has an angular distribution of ∼2° (FWHM) and energy distribution of ∼2.5 eV (FWHM). The energy resolution for the present experiments is set to be $E/\Delta E = 50$ and the angular resolution is 3°. All angle measurements are made with respect to the surface normal.

The energy analyzer is operated in constant transmission mode and constant energy resolution mode to avoid any discrimination of low energy ions by the analyzer. This requires that all ions pass through the energy analyzer at the same ion energy, 100 eV for the present experiments. As primary ions dissociate, their kinetic energy is reduced by the mass ratio of the fragment and the parent ion (43/58 for acetone ions). In order for these fragment ions to pass through the energy analyzer at fixed ion energy of 100 eV, these lower energy ions are accelerated by the energy difference between the primary ions and the fragment ions in addition to any energy lost in the collisional activation step. The primary ions are similarly accelerated after surface collision to pass through the energy analyzer if they lose energy on collision. For this reason, all scattered ions are observed at higher ramp voltages than primary ions.

The SAM surface was prepared from the fluorinated alkyl thiol ($F_3C(CF_2)_9(CH_2)_2SH$) by immersing the gold crystal (Au, 1 1 1) in 1 mM ethanol solution of the SAM material for 48 h after cleaning it in a UV cleaner and in ethanol using an ultrasonic cleaner. Excess SAM material was removed from the surface by sonicating the surface in ethanol for another 5 min before transferring it into the vacuum system. The vacuum chamber was pumped at least overnight before any SID experiments were performed so that remaining solvent is removed from the surface. The mass spectrometer and the collision chamber are all pumped by turbo molecular pumps and the background pressure in the collision chamber is $\sim 2\times10^{-7}$–3×10^{-7} Torr. The SAM surfaces are covalently bonded on gold (Au–S bond) and it has been demonstrated that these are not easily contaminated under the vacuum conditions of our experiments [29].

3. Results and discussion

3.1. Inelastic scattering of acetone cations

Since the common model for surface-induced dissociation is a stepwise process of impulsive scattering of internally excited ions which subsequently decompose unimolecularly [1,4–8,30], it is instructive to examine the scattering dynamics of parent acetone ions before considering the major fragmentation channel to generate acetyl ions. Fig. 1 shows the kinetic energy distributions at several angles, ranging from 90° (parallel to the surface) to 75° at which the intensity has dropped to a very low value for ion collision energy of 49.6 eV. Except for some broadening at the base of the peak, suggesting a very modest contribution from a second dynamics feature we may infer that the scattering dynamics responsible for this peak is quite specific and quite similar to our findings for ethanol cations [2]. Clearly the kinetic energy shift relative to primary ions is modest, as shown in more detail in Fig. 2. It ranges from about 2 eV close to the surface to about 6 eV where the intensity drops to zero. An arrow in Fig. 2 marks the energy loss at the most probable scattering angle of ∼87°.

Fig. 3 illustrates the angular scattering of acetone cations at the same collision energy of 49.6 eV. The

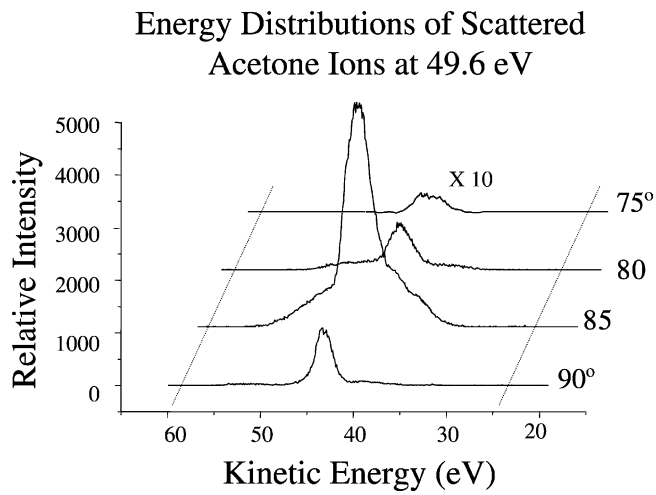

Fig. 1. Kinetic energy distributions of scattered acetone cations at 49.6 eV energy plotted at several scattering angles as marked. Successive angular scans are displaced for clarity and parallel dotted lines denote the same kinetic energy.

extremely sharp peaked distribution is a signature for very well defined dynamics. Remarkably, the angular distribution of scattered acetone ions is essentially identical to the angular distribution of parent acetone ions prior to the collision event. We may therefore describe this dynamics event as shifting the ion beam from its angle of impact, shown in Fig. 3, to nearly parallel to the surface without significantly affecting the angular distribution of the scattered ions from the original ion beam. At the same time the kinetic energy of the ion beam is shifted by a modest amount—between 2 and 6 eV with respect to the original kinetic energy of the impacting ion beam.

