

**SPECIAL FEATURE:
TUTORIAL†**

Translational Energy Spectroscopy

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The technique of translational energy spectroscopy (TES) is described, whereby a collision of a fast ion (a few keV in energy) with a neutral target gas can reveal spectroscopic information on the states of the participating species. Information on the dynamics of the collision, lifetimes of species, collision cross-sections and populations of states can be revealed. Classification of collisional processes amenable to TES are given together with simple aspects of relevant collision theory, an appraisal of quantum selection rules for collisions, a description of typical high resolution instrumentation and two simple examples of TES experiments.

INTRODUCTION

Throughout its long development mass spectrometry has drawn heavily from the work of physicists and physical chemists for advances in instrumentation and techniques. In recent times, the converse has also been true with physical chemists taking advantage of the highly developed instrumentation of commercial mass spectrometers to conduct an ever-increasing range of sophisticated experiments. Pivotal to many techniques in mass spectrometry is the interaction (collision) of an ion with a neutral molecule or atom. Collisions of low energy ions (thermal to a few eV) with neutral species are familiar to us in such ionization processes as chemical ionization and atmospheric pressure ionization and occur in the many instruments used to perform ion–molecule reactions. Collisions at higher energies (where the ion has a laboratory translational energy ranging from tens of eV to tens of keV) are encountered in experiments employed to fragment a mass-selected ion. This collision-induced dissociation experiment forms the basis of the well-known technique of mass spectrometry/mass spectrometry (MS/MS). This method was initially developed for mixture analysis and structural elucidation or confirmation, and is now being employed in quantitative analysis too.

† Editor's Note: This is the second of several 'Tutorial' articles which will appear this year in the Special Features section of the journal. These tutorials will describe fundamental aspects and applications of mass spectrometry with the general reader, not the author's peer group, in mind. The aim will be to cover some specific areas of mass spectrometry in a manner in which a teacher might present the subject in a graduate level course. Although these articles are normally invited, comments and suggestions from readers are welcome. Please address these to the Special Features Coordinator; Graham Cooks, Dept of Chemistry, Purdue University, W. Lafayette, IN, USA, 47907. Further, as a special offer to readers, copies of the figures of this 'Tutorial' article, as color slides, are available free of charge on request from the editor-in-chief's office. Supplies are limited and slides will be sent out in the order requests are received.

The physical chemistry of ion–molecule and ion–atom collisions in this higher collision energy domain, has been commonly referred to as collision spectroscopy. Translational energy spectroscopy (TES) is a closely related term, often adopted when high resolution studies (in energy, angle or time) are undertaken. In TES the goal is to glean spectroscopic information on the states of the participating species and in some cases to determine detailed information on the scattering process, such as its dynamics, the lifetimes of species, collision cross-sections and populations of states. For simplicity, the collision process will be considered to be between a fast ion and a neutral species at thermal energy, unless otherwise stated. The projectile ion and target may be either atomic or molecular in nature.

In simple terms translational energy spectroscopy can be classified into two major categories (Cases I and II), both of which provide the experimentalist with direct spectroscopic measurements of the energy levels of the molecular or atomic ion and, in some experiments, also of the target species.

Case I

Precise measurement of the translational energy loss (or gain) of the fast ion as a result of its collision with a neutral target species: in this case it is a necessary condition that the energy loss messenger—the ion—does not dissociate before reaching the detector.

Case II

Determination of the kinetic energy release distribution (KER) associated with dissociation processes: this measurement is made by examining the products of the fast projectile ion. [We will come back to define KER].

The outcome of a TES measurements is to provide information on electronic, vibrational and, in favourable cases, the rotational states of the collision partners. This might seem unremarkable as one would argue that

there already exist many well developed spectroscopic techniques which achieve these aims, including a few which are applicable to populations of trapped ions. However, a simple estimate shows that ions cannot easily be formed in high concentrations and in ion beams in particular, fluences are typically 10^{12} ions $\text{m}^{-3} \text{s}^{-1}$. Thus mass-selected ion beam concentrations are easily ten orders of magnitude lower than the concentrations of analyte typically encountered in other spectroscopic experiments. This makes direct structure determination of ions difficult or impossible, except, by a few specialised methods such as TES.

