Surface-induced reactions and dissociations of small acetone, acetonitrile and ethanol cluster ions: competitive chemical reactions, dissociation mechanisms and determination of dissociation energy

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New Journal of Physics 5 (2003) 9.1–9.18 (http://www.njp.org/)
Received 10 July 2002, in final form 27 October 2002
Published 23 January 2003

Abstract. Using a recently commissioned tandem mass spectrometer system, BESTOF, we have carried out systematic investigations (using also deuterated molecules) on the interaction of various molecular cluster ions (including stoichiometric acetone and acetonitrile cluster ions and protonated ethanol cluster ions) with a hydrocarbon-covered stainless steel surface. Besides observing competitive chemical reactions for the stoichiometric cluster ions driven by the energy transfer in the surface collision (intra-cluster reactions versus surface H-atom pick-up reactions), we were able to see clear evidence that unimolecular dissociation kinetics determines the production of the observed decay patterns in collision energy-resolved mass spectra (CERMS). From characteristic shifts in these CERMS we can deduce corresponding binding energies, i.e., $D((\text{CD}_3\text{CN})_2^-\text{CD}_3\text{CN}) = 0.66 \text{ eV}$, $D((\text{C}_2\text{H}_5\text{OH})_2^+\text{H}^+\text{--C}_2\text{H}_5\text{OH}) = 0.95 \text{ eV}$, and for the protonated dimer $D((\text{C}_2\text{H}_5\text{OH})\text{H}^+\text{--C}_2\text{H}_5\text{OH}) = 1.6 \text{ eV}$. The first value is in good agreement with values currently calculated using the B3LYP (Becke–

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Lee–Yang–Parr) density functional and the 6-311G(d, p) basis set, the latter values are in good agreement with values derived earlier from thermochemical data.

Moreover, in the case of the protonated ethanol cluster ion, it is possible to arrive at a single (universal) breakdown graph for the trimer composed of data derived from monomer, dimer and trimer CERMS. This can be achieved by renormalizing the energy scale in the CERMS for the monomer, dimer and trimer ions (taking into account the conversion from translational to internal energy and assuming that the clusters behave like a statistical ensemble with the corresponding degrees of freedom).

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1. Introduction

Fragmentation of finite-size systems is a widespread phenomenon in nature, including such diverse phenomena as the break-up of microscopic objects and collisions between asteroids [1, 2]. The study of fragmentation of systems such as nuclei, molecules and clusters has attracted much interest recently and one intriguing result is the recognition that the general features of this phenomenon (e.g. fragmentation patterns; see figure 1) are rather independent of the actual system studied and its corresponding interaction forces [3]. It is thus not surprising that one important field in cluster science (recently attracting growing interest) is the study of the fragmentation behaviour of excited cluster ions, \( \text{X}_{n}^{z+,n} \)

\[
\text{X}_{n}^{z+,n} \rightarrow \Sigma \text{X}_{p}^{q+}
\]  

produced by such means as photon, electron and ion impact or surface collisions.

Whereas cluster ion fragmentation induced by low-energy deposition has usually been interpreted in the framework of the evaporative ensemble model [4]–[7] (curve 1 in figure 1), recently reported fragmentation patterns exhibiting bimodal (U-shaped) decay patterns (curve 2 in figure 1) obtained in high-energy atom/cluster collisions [8]–[11] and multiply charged ion/cluster collisions [12, 13] have been interpreted in terms of the occurrence of both evaporative cooling reactions and multi-fragmentation processes. These bimodal distributions, sometimes exhibiting a U shape (see figure 1), sometimes consisting of two peaks separated by a strong and extended minimum, have also been observed for primary mass spectra after electron impact [14] or photon impact [15] ionization of \( \text{C}_{60} \) or for \( \text{C}_{60} \) ions impinging on a surface (see [16]).
Figure 1. Schematic representations of the normalized fragmentation yield versus normalized fragment size $p/n$ for four different fragmentation regimes after [9]. Regime (1): monomer evaporation in low-energy collisions; regime (2): the bimodal regime (evaporation and multi-fragmentation); regime (3): the intermediate regime (multi-fragmentation); regime (4): complete disintegration (shattering).

Moreover, beam foil experiments [17] have led to a complete disintegration of the projectile (curve 4 in figure 1); in a similar manner, high-energy impact of cluster ions on surfaces has also been described in terms of complete shattering of the clusters [18]. It is interesting to note here that these distribution patterns obtained in cluster ion fragmentation studies are similar to what has been observed earlier in nuclear fragmentation reactions [19].

Nevertheless, an intermediate regime (see the dashed curve in figure 1) observed in nuclear reactions and characterized by a fragment distribution described solely by a decreasing power law function $F_p$:

$$F_p \propto (p/n)^{-\tau}$$

had until recently not been observed in cluster experiments. This intermediate regime is of particular importance because of the predicted presence of a critical behaviour in nuclear fragmentations, i.e., involving liquid–gas phase transitions in the course of the decay of hot-nuclear-reaction compounds [20]–[23]. In recent studies by Farizon and co-workers involving high-energy cluster–cluster collisions in which all the fragments are mass analysed on an event-by-event basis using a novel multi-coincidence technique, this intermediate regime was explored for the first time for the cluster case. This work gave clear evidence for a liquid–gas-like phase
transition in the excited cluster ions during the decay reactions [9, 24]–[27].