Since the threshold energy for dissociation of acetone ions to acetyl ions is only 0.7 eV [31], the most plausible interpretation of the energy shift is that it is mainly dissipated into the surface, as several earlier studies have reported for a number of molecular ions [1–7]. There are, however, additional possibilities for acetone molecular ions to take up internal energy in excess of 0.7 eV. In a series of previous studies we have demonstrated that it is possible to induce by collisions intrastate conversion of internal energy between the X state and the A state of acetone cations [20,21,32]. The barrier height to access this energy level is approximately 2.2 eV, well within the range of energy shift

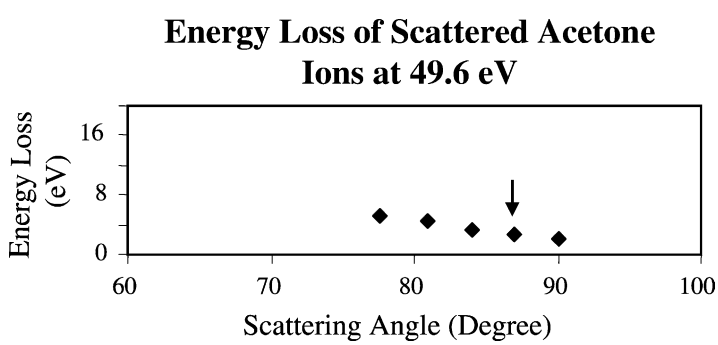

Fig. 2. A plot of kinetic energy lost by scattered acetone cations in collision with the SAM surface at 49.6 eV kinetic energy. The arrow indicates the most probable scattering angle.

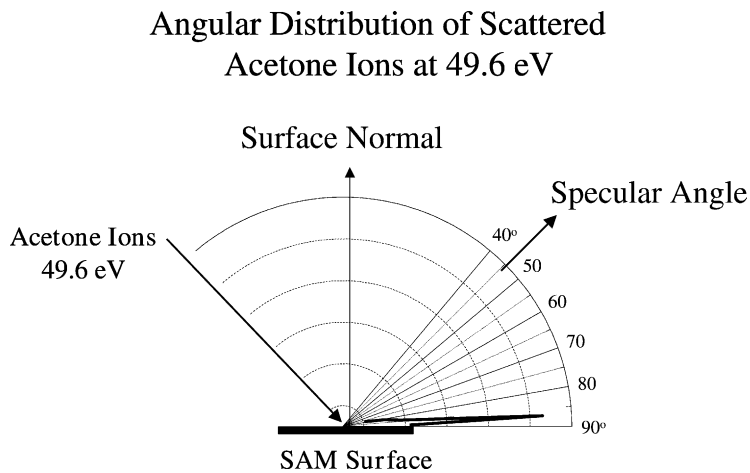

Fig. 3. Angular distribution of scattered acetone cations in collision with the SAM surface at 49.6 eV kinetic energy. The impact angle, surface normal and specular angle are shown for reference.

noted for the majority of inelastically scattered acetone ions. The radiative decay lifetime of this state is of the order of 15 ms, exceeding the transit time in our energy analyzer/mass detector. In addition, the barrier for keto–enol conversion of acetone ions lies at almost the same level. As we have shown previously in a molecular beam study of collision-induced dissociation of the enolic acetone cation the lifetime of enolic acetone cation is also long enough for dissociation to occur after the ion has left the collision region [33].

We should also point out that acetone cations are generated by 70 eV electron impact in our experiments. Earlier work has suggested that 5–10% of the ions are in the electronically excited A state when they collide with the surface [23]. We first detected these ions in a crossed-beam scattering experiment in which a non-adiabatic transition was triggered by collision and the ions dissociated very rapidly on the ground X state surface. In the next section we shall discuss fragmentation processes and point out that no evidence was found for promptly dissociating acetone cations following the same scattering dynamics. For these reasons we are not inclined to invoke the electronic state excitation process to rationalize our SID results.