This article will provide a classification of collisional processes that are amenable to TES, give relevant but simple aspects of collision theory, briefly review quantum selection rules and appraise their applicability to two body collisions, describe TES hardware and conclude with two simple examples of TES experiments. Before these tasks are undertaken we need to address one important question: ‘What defines the collision energy range of interest?’ In practice this is found to lie from a few hundred eV to tens of keV for a singly-charged ion. Briefly, the main reasons for this are:

- (i) The collisional cross-sections for many simple electronic excitations and charge transfer processes frequently maximise in this energy range, thus greatly increasing the product signal intensity.
- (ii) The time an ion interacts with the target species is very short ($< 10^{-14}$ s) at keV energies and nuclear motion within a molecular ion and (molecular) target is essentially frozen out on this time scale. In these circumstances, excitation and de-excitation are described as vertical processes (also called non-adiabatic) which offers the advantage of allowing direct comparisons with optical spectroscopy.
- (iii) Momentum transfer to the target is almost always very small (0.1 eV or less), for small scattering angles at these energies, allowing the energy loss to be directly related to the states of the ion alone.
- (iv) Excitations usually involve valence electrons which are of course of chemical interest.
- (v) Ion acceleration voltages below a few tens of keV are readily generated and relatively easy to handle experimentally.
- (vi) For reactions in which the product ion dissociates, the internal energy stored in the ion, either as energy obtained during ionization or in the collision event, may be released as translational energy of the dissociation products. This quantity is referred to as the kinetic energy release distribution (KER). It turns out that the translational energy released in the center-of-mass system is greatly amplified (by as much as five orders of magnitude) in the lab system. Thus the measurement of the KER of the product ions allows a very precise probe of a quantity related to the internal energy distribution of the precursor ion.

For simplicity TES will be considered as a spectroscopic method that does not rely at any juncture upon photon absorption or emission, for example, by the use of laser radiation. However, there are many excellent examples that can be cited where the specificity of the photon can be employed, for example, to prepare a system in certain specified state(s) prior to reaction.

THE TECHNIQUE

Briefly, the TES technique utilises a monoenergetic beam (typically $3000 \text{ eV} \pm 0.1 \text{ eV}$) of mass-selected ions which are focused into a collision cell containing a suitable target gas or vapour. It is important that the pressure within the cell is maintained at a value which is low enough (typically $< 10^{-3}$ Torr for a cell of only a few mm in length) to ensure the ions will suffer a maximum of one collision. This is referred to as the single-collision condition and when it applies the majority of the ions passing through the cell do not collide at all. The extent to which a collision process will occur depends on the thickness of the attenuating target gas, π ($\pi = nl$, where n is the number density of the target gas and l the collision path length). The effective collision area the two colliding bodies present to each other, is called its cross-section, σ . For a beam of intensity I_0 passing through a gas of target thickness π , the reduction in the intensity of the beam, ΔI , is given by

$$\frac{\Delta I}{I_0} = 1 - \exp(-\pi\sigma)$$

Cross-sections are independent of pressure and have traditionally been quoted in cm^2 , although SI units are recommended and typical values are in the vicinity of 10^{-20} m^2 per collision.

In the cell a collision will either be an elastic or inelastic process. Elastic collisions are those in which there is no change in the internal energy of any of the collision partners, and the translational energy loss of the projectile ion will generally be very small, typically $< 1 \text{ eV}$ (again assuming keV energies and small angle scattering). Inelastic collisions occur when the internal energy of one of the collision partners changes; in special cases this energy may be transferred between the collision partners or converted to translational energy, or even result in photon emission, particularly when atomic excitation takes place. It is important to note that for inelastic collisions three outcomes are possible; the translational energy of the ion may: (i) decrease (endothermic reaction), (ii) increase (exothermic reaction), or (iii) remain unchanged (e.g. in resonant charge exchange). Reactions in which the translational energy increases are frequently described as superelastic. Energy changes in inelastic processes typically are a few eV, but cover the range 0 up to a maximum of 50 eV. The probability, P_E , that an inelastic energy loss will be ΔE is approximately given by the Hasted relationship

$$P_E = A \exp\left(\frac{-B|\Delta E|}{hv}\right)$$

where A and B are constants, h is Planck’s constant and v is the collision velocity.

As the collision system is isolated, there is only one source of the necessary energy to drive these reactions, the translational energy of the ion. Thus a direct connection is established between the translational energy loss (or gain) and the internal energy states of the system. The discrete changes in the translational energy of the incident ion are recorded by precise energy analysis of the ion beam after collision. At keV energies,

Table 1. Classification of some of the major collisional processes

Selected Non-dissociative Collisional Processes		
Energy loss	$M^+ + G \rightarrow M^{+*} + G$	Ia
	$M^{+*} + G \rightarrow M^+ + G$	Ib
Charge transfer	$M^{x+} + G \rightarrow M^{(x-y)+} + G^{y+}$	II
Charge stripping	$M^{x+} + G \rightarrow M^{(x+y)+} + G^{z+} + (y+z)e$	III
Charge inversion	$M^{x+} + G \rightarrow M^{y-} + G^{z+} + (z - \{x+y\})e$	IV
Neutral spectroscopy	$F^+ + M \rightarrow F^+ + M^{*..*.(+)}$	V
Selected Dissociative Collisional Processes		
Unimolecular dissociation	$AB^{+*} \rightarrow A^+ + B$	
Collisional induced dissociation	$AB^{+*} + G \rightarrow A^+ + B + G$	
Dissociative ionization	$AB^{+*} + G \rightarrow AB^* + G^+ \rightarrow A + B + G^+$	
Dissociative charge exchange	$AB^{2+*} + G \rightarrow AB^{+*} + G^+ \rightarrow A^+ + B + G^+$	

and small scattering angles, these measured energy changes can be directly related to excitation and de-excitation the low-lying electronic states of the collision partners.