The present series of studies is another attempt to access this intermediate regime. We, however, employ low-energy collisions between polyatomic cluster ions and a surface. The present results show that in this case surface collisions do not lead to a total shattering of the cluster ions, but instead to a fragmentation pattern reminiscent of this intermediate regime.

In this communication we present results on three different cluster systems including stoichiometric acetone cluster ions, stoichiometric acetonitrile cluster ions and protonated ethanol cluster ions up to cluster size 4 and in an energy range from about a few electron volts up to about 80 eV. Employing a recently constructed tandem mass spectrometer system, BESTOF [28], we have carried out systematic investigations (using also deuterated clusters) on the interaction of these molecular cluster ions (see also some earlier studies involving benzene dimer ions [29]) with a hydrocarbon-covered stainless steel surface including surface-induced dissociation (SID) and surface-induced reactions (SIR). Besides observing competitive chemical reactions for the stoichiometric cluster ions driven by the energy transfer in the surface collision (intra-cluster reactions versus surface H-atom pick-up reactions), we were able to see for all of the cluster ions (stoichiometric and non-stoichiometric) clear evidence of a fragmentation pattern as in the intermediate case mentioned above. We were also able to observe its transition with increasing collision energy towards a complete disintegration of the impinging cluster ions. Some of the results concerning the acetone clusters have already been published [30, 31] and some of the data concerning the acetonitrile cluster ions have recently been submitted for publication [32].

2. Experimental details

Experiments were carried out with the recently commissioned tandem mass spectrometer apparatus BESTOF (see figure 2). It consists [28] of a double-focusing two-sector-field mass spectrometer (reversed geometry) combined with a linear time-of-flight mass spectrometer. Neutral clusters are produced by supersonic expansion through a 20 µm nozzle in a continuous, cooled or heated, cluster source. The pressure of the expanding gas can be as high as 2.5 bars and the temperature in the expansion vessel can be controlled in the range from −180 to 120 ºC. After passing through a skimmer, the neutral beam enters transversely into a Nier-type electron impact ion source. Besides that, a direct gas inlet may be utilized to prepare a stagnant monomer gas target in this Nier-type source. Neutral molecules or clusters are ionized in this ion source by impact of electrons whose energy can be varied from below the ionization energy up to about 500 eV. The ions produced are extracted from the ion source region and accelerated to 3 keV for mass (and energy) analysis by a double-focusing two-sector-field mass spectrometer. Figure 3 shows as an example a typical primary mass spectrum taken at the exit of the first mass spectrometer with a detector which can be moved into the beam line, demonstrating the resolving power of this instrument, which thus allows us to select isotopically separated primary ion beams.

After passing the mass spectrometer exit slit, the mass-selected ions are refocused by an Einzel lens and decelerated to the required collision energy before interacting with the target surface. Shielding the target with conical shield plates minimizes field penetration effects. The incident impact angle of the projectile ions is usually kept at 45º and the scattering angle (defined as a deflection from the incident beam direction) is fixed at 91º (for possible variation of the incident and scattering angles and the influence of this on the product ion yields, see for instance [33]). The collision energy of ions impacting on the surface is defined by the potential

New Journal of Physics 5 (2003) 9.1–9.18 (http://www.njp.org/)
**Figure 2.** A schematic view of the tandem mass spectrometer BESTOF consisting of a $B$-sector field, an $E$-sector field, a surface and a time-of-flight mass spectrometer.

**Figure 3.** The primary mass spectrum obtained by electron impact ionization with 80 eV electrons of a neutral ethanol cluster beam seeded in helium.

Difference between the ion source and the surface. The potential difference (and, hence, the collision energy) can be varied from about 0 to 2 keV with a typical resolution of about 200 meV (full width at half-maximum). The collision energy and the projectile beam energy spread was determined by applying to the target a retarding potential and measuring the (reflected) total ion signal as a function of the target potential. A fraction of the product ions formed at the surface exit the shielded chamber through a 1 mm diameter orifice. The ions are then subjected to a pulsed extraction- and-acceleration field which initiates the time-of-flight analysis of the ions. The second mass analyser is a linear time-of-flight mass selector with a flight tube of about 80 cm length. The mass-selected ions are detected by a double-stage multi-channel-plate which is connected to a multi-channel scaler (time resolution of 5 ns/channel) and a laboratory computer.