The simplest explanation for our results, supported by almost identical dynamics observed for ethanol cation (and for Ar^+ scattering from the same surface), is that the mechanism for this remarkable dynamics feature is turning of the ion by impact on a surface moiety, followed by “skittering” of the ion along the highly regular FC_{12} SAM deposited on a Au (1 1 1) single crystal [2]. The mechanism has certain analogies in previous suggestions of Snowdon [34] and Akazawa and Muarata [35] that ions reflected from a highly attractive conductor undergo surface trapping and interact multiple times with the surface until they are deflected away closer to the parallel. Since our SAM surface is only slightly attractive and the Fermi level is never accessed by these ions, surface trapping cannot be the explanation. Rather we adopted the concept of multiple interactions with a non-attractive surface which removes modest amounts of translational energy from the ion after it is deflected by the terminal group. It is our expectation that this class of mechanism is most important at relatively high kinetic energy and would decline in importance as ion collision energy is reduced. Our lower collision energy experiments support this hypothesis.

Our results for acetone cation scattering at 25.2 eV collision energy for energy loss and angular distributions of scattered acetone ions are shown in Figs. 4 and 5. As before, the predominant inelastic scattering mechanism is quasi-elastic “skittering” of the ion nearly parallel to the surface. However, there is a

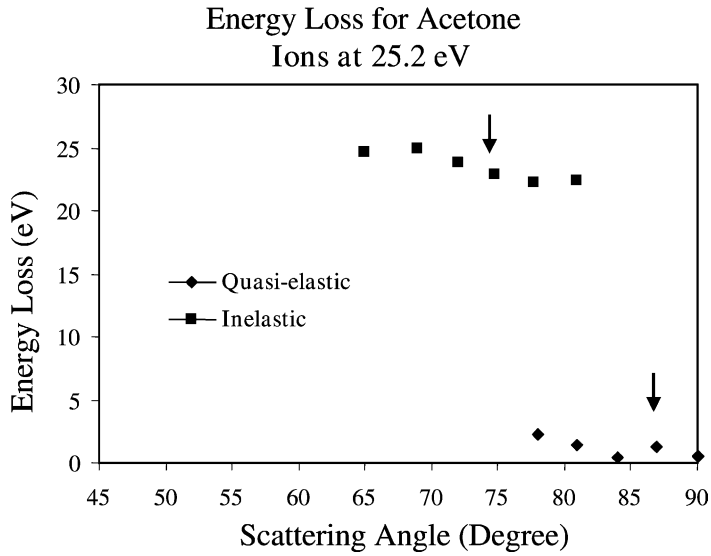

Fig. 4. A plot of the kinetic energy lost by scattered acetone cations in collision with the SAM surface at 25.2 eV kinetic energy. Arrows indicate the most probable scattering angles for the two dissociation processes.

second, highly inelastic mechanism which develops at this collision energy. It is somewhat broader in both energy and angle, maximizing at about 75° where the surface parallel mechanism has essentially vanished. The energy loss for this mechanism is almost 25 eV, a totally inelastic collision, contrasting with ∼2 eV for the surface parallel mechanism. It is evident that this is a "hard collision" with the SAM surface in which almost all the kinetic energy of impact is dissipated in the fluoro-alkyl surface.

On further decreasing collision energy to 13 eV, as illustrated in Figs. 6 and 7, we find that the relative intensity has shifted from the surface parallel mechanism favored at higher energy to the totally inelastic scattering mechanism. The most probable scattering angles for both mechanisms move further from the surface towards but never approaching the specular angle. These observations are quite consistent with the explanation put forward for the "skittering" mechanism in which the initial scattering event is favored by higher

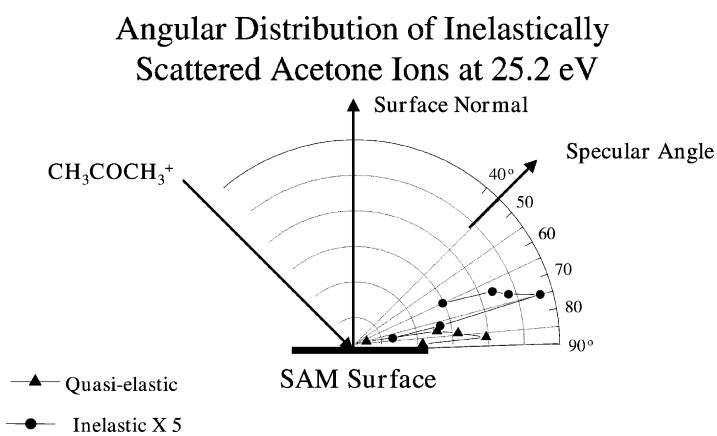

Fig. 5. Angular distribution of scattered acetone cations in collision with the SAM surface at 25.2 eV kinetic energy.