CLASSIFICATION OF COLLISIONAL PROCESSES

It is useful to classify the main collisions processes that TES is applied to. These fall into two categories: (i) non-dissociative collisions, that is, where the projectile ion does not break up as a consequence of the collision; and (ii) dissociative collisions, where the ion fragments before reaching the detector. Table 1 lists some of the major collisional processes that fall into these two categories. For non-dissociative processes that are five main reactions the most important of which is the energy loss reaction (Ia) where the molecular ion, M^+ , is excited to higher energy levels in the collision. When the projectile has undergone electronic excitation a convention is

used to denote this: M^{+*} , with a single "*" indicating that a single electron is excited, whereas excitation involving two electrons is denoted by "**", and so on. Reaction Ib in Table 1 represents a super elastic collision where the internal energy stored by the ion is given out to translational energy. Reactions II, III and IV represent classes of reactions where electrons are exchanged between the fast projectile and the target. In some cases electrons are emitted as free particles, for example, in charge stripping (III). In all of the reactions I–IV it is an essential condition that the product ion remains intact before reaching the detector, otherwise the apparent resolution of the experiment (typically 0.1 eV for a translational energy of 3000 eV) falls off dramatically and for a dissociated ion the resultant peak may be 50 to several hundred eV wide, instead of 0.1 eV! The magnitude of this broadening depends on the amount of internal energy converted to translational energy and just a 1 eV energy release can broaden a collision induced dissociation (CID) peak by 100 eV or more. Reactions II–IV have been widely studied to provide information on the ionization energies of singly-and-multiply-charged ions.

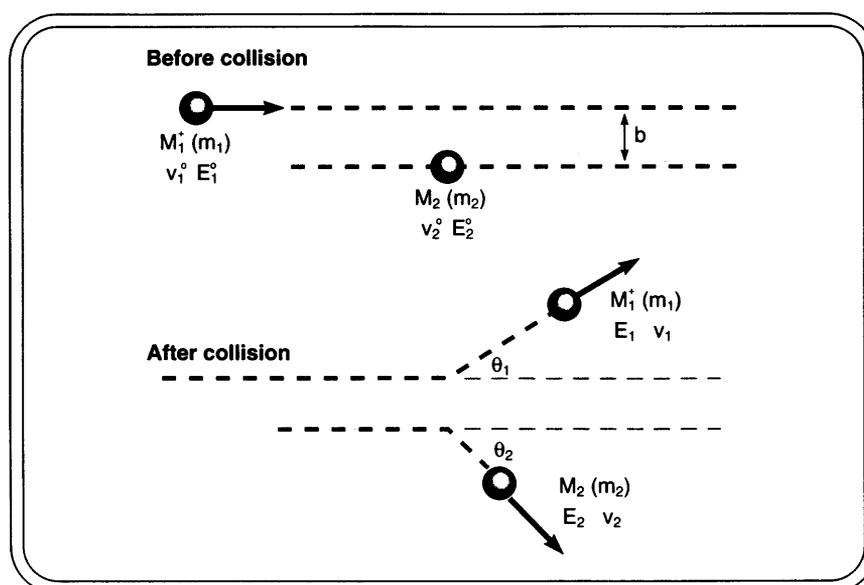


Figure 1. Schematic representation of a binary collision between a fast ion, M_1^+ , of mass m_1 , velocity v_1^0 and translational energy E_1^0 and a neutral target species, M_2 , of mass m_2 , velocity v_2^0 and a translational energy E_2^0 . The collision is at an impact parameter of b . After the collision the ion, M_1^+ , is scattered through an angle of θ_1 radians and has a velocity v_1 and translational energy E_1 , the target species, M_2 , is scattered through θ_2 radians and has a velocity v_2 and a translational energy E_2 .

One method to ensure the condition that the product ion, M^+ , does not dissociate is to make it an atomic ion. Whilst atomic systems may be less interesting than molecular species, atomic ion projectiles can be used to gain information about molecular target species. An example of this is the reaction IV. Let us assume the projectile ion is H^+ and the product is H^- , then the target will become doubly ionized, G^{2+} . This sub-area is referred to as double-charge transfer spectroscopy and it provides information on the ionization energies of doubly-charged ions and their higher electronic states. An added benefit is that the information on the higher electronic states is captured within $<10^{-14}$ s and registered in the translational energies of the negatively-charged hydrogen atoms. It is not a condition of this type of spectroscopy that the doubly ionized target be stable after the information about its higher states has been transferred. Similar strategies have been employed for other collision types to allow information to be gathered about electronic states with lifetimes as short as the collision period itself. Reaction V specifically aims at making spectroscopic measurements on molecular target species in their neutral form, in this case denoted by M. The fast projectile is denoted by F^+ and is used as an ion 'hammer' to excite the molecular target. To ensure the energy loss spectrum reflects the electronic structure of the species M, the fast ion is preferentially a simple atomic ion. This type of spectroscopy is still under development, and demands very high sensitivity and energy resolving power from the apparatus.