In the present experiments, neutral acetone as well as acetonitrile cluster beams were produced by supersonic expansion of an argon/acetone (argon/acetonitrile) mixture (prepared...
by bubbling argon through liquid acetone or acetonitrile at room temperature) at a pressure of the Ar seeding gas of about 1.5 bar and at a stagnation temperature in the expansion vessel of about 300 K. In the case of ethanol clusters, helium was employed as the carrier gas. The surface used was a polished stainless steel surface maintained under ultrahigh-vacuum conditions (about $10^{-9}$ Torr or better) in our bakeable turbo-pump-evacuated target collision chamber. However, even these conditions did not exclude deposition of multi-layers of hydrocarbon contaminants on the surface whenever the valve between the mass spectrometer and the target collision chamber was opened and the pressure in the target region increased to the $5 \times 10^{-9} - 10^{-8}$ Torr range.

3. Results and discussion

3.1. Competitive chemical reactions

Figure 4 illustrates the surface collision reaction products for the impact of mass-selected acetone dimer radical cations $(\text{CH}_3\text{COCH}_3)_2^+$ at the collision energies of 15, 20 and 30 eV. Figure 5 shows the corresponding CERMS for this projectile ion, where the relative abundances of all product ions are plotted as a function of the collision energy. At around 20 eV the major secondary ions are the protonated monomer ion $(\text{CH}_3\text{COCH}_3)^+$ as well as the monomer ion $(\text{CH}_3\text{COCH}_3)^+$, the latter very likely arising from simple collision-induced decomposition of the dimer projectile ion. Both types of product ion are observed at collision energies as low as 10 eV. The abundance of the acetyl cation $\text{CH}_3\text{CO}^+$, which is a minor secondary ion at 20 eV, increases monotonically with collision energy. The acetyl ion is the major collision-induced decomposition product for the acetone molecular ion in the gas phase [34]. It is also a major dissociation product formed in low-energy SID upon impact of the acetone monomer ion on a surface [35]. Consequently, we identify the acetyl cation with the break-up of molecular acetone ions present after the surface impact of the dimer ion. In addition to the acetyl ion, several other fragment ions, $\text{CH}_3^+$, $\text{C}_3\text{H}_7^+$ and $\text{CH}_2\text{OH}^+$, are observed in appreciable amounts at higher collision energies. $\text{CH}_3^+$ is known to be a fragment ion of the acetone monomer ion, whereas $\text{CH}_2\text{OH}^+$ is known to be a secondary dissociation product of protonated acetone cations when collision energy is increased. As both the acetone monomer ion and the protonated acetone ion are present in the secondary-ion mass spectrum and both are decreasing in relative abundance as the other fragment ions, i.e. $\text{CH}_3^+$, $\text{C}_3\text{H}_7^+$ and $\text{CH}_2\text{OH}^+$, are increasing in relative abundance with increasing collision energy, the production pathways of these fragment ions appear to be straightforward.

Nevertheless, these reactions of the acetone dimer ion with the surface yield as the major product ion the protonated acetone monomer ion $(\text{CH}_3\text{COCH}_3)^+$. Important insight into the origin of this protonated acetone ion formation can be gained by performing experiments using completely deuterated acetone dimer ions $(\text{CD}_3\text{COCD}_3)_2^+$ as projectiles (see figure 6). In this case (for details on this identification, see [30, 31] and the inset in figure 6(a)), it turns out that the monomer ion group in the product ion mass spectrum consists of three peaks, corresponding to the deuteronated acetone ion $(\text{CD}_3\text{COCD}_3)_2^+$, the protonated acetone ion $(\text{CD}_3\text{COCD}_3)^+$ and the acetone monomer fragment ion $\text{CD}_3\text{COCD}_3^+$. The explanation is that the deuteronated acetone ion $(\text{CD}_3\text{COCD}_3)_2^+$ is produced in a surface-induced intra-cluster ion–molecule reaction:

\[(\text{CD}_3\text{COCD}_3)_2^+ + \text{S/RH} \rightarrow (\text{CD}_3\text{COCD}_3)_2^* \rightarrow (\text{CD}_3\text{COCD}_3)^+ + \text{CD}_2\text{COCD}_3 \quad (3a)\]

where reaction (3a) represents a collisional activation of the impinging dimer ion followed by an intra-cluster ion–molecule reaction between the acetone ion and its neighbouring neutral
molecule. In contrast, the protonated acetone ion (CD\textsubscript3COCD\textsubscript3)\textsuperscript{H+} originates via a reaction of the impinging dimer ion with hydrogen-containing surface adsorbates:

\[
\text{(CD\textsubscript3COCD\textsubscript3\textsuperscript{+})\textsubscript{2} + S/RH \rightarrow (CD\textsubscript3COCD\textsubscript3)\textsuperscript{H+} + CD\textsubscript3COCD\textsubscript3.}
\] (3b)

This is in line with information from earlier studies on the reaction of acetone monomer ions with a surface, where the protonated acetone ion was formed exclusively by H abstraction from hydrocarbon adsorbates on the surface [35].