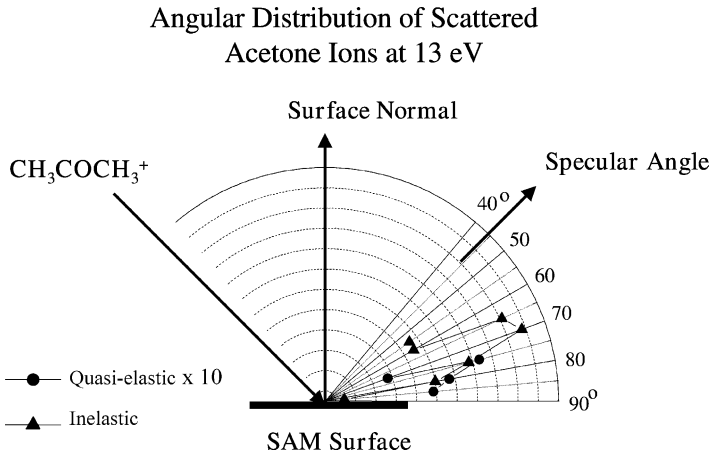

Fig. 6. Angular distribution of scattered acetone cations in collision with the SAM surface at 13 eV kinetic energy.

energy, impulsive collisions and multiple interactions with an essentially flat potential surface modestly reducing the kinetic energy of the ion. It will be shown in the next section that a dissociation channel mimics the same dynamics.

3.2. Dynamics of formation of acetyl product ions

Fig. 8 illustrates the kinetic energy distributions of acetyl ions formed on collision of acetone cations with the SAM surface at 49.6 eV collision energy. It consists of a main peak with apparent shoulders and a tail of intensity corresponding very closely to the surface parallel mechanism in inelastic scattering of primary ions accompanied by highly inelastic and broadly scattered peaks. These lower intensity peaks are amplified by a factor of 10 in the figure to demonstrate that two different kinetic energy distributions are formed. The close correspondence in scattering dynamics of the quasi-elastic peaks is further illustrated in Fig. 9, which plots the angular distributions of acetyl ions at this collision energy. The much broader angular scattering characteristics of the highly inelastic mechanisms are clearly evident in this figure.

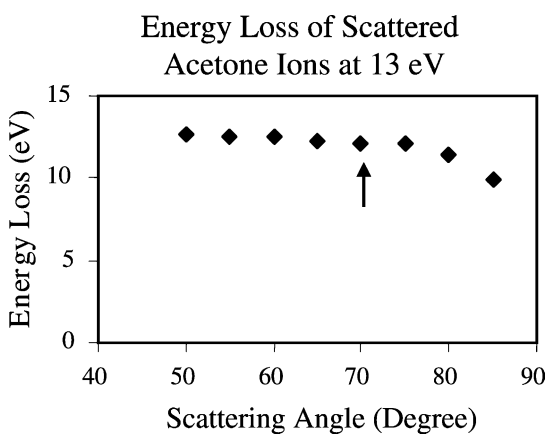

Fig. 7. A plot of the kinetic energy lost by scattered acetone cations in collision with the SAM surface at 13 eV kinetic energy. Arrows indicate the most probable scattering angles for the two dissociation processes.

Fig. 9 labels the quasi-elastic parallel scattering mechanism as “delayed dissociation” for reasons which become evident on consideration of Fig. 10. This is a plot of the energy distribution of acetyl ions at 85°, near the maximum for this dynamics mechanism. Shown as arrows in this figure are the parent ion, labeled P^+, the peak maximum at 47 eV, a theoretical fragment ion location designated F^+ and the very weak signals at much lower ion kinetic energy. The location of F^+ is a calculated number, the maximum kinetic energy the fragment can have following dissociation; specifically it is the ion kinetic energy multiplied by the ratio of [daughter ion