BASIC SCATTERING THEORY

Consider a high velocity (keV) projectile ion (M_1^+) colliding with a thermal atomic or molecular target (M_2), as shown schematically in Fig. 1. The velocity of the target, before collision, due to its thermal motion is <500 m s $^{-1}$. The velocity of a typical keV atomic projectile ion is around 100 000 m s $^{-1}$. In these instances, the kinetic energy and momentum of the thermal target before collision can be assumed to be approximately equal to zero and hence neglected. For an isolated collision system, total energy and linear momentum are conserved during the binary collision. Two main laws apply.

Conservation of Energy, gives

$$E_1^0 = E_1 + E_2 + Q$$

Conservation of Linear Momentum, gives

$$m_1 v_1^0 = m_1 v_1 \cos \Theta_1 + m_2 v_2 \cos \Theta_2$$

$$0 = m_1 v_1 \sin \Theta_1 - m_2 v_2 \sin \Theta_2$$

where

m_1 = mass of the projectile ion

m_2 = mass of the target

E_1^0 = translational energy of m_1 before collision

E_1 = translational energy of m_1 after collision

E_2^0 = translational energy of m_2 before collision

E_2 = translational energy of m_2 after collision

Q = amount of kinetic energy converted to internal energy in the collision

v_1^0 = velocity of m_1 before collision

v_1 = velocity of m_1 after collision

v_2^0 = velocity of m_2 before collision

v_2 = velocity of m_2 after collision

Θ_1 = angle through which m_1 is scattered

Θ_2 = angle through which m_2 is scattered

Many mathematical formula derive from the above. In the case of small angle scattering, two approximate results of general interest give the energy transferred to the target

$$E_2 \approx (m_1/m_2)E_1^0\Theta_1^2$$

and the energy loss experienced by the projectile ion, $\Delta E = E_1^0 - E_1$,

$$\Delta E \approx (m_1/m_2)E_1^0\Theta_1^2 + Q$$

QUANTUM SELECTION RULES FOR COLLISIONAL PROCESSES

Quantum selection rules are critical in the interpretation of optical spectroscopy and in the rationalisation of the spectra obtained. However, for collision spectroscopy the picture is considerably less clear. The main quantum selection rules for optical spectroscopy are very well documented (refer to Herzberg's encyclopedic treatise, given in the reference list, or a standard text).

Selection rules are based on symmetry conditions and provide numerate guidelines for the determination of allowed and disallowed transitions. In collision spectroscopy the main quantum selection rule that can be applied deals with the total spin of the system (S). TES spectra have shown that the spin conservation rule needs to be extended when dealing with collisions rather than optical spectroscopy. Allowed collisions now occur when spin changes by 0, ± 2 , ± 4 etc. This rule holds rigorously for light systems, that is, for low mass atomic ions (smaller than Cl) and for molecular ions incorporating low atomic mass atoms. For heavier atoms the rule is progressively less reliable, breaking down completely at some point. The reason why it breaks down is analogous to the situation in optical spectroscopy where ls-coupling changes to jj-coupling and S becomes a weak quantum number. Other well-known quantum selection rules, such as that which constrains the total orbital angular momentum to 0 or ± 1 in spectroscopy, hardly apply in collision spectroscopy. Thus, Σ to Δ transitions, where the orbital angular momentum changes by two, are frequently observed as major processes in TES experiments. Only in the very simplest of systems have quantum selection rules, other than for spin conservation, been observed to hold. This can be pictorially imagined by the fact that the target species can take random orientations with respect to the incoming ion and that any molecular symmetry occurring in one collision may not arise in most others, since the target species are randomly oriented.

Vibrational excitation, however, appears to follow very similar patterns for infrared excitation and col-

lisional excitation. In infrared spectroscopy the vibrational state may change by $\Delta v = \pm 1$, and for anharmonic systems by $\Delta v = \pm 2, \pm 3$ etc. Transitions for changes greater than ± 1 are extremely weak in infrared spectra. An exactly similar pattern is found for vibrational collisional excitation where transitions to $\Delta v = \pm 1$ are strongly preferred over transitions changing Δv by $\pm 2, \pm 3$. Collisions in which vibrational excitation occurs are referred to as momentum transfer collisions.