In order to rationalize the occurrence of these reaction products for the interaction of the acetone dimer ion with the surface, we have to assume that the hydrogen-bonded dimer ion may alternatively exist before the impact in two different isomeric configurations separated by a barrier (i.e., utilizing the picture of the Brauman double-well potential [36]; for details see [30, 31]), i.e., one consisting of (CD\textsubscript3COCD\textsubscript2)\textsuperscript{D+}(CD\textsubscript3COCD\textsubscript3) and one consisting of (CD\textsubscript3COCD\textsubscript3)\textsuperscript{+}(CD\textsubscript3COCD\textsubscript3). As demonstrated in many earlier studies [37]–[40], surface collisions convert translational energy efficiently into internal energy, a typical conversion factor for the hydrocarbon-covered stainless steel surface being approximately 6\% [39, 41, 42]. For the present example, the sudden increase in internal energy results in dissociation with localization of the charge on either the deuterated acetone structure (CD\textsubscript3COCD\textsubscript3\textsuperscript{D+} (reaction (3a)) or on the molecular ion (CD\textsubscript3COCD\textsubscript3\textsuperscript{+}). Similarly to in the monomer case discussed above, in the latter
case most of the molecular acetone cations may then react with surface hydrocarbons to give the 
hydrogen abstraction protonated acetone (CD₃COCD₃)H⁺ (reaction (3b)) as its major product. The 
intact molecular ion, (CD₃COCD₃)⁺, is also observed as a less abundant dissociation product. Some 
of those ions may be ions which after dissociation at the surface have not reacted to 
(CD₃COCD₃)H⁺, but some of those ions may also have been formed in slow dissociations of 
the receding dimer ion to (CD₃COCD₃)⁺ + (CD₃COCD₃) after the interaction with the surface.

The results for the acetone trimer and tetramer cluster projectiles are very similar, as can 
be seen in figure 6. Also in these cases the most abundant reaction products are the protonated 
monomer as well as the deuterated monomer cation. Only the relative abundance of those 
product ions changes with cluster size. A likely reason is that attaching additional neutral acetone 
molecules changes the relative depths of the minima in the double-well potential invoked above 
to rationalize the occurrence of these competing reactions.

An analogous study with acetonitrile cluster ions (see examples of the mass spectra of 
product ions formed in surface interactions of deuterated acetonitrile dimer ions (CD₃CN)₂⁺ at 
collision energies of 15, 25 and 35 eV in figure 7) confirms the occurrence of these competing 
reactions, too. The mass spectra show, similarly to in the case of the non-deuterated dimer 
cation (CH₃CN)⁺ (not shown and discussed here; for details see the forthcoming paper [32]), 
a considerable amount of the non-dissociated dimer ion. This ion quickly disappears with 
increasing collision energy (when going from 15 to 25 eV) in favour of several smaller ions, one 
being the direct dissociation product, i.e., the acetonitrile molecular ion CD₃CN⁺. However, as 
the main dissociation product of surface collisions of (CD₃CN)₂⁺ (which in the case of surface 
interactions of (CH₃CN)⁺ was the protonated acetonitrile ion CH₃CNH⁺) there appear here 
both the deuterated molecular ion, CD₃CND⁺, and the protonated molecular ion, CD₃CNH⁺. 
Similarly to in the case of the acetone clusters discussed above, we can interpret the occurrence 
of both CD₃CND⁺ and CD₃CNH⁺ as products of two different reactions induced by the surface.
Figure 6. Secondary-ion mass spectra after surface collisions of deuterated acetone dimer (a), trimer (b) and tetramer (c) cations at collision energies of (a) 30 (b) 40 and (c) 55 eV, respectively.

collision, i.e., CD₂CND⁺ as a product of an intra-cluster chemical reaction in the dimer, induced by the surface collision

\[
(\text{CD}_3\text{CN})_2^+ + \text{S/RH} \rightarrow (\text{CD}_3\text{CN})_2^{++} \rightarrow \text{CD}_3\text{CND}^+ + \text{CD}_2\text{CN}
\]  

(4a)

and CD₃CNH⁺ as a product of an H-atom pick-up reaction from the surface material during the cluster–surface interaction, presumably between the dissociated molecular ion and the surface hydrogen:

\[
(\text{CD}_3\text{CN})_2^+ + \text{S/RH} \rightarrow \text{CD}_3\text{CNH}^+ + \text{CD}_3\text{CN}.
\]  

(4b)

As in the case of acetone cluster ions, the competition of the two processes, dissociation of the acetonitrile dimer ion to either the deuteronated product CD₂CND⁺ plus CD₂CN (reaction (4a)) or to the molecular ion CD₃CN⁺ (reacting in part subsequently with the surface hydrogen via reaction (4b))) plus a neutral acetonitrile molecule can be explained with the help of the Brauman double-well potential [36]. In this case the acetonitrile dimer ion, relaxed by monomer evaporation from larger cluster ions to a low internal energy, exists prior to its interaction with the surface in two different configurations, symbolized as (CD₂CN)–(CD₃CND)⁺ and (CD₃CN)–(CD₃CN)⁺, separated by a barrier. In the surface collision a fraction of the collision
energy is converted into internal energy of the dimer ion and this leads to its dissociation to the ion moieties CD$_3$CND$^+$ or CD$_3$CN$^+$, depending on the initial population of the configurations in the two potential energy minima.

