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Charge permutation reactions

Charge permutation reactions in beam type mass spectrometers

Allison S. Danell, Gary L. Glish

Department of Chemistry, University of North Carolina, Chapel Hill, North Carolina 27599-3290

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Abstract

This is a review of the gas-phase reactions, in beam type mass spectrometers, that change the charge states of ions. The Cooks research group has been a leader in both the understanding and use of these charge-changing reactions. The charge of ions can be manipulated in beam type instruments via collisions with neutral gas atoms or molecules in the high ion kinetic energy regime. The two major processes, charge inversion and charge stripping due to high energy ion/neutral collisions, are discussed. Charge permutation reactions often result in the formation of unique ion structures that aid in the differentiation of isomers. The products of charge permutation reactions may possess excess internal energy that cause the ions to fragment, and these fragment ions may provide complementary information to that obtained from high energy collision-induced dissociation. The charge of ions also can be changed as a result of a collision with a surface in the low ion kinetic energy regime. Charge exchange and charge inversion processes that occur as a result of low energy ion/surface collisions are presented. (Int J Mass Spectrom 212 (2001) 219–227) © 2001 Elsevier Science B.V.

Keywords: Charge stripping; Charge inversion; SID; High-energy CID; Sector; Quadrupole

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1. Introduction

In tandem mass spectrometry (MS/MS) experiments, a parent ion is selected in the first stage of analysis. This ion subsequently undergoes some type of reaction and the mass-to-charge ratios of the product ions are measured with the second stage of mass spectrometry. The conventional reactions involve changes in mass, most commonly dissociation into smaller mass ions in collision-induced dissociation (CID), but in some cases product ions of increased mass are observed as a result of ion/molecule association reactions. The term “mass spectrometry” thus appears to be an apt description. However, it is the mass-to-charge ratio that is typically being measured, not just the mass. Often overlooked are reactions in which the charge state of an ion changes.

The emergence of electrospray ionization combined with ion trapping instruments (both quadrupole ion traps and ion cyclotron resonance instruments) increased the use of charge permutation reactions. With the long trapping times that are possible, ion/molecule [1–5] or ion/ion reactions

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* Corresponding author. E-mail: glish@unc.edu

Dedicated to R. Graham Cooks on the occasion of his sixtieth birthday.

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[6–10] can readily be performed. However, these are relatively new entrants into the charge permutation reaction repertoire. The first charge permutation reactions were electron-stripping reactions that occurred upon ion/neutral collisions at kiloelectron volt ion kinetic energies in beam instruments. An advantage of these reactions is that with beam instruments, unique scans can be done to screen samples for compounds that undergo characteristic charge permutation reactions, unlike ion trapping instruments. Subsequent to the charge permutation reactions observed with ion/neutral collisions at kiloelectron volt ion kinetic energies, other charge permutation reactions have been observed in surface-induced dissociation (SID) experiments with ions having tens of electron volts of kinetic energy.

This article provides an overview of charge permutation reactions performed on beam instruments. As will be seen, G. Cooks and coworkers were major contributors to the development and application of charge permutation MS/MS reactions in beam instruments as well as providing insight into the fundamentals of such reactions.

2. Charge permutation reactions in gaseous collisions

2.1. Charge inversion of negative ions

In the kiloelectron volt (keV) collision energy range, when a negatively charged ion collides with a neutral target gas molecule, N, two electrons may be removed from the anion. As shown in reaction (1),

$$M^{-\cdot} + N \rightarrow M^{+\cdot} + N + 2e^{-} \tag{1}$$

the charge of a molecular anion is inverted; thus, the products of the reaction include the molecular cation, the neutral target, and two free electrons.

It is possible for the neutral target gas molecule to capture one of the free electrons. Reaction (1) is highly endothermic. The minimum energy (E_{min}) required by reaction (1) is given by equation (2)

$$E_{min} = EA(M) + IE(M) \tag{2}$$

where EA(M) is the electron affinity of the molecule and IE(M) is the ionization energy of the molecule. Eq. (2) assumes that the reactants are in their respective ground states. The minimum energy would be lowered if the reactants were to possess any excess internal energy prior to the collision. If the minimum energy required for charge inversion is exceeded, the excess energy deposited can cause subsequent fragmentation of the newly formed molecular cation. The energy to effect charge inversion comes from conversion of some of the kinetic energy of the ion into internal energy. The change in kinetic energy of an ion can be measured readily using an electric sector.