INSTRUMENTATION FOR HIGH RESOLUTION ENERGY ANALYSIS

Conventional energy analysers

There are many types of charged-particle energy (strictly energy/charge ratio) analysers. They usually involve electrostatic fields but sometimes magnetic fields are employed. A simple energy analyser is a retarding field analyser in which an electrical potential is developed across two parallel grids. This potential is varied and the ions that are capable of traversing this field must have an appropriate translational energy determined by the applied voltage. Energy spectra recording using a retarding field analyser show abrupt steps when ions of a particular energy are prevented from crossing the potential barrier. Differentiation of the ion retardation profile produces a conventional energy spectrum (with peaks), although one with relatively low resolution. Other types of kinetic energy analysers are based on deflection and dispersion of the beam. Cylindrical sector analysers (electric sectors) are a favoured choice; these devices consist of a pair of cylindrical electrodes one with a positive voltage and the other with an equal but negative voltage. They have direction focusing properties in one plane (x - y), and produce an

energy dispersion. A variant on this is the hemispherical analyser which focuses for beam direction in three dimensions (stigmatic focusing) and so provides greater beam transmission while dispersing the beam according to translational energy. A typical ESA can give an energy resolution ($E/\delta E$) up to 10 000, where this value is measured as the translational energy E divided by the width of the translational energy peak measured at half height (δE). The energy resolution is related to instrumental parameters by

$$E/\delta E \approx R/A_x s + w + \Delta_i$$

where R is the mean radius of the analyser, s is the source object slit width, w is the image slit width, A_x is the magnification of the object size and Δ_i includes all ion-optical aberrations of the lens system.

Figure 2 schematically shows a high resolution energy loss spectrometer based on cylindrical electrostatic analysers. In addition Fig. 2 depicts a system which incorporates deceleration prior to energy analysis. The primary ion beam, M^+ , has been mass selected and energy selected before introduction to the collision cell. The energy monochromatization process can be either by a conventional cylindrical or spherical energy analyser and, in an attempt to significantly improve energy resolution, by decelerating the ion beam to a low translational energy (10 to 100 eV) before it enters the sector. Deceleration can greatly reduce the resolution requirement of that particular energy analyser and hence its size, whilst still achieving the required energy monochromatization of the initial ion beam. For example, consider an energy analyser of nominal resolution 1000. If a beam of 1000 eV is passed through this analyser a resolution of 1 eV will be achieved without deceleration. With deceleration to 10 eV the 1000 resolving power will be in principle lead to an energy resolution of 0.01 eV. Thus, deceleration can greatly enhance the energy separating power of the analyser. The ion beam is re-accelerated to its original

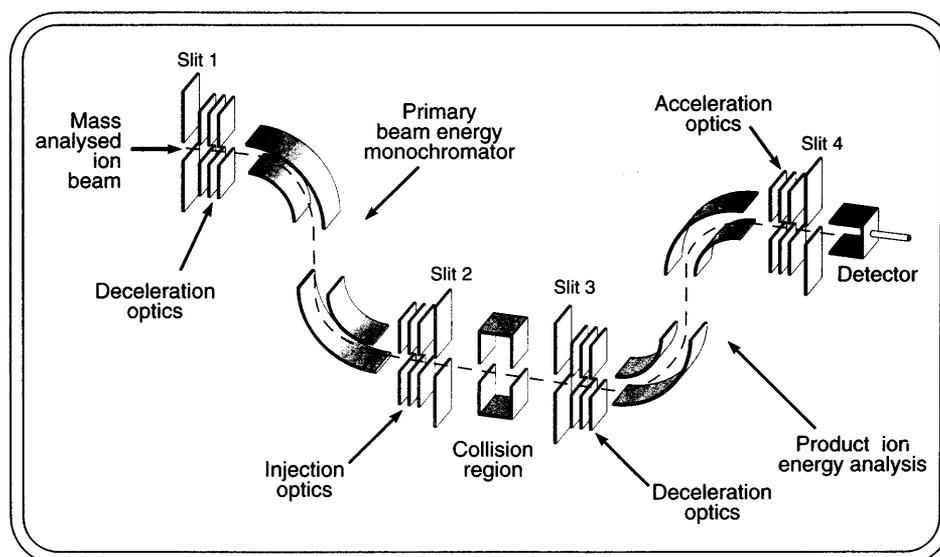


Figure 2. An illustration of a typical arrangement of a high resolution energy loss spectrometer utilizing energy monochromatization, and ion retardation, before and after the collision process to obtain high resolving power. The ion beam will usually be mass selected before injection into the system. It is energy monochromatized prior to collision, often using ion retardation techniques to improve the resolving power of the pre-collision energy analyser. Energy loss processes occurring in the collision cell are recorded by scanning the energy range of the post-collision energy analyser before passing to a sensitive single ion detector.