3.2. Surface-induced dissociation: sequential unimolecular decay and determination of binding energy

So far our discussion concerned chemical reactions of the cluster ions upon interaction with the surface. The acetone cluster ion system represents a case where the ion/surface collisions lead to the complete disintegration of the impinging cluster ion and the product ions observed are either monomer or protonated monomer ions or fragment ions thereof. No cluster product ions with monomers attached to the product monomer ion or protonated monomer ions (and their fragments) were observed.

The situation is different for the acetonitrile cluster ions. In this case the dimer projectile ions (CD$_3$CN)$_2^+$ are still present in the product ion spectrum (see the upper panel in figure 7) in considerable abundance, even when the collision energy is already high enough to yield appreciable amounts of the monomer ions. As a matter of fact, it is possible to observe a crossover in the CERMS plot (figure 8(a)) between the decreasing abundance curve of the

**Figure 7.** Product ion mass spectra from surface interactions of the deuterated acetonitrile dimer ion (CD$_3$CN)$_2^+$ at collision energies of 15, 25 and 35 eV.
undissociated product dimer ion \((\text{CD}_3\text{CN})_2^+\) and the increasing ‘protonated’ monomer product ion \((\text{CD}_3\text{CN})_D^+\) at about 8 eV, thus demonstrating the direct relationship between the loss of the reactant ion in favour of the production of the product ion. Even more exciting is that, in the case of the acetonitrile trimer ion (see figure 8(b)), we are able to observe at low energies besides the decreasing dimer ion the decreasing trimer ion. In addition, the change of the relative abundance of the dimer ion curve in figures 8(a) and (b) with collision energy and the shape of the corresponding trimer ion curve in figure 8(b) and also of the other CERMS curves in figure 8 clearly indicates the sequential nature of the break up, i.e., the trimer ion decaying into the dimer ion and the dimer ion then decaying into various monomer ions. Moreover, it is interesting to note that the crossover between the dimer ion and the (dominant) monomer ion produced is shifted in the case of the trimer projectile ion \((\text{CD}_3\text{CN})_3^+\) (see figure 8(b)) by approximately 11 eV to the collision energy of 19 eV. This shift indicates that energy transferred from translational to internal energy of the collision complex is first used to break away a monomer from the trimer ion and then in a sequential manner the dimer ion produced dissociates to further products. Therefore, under the condition that this trimer-to-dimer ion dissociation is the only decomposition process of the trimer ion and that the dimer ions are dissociating in a similar manner, it can be argued that this shift (approximately 11 eV) between the crossover points in the two cases is proportional to the binding energy of the trimer decaying into the dimer ion. Assuming an efficiency of about 6% for the collision-to-internal energy conversion on the hydrocarbon-covered stainless steel surface (see for details [39, 41, 42]), one obtains about 0.66 eV for the binding energy between a neutral acetonitrile monomer and the acetonitrile dimer cation. Note that the initial dominant monomer products are, however, different in these two cases. For the dimer case the prevailing product at low energies is the \(\text{CD}_3\text{CND}^+\) fragment ion, whereas in the trimer case it is the \(\text{CD}_3\text{CNH}^+\) fragment ion (a similar observation has been discussed already above for the competitive reactions in acetone cluster ions). In order to take this into account we have plotted in figure 9 CERMS curves for the two cases, however summing over the different monomer fragment channels. The resulting shift in this case is approximately 10 eV, yielding a corresponding binding energy of about 0.6 eV. It is interesting to note that the present method is reminiscent of the so-called model-free approach presented recently at this year’s ISSPIC meeting by Schweikhard et al [43].

The interaction between the acetonitrile dimer cation and one neutral acetonitrile molecule was also investigated by means of quantum chemical calculations. Since the energy surface of the trimer and dimer cations is of considerable complexity, we tried to scan its important parts by performing a series of unrestricted Hartree–Fock (UHF) geometry optimizations starting from plausible structures. For this, the 3-21G basis set [44] was used, which is small but is known to give reliable results for systems containing second-row atoms.

All intermolecular and intramolecular degrees of freedom were optimized. We found three stable conformations for the acetonitrile dimer cation. They are shown in parts (a)–(c) of figure 10, annotated with the Mulliken partial charges. In structure (c) a bond from one N atom to the C atom of the cyanide group of the second acetonitrile molecule is formed and the positive charge resides mostly on this carbon atom. This structure is about 1.1 eV more stable than (a) and about 2.2 eV more stable than (b). The large differences in energy can be attributed to the fact that (a)–(c) are really different molecules: (a) is an unusual structure with the spin density localized at the two nitrogen atoms which are partially bonded with a N–N distance of only 1.98 Å; (b) is a hydrogen-bonded complex (parts of the spin density reside on every atom) while (c) is an amidine cation. For the trimer cation two stable structures could be identified.
Figure 8. CERMS for product ions from surface interactions of the (deuterated) acetonitrile dimer ions \((\text{CD}_3\text{CN}^+)\) \_2\ (upper panel) and of the (deuterated) acetonitrile trimer ions \((\text{CD}_3\text{CN}^+)\) \_3\.