One fundamental application of negative ion charge inversion is the determination of a molecule's electron affinity. For example, the peak resulting from charge inversion of Cl^{-} to form Cl^{+} was compared to the peak arising from Cl^{-} [11]. The difference in ion translational energy between the two peaks should correlate to the sum of the electron affinity and ionization energy of Cl^{-}, as indicated by Eq. (2). Provided the ionization energy is known, the electron affinity can be calculated.

Charge inversion of negative ions was first performed by Stapleton and Bowie [12] and is observed nearly exclusively in sector instruments. Early work involving the investigations of charge inversion reactions took place using forward geometry sector instruments [12–15]. The direction of the electric (E) and/or magnetic (B) field of the individual sector(s) may have to be reversed with respect to that required to pass negatively charged ions extracted from the ion source (see Table 1), depending upon where the reaction occurs. If the charge inversion happens in the first field free region, the direction of the electric sector field is reversed (positive). The positively charged ions can be detected at an intermediate detector between the electric and magnetic sectors, or alternatively, the field direction of the magnetic sector can be reversed to pass the positively charged ions to the final detector. This class of spectra is generally called "+E" spectra, designating the direction of the electric sector field. The charge inversion can occur in

Table 1
Summary of instrumental settings necessary to observe products of charge inversion reactions; The location of where the charge-changing collisions occur is denoted by (*), and the possible use of an intermediate detector between the two sectors to observe the ions formed by charge-changing collisions is denoted by (◆)

	Polarity of ions created in source	First field-free collision region	Polarity of ions passed by electric sector	Second field-free collision region	Polarity of ions passed by magnetic sector	Information obtained
Charge inversion of negative ions	−	*	+	◆	+	+E spectrum
	−		−	*	+	Scan magnetic sector to observe dissociative charge inversion
Charge inversion of positive ions	+	*	−	◆	−	−E spectrum
	+		+	*	−	Scan magnetic sector to observe dissociative charge inversion

the second field free region, requiring no change in the direction of the electric sector field, but a reversal of the magnetic field direction. A scan of the magnetic sector records dissociation products (both metastable and collision-induced) originating from parent ions that undergo charge inversion and subsequent fragmentation in the second field free region.

Charge inversion experiments became more prevalent with the advent of reverse geometry sector instruments [16]. The mass-selected negative ions undergo charge inversion in a collision cell between the magnetic and electric sectors. The undissociated positively charged ions possess the same kinetic energy-to-charge ratio as the negative parent ions extracted from the ion source, but opposite polarity, and thus require a reversal of the electric sector field (positive) to pass to the detector. This is the most common way of acquiring a +E spectrum. With the reverse geometry configuration, the magnetic sector is scanned and the electric sector acts as a final filter to avoid interferences (peaks resulting from metastable or CID processes). This instrumental setup is a common approach used for examining dissociative charge inversion processes because mass-analyzed kinetic energy spectrometry (MIKES) can be used to measure the *m/z* values of any positively charged product ions that are formed following charge inversion [15]. These product ions are detected simply by selecting the negatively charged parent ion of interest with the magnetic sector and then scanning the electric sector (after reversing the field direction).

Negative ion charge inversion has proved useful because fragmentation of some negative ions yields few if any structurally informative ions. Positively charged ions formed by charge inversion often dissociate to produce a variety of fragment ions. For example, negative ion CID of fluoranthene produced no detectable product ions, whereas charge inversion of negatively charged fluoranthene produced an abundance of positively charged fragment ions [17]. Some classes of compounds are readily ionized by negative ionization techniques. Negative chemical ionization techniques also can be very selective, making them attractive ionization methods for the analysis of certain classes of compounds in complex mixtures. Only the desired components are ionized, greatly simplifying mass spectra. Consequently, the negative ion mode may be the preferred analysis mode of some compounds by mass spectrometry. Charge inversion of these negative ions can provide much needed structural information from the subsequent dissociation. In the fluoranthene example discussed previously, selective negative chemical ionization was combined successfully with charge inversion to verify the presence of fluoranthene in a complex mixture [17].

Extensive fragmentation may occur during charge inversion that does not occur during conventional CID of the positively charged ions. This is because of the nature of the high-energy collision resulting in the formation of $M^{+\cdot}$. The duration of a kiloelectron volt collision event is shorter than that of a molecular vibration, allowing the removal of the two electrons to be a vertical process. Consequently, the structure of the resulting cation closely resembles that of the anion [12]. If the most stable structure of the cations is significantly different than that of the anions, then the cations formed during charge inversion will be created in an excited state and possess excess internal energy that is available for fragmentation. The formation of cations through this process may yield cations not available by any other means. Polyaromatic hydrocarbons (PAHs) such as fluoranthene exhibit little or no fragmentation in their negative fragment ion (CID) spectra because of the inherent stability of their conjugated ring systems. However, the charge inversion experiment provides extensive fragmentation, allowing different ring structures to be differentiated.

Ions that undergo dissociation following charge inversion may yield unique fragment ions because of the nature of the ions sampled by charge inversion. Because reaction (1) is highly endothermic, a more representative sampling of the total ion population occurs with dissociative charge inversion than with conventional CID. During CID, higher internal energy ions are preferentially sampled, and these ions are more likely to have already isomerized [18].

Dissociative charge inversion of negative parent ions has played an important role in ion structure elucidation. The earliest application of negative ion charge inversion in the study of isomers was the differentiation of dinitrobenzenes [12]. In an attempt to determine the identities of PAHs in solvent-refined coal, charge inversion was used to distinguish isomers such as pyrene and fluoranthene [17]. The charge inversion MS/MS spectra of the $M^{-\cdot}$ parent ions of pyrene and fluoranthene were distinctive enough to tell them apart. Another example involved characterizing alkylbenzenes with the molecular formula C_8H_{10} by the unique fragment ions that appeared in the charge inversion spectra. Ethylbenzene was differentiated from xylenes via charge inversion of the $(M\text{-}H)^-$ ions, whereas all of the isomers were identified via charge inversion of the $(M\text{-}H_2)^{-\cdot}$ ions [19]. Similarly, the degree to which different isomers undergo reaction (1) could be used to differentiate them. The ortho and para isomers of hydroxybenzoic acid were differentiated by comparing their charge inversion spectra [18]. The relative intensities of the $(M\text{-}H)^+$ ions, formed by charge inversion of o- and p-hydroxybenzoic acid $(M\text{-}H)^-$ ions, were 20:1, respectively. In this example, the presence of unique fragment ions generated from the charge inversion of the two isomers was not necessary to be able to differentiate them. Structural information on nitrobenzoyl derivatives of amino esters was provided by combining data from negative ion mass spectra and dissociative charge inversion spectra [13]. Charge inversion spectra of polypeptides provided amino acid composition information that proved complementary to the sequence information found in conventional CID spectra [20]. Structures of ions undergoing gas-phase Dieckmann condensation were established using charge inversion spectra, and the proposed condensation mechanism was verified, in part, by these results [21]. These examples highlight charge inversion spectra as sources of unique information that is often complementary to the data obtained by other methods, such as CID.

On occasion, however, the extensive fragmentation observed in charge inversion can obscure low energy fragmentation processes that might differentiate isomers. As an example, the isobars 9-methylfluoranthene and 9-fluoranone give indistinguishable charge inversion spectra yet the standard negative ion CID spectra readily differentiate these species [22].

2.2. Charge inversion of positive ions

A similar process to reaction (1) can occur for positive ions. An example is shown in reaction (3)

$$M^{+\cdot} + N \rightarrow M^{-\cdot} + N^{2+} \tag{3}$$

The minimum energy (E_{min}) required by reaction (3) is given by

$$E_{min} = IE^{II}(N) - EA(M) - RE(M^{+}) \tag{4}$$

where $IE^{II}(N)$ is the double ionization energy of the neutral target gas, EA(M) is the electron affinity of the molecule, and $RE(M^{+\cdot})$ is the recombination energy of the positively charged molecule. A two-step charge inversion process is also possible, as illustrated in reaction (5)

$$M^{+} + N \rightarrow M + N^{+} \tag{5a}$$

$$M + N \rightarrow M^{-\cdot} + N^{+} \tag{5b}$$

A single electron is transferred to a neutral target molecule in reactions (5a) and (5b) as opposed to the double electron transfer occurring in reaction (3). The minimum energy (E_{min}') required by reactions (5a) and (5b) is given by

$$E_{min}' = 2IE(N) - EA(M) - RE(M^{+\cdot}) \tag{6}$$

where the ionization energy of the neutral target gas molecule is doubled instead of including its double ionization energy. Because the double ionization energy of a molecule is larger than twice its single ionization energy, the E_{min} value required for the one-step charge inversion process is larger than the E_{min}' value required for the two-step charge inversion process. Experimentally, the two mechanisms of positive ion charge inversion can be distinguished by evaluating the intensity of the charge-stripping peak as a function of the target gas (N) pressure [23]. Reaction (4), the one-step mechanism, shows first order dependence on the target gas pressure. The sequence of reactions (5a) and (5b), the two-step mechanism, shows a squared law dependence on the target gas pressure.

The instrumental configuration necessary to observe charge inversion of positive ions was first reported by Keough and colleagues [24]. As was the case for the observation of charge inversion of negative ions, the directions of the electric and magnetic sector fields must be set correctly to pass the ions of interest, which depends on where in the mass spectrometer the charge inversion of the positive ions occurs (Table 1). Forward geometry instruments were used because charge inversion of positive ions was first characterized prior to the development of reverse geometry instruments. The direction of the electric sector field must be reversed (negative) to pass the anions formed by charge inversion in the field free region preceding the electric sector. The ions can be detected at an intermediate detector, between the two sectors, to obtain an ion kinetic energy spectrum without performing mass analysis [25]. The direction of the magnetic sector field can be reversed, and ions can be mass analyzed at the final detector [24]. Charge inversion spectra of positive ions are generically referred to as "−E" spectra, specifying the direction of the electric sector field needed to pass the product anions.

Table 2
Comparison of ions appearing in positive ion, negative ion, and −E mass spectra of toluene[24,42]; The asterisk (*) denotes the base peak of the mass spectrum

Spectra of Toluene	*m/z* Values of Abundant Ions
Positive Ion Mass Spectrum	92, 91*, 65, 39
Negative Ion Mass Spectrum	84, 73, 49, 25*
−E Mass Spectrum	65*, 61, 49, 48, 39, 37, 36, 25, 24

Charge inversion also can occur in the second field free region, between the two sectors of a forward geometry instrument. In this case, the direction of the electric sector field is left unchanged to pass positively charged ions. The direction of the magnetic sector field must be reversed to pass negatively charged ions. A spectrum acquired in this manner would not be called a −E spectrum because the direction of the electric sector field passes ions with the same polarity exiting the ion source. Typically, it is called a charge inversion mass spectrum [25].

Although charge inversion of positive ions has not been exploited as extensively as charge inversion of negative ions, the same feature of unique ion formation is observed. The structure of the anion formed by charge inversion will be the same as the structure of the parent cation because charge inversion is a vertical process. The structure of the anion may not be the most stable structure the anion would normally adopt [24]. Thus, extensive fragmentation of the uniquely structured anion is observed, resulting in the formation of fragment ions not necessarily seen in conventional CID spectra (see Table 2). Again, the complementary nature of spectra arising from charge inversion and CID is asserted [25]. The position of the charge inversion peak in the −E spectrum can be compared to the absolute value of E to determine

Table 3
Summary of instrumental settings necessary to observe products of charge stripping reactions; The location of where the charge-changing collisions occur is denoted by (*)

	Polarity of ions created in source	First field-free collision region	Polarity of ions passed by magnetic sector	Second field-free collision region	Polarity of ions passed by electric sector	Information obtained
Charge stripping	+	*	+½		+½	E/2 spectrum
	+		+	*	+½	E/2 spectrum; Mass selection can occur in magnetic sector

unknown values in Eq. (4) or (6) [26]. For example, for charge inversion processes occurring through the one-step mechanism, the double ionization energy of the target molecule can be determined, given the other quantities present in Eq. (4) are known [27].

Applications of charge inversion of positive ions include the investigation of excited states of halogen ions [23] and the determination of double ionization energies of target gas molecules, as well as the evaluation of the stability of anions based on the propensity of cations to undergo charge inversion [25]. For example, ions of the general formula C_nH^- ($n=1-6$) were readily formed from benzene cations, whereas $C_6H_6^{-\cdot}$ ions were not [24]. These results were attributed to the effect that the instability of certain negatively charged ions could have on the likelihood of positively charged ions to undergo charge inversion.

2.3. Charge stripping

In the keV collision energy range, when a singly charged ion collides with a neutral target gas molecule, N, an electron may be removed from the ion. An example is shown in reaction (7)

$$M^{+\cdot} + N \rightarrow M^{2+} + N + e^- \tag{7}$$

The minimum energy (E_{min}) required by reaction (7) is given by

$$E_{min} = IE(M^{+\cdot}) \tag{8}$$

where $IE(M^{+\cdot})$ is the ionization energy of the singly charged ion. Eq. (8) is written assuming the reactant $M^{+\cdot}$ is in its ground state [28].

Charge stripping events are observable on both forward and reverse geometry instruments by setting the electric sector to half of the value needed to pass $M^{+\cdot}$ (see Table 3). The newly formed doubly charged ion will be passed at this value because it possesses the same kinetic energy as $M^{+\cdot}$ but twice the charge, so the kinetic energy-to-charge ratio is one half of the original value for $M^{+\cdot}$. Hence, the spectrum produced is termed an “E/2” spectrum. Fragment ions may be detected when the magnetic sector is scanned to mass-analyze charge-stripping ions formed in the first field free region in forward geometry instruments. A method to avoid the confusion of charge stripping peaks with fragmentation peaks has been established. By scanning the accelerating voltage and performing an E/2 scan, any overlapping peaks due to charge stripping and fragmentation can be resolved [29]. Because fragment ions release energy during fragmentation (kinetic energy release), they have a broad kinetic energy distribution and thus a broad peak in the mass spectrum, whereas the charge-stripping peak appears as an intense, narrow peak readily distinguishable from the broad peak due to fragmentation.

Performing charge stripping experiments on reverse geometry instruments avoids most interference problems, except in the case when the ion of interest dissociates exactly in half and appears at the same mass-to-charge as the charge stripping peak [15]. Charge stripping experiments are observed most easily when they occur in a collision cell between the magnetic and electric sectors, with mass selection occurring in the magnetic sector and the electric sector set to E/2 [30]. It has been reported that oxygen is one of the most efficient choices for the collision

Table 4
Relative abundances of products of charge stripping or CID processes for three $C_6H_6^{+\cdot}$ isomers: benzene, 1,5-hexadiyne, and 2,4-hexadiyne[33]

Reaction	Process	Benzene	1,5-Hexadiyne	2,4-Hexadiyne
$[78]^{+\cdot} \rightarrow [78]^{++}$	Charge stripping	8	2	1
$[78]^{+\cdot} \rightarrow [52]^{+}$	CID	10	10	10
$[78]^{+\cdot} \rightarrow [39]^{+}$	CID	4	2	3

gas [31]. As is the case with dissociative charge inversion, MIKES can be employed to detect fragment ions (both doubly and singly charged ions being possible) resulting from charge stripping.

Charge stripping experiments can be used in fundamental studies of ion energetics. If the ionization energy of the neutral molecule of interest is known, the position of the charge-stripping peak in an E/2 spectrum relative to the actual value of E/2 can be used to calculate the double ionization energy of the molecule. The determination of the double ionization energy is difficult to achieve otherwise [26,30]. The internal energy distributions of doubly charged ions are also of interest. The internal energy distributions of singly charged ions formed by electron ionization have been well characterized, but those of doubly charged ions formed by the same ionization method had been little studied. A method previously used to approximate the internal energy distributions of singly charged ions was applied to doubly charged ions formed by charge stripping [32]. First, dissociative charge stripping experiments of the thermometer ion $W(CO)_6^{+\cdot}$ were performed. Critical energies for the fragmentations of $W(CO)_6^{+\cdot}$ were determined separately, and it was assumed that $W(CO)_6^{+\cdot}$ ions resided in their ground states because the ions have such long lifetimes that it was likely that they were not excited. This information, together with the charge stripping spectra, led to the determination of the internal energy distributions of $W(CO)_6^{2+}$.

As was discussed with the case of charge inversion processes, ions formed by charge stripping that subsequently fragment might yield different fragment ions than ions dissociated by conventional CID. Again, higher energy ions that are more likely to have undergone isomerization are preferentially sampled during CID. Because of the high endothermicity of the charge stripping reaction, stable isomers that have not interconverted are included in the population of ions that undergo charge stripping [30,33,34]. The ions sampled by charge stripping are a more uniform representation of all ions present than the population of ions that undergo CID. Consequently, charge stripping can be a useful tool in differentiating isomers based on differences in fragmentation patterns. For example, $C_6H_6^{+\cdot}$ isomers have been distinguished based on the relative propensities of the isomers to undergo charge stripping. High-energy CID spectra of these isomers did not include any marked differences among the spectra [33] (Table 4). The extent to which certain compounds undergo charge stripping also was used to determine the site of cationization of ions formed by chemical ionization [34]. The compounds studied included dihydroxybenzoic acids, cresols, and methylanilines. Chemical ionization reagents transferred protons, methyl cations, or ethyl cations to the compounds of interest and charge stripping spectra were acquired. Two sites of protonation or alkylation were possible: on the ring or the substituent. By performing charge stripping, it was determined that the compounds that produced significant charge stripping peaks in the E/2 spectra were protonated or alkylated on the ring, and the compounds that produced little or no charge stripping peaks were protonated or alkylated on the substituent.