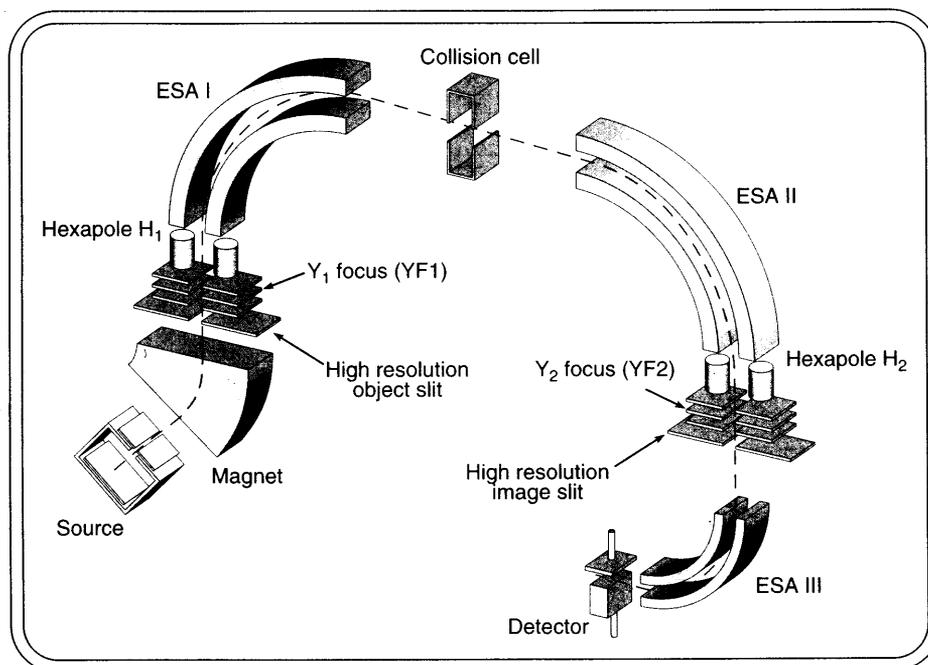


Figure 3. Schematic representation of a high energy resolution energy-loss spectrometer using a pair of symmetrical electrostatic analysers arranged as a double focusing combination. The ion beam is mass-selected by the magnetic sector before passing through to the double electric sector system. The collision cell is located in the central plane of symmetry. In this combination high resolution resolving slits are only required at the two positions indicated. Additional lenses, Y_1 and Y_2 , adjust first order focusing and second order beam correction by hexapoles, H_1 and H_2 . A third electric sector (ESA) is essential to remove unwanted specular reflections from the second ESA and from the final high resolution slit blades.

translational energy before it passes into the collision region. Reaction products from collision within the cell pass towards the final energy analyser and, again, the use of deceleration of the ion beam can greatly enhance the nominal resolving power of the final energy analyser. By no means do all systems incorporate ion deceleration.

The very best energy resolution that has been achieved with this type of arrangement (Kobayashi 1991) has been reported to be 0.01 eV for scattering experiments using ion beams at 50 to 1000 eV. The results reported also indicate that the technique requires

a long acquisition period due to the low ion signals recorded.

Double focusing arrangements

The combination of magnetic and electrostatic analysers to obtain simultaneous velocity focusing has long been the foundation of high resolution mass spectrometry. However, it is possible to use a reversed-geometry mass spectrometer, normally used for organic chemical analysis, effectively for high resolution TES

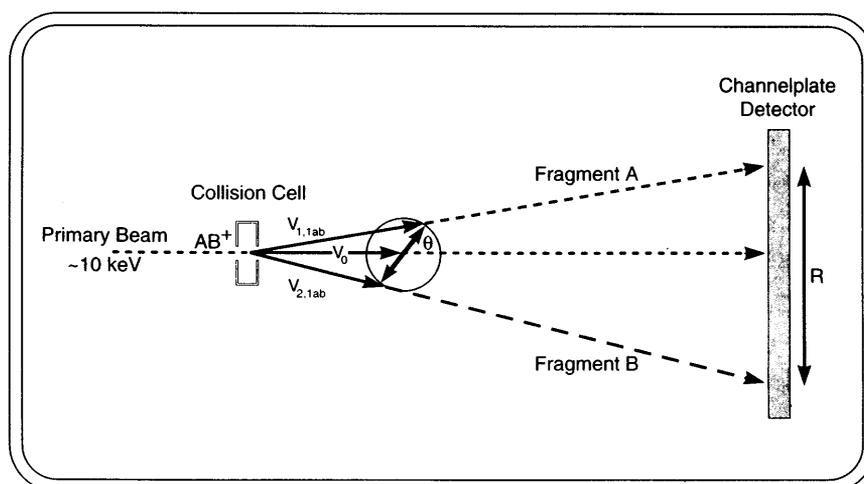


Figure 4. An illustration of a time and position sensitive detector used for translational spectroscopy measurements on both the fragmentation products simultaneously. A fast ion, AB^+ , of velocity, v_0 , undergoes collisional dissociation to fragments A and B, which may or may not be charged species. The velocities, $v_{1,1ab}$ and $v_{2,1ab}$ of each fragment can be measured from the time and position at which they arrive on the detector allowing kinetic energy release distributions to be measured.

experiments. The double focusing combination of a magnetic and electrostatic sector provides reasonably high energy resolution, up to 0.1 eV in 8000 eV. However, a completely new combination of two symmetrical electrostatic analysers could provide even greater energy resolution. An instrument of this configuration is shown in Fig. 3.