(we did not consider structures obtained by abstraction of \(\text{H}^+\) from the methyl groups). They are shown in parts (d) and (e) (figure 10). Other plausible starting geometries, for example a prismatic structure with the three acetonitrile molecules aligned parallel or antiparallel to each other along the edges of a prism and a triangular structure which allows for C–H hydrogen bonding, are apparently not local minima of the global potential energy surface, but converge to structures (d) or (e). Structure (e) (which contains the dimer cation subunit shown in (c)) is more stable than (d) by about 1.4 eV. The binding energy between a neutral acetonitrile molecule and the dimer cation, obtained as the difference between the energies of structure (c) plus a neutral acetonitrile molecule and structure (e), is \(-0.85\) eV. For this complex, we performed a more accurate calculation with the B3LYP [45] density functional and the 6-311G(d, p) basis set [46]. With fully optimized geometries, a slightly lower value of \(-0.75\) eV for the binding between one acetonitrile molecule and the dimer cation is obtained. In particular the lower value of \(-0.75\) eV is in good agreement with the experimental values.

Thus, the fragmentation and the reaction patterns of the trimer acetonitrile ions show (in contrast to some of the earlier cluster ion studies leading to a complete shattering of the cluster
Figure 9. As figure 8, but for fragment ions with mass-to-charge ratios 46, 45 and 44 summed together (see the text).

Figure 10. Optimized geometries of the dimer ((a)–(c)) and trimer ((d), (e)) cations of acetonitrile, together with the Mulliken charges of C and N atoms of the cyanide residues and the methyl groups. See the text for explanations.
ions; see [18, 19] and references therein) that unimolecular dissociation kinetics determines the formation of product ions in the acetonitrile cluster ion surface-induced decomposition. Moreover, the data offer a possibility of deducing the binding energy of the clusters in a novel way.

Studies of the surface-induced decomposition of protonated ethanol cluster ions provide another example of the decay mechanisms governed by unimolecular rate kinetics. The primary mass spectrum obtained by ionization of neutral ethanol clusters by impact of 80 eV electrons (see figure 3) exhibits only protonated ethanol cluster ions; the stoichiometric cluster ions were absent in the mass spectrum. This observation is in agreement with earlier observations of Lifshitz and co-workers [47] as well as Stace and co-workers [48] on ethanol cluster ions. Protonated ethanol cluster cations are produced by an ion–molecule reaction of a larger intermediate cluster, and are then stabilized by successive evaporations of monomers. As seen in figure 3, electron impact ionization of the ethanol cluster beam, besides leading to the production of the monomer ion and some impurities, also leads to a small signal of the protonated monomer ion at \( m/z = 47 \) and the protonated dimer ion \((\text{C}_2\text{H}_5\text{OH})_2\text{H}^+ \) \((m/z = 93)\). The stoichiometric dimer ion \((m/z = 92)\) is clearly missing in this spectrum.

Figure 11 shows the CERMS curves of the protonated ethanol trimer \((\text{C}_2\text{H}_5\text{OH})_3\text{H}^+ \), dimer \((\text{C}_2\text{H}_5\text{OH})_2\text{H}^+ \) and monomer \((\text{C}_2\text{H}_5\text{OH})\text{H}^+ \) ion, as obtained from the series of mass spectra measured at a series of collision energies. The CERMS curves are plotted above each other, but are shifted against each other so that the characteristic features, i.e., crossings of the major product ion abundances, will fit above each other. Thus, the crossings between the product ion \((\text{C}_2\text{H}_5\text{OH})\text{H}^+ \) and \( \text{C}_2\text{H}_3^+ \) curves lead to the shift of the CERMS plots of the protonated dimer \((\text{C}_2\text{H}_5\text{OH})_2\text{H}^+ \) with respect to the protonated trimer by 17 eV, and the crossings between the product ion \((\text{C}_2\text{H}_5\text{OH})\text{H}^+ \) and \( \text{C}_2\text{H}_3^+ \) curves to a shift of the protonated monomer CERMS plots with respect to the trimer curve by about 41 eV and with respect to the dimer CERMS plots by about 25 eV (see figure 11). There is an obvious similarity in the CERMS patterns in figure 11, if shifted in the way described. However, the patterns seem to be more and more compressed when going from the protonated trimer to the protonated monomer.

The shifts of the collision energy scale for the three projectiles evidently indicate energy differences required to achieve the same degree of fragmentation in the projectile and thus they should be related to the energy of binding of the dissociating monomer molecule to the respective cluster ion. Assuming—as stated earlier—the collisional-to-internal energy transfer of 6% for this type of surface [39, 41, 42], we can derive from the shifts of the energy scale in figure 11 an approximate value of the dissociation energy of an ethanol molecule from the protonated ethanol trimer \( D((\text{C}_2\text{H}_5\text{OH})_3\text{H}^+ − \text{C}_2\text{H}_5\text{OH}) = 0.06 \times (41 − 25) = 0.95 \text{ eV} \), and for the protonated dimer \( D((\text{C}_2\text{H}_5\text{OH})_2\text{H}^+ − \text{C}_2\text{H}_5\text{OH}) = 0.06 \times (45 − 18) = 1.6 \text{ eV} \). These values are in fair agreement with calculated binding energies of about 0.9 eV for the trimer and about 1.35 eV for the dimer ion obtained by Jarvis et al [49] and a value of 1.37 eV for the dimer ion estimated from thermochemical data by Bomse and Beauchamp [50].

The evident compression of the CERMS curve pattern in figure 11 when going from the protonated trimer projectile to the protonated monomer is due to the fact that for different projectiles the same energy is distributed over a different number of internal degrees of freedom. A unification of the picture can be achieved by normalizing the energy scale to the energy pertinent to a single degree of freedom. For a system behaving like a statistical ensemble, the number of internal degrees of freedom is \((3N − 6)\), where \(N\) is the number of atoms in the system. For the protonated trimer \((N_3 = 28)\), dimer \((N_2 = 19)\) and monomer \((N_1 = 10)\), these numbers are 78, 51 and 24, respectively. The relation between the energy pertinent to one internal degree...
Figure 11. CERMS for product ions from surface interactions of the protonated monomer (lower panel), dimer (middle panel) and trimer (upper panel) ethanol cluster ion. The collision energy has been shifted to fit the characteristic crossing of abundances of certain specific ions.

of freedom (idf) and the collision energy is then $\langle E_{\text{int}} \rangle_{\text{idf}} = 0.06 E_{\text{coll}} / (3N_i - 6)$. The CERMS curves from figure 11 are re-plotted in the new energy scale in one picture in figure 12, using the relation between $\langle E_{\text{int}} \rangle_{\text{idf}}$ and the absolute value of $E_{\text{coll}}$ (the collision energy scale now starts at zero; there is no shift). The mutual overlap of data from surface collisions of three different projectiles, the protonated trimer, dimer and monomer, is remarkably good. We thus obtain a unimolecular decomposition pattern of the protonated trimer over a wide range of energies by a combination of data from experiments on SID of the three different projectiles. The internal energy of the trimer is then simply $\langle E_{\text{int}} \rangle_3 = (3N_3 - 6) \langle E_{\text{int}} \rangle_{\text{idf}} = 78 \langle E_{\text{int}} \rangle_{\text{idf}}$ (the upper scale in figure 12) and in figure 12 it covers the range of $\langle E_{\text{int}} \rangle_3$ from zero to about 9.8 eV.

Recent experiments [38]–[42] clearly show that the energy transformed in a surface collision to the internal energy of a polyatomic projectile increases linearly with the collision energy and that the width of its distribution does not change much with the collision energy. Thus in a surface collision a certain specific internal energy can be imparted to the projectile. It appears that surface collision excitation may possibly be used to obtain information on the breakdown pattern of an excited polyatomic ion analogously to how charge transfer was used many years ago (see, e.g., [51, 52]). The necessary requirement, however, is that the width of imparted energy
distribution should not be too wide in comparison with the changes of relative abundance of fragment ions in the breakdown pattern. A typical energy distribution imparted to a polyatomic projectile in a surface collision, as derived from recent data for this type of surface [39, 42], has a full width at half-maximum of about 1.5 eV. The situation is not ideal, but the data suggest that the recalculated CERMS curves in figure 12 may be regarded as a relevant breakdown pattern of the protonated ethanol trimer.

4. Conclusions

The data on the SID of the protonated ethanol clusters clearly show that unimolecular decomposition kinetics of the surface-excited projectile ion governs the formation of the product ions over the collision energy range studied. The mutual consistency of the data indicates that the cluster can be regarded as a statistical ensemble with all internal degrees of freedom involved. The CERMS curves seem to provide a good source of information on the breakdown pattern of the polyatomic cluster projectile.
Acknowledgments

Partial support of this work by the FWF, ÖNB and ÖAW, Wien, Austria, by the European Commission, Brussels, by the Socrates/Erasmus Programme (JF), by the grant No 203/00/0632 of the Grant Agency of the Czech Republic, by the Slovak–Austria Cooperation Programme in Science and Technology (No 25s19), by the Czech–Austria Cooperation Programme in Science and Technology (Kontakt 2000-01, No 6) and by RFBR Project 01-03-02006 is gratefully acknowledged.