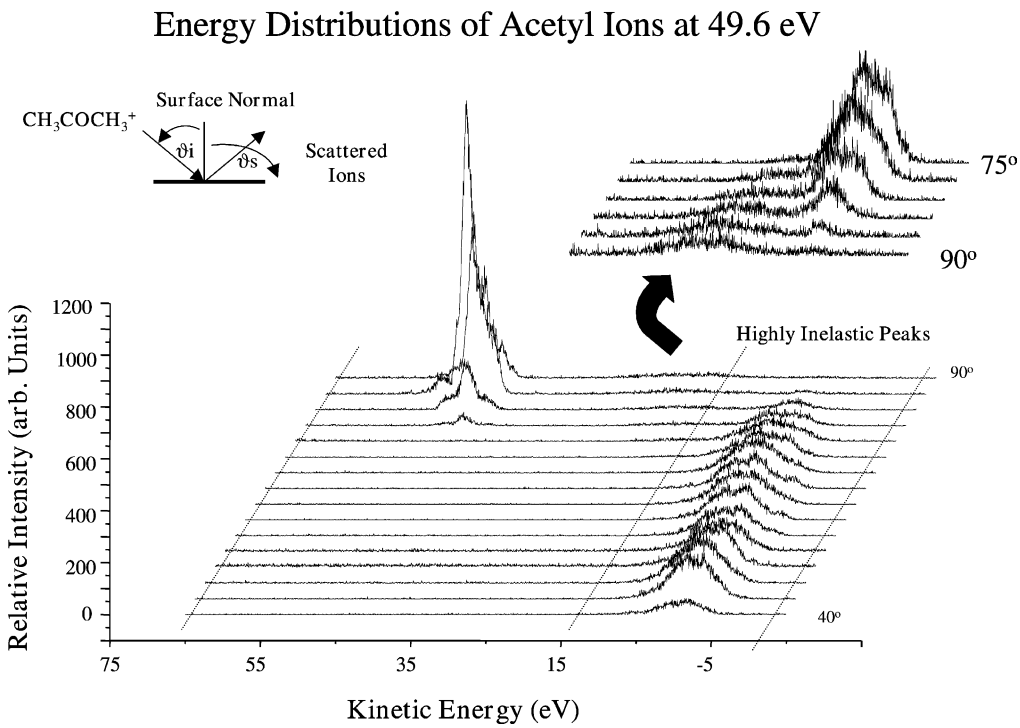

Fig. 8. Kinetic energy distributions of acetyl cations from the SID of acetone cations at 49.6 eV kinetic energy, plotted as a function of scattering angle. The spectra between 75 and 90° were amplified (not normalized) in the inset to clearly show the smaller intensity peaks. Also shown for reference are the impact angle and surface normal, the reference points for scattering angles.

mass (43)/parent ion mass (58)]. For endothermic processes, such as SID, it is normally presumed that the highest energy a product ion can have is located below this value. Clearly the major peak is located at 47 eV, much higher than allowed by the assumption of prompt dissociation after leaving the surface and before the ion energy analyzer/mass analyzer stage of our beam apparatus.

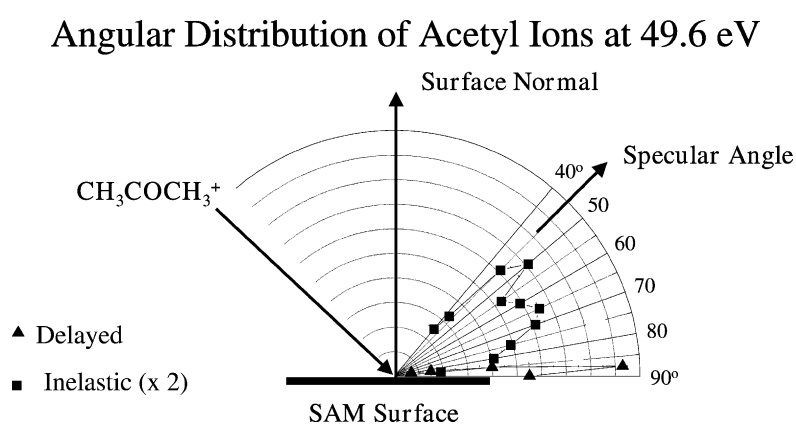

Fig. 9. Angular distribution of acetyl fragment ions from the SID of 49.6 eV energy acetone cations.