This type of high energy resolution energy analyser is based on a pair of symmetrical electrostatic analysers and is found to provide an energy resolution of 0.01 eV on a beam of 5000 eV energy. This system does not employ deceleration for energy monochromatization of the primary ion beam as in the above cases and so affords considerably higher sensitivity (Refer to Hamdan and Brenton 1991). Energy loss processes differing by 0.01 eV can be resolved when the intrinsic energy spread of the ion beam is as great as 1 eV.

Position sensitive analysers

These analysers are mainly research devices, and Fig. 4 shows the position sensitive detector developed at the FOM Institute, Amsterdam. A property of a fast ion (or fast neutral) when it dissociates is that there is a relationship between the velocity (and thus position where an ion lands on the detector) spread of the fragments, and the kinetic energy release. (The primary ion beam must be reasonably mono-energetic with very small angular spread.) This method is generally applicable to diatomic ions, and with restrictions, to other small ions. Kinetic energy release distributions (KER) can be measured to very high accuracy and this is one of the preferred techniques for such measurements. Another reaction which has been studied in this way is dissociative ionization (refer to Table 1). It may be noted that the very high energy (MeV range) coulomb explosion experiment, used to precisely measure inter-

atomic distances in gas phase ions, uses this type of detector.

Time-of-flight energy analysers

It is usual to think of time-of-flight systems in the context of high mass analysers. Several designs exist where the energy of an ion is measured to high accuracy. One essential condition is that the mass of the ion does not change the energy scale (E) and is related to time (t) by

$$E = \frac{1}{2} \frac{ml^2}{t^2}$$

where l is the distance travelled. Time-of-flight can give reasonable energy resolution of several hundred and time focusing instruments have been designed and built which increase this value many times. A major advantage of time-of-flight is its relative simplicity.

TYPICAL DATA

Two spectra have been selected to illustrate some of the main features of TES, both illustrate inelastic collision processes of type Ia (Table 1).

N^+ -NO collision system

NO has no excited states below approximately 5.5 eV and consequently the spectrum is relatively free of interferences caused by molecular excitation of the target. The main feature in the spectrum (Fig. 5) is the central

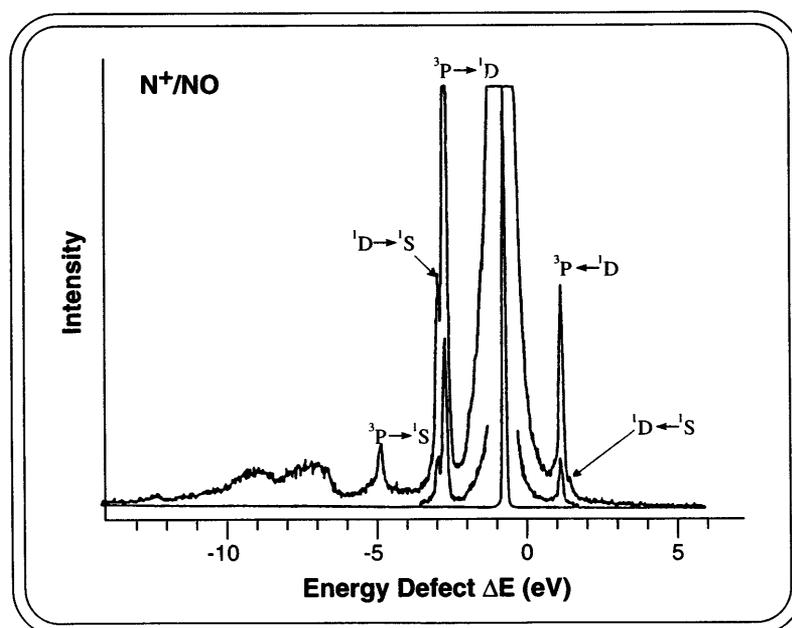


Figure 5. TES spectrum of N^+ colliding with nitric oxide, at 3000 eV collision energy. Excitation between the atomic states $^3P \rightarrow ^1D$, $^1D \rightarrow ^1S$, $^3P \rightarrow ^1S$ are seen on the energy loss side while the atomic de-excitation $^3P \leftarrow ^1D$, $^1D \leftarrow ^1S$ are observed on the superelastic side (energy gain).