References

[1] Hutchinson H 1998 Science 280 693
[2] Binzel R P 1997 Nature 388 516
[3] Beyson D, Campi X and Pfefferkorn E (ed) 1995 Fragmentation Phenomena (Singapore: World Scientific)
[4] Van Lunig A and Reuss J 1978 Int. J. Mass Spectrom. Ion Phys. 27 197
[5] Klots C E 1988 J. Phys. C: Solid State Phys. 92 5864
[6] Märk T D 1994 Linking Gaseous and Condensed Phases of Matter ed L G Christophorou, E Illenberger and W F Schmidt (New York: Plenum)
[7] Wörgötter R, Dünser B, Scheier P, Märk T D, Foltin M, Klots C E, Laskin J and Lifshitz C 1996 J. Chem. Phys. 104 1225
[8] Ehlich R, Westerburg M and Campbell E E B 1996 J. Chem. Phys. 104 1900
[9] Farizon B et al 1997 Int. J. Mass Spectrom. 164 225
[10] Vandenbosch R et al 1998 Phys. Rev. Lett. 81 1821
[11] Opitz J et al 2000 Phys. Rev. A 62 022705
[12] LeBrun T et al 1994 Phys. Rev. Lett. 72 3965
[13] Schlathölter T, Hoekstra R and Morgenstern R 1998 J. Physique B 31 1321
[14] Scheier P, Dünser B and Märk T D 1995 J. Phys. Chem. 99 15428
[15] Hohmann H, Callegari C, Furrer S, Grosenick D, Campbell E E B and Hertel I V 1994 Phys. Rev. Lett. 73 1919
[16] Campbell E E B and Levine R 2000 Rep. Prog. Phys. 63 1061
[17] Mazuy B, Elkacem A, Chevallier M, Gaillard M J, Poizat J C and Remillieux J 1987 Nucl. Instrum. Methods B 28 497
[18] Raz T, Even U and Levine R D 1995 J. Chem. Phys. 103 5394
[19] Christen W and Even U 1998 J. Phys. Chem. 102 9420
[20] Campi X 1992 Nucl. Phys. A 545 161
[21] Gross D H E, DeAngelis A R, Jaqaman H R, Jicai P and Heck R 1992 Phys. Rev. Lett. 68 146
[22] Latora V, Belkacem M and Buonasera A 1994 Phys. Rev. Lett. 73 1765
[23] Gross D H E and Hervieux P A 1995 Z. Phys. D 35 27
[24] Farizon B et al 1998 Phys. Rev. Lett. 81 4108
[25] Farizon B et al 1999 Eur. Phys. J. D 5 5
[26] Gobet F et al 2001 Phys. Rev. Lett. 86 4263
[27] Gobet F et al 2001 Phys. Rev. Lett. 87 203402
[28] Mair C, Fiegele T, Biasioli F, Wörgötter R, Grill V, Lezius M and Märk T D 1999 Plasma Sources Sci. Technol. 8 191
[29] Wörgötter R, Mair C, Fiegele T, Grill V, Märk T D and Schwarz H 1997 Int. J. Mass Spectrom. Ion Process. 164 L1
[30] Mair C, Fiegele T, Biasioli F, Futrell J H, Herman Z and Märk T D 1999 Int. J. Mass Spectrom. Ion Process. 188 L1
[31] Mair C, Fiegele T, Biasioli F, Herman Z and Märk T D 1999 J. Chem. Phys. 111 2770

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[32] Mair C, Herman Z, Fedor J, Lezius M and Märk T D 2003 Chem. Phys. in press.
[33] Wörgötter R, Kubišta J, Zabka J, Dolejšek Z, Märk T D and Herman Z 1998 Int. J. Mass Spectrom. Ion Process. 174 53
[34] Futrell J H 1998 private communication
[35] Wörgötter R, Grill V, Herman Z, Schwarz H and Märk T D 1997 Chem. Phys. Lett. 270 333
[36] Brauman J I 1979 Kinetics of Ion–Molecule Reactions ed P Ausloos (New York: Plenum) p 153
[37] Cooks R G, Ast T and Mabud M A 1990 Int. J. Mass Spectrom. Ion Process. 100 209
[38] Grill V, Shen J, Evans C and Cooks R G 2001 Rev. Sci. Instrum. 72 3149
[39] Kubišta J, Dolejšek Z and Herman Z 1998 Eur. Mass Spectrom. 4 311
[40] Zabka J, Dolejšek Z and Herman Z 2003 J. Phys. Chem. B at press
[41] Biasioli F, Fiegele T, Mair C, Herman Z, Echt O, Aumayr F, Winter H-P and Märk T D 2000 J. Chem. Phys. 113 5503
[42] Mair C 2001 PhD Thesis University of Innsbruck
[43] Schweikhard L, Hansen K, Herlet A, Marx G and Vogel M 2003 Eur. Phys. J. D at press
[44] Binkley J S, Pople J A and Hehre W J 1980 J. Am. Chem. Soc. 102 939
[45] Becke A D 1993 J. Chem. Phys. 98 5648
[46] McLean A D and Chandler G S 1980 J. Chem. Phys. 72 5639
[47] Feng W Y and Lifshitz C 1995 Int. J. Mass Spectrom. Ion Process. 149/150 13
[48] Crooks J, Stace A J and Whitaker B J 1988 J. Phys. C: Solid State Phys. 92 3554
[49] Jarvis V M, Villanueva M A, Bostwick D E and Moran T D 1993 Org. Mass Spectrom. 28 595
[50] Bomse D S and Beauchamp J L 1981 J. Am. Chem. Soc. 103 3292
[51] Čermák V and Herman Z 1961 Nucleonics 19 106
[52] Lindholm E 1972 Ion–Molecule Reactions vol 2, ed J L Franklin (New York: Plenum) p 457