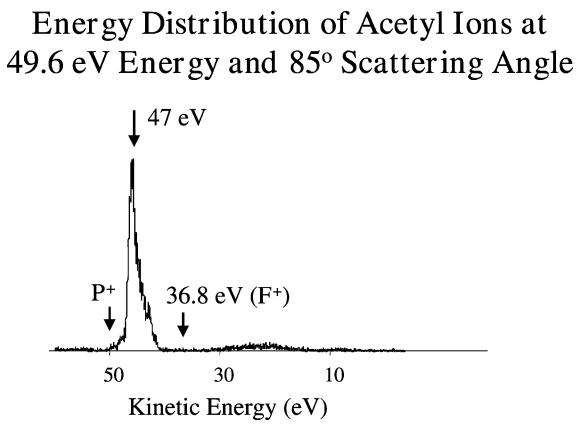

Fig. 10. A plot of the kinetic energy distribution of acetyl cations from the SID of acetone cations at 49.6 eV kinetic energy and 85° scattering angle. The arrow marked P^+ corresponds to the location of the primary ions and the other marked F^+ corresponds to the expected location of the fragment ions if there is no energy transfer from kinetic into internal modes in the collision process. The most abundant peak found at ~47 eV on the energy scale cannot be due to prompt dissociation from a normal SID process. See text for details.

The only plausible rationalization for the observed sharply peaked distribution at an energy which is too high when analyzed in the usual way is that the ion passes through the energy analyzer as an undissociated parent ion and dissociates into acetyl ion prior to entering the mass analyzer. For this apparatus this requires a minimum time of ~5 μs. If we make the plausible assumption this location corresponds to its parent ion precursor an energy shift of about 3 eV is deduced. Clearly the dynamics of this process matches very well the unique "skittering" dynamics of the acetone cation at this collision energy.

Energy loss data for SID at 49.6 eV are summarized in Fig. 11 using the concepts we have discussed above. Diamonds in this figure designate the delayed dissociation mechanism discussed above and the arrow designates the energy shift of about 3 eV associated with it. The two peaks in the angular distribution shown in Fig. 9 correspond to sharp peaks near the surface parallel and combined intensities of the two broader peaks (since the intensity of the middle peak is not high enough to make a significant difference to the overall distribution). The highly inelastic peaks appear to represent similar dynamics processes to highly inelastic scattering of acetone ions in that the energy shift is almost the same as the parent ions but with a broader angular distribution. It is very interesting that four points labeled as inelastic are a shoulder which underlies the delayed dissociation mechanism and are widely

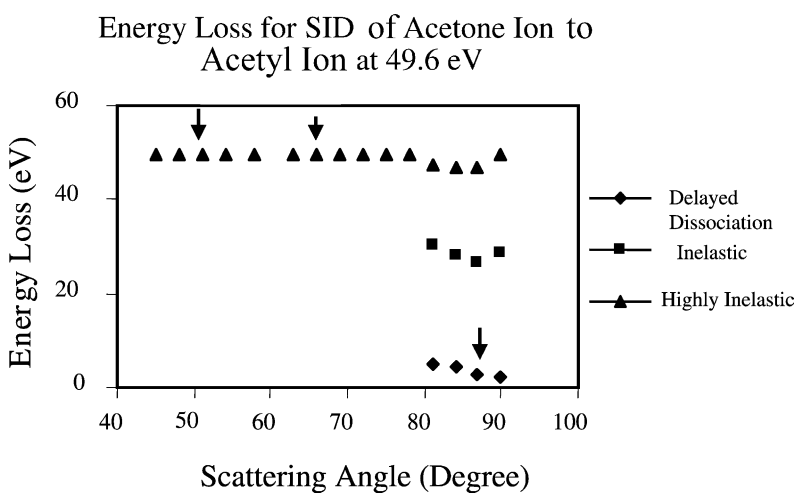

Fig. 11. A plot of kinetic energy lost by acetone cations dissociating into acetyl cations at 49.6 eV, corresponding to three peaks in the energy distributions of Fig. 8, plotted as a function of scattering angle. Arrows indicate the most probable scattering angles for the two dissociation processes. The data points marked delayed dissociation correspond to dissociation of excited acetone cations after passing through the energy analyzer. See text for details.

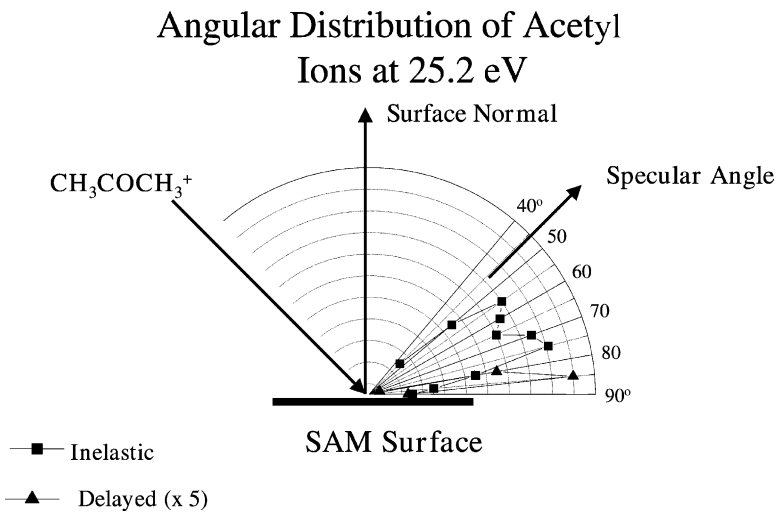

Fig. 12. Angular distributions of acetyl fragment cations from the SID of acetone cations at 25.2 eV kinetic energy.

separated from it energetically. It is plausible to interpret these peaks as resulting from prompt dissociation of parent ions scattered nearly along the surface parallel which fragment before the parent ions enter the energy analyzer—in other words, a normal dissociation mechanism rather than a long-lived decay mechanism. If this is correct, the "skittering" mechanism at this energy forms a continuum of states, some of which dissociate promptly and some of which have lifetimes exceeding the transit time through the energy analyzer.

SID dynamics data for our 25.2 eV experiment are summarized in Figs. 12 and 13. Fig. 12 shows

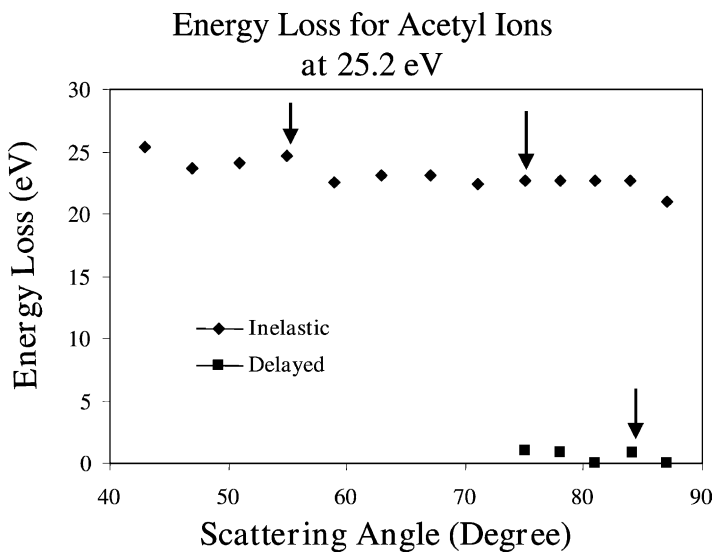

Fig. 13. A plot of the kinetic energy lost by dissociating acetone cations at 25.2 eV kinetic energy. Arrows indicate the most probable scattering angles for the two dissociation processes. The data points marked delayed dissociation correspond to ions dissociating after passing through the energy analyzer. See text for details.

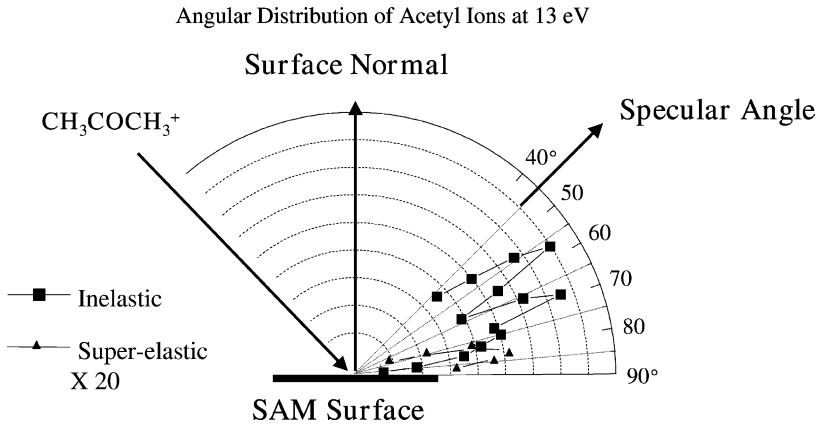

Fig. 14. Angular distribution of acetyl fragment ions from the SID of acetone cations at 13 eV kinetic energy.

the angular distribution of dissociatively scattered ions, largely confirming the results discussed above for 49.6 eV collision with the SAM surface. As indicated in the figure, the inelastic scattering peaks are now much more intense than the delayed dissociation surface parallel component. The energetics as summarized in Fig. 13, confirming the very small energy shift associated with the delayed dissociation mechanism and that the highly inelastic scattering mechanism dissipates nearly all the collision energy into the surface.

Figs. 14 and 15 summarize our results for 13 eV SID and further support the general conclusions discussed above. Fig. 14 presents clear evidence for three distinguishable scattering processes with distinct separations in most probable scattering angle even though there are only two peaks in the energy distributions. We have also observed similar bimodal distribution of intensities at higher ion energies although it was not as pronounced as observed at 13 eV. Such a variation in the scattered ion intensities as a function of scattering angle has often been related to the geometric structure of the target surface [36]. SAM molecules stick out on the gold surface at ∼30° tilt angle and therefore it may be possible that acetone ions are interacting with different parts of the SAM molecular chains or with more than one SAM molecule simultaneously resulting in such angular distributions. For the highly inelastic peaks the recoil energy of the ion ranges from 5 eV near the surface to 2 eV at 40°. These values are not dissimilar to the recoil energy for large angle scattering at higher ion impact energy. The delayed dissociation mechanism has almost disappeared at this energy, down by a factor of 4–5 at 13 eV compared with 25.2 eV. Both contrast with the 49.6 eV experiment, for which this is the dominant mechanism.

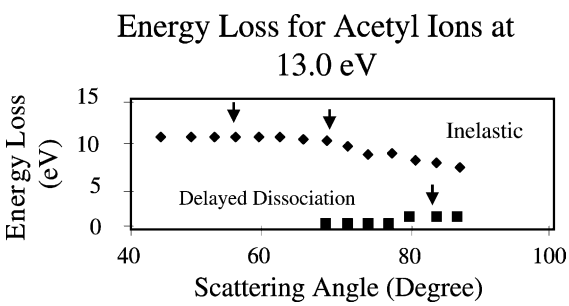

Fig. 15. A plot of kinetic energy lost by dissociating acetone cations for the formation of acetyl fragment cations at 13 eV kinetic energy. Arrows indicate the most probable scattering angles for the two dissociation processes. The data points marked delayed dissociation correspond to ions dissociating after passing through the energy analyzer. See text for details.

4. Conclusions

Low energy SID of acetone cations with a fluorinated SAM surface on gold has been demonstrated to

proceed via three energetically and spatially distinct dissociation pathways depending upon the ion's kinetic energy. Our results suggest that ion-surface collisions leading to dissociation involve a combination of a "skittering" reaction following impulsive scattering and multiple interactions with surface groups of the SAM molecular chain and a stronger interaction in which essentially all of the ion kinetic energy is transferred to the surface. These mechanisms result in uniquely different energetics and dynamical features. The "skittering" mechanism has several distinctive features—(1) quasi-elastic scattering of the molecular ion and the dissociation channel have indistinguishable angular scattering and energetics; (2) extremely narrow angular distributions, comparable to that of the reactant ion beam, scattered nearly parallel to the surface; and (3) a dominant long-lived decay of internally excited acetone cations, accompanied by a lower intensity prompt dissociation. The large scattering angle highly inelastic scattering peaks are always dissociative with short lifetimes. The explanation for the clearly resolved angular scattering of low recoil energy product ions—especially evident at 13 eV impact energy—is not entirely satisfactory. We have suggested a diffraction effect of shadowing by surface groups. Finally, we see no evidence in our SID experiments for a dominant role of excited states, as was found for gas phase CID. The most likely place for long-lived excited states present in the ion beam to manifest themselves is the 13 eV experiment, which should correspond to low energy in the CM reference frame where such behavior was observed for dissociation from gas phase collisions. No evidence for superelastic scattering was found, contrasting with our low energy CID experiments in which superelastic scattering was the predominant mechanism.

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