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Translational-energy spectroscopy: A personal perspective of its development

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Abstract

Translational-energy spectroscopy (TES) has been widely employed over the last 30 yr to characterize the collision-induced and unimolecular reactions of ions. A personal view is taken of the breath of the field and some of the landmark events that have helped shape it. In this article, the description of the technique is confined to applications for ion beams with translational energies from 0.1 to 10 keV and those not relying on the absorption or emission of radiation. Collisions of ions with a neutral target gas can reveal spectroscopic information on the states of the participating species, dynamics of the collision, lifetimes of species, collision cross sections, and populations of states. The work from six key laboratories is included to illustrate the range of applications. (Int J Mass Spectrom 200 (2000) 403–422) © 2000 Elsevier Science B.V.

Keywords: Translational-energy spectroscopy; Excited states; Collisional excitation; Energy loss

1. Introduction

In 1973, Cooks, Beynon, Caprioli, and Lester [1] published a definitive treatise titled *Metastable Ions*. It reflected the increasing number of mass spectrometers being used for research in physical chemistry. This and other scholarly texts, *Collision Spectroscopy* [2] and *Tandem Mass Spectrometry* [3], provided a starting point for many who have contributed subsequently to mass spectrometry and the field of gas-phase ion chemistry. These seminal works were published in a golden era of ion/molecule collision studies and laid the fundamental basis for the field we now refer to as MS/MS. Translational-energy spectroscopy (TES) is but one specialized branch of MS/MS and is primarily concerned with the characterization of electronic, vibrational, and in special circumstances, rotational states of ions undergoing high-energy collisions (~0.5–10 keV) with a gas phase target. From my own recollections, the specific term TES was coined in the early 1980s by Illies and Bowers [4] in a paper titled *High-resolution translational energy spectroscopy—Electronic transitions in* Kr^+ *and* I^+ *and vibronic transitions in* N_2^+. In this paper, they demonstrated that high-energy-resolving power could be obtained on a commercial mass spectrometer for ion energy-loss studies.

My research focuses on such thousand electron Volt ion/molecule collisions, employing instrumentation providing energy resolution of ~0.03 eV (i.e., $\leq 1 : 10^5$) and is therefore mainly concerned with electronic spectroscopy, observable through the scattering events occurring. This is not high-resolution

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spectroscopy in the sense normally associated with the emission or absorption of radiation; this is another more specialized and separate field of study. It is commonly referred to as ion spectroscopy [5], where line widths are talked of in terms of megahertz (1 MHz$=4.135\times10^{-9}$ eV), rather than the electron Volts usually associated with MS/MS. Collision spectroscopy is perhaps a better term for the type of work physical chemists do when they are investigating high-energy ion/molecule–atom collisions. It refers to cases where the ion can fragment and the energy resolution need not be high, whereas TES generally refers to situations where high-energy-resolution is required. Our work has concerned small ions, frequently multiply charged, that are generally in their ground electronic state before undergoing collisions. Changes in the electronic and vibrational configuration of the ion (and target) can be measured directly from the energy loss suffered by the ion during collision, exact measurement of which leads to the assignment of the electronic structure of the species partaking in the collision. When this program of work started some 20 yr ago, there was a paucity of data on the higher electronic structure of ions, excited states of dications, and multiply charged ions. One attraction was that while ground state equilibrium configurations could be understood by existing models, molecules in higher states could not, particularly those closer to the dissociation limit. This new area of research was attracting the attention of theorists and experimentalists, and TES was providing other information: state-to-state cross-sections; applicability of quantum selection rules in collisions; metastable fractions in an ion beam; and thermochemical data such as ionization, excitation, and electron attachment energies.

My introduction to mass spectrometry was as a young and fresh-faced postdoctoral student when in late 1977 I had an opportunity to work in John Beynon's newly formed research unit. I had come from a traditional experimental physics background, where experiments and apparatus were built from the ground up, and I had just labored through a Ph.D. program measuring total cross sections for positron/atom scattering. It was extremely exciting when I realized that a mass spectrometer, which I had previously thought had been built solely for the use of organic chemists, could be a physical laboratory in its own right. More than that, someone else built the instrumentation to professional standards, which gave unheard of performance and sensitivity, and without a single line of computer code to write to control the device. That instrument was the new ZAB-2F mass spectrometer (supplied by VG Organic, Altrincham). My initial work on the ZAB-2F was concerned with the collision-induced dissociation (CID) of organic molecules, but I soon started to study smaller molecular ions. I was encouraged by the many extras Beynon had persuaded VG to add to his ZAB, which coincidently was the first production model incorporating so-called reversed geometry in a horizontal format. It was an innovative design giving the experimentalist unhindered access to the instrument, which Beynon had very carefully specified to have numerous extra slits, detectors, and controls of various descriptions and uses as yet unknown to me [6]. Some of our early work was concerned with relating the profiles of collision-induced and metastable peak shapes to the internal energy-release distribution of the ion, using the mass-analyzed ion kinetic energy spectrometry (MIKES) scanning technique. A theoretical model was developed that allowed us to get at the internal energy-release distribution [7]. In general, these distributions were continuous functions and without some smart theory, we could not progress further. However, it was soon realized that for certain reactions, structure appeared in the peak shape and the new ZAB had collimating slits just a few inches from each focal point, allowing angular collimation to be applied both to the primary ion beam before fragmentation and to the ions formed after fragmentation. This had the effect of enhancing any discrete structure within a peak, for example, allowing isomeric products with different reverse activation energies to be resolved. A classic paper [8] from Keith Jennings's laboratory attracted my attention, it described the unimolecular charge separation of $C_7H_7^{2+}\rightarrow C_4H_4^{+}+C_3H_3^{+}$, where the propargyl and cyclopropenium forms of $C_3H_3^{+}$ lead to two superimposed dish-topped peaks, from which their identity was deduced.

Considerable experimental effort was given to the underlying instrumental effects that were responsible for achieving a high degree of angular collimation and how peaks' shapes would vary over a wide range of instrumental conditions and energy releases. This research into angular resolution/collimation was essential to ensure that the energy-release distribution, measured for a fragmentation process, could be accurately connected to the MIKE peak shape and that any deconvolution procedure to remove instrumental effects was being accurately applied.