Complex mixture analysis also has been achieved with charge stripping. The analysis of nitrogen-containing compounds in coal liquids has been carried out successfully [35]. Nitrogen-containing compounds tend to undergo charge stripping because nitrogen can stabilize the additional charge acquired by the ion. The presence of nitrogen-containing compounds was verified in the coal liquid sample by the presence of a peak in the E/2 spectrum. Further analysis was required to identify the species undergoing charge stripping, because the isomers tetrahydroquinoline and tetrahydroisoquinoline would appear at the observed *m/z* value. Based on each isomer's propensity to undergo charge stripping, tetrahydroquinoline was identified as the compound present in the real world sample.

3. Charge permutation collisions in surface collisions

The early development of SID occurred exclusively in the Cooks' group [36–38]. Although the primary goal, as in CID, is the changing of the mass of the ion colliding with the surface, the charge of the ion can also change. A major experimental difference between the gaseous collisions leading to charge permutation discussed previously and ion/surface collisions is the kinetic energy of the ion. All the gaseous reactions discussed previously occur with ion kinetic energies of at least several kilovolts. Ion/surface reactions typically are at ion kinetic energies of tens of eV. Thus, whereas sector mass spectrometers are used for gaseous charge permutation reactions, quadrupole based instruments are typically used for ion/surface collision experiments [39]. Due to this huge difference in ion kinetic energy, several reactions analogous to those observed in the gas phase have been observed.

Perhaps the most common charge permutation reaction occurring in ion/surface collisions is charge exchange between a positive singly charged ion and the surface [36]. This reaction depends upon the nature of the surface and the ion, with clean metal surfaces being the most favorable for promoting this process. In most cases, this is an undesirable reaction because there is no ionic species left to detect in the mass spectrometer. However, one class of ions promote a unique chemical sputtering process [40,41]. When organofluorine ions impinge on a "dirty" surface at collision energies between 50 and 150 eV, a mass spectrum containing even electron C_2, C_3, and C_4 hydrocarbon ions is obtained, with no organofluorine ions observed. Simple thermodynamics is insufficient to explain the observation as nonfluorinated ions with similar thermodynamic properties are not observed to promote this chemical sputtering process.

For doubly charged positive ions, charge exchange with the surface results in a singly charged ion that can subsequently be detected in the mass spectrometer. In a study of ions from toluene (C_7H_n $n=6-8$) the data suggest that the doubly charged ion first undergoes charge exchange and then dissociates. As the charge exchange process is quite exothermic, this could provide a source of energy for fragmentation in addition to energy from the collision of the ion with the surface. The reverse charge permutation reaction, charge stripping to go from a singly charged to a doubly charged ion, is not observed in ion/surface collisions. This is perhaps not surprising given the exothermicity of the electron transfer from the surface to a doubly charged ion. So, whereas energies can be accessed that should be sufficient to strip an electron from the ion, such species are not observed.

The other electron stripping process, charge inversion where a negative ion is converted to a positive ion, can be observed in ion/surface collisions [40]. For the deprotonated benzoate anion, some intact positively charged parent ion is observed, but the dominant peak in the spectrum is the phenyl cation. The charge inversion reaction in which a positive ion is converted to a negative ion has also been observed in ion/surface collisions. $C_3F_5^+$ can pick up two electrons from the surface. The corresponding anion is not observed but fragment ions $C_2F_3^-$ and F^- are observed. Both these charge inversion reactions should be endothermic, although the positive to negative reaction could be exothermic if the ion is interacting with a clean metal surface.

Overall, the charge permutation reactions occurring during ion/surface collisions have not been demonstrated to be nearly as useful as the gaseous charge permutation reactions. Although charge permutation reactions in beam instruments are rarely used today, they have the capability of providing complementary information to CID and SID and have played an important role in gaining an understanding of fundamental ion energetics and gas phase chemistry.

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