peak which represents those ions that have not undergone an inelastic collision. This situation can be compared to that which obtains in Raman spectroscopy. The translational energy spectrum of 3000 eV N^+ ions scattered off NO is dominated by excitation and de-excitation processes between the $2p^2\ ^2P$ ground state and the first metastable state $2p^2\ ^1D$ (1.90 eV) of the N^+ ion, represented by the smaller intensity peaks on either side of the unscattered signal. The intensity of the energy loss/gain peaks is typically 10^{-2} to 10^{-5} that of the unscattered signal. Other atomic features in the spectrum are excitation of the ground state $2p^2\ ^3P$ to the second metastable state $2p^2\ ^1S$ (4.05 eV) and excitation and de-excitation processes occurring between the two lowest metastable states $2p^2\ ^1D$ and $2p^2\ ^1S$ (2.15 eV). The superelastic peaks indicate the presence of projectile ions in the $2p^2\ ^1D$ and $2p^2\ ^1S$ metastable states prior to collision. These spectra provide several pieces of information: (i) the collisional cross-section can be calculated, (ii) the lifetimes of the product states estimated, and (iii) the population of projectile states in the ion beam can be deduced. In this case it was found the 1S state is clearly small ($\approx 0.3\%$ of the beam) and can be neglected, hence the fractional populations of the ground ($2p^2\ ^3P$) and metastable ($2p^2\ ^1D$) states are 0.87 and 0.13, respectively.

C^+-N_2 collision system

C^+ ions scattered off N_2 produce an intriguing and aesthetically pleasing spectrum (Fig. 6) revealing several electronic transitions of N_2 each of which displays rich vibrational features. It is beyond this article to provide a detailed description but the salient features are: new conclusions on spin conservation were gleaned from this spectrum, spectroscopic constants were calculated

from the band structure and evidence was provided for simultaneous atomic and molecular excitations as major processes.

PROSPECTUS

The marriage of physics and mass spectrometry will continue. In many areas of current research the fundamental understanding of the processes involved is still at an elementary level. For example, routine or automated structural interpretation of mass spectra are still hindered by the non-thermal nature of many ionization techniques. Whereas other spectroscopic methods deal with essentially thermal systems and provide direct information on the neutral moiety, mass spectrometry usually deals with ionic species in non-Boltzmann energy distributions. New physical methods such as TES may impact on this situation by providing methods which will allow the acquisition of structural information on thermal neutral species without prior ionisation.

Translational energy spectroscopy has an important role to play in the spectroscopy of ionic systems. Due to its extraordinarily high sensitivity it allows characterisation of ionic systems whilst most other spectroscopic methods fail due to the extremely low concentration of the ion under investigation. Methods to overcome collision broadening are maturing, again increasing the technique's sensitivity. Very high spatial resolution arrays (15 micron electrode interspacing) for detecting a whole TES spectrum simultaneously already exist in prototype form, and show the ability to reduce data acquisition times from many minutes to seconds. Coincidence monitoring of the projectile ion and the scattered target will herald further improvements to energy resolution and also offer a more complete description of the collision process.

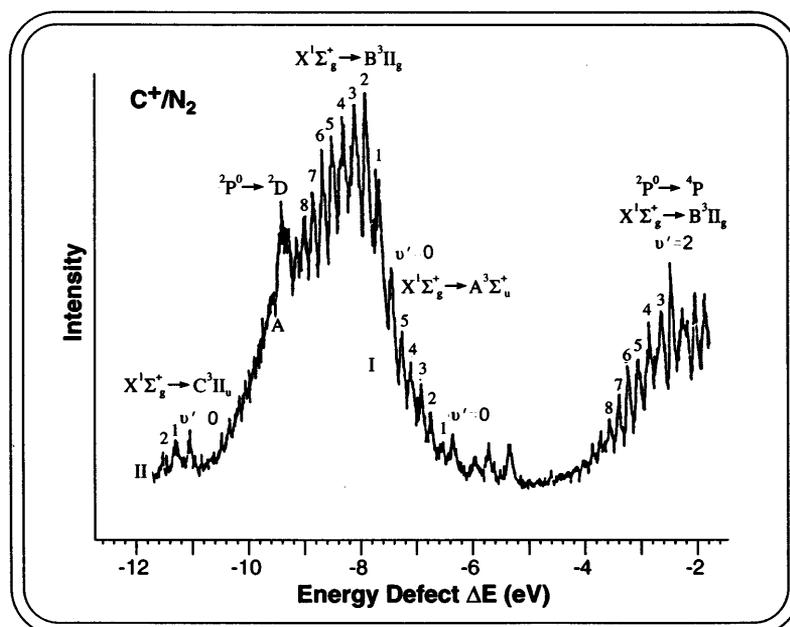


Figure 6. TES spectrum of C^+ colliding with molecular nitrogen, at 3000 eV collision energy. Excitation between the X and A, B and C molecular states are observed together with their associated vibrational progressions. Simultaneous de-excitation of the $^2P^0 \rightarrow ^4P$ state of C^+ and molecular excitation of the target is observed to occur as a single process.

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