I have described, at some length, the background to my thoughts on how best to achieve high-angular and -energy resolution, for studying fragmentation reactions, with a commercial double-focusing mass spectrometer. Instrumental improvements were always of interest to our ongoing program of work. The ZAB mass spectrometer was in continuous use by a group of a dozen or more workers, and its mass resolution was difficult to maintain beyond a few thousand, and as such, we did not achieve energy resolution better than 0.5 eV. Thus, high-energy-resolution TES experiments were not feasible during this period. However, one exception was a final experiment I engaged on as a postdoctoral student. It involved charge-stripping He^+ to He^{2+} on helium collision gas under conditions of very high angular collimation $<10^{-4}$ rad and energy resolution of $\sim$0.5 eV. The choice of the system was deliberate: As we were looking for an ideal calibration system for our charge-stripping studies, the states of He, He^+, and He^{2+} are such that there should be no energy-loss processes within $\leq$5 eV of the charge stripping of He^+ from its ground state to the electronless He^{2+}. Unexpectedly, the charge-stripping process experimentally observed showed rich fine structure, which led to an interpretation not based on excited states [9]. It is perhaps surprising that a one-electron collision system can still reveal new facets of collision phenomena.

At this time, I left to work with Kratos Analytical (Manchester) for a couple of years before being tempted back to academia by Beynon. When I returned, I was better equipped with new knowledge on how high-resolution sector instruments functioned after having worked in the research and development team on a range of high-resolution spectrometers manufactured by Kratos. In conjunction with the recently published TES studies by Bowers [4], I finally realized that a double-focusing mass spectrometer could be applied to record high-quality TES data. However, we still continued to study ion fragmentation; for example, H_2^+ is an interesting case. The molecular ion becomes highly vibrationally and rotationally excited when it is formed from an alkane or almost any precursor capable of generating a H_2^+ signal. Those ro-vibronic states with lifetimes in the "metastable window" of the instrument can be resolved under conditions of high angular collimation and modest energy resolution.

In 1985, we had thought up a superior design for a translational-energy spectrometer based on two identical electrostatic sectors, and this heralded the start of a period when we were able to perform high-quality TES on a range of ionic systems, which was not possible with the ZAB. Some key experiments undertaken are described later in this article. Most of the early work was carried out with John Beynon as my main coworker, but later collaborators who contributed extensively were Deepak Mathur, Mahmoud Hamdan, and Anthony Lee.

Now that I had identified TES as a subject area that I thought an interesting topic to research, I became more mindful of the activity of other workers past and present in the field. Half a dozen groups have shaped and driven the field forward; some of the major events and milestones that have occurred will be presented later within this article. The early reference work in this area is the volume *Collision Spectroscopy*, edited by Graham Cooks [2]. Its scope is far wider than what I will attempt to cover here, as I will limit my comments to studies within a collision energy regime from $\sim$0.5–10 keV. Depending on what body of scientists you address, this is called anything from a low-energy regime to a high-energy regime. In the context of mass spectrometry and physical chemistry, it will be subsequently referred to as a high-energy regime and defines collisions where electronic excitation dominants. There is a huge body of work on the physics of ion atom/molecule work that I will not deal with. I intend to focus on applications of interest in chemical physics where high-energy and angular resolution has been applied, generally to small ions. The ion optical properties and physics of these spectrometers have also been of considerable interest in my research, and I will briefly discuss some of the main features of the novel ion optics we developed during this work.

The origin of TES may be traced to a number of sources; applications to chemical compounds were pioneered in the work of Moore and Doering between 1969 and 1974. A landmark investigation of the low-energy singlet–triplet and singlet–singlet transitions observed in ethylene derivatives by ion impact was reported by Moore [10] in a comprehensive study of 3 keV He^+ and H^+ ion-impact energy loss. The technique employed a spectrometer incorporating ion retardation, thus improving the resolving power. The ground states of H^+ and He^+ are, respectively, singlet and triplet in nature, enabling Moore to investigate the role of spin conservation. Before this, Moore and Doering had reported cross sections for vibrational excitation processes in ion/molecule collisions [11] and Herrero and Doering [12] had reported superelastic collisions of vibrationally excited $H_2{}^+$ carried out at an energy resolution of 1 : 10^4. The latter study demonstrated how vibrational excitation cross sections, within a given electronic state, varied with $\Delta\upsilon=0, \pm1, \pm2$, and so forth ($\Delta\upsilon$ being the change in vibrational quantum number during excitation). At the same time, Durup's group, in the Universitié de Paris-Sud, were developing a high-resolution translational-energy spectrometer based on a modified magnetic-sector mass spectrometer for double-charge transfer spectroscopy [13]. Another study I will focus on is the work of Bowers's group; in particular, the observation of the $C^2\Pi_u$ excited state of $H_2{}^+$ by TES, using a commercial ZAB mass spectrometer [14]. Within the atomic physics community, Kaneko's research group at the Tokyo Metropolitan University observed rotational excitation by TES [15] on a custom-built retarding ion–energy loss spectrometer. The most outstanding work came, unsurprisingly, from the FOM Institute in Amsterdam, initiated by Los's group. In 1982, de Bruijn and Los [16] reported a time- and position-sensitive detector for studying charge-transfer dissociative processes, and a series of high-quality studies arose from this development over the subsequent 10 yr or so. I will take the opportunity to discuss a few examples of our own work [17,18]. I was asked to give highlights of the major work contributing to the field. There is other work I would like to bring to the attention of the reader, and that is the group of Mathur (Bombay) and the work from Queen's University Belfast (McCullough and Gilbody). The latter have recently enhanced their facility to carry out so-called double TES (DTES). Here the primary ion beam is state selected through a preliminary energy-loss selection process before the main energy-loss processes are investigated. This work, if nothing else, is at the limit of sensitivity of the technique and shows the boundaries for the method.

TES is almost exclusively applied to positive ions, at least in respect of the charge state of the primary ion beam. This is not unsurprising because of the relative stability of positive ions vis à vis negative ions. Hence, apart from double-charge transfer spectroscopy, this article will refer only to investigations concerning positive ions.

2. Principles of TES and experimental methods

2.1. Classification of collisional reactions

Translational-energy spectroscopy can be classified into two main categories (cases 1 and 2, refer to Table 1): Case 1 (nondissociative reactions) involves the precise measurement of the translational-energy loss (or gain) of the projectile ion after collision with a neutral target species. It is a necessary condition that the ion does not dissociate before reaching the detector. Case 2 (dissociative reactions) involves the determination of the kinetic energy release distribution (KER) from the translational-energy distribution of the ionic dissociation product(s) from the fast projectile ion. The outcome of a TES measurement is to provide physical and structural information on the ion and, in certain experiments, on the target moiety. Typically, the collision energy range lies between a few hundred electron Volts to tens of thousands of

Table 1
Classification of the major collisional reactions arising in TES

Case 1: Non-dissociative reactions:		
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
Case 2: Some selected dissociative reactions:		
Unimolecular dissociation	$AB^{+,*} \rightarrow A^+ + B$	
Collision induced dissociation	$AB^{+,*} + G \rightarrow A^+ + B + G$	
Dissociative ionization	$AB^{+,*} + G \rightarrow AB^* + G^+ \rightarrow A + B + G^+$	
Dissociative charge exchange	$AB^{2+,*} + G \rightarrow AB^{+,*} + G^+ \rightarrow A^+ + B + G^+$	

Note. Classification of the major collisional reactions arising in TES. M^+, fast projectile ion; x, y, z, number of charges; G, collision gas; * excited state species or an ion with sufficient internal energy to undergo dissociation; AB^+, molecular ion capable of dissociating into its constituent parts A and B.

electron Volts for a singly-charged ion, which is defined for the following reasons: The collisional cross sections for electronic excitation and charge transfer are large or maximize in this energy range; the collision interaction time between the ion and the target species is very short ($<10^{-15}$ s) leading to Franck-Condon behavior, where excitation and deexcitation are described as vertical (nonadiabatic) processes; momentum transfer to the target is very small for small scattering angles, allowing the energy loss to be directly related to the states of the ion alone; excitation involves valance electrons, which are of chemical interest; and for case 2 reactions the kinetic energy release distribution (KER) is greatly amplified at high translational energies and can be readily determined from the peak shape giving a very precise probe of the internal energy distribution of an ion.

For nondissociative reactions there are five main processes (refer to Table 1). Energy-loss reactions (I*a*) and superelastic reactions (I*b*) feature prominently in TES, where the ion, M^+, is excited or deexcited between its energy levels. Reactions II, III, and IV represent another class of reaction where electrons are exchanged between the fast projectile and the target. When electrons are emitted as free particles, this is referred to as charge stripping. In all of the reactions I–IV, it is an essential condition that the product ion remains intact before reaching the detector; otherwise, the resolution and sensitivity deteriorate excessively. Reactions II–IV provide information on ionization energies and electron affinities as well as on the excited states.

If M^+ is chosen to be an atomic species, then there is no fear of the projectile ion breaking. This was our starting point in our early investigations. H^+ is an obvious option; however, it may be a restrictive choice, as a proton is a permanent singlet state and TES will only allow observation of singlet systems. We have recently found $H_2{}^+$ to be an excellent projectile for high-resolution studies, and examples of this work will be given, contrasting both projectiles that provide complementary information on the target.

However, the fate of the target after excitation is unimportant, as the information has been transferred into translational-energy changes in the projectile. In double-charge transfer spectroscopy (IV), highly excited states of any lifetime can be observed; typically, H^+(singlet) and OH^+(triplet) are common choices for the projectile for studying the electronic structure of dications by this method [19].

2.2. Some basic collision theory

Classical theory of high-velocity (keV) ions ($M_1{}^+$) colliding with a thermal energy atom or molecule (M_2) is well developed and extensively written about. However, it is worthwhile recalling three basic relationships (Eqs. [1], [2], and [3], given below), which

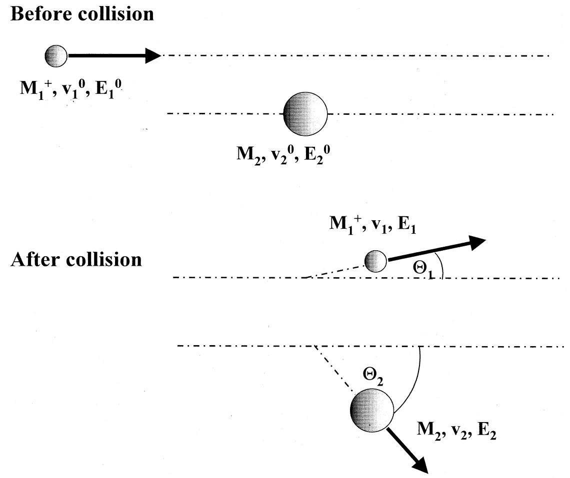

Fig. 1. Schematic representation of a binary collision between a fast ion of mass, M_1^+, velocity v_1^0, and translational energy E_1^0 with a neutral target of mass M_2, velocity v_2^0, and translational energy E_2^0. After collision, the projectile ion has been scattered through an angle, Θ_1, and has a velocity v_1 and translational energy E_1. The target species is scattered through the angle, Θ_2, and has a velocity v_2 and translational energy E_2.

relate the energy loss of the projectile and target. Refer to the schematic diagram for the idealized collision process shown in Fig. 1. The main results are that the translational energy of the ion after collision (E_1) is given by

$$E_1 = E_1^0 - (E_2 + Q), \tag{1}$$

where Q is the amount of kinetic energy converted to internal energy in the collision. For small angle scattering, Θ_1, the energy converted into translational motion of the target (E_2) is

$$E_2 \approx (M_1/M_2)\, E_1^0 \Theta_1^2, \tag{2}$$

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

$$\Delta E \approx (M_1/M_2)\, E_1^0 \Theta_1^2 + Q. \tag{3}$$

In view of Eq. (2), the choice of a very light projectile ion such as H^+ or H_2^+ will keep the translational-energy transfer to the target very small and, thus, enable high resolution to be maintained. E_2 will not be single valued in a real collision process but as a distribution dependent on the differential scattering cross section for the system, and it is essential to keep E_2 small.

2.3. Experimental methods

The technique together with the types of instrument have been described in detail elsewhere [17]. For simplicity, TES will be considered as a spectroscopic method that does not rely on photon absorption or emission, for example, by the use of laser radiation, as is the case in photofragment spectroscopy. All the work reported in this article, except that from the FOM Institute with their time- and position-sensitive detector, uses the same basic technique. A monoenergetic beam of mass-selected ions is focused into a collision cell containing a suitable target gas or vapor maintained at a pressure low enough to ensure that single-collision conditions apply. Different strategies have been developed to ensure that high energy resolution is available, by using either energy selectors before and after the collision cell or by employing double-focusing properties of two sectors in a conventional sector mass spectrometer or, ideally, two identical electrostatic analyzers used in an ultra-high-resolution arrangement [18].

The primary ionization method has frequently been electron impact (EI), although chemical ionization (CI) was employed to generate more exotic species. EI will produce ions with a wide range of internal energies, which can be a severe drawback if hot bands are to be avoided. CI is useful to render an ion cold, and low-temperature CI sources were built to further cool ions into their lower vibrational states of the ground state. Careful manipulation of the electron energy in EI can crudely regulate the fractional population of an excited state, but as it is a threshold control, it is only effective for widely spaced excited states in atomic ions. However, it is very useful to be able to vary the electron energy, up to 1000 volts, for example, in studies of multiply charged rare gas ions.

Most TES spectrometer designs employ a mass-selective device; it is not chosen to have high performance, as the masses generally used are low and even a permanent magnet could successfully be employed for mass selection. The key part of the instrument to

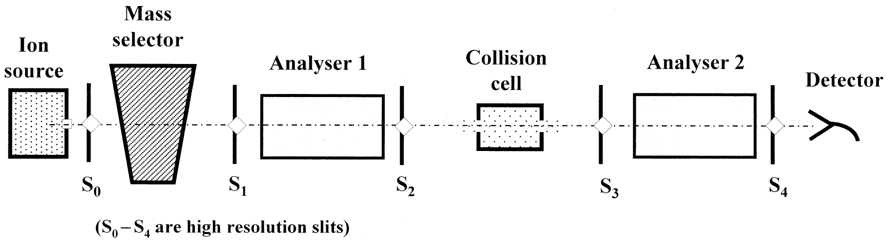

Fig. 2. Schematic diagram of the generic design of a translational energy-loss spectrometer. S_0–S_4 are high-resolution resolving slits. Analyzers 1 and 2 are energy analyzers, discussed in the text and in Table 2.

achieve highly resolved spectra are the energy analyzer(s). This section will very briefly describe the most successful of these designs.

Fig. 2 schematically shows the generic design of a translational-energy-loss spectrometer; the specific variants, which have been developed, are referred to in Table 2. The classical physicists' design is to use separate energy analyzers placed before and after the collision region, each analyzer having its own resolving slits so that high resolution is obtained on each device. The first will monochromate the primary ion beam (analyzer 1 shown in Fig. 2), and the second analyzer (analyzer 2 shown in Fig. 2) will measure the energy loss encountered. To improve sensitivity, stigmatic focusing has been employed. Another popular design has been to employ a pair of 180° cylindrical electrostatic analyzers, placed in an S-shape configuration. To reduce the requirement of high performance with each analyzer, retardation of the ion beam before it enters an analyzer is often applied; here, the ion beam is typically decelerated ~10 eV in translational energy. One of the best examples is the work of Kaneko and Kobayashi [15], whose optics achieve an energy resolution of ~0.007 eV at a collision energy of 50 eV and in-analyser translational energy of 3 eV.

Commercial double-focusing mass spectrometers can provide energy resolution of ≥0.1 eV for 8-keV collisions [4]. However, this is often at the limit of sensitivity and necessities signal averaging over quite long periods. It should be noted that double focusing has a different meaning in the physics community compared to mass spectrometrists; the latter have an extended view, where the term refers to compensation of energy and angular distributions of the ion beam to full second-order compensation. The above mass spectrometer comprises a magnetic sector and a cylindrical electrostatic sector, with the collision placed in the drift region between them. A magnetic sector is mandatory for a mass spectrometer but is a mismatched ion optical device when compared to the

Table 2

Description	Slits Used	Retardation	Remarks	Reference
Classic energy loss with energy analysis before and after the cell	S_0,S_1,S_2,S_3,S_4	No	Each analyzer can be either a single-energy selector or dual S-energy selector	None
Classic energy loss with energy analysis before and after the cell except ion retardation is incorporated in the analyzers 1 and 2	S_0,S_1,S_2,S_3,S_4	Yes	Each analyzer can be either a single-energy selector or dual S-energy selector	[11,15]
Magnetic electrostatic double-focusing mass spectrometer	S_0,S_1, S_4	No	Commercial mass spectrometers	[4]
Double-focusing symmetrical pair of electrostatic analyzers	S_0,S_1, S_4	No	Two machines built	[17,18]

Note. Classification of four main variants of translational energy spectrometer based on sector technology.

electrostatic analyzer. A superior focusing system is a symmetrical pair of electrostatic analyzers, which have very low imaging aberrations [18].

3. Landmark TES studies

In this section, I have tried to bring together examples of major contributions of the leading practitioners of TES, in general, with what I consider to be highlights of their research. I have not discussed my choice with these individuals and, therefore, it must be regarded purely a personal opinion. Some have made major contributions, while others have broader interests where TES is only one. Again, my own opinion is that the field has grown from an interest of physicists who have moved closer to the chemical community as well as from physical chemists and mass spectrometrists. Technological developments with commercial mass spectrometers had given impetus to the field because of the versatility of some of the designs of sector mass spectrometers. However, the subject has now matured and largely entered the textbooks and, with the ever-increasing demand toward applied science, this type of work is less favored. I personally became involved in TES because of both the scientific challenges I saw and of their stimulus. I hope that I have succeeded to some extent.

3.1. Moore and Doering (Johns Hopkins University and the University of Maryland)

The early work by Moore and Doering at Johns Hopkins University was on an ion energy spectrometer fitted with a Bausch and Lomb diffraction grating to record the emission spectra of the N_2^+ first negative band (0,0) [20]. They soon developed an ion energy–loss spectrometer capable of resolving ∼0.1 eV for 0.1–10 keV ion beams using 120° spherical electrostatic analyzers operated in retardation mode (ion energy in-analyzer 6-12 eV), and they undertook high-resolution studies of the vibrational excitation of H_2, D_2, and N_2 by H^+ and H_2^+ impact. Cross sections were measured for collisions energy at 150 and 200 eV for the first few vibrational levels. I have classified this work as one of the earliest TES measurements. Moore went on to the University of Maryland and continued his work with a landmark study "An investigation of the low-energy singlet–triplet and singlet–singlet transitions in ethylene derivatives by ion impact" [10]. Moore had developed an apparatus [21] that used a collision energy of 3 keV and gave an energy resolution of 0.35 eV. The projectiles were chosen so that singlet–singlet transitions could be observed on their own using H^+(singlet), and singlet–triplet transitions observed using He^+ (triplet ground state).

Fig. 3 reproduces the classic spectra taken by Moore; the lower-energy singlet–triplet reactions are clearly observed for all substituted ethylenes, and their structural differences lead to distinct differences in the corresponding TES spectra. The work clearly allowed the singlet–triplet splitting between the T and V states to be evaluated as 3.5 eV in ethylene, which reduces to ∼3 eV for most of the substituted ethylenes. Moore also commented that the dipole allowed first Rydberg transition, which is an intense feature in optical and electron impact spectra, was not an obvious feature, if at all present. The absence of Rydberg transitions in small-angle scattering TES is a characteristic and has been discussed by Lock, Brenton, and Mathur [22].

The role of the Wigner spin rule was shown by Moore to hold for scattering of N^+ on He, Ne, Ar, and O_2 [23], and in a later study on the spin forbidden reactions, $^1D \leftrightarrow {}^3P$ in N^+ on Kr and N^+ on Xe [24] were observed. This result is in analogy to the observation in optical spectroscopy that ls coupling is prevalent in light atoms, while jj coupling is more important in the excited states of heavier atoms.

3.2. Durup et al. (Universitié of Paris-Sud)

Durup, together with Appell, Fehsenfeld, and Fournier, in the early 1970s developed double-charge transfer spectroscopy where the electronic states of doubly charged ions can be measured by a beam of protons interacting with the neutral vapor of the compound. The translational-energy spectra of the

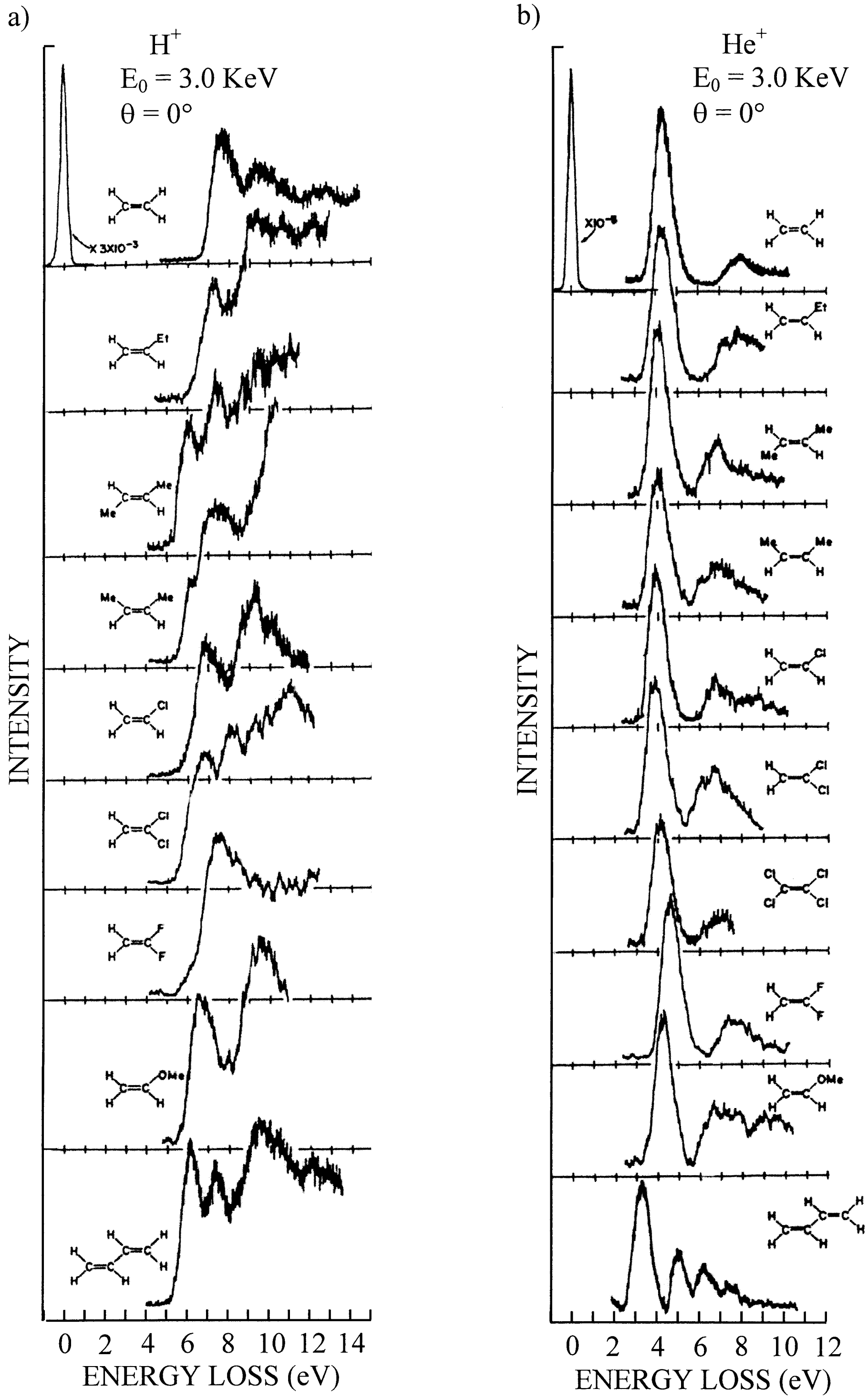

Fig. 3. 3-keV (*a*) H^+ and (*b*) He^+ energy-loss spectra of ethylene and some substituted ethylenes and 1, 3-butadiene. (Reproduced with permission, [10].)

Table 3

	I^{++} (eV)			
Target and States of M^{2+}	Theory	Appell et al. data [13]	Electron impact data	Auger electron spectroscopy
O_2				
$\tilde{X}\ {}^3\Sigma_g^-$:				
$\tilde{X}\ {}^1\Sigma_g^+$	35.5		36.3 ± 0.5	37.4
$\tilde{A}\ {}^3\Sigma_u^+$	39.6			
$\tilde{B}\ {}^3\Pi_g$	42.15	43.0 ± 0.5		
$\tilde{B}'\ {}^3\Sigma_u^-$	42.5			
$\tilde{a}'\ {}^1\Sigma_u^-$	42.9			
$\tilde{a}\ {}^1\Pi_g$	43.7			
$\tilde{W}\ {}^1\Delta_u$	43.6			
$\tilde{C}\ {}^3\Pi_u$	48.4	48.0 ± 1.0		
N_2				
$\tilde{X}\ {}^1\Sigma_g^+$:				
$\tilde{X}\ {}^3\Pi_u$	42.6		42.7 ± 0.1	43.0
$\tilde{a}\ {}^1\Sigma_g^+$	42.7	43.1 ± 0.5		
${}^3\Sigma_g^-$	43.8		43.8 ± 0.1	
$\tilde{b}\ {}^1\Pi_u$	44.0	45.2 ± 0.5		
$\tilde{A}''\ {}^3\Sigma_u^+$				46.2
$\tilde{A}'\ {}^3\Pi_g$	46.1			47.2
NO				
$\tilde{X}\ {}^2\Pi$:				
$\tilde{X}\ {}^2\Sigma^+$	38.1	39.3 ± 0.5	39.8 ± 0.3	40.1
$\tilde{A}\ {}^2\Pi$	38.7			
$\tilde{B}\ {}^2\Sigma^+$	42.9	42.4 ± 1.0		
$\tilde{C}\ {}^2\Sigma^+$				
$\tilde{D}\ {}^2\Pi$		47.2 ± 0.5		

Note. Double-charge transfer data taken form the work of Appell et al. [13].

product H^- ions formed reveal the vertical excitation energies of the doubly charged target. This has been shown to be a robust method for obtaining data on doubly charged ions, so long as the ionization energy and electron affinity of the fast projectile are known, and it compares favorably with data from Auger spectroscopy. The method is accurate to better than 0.5 eV. Table 3 shows a typical set of data obtained by double-charge transfer spectroscopy [13]. The apparatus built by this group was based on a magnetic sector, and the key feature was the extensive angular collimation that was fitted. This philosophy marks my earlier comments in this article on the spectrometers' requirements; for case 2, TES angular collimation is essential for obtaining high-quality spectra.

Harris et al. [19] have continued with this technique using a commercial mass spectrometer and have extended the technique to the measurement of triply charged ion species through the process of three-electron transfer in allene [24]. This application understandably suffers from limited sensitivity but is feasible in selected cases.

3.3. Bowers's group (Santa Barbara, California)

Bowers's group was the first to conclusively show that a commercial double-focusing mass spectrometer could be used for high-resolution TES. Illies and Bowers [4] published an early article demonstrating this on the electronic transitions in Kr^+, I^+ and N_2^+. A remarkable paper was published by Kirchner at al. in 1984, titled "First spectroscopic observation of the $C^2\Pi_u$ excited state of H_2^+" [14]. While it had been theoretically predicted that there were at least two bound excited states, $B^2\Sigma_g^+$ and $C^2\Pi_u$, these had not been experimentally observed, even though the $C^2\Pi_u$ is optically allowed. It was known from theory that the equilibrium internuclear distances for these states was much larger than the ground state of $H_2^+(X^2\Sigma_g^+)$: $r_e(X^2\Sigma_g^+)=1.06$ Å; $r_e(B^2\Sigma_g^+)=4.7$ Å; $r_e(C^2\Pi_u)=4.2$ Å. Thus, the Franck-Condon factors will be very small for transitions from the lower vibrational levels of $H_2^+(X^2\Sigma_g^+)$, making its observation unlikely. A method had been found by Brenton et al. [25] where H_2^+ $(X^2\Sigma_g^+)$ could be formed in very high vibrational states and even populate levels above the dissociation limit because of the associated rotational excitation. These levels are quasibound, and they are lifetime dependent on the rate of predissociation through the rotational barrier. Fig. 4a shows the TES spectrum for H_2^+ on He, and Fig. 4b the potential energy curves. The evidence is compelling for the first recorded observation of the $C^2\Pi_u$ state: TES has shown its power to fill some of the gaps that optical spectroscopy leaves. Bowers's work was pioneering even though the energy resolution that could be applied was 0.65 eV because of limited sensitivity. Further studies by Bowers were on small di- and triatomic ions: C_2^+ [26], C_2D^+ [26] and NO^+ [27]. When we commissioned our double-electric sector instrument, with its greatly improved sensitivity at high resolution

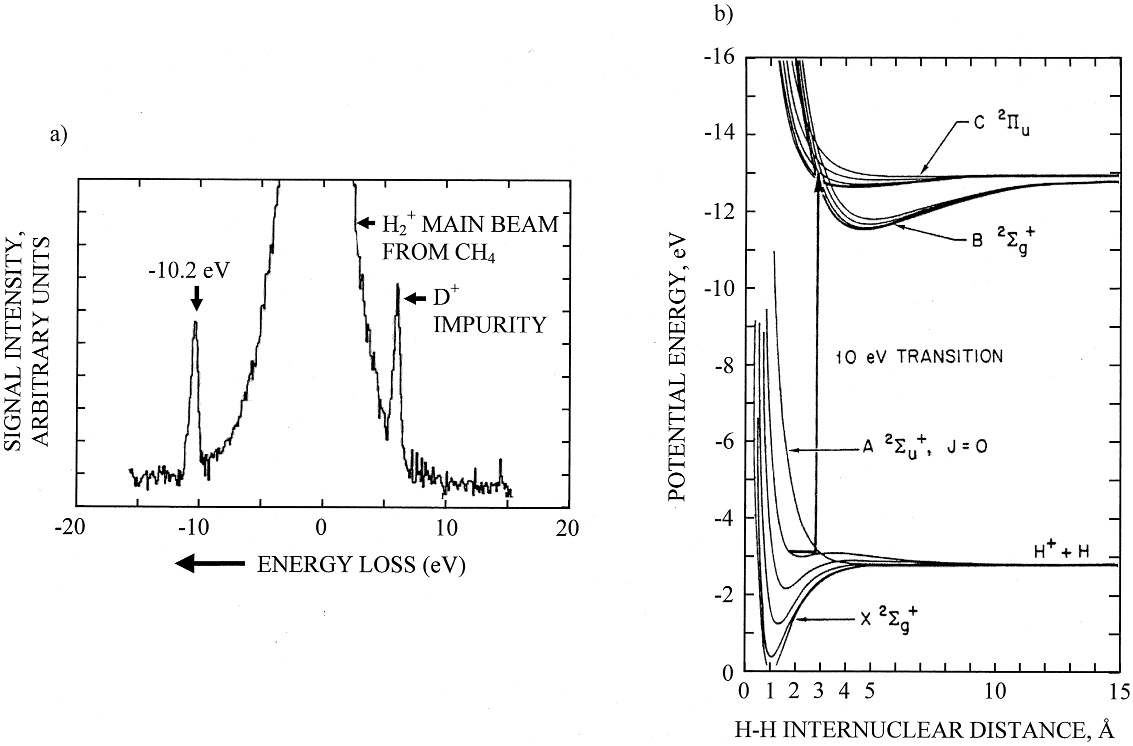

Fig. 4. (*a*) Energy loss spectrum of $H_2{}^+$, formed from methane, at 8-keV collision energy and 0.65-eV energy resolution; (*b*) potential energy curves for excitation from the high-lying ro-vibronic states of ground state $X^2\Sigma^+{}_g$ to the $B^2\Sigma^+{}_g$ and $C^2\Pi_u$ states. (Reproduced with permission, [14].)

showing the technique could move further on, one striking example of the improved performance we obtained is the TES of NO^{2+}, which in shown later in this article.

3.4. Kaneko and Kobayashi (Metropolitan University, Tokyo)

Kaneko and Kobayashi developed an ion energy–loss spectrometer having an ultimate resolution of 0.007 eV for 50 eV collision energy. The instrument uses ion retardation, with the ion energy being decelerated down to 3 eV for transmission in the two energy analyzers. A great deal of their work involved state-resolved measurements, including measurements of cross sections. Rotational cross sections for Li^+ on H_2 were reported between 50 and 400 eV [15]. Fractional populations of excited states as a function of electron ionizing energy can now be routinely measured by this technique [28]. The design of their spectrometer is particularly useful for energy losses that are relatively small (<0.5 eV), as these are less accessible on double-focusing instruments because of peak tailing effects. Fig. 5 shows the energy loss spectrum for 203 eV Li^+ on CO_2, a loss of between 0 and 0.5 eV; the excitation of overtones of the bending and stretching modes are clearly identified.

3.5. Brenton's group (University of Wales, Swansea)

I would like to discuss three examples illustrative of our studies.

3.5.1. Rotational predissociation of $H_2{}^+$

The $H_2{}^+$ molecular ion, the simplest three-particle system, has been extensively studied since the 1930s.

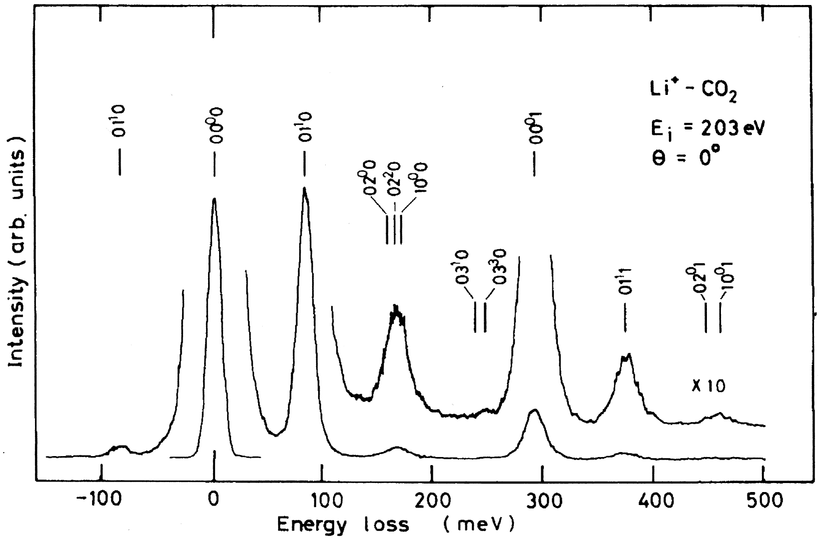

Fig. 5. TES spectrum of 203 eV Li^+ incident on CO_2. (Reproduced with permission, [15].)

In our 1982 investigation titled "*Rotational predissociation of H_2^+ ions of different precursor origins*," it was found that the ro-vibronic population of H_2^+ could be increased dramatically by forming it as a fragment of a higher precursor with EI [25]. Ordinarily metastable unimolecular dissociation of H_2^+, formed by EI, does not occur. Rotational predissociation is possible for ro-vibronic states lying above the dissociation limit (usually high J; refer to Fig. 4b) for metastable states with lifetimes between 10^{-3} and 10^{-7} s. Our calculations identified 56 quasibound states lying above the dissociation limit; the energy release and lifetimes for each were calculated and the uncertainty in the higher ro-vibronic states was judged to be 12 cm^{-1}, at low values of (v, J) the accuracy was estimated at 0.2 cm^{-1}. All but 14 have lifetimes well outside the metastable window. Methane was found to give the most intense signal for rotationally excited H_2^+ and the unimolecular mass-analyzed ion kinetic energy spectrometry (MIKES) spectrum under conditions of high-angular collimation and with energy resolution of ~0.5 eV are shown in Fig. 6. A MIKE peak should be symmetrical about its center. From Fig. 6, the transitions identified are labeled *a* to *i*, and each are symmetrical features that should be observed on both sides of the peak (sometimes called horns). This experimental data is listed in Table 4. The long drift-free regions of the ZAB-2F mass spectrometer

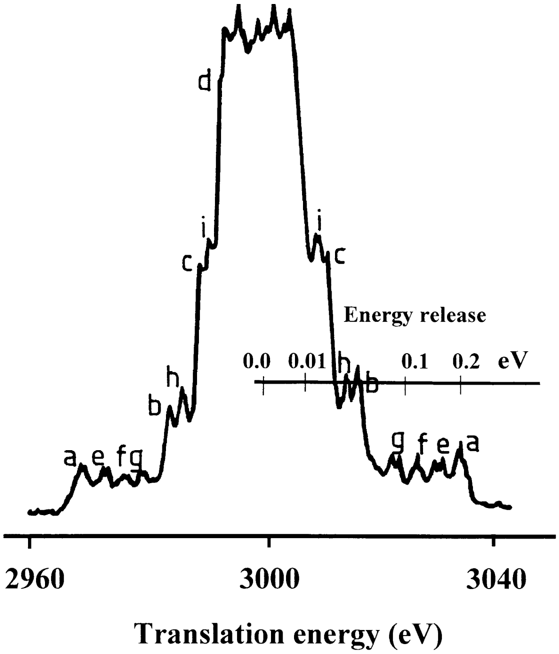

Fig. 6. Translation-energy spectrum for the rotational predissociation of $H_2^+ \rightarrow H^+$, when H_2^+ is formed from methane. Accelerating voltage is 6000 eV.

Table 4

Quasibound states of H_2^+		Feature in Fig. 6	Relative Populations from Theroretical Data	Relative Populations from Experimental Data
v	J			
0	39	a	1	1
1	37	e	2	2.2
2	35		<19	<24
3	34	f	0.75	0.4
4	32	g	1.1	0.7
5	30		<50	<70
6	29		<2	<0.7
7	27	b	1.6	1.9
8	25		<30	<60
10	22	h	400	40
11	20	c	0.8	0.75
12	18	i	0.5	0.75
13	16		<0.3	<0.5
14	14	d	0.35	0.4

Note. Populations deduced form the rotational predissociation of H_2^+ for its various ro-vibronic states, rotational (J) and vibrational (v), based on experimental data [25] and available theoretical data (J.M. Peek, J.G. Maas, J. Los, Chem. Phys. 8 (1975) 46).

were important in improving the sensitivity of the experiment. Even so, signal averaging >30 min was required for each metastable peak. Using this method, we were able to determine the relative populations of ro-vibronic states that have lifetimes in the range 10^{-3} to 10^{-7} s for a variety of precursors.

Two excellent experimental and theoretical studies of metastable ion fragmentation are from Bowers's group for the following precursor ions CH_4^+ [29] and H_n^+ ($n=3$, 5, 7, and 9) [30] and their isotopic analogues. Both CH_4^+ and H_n^+ showed that the origin of the metastable processes is tunneling through the centrifugal barrier. High-resolution kinetic energy release (KER) distributions were measured using a highly specialized signal averaging system and interpreted in terms of statistical theory. For the metastable hydrogen ion clusters, a higher-order WKB tunneling formulism had to be employed to interpret the rich fine structure observed in the KER of clusters with $n=5$ and 7.

3.5.2. He_2^{2+} and NO^{2+} doubly charged ions

He_2^{2+} and H_2 are both two-electron systems and, as, such should have the same molecular states, although the Coulomb repulsion in He_2^{2+} will greatly change its potential energy curves. In 1984, we published "*First direct observation of He_2^{2+}: charge stripping of He_2^+ using a double-focusing mass spectrometer*" [31]. The experiment was extremely demanding, requiring isotopic labeling, $^3He^4He^{2+}$, and a second electrostatic analyzer to remove two major artifact peaks obscuring the charge-stripping signal. Experimentally, we found the charge-stripping signal to be $\sim 1 : 5\times 10^7$ less intense than the $^3He^4He^+$ signal. However, this experiment did show the high sensitivity of the ZAB-2F in situations where energy resolution was not too important. The experimental energy loss was measured to be 35 eV, and the potential energy curves of the three excited states ($E_1[^1\Sigma_g^+]$, $E_1[^1\Sigma_u^+]$, and $E_2[^1\Sigma_g^+]$) [32] are shown in Fig. 7. Clearly, the weak signal observed is caused by the high excitation energy and poor Franck-Condon factors, as He_2^{2+} has the same equilibrium geometry as H_2 at 0.7 Å, while the ground state of He_2^+ is 1.08 Å.

During 1985–1987, we built our first high-resolution TES spectrometer based on two identical electrostatic analyzers placed in a symmetrical configuration [33]. Its performance greatly exceeded that of the ZAB-2F, routinely giving high sensitivity on most ionic system studied, to a resolving power of ~ 0.06 eV. A great deal of the work on this new instrument is summarized in the literature [17].

Diatomic cations have attracted the attention of many groups; one ion we visited several times, each time at higher resolving power, was NO^{2+}. This species has been examined by a number of workers between 1983 and 1995 [34–36]. I will report the latest work we undertook [37]. NO^{2+} was chosen, as very few studies had been able to observe its spectroscopy. Photofragment spectroscopy is in principle the most accurate TES method, but use of the method failed to observe discrete transitions in NO^{2+}. However, high-resolution TES measurement shows discrete vibrational structure on the energy loss and energy gain sides of the unreacted ion beam (Fig. 8a). The $X^2\Sigma^+$ and $A^2\Pi$ states overlap, and the transition probabilities for $A^2\Pi \leftrightarrow X^2\Sigma^+$ transitions were calculated; Franck-Condon factors are shown as vertical bars in Fig. 8a. Convoluting the Franck-Condon

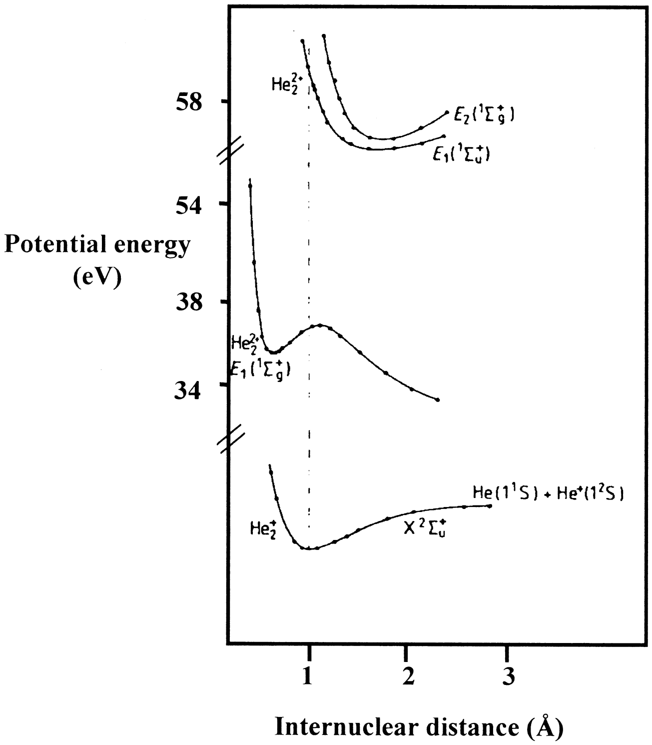

Fig. 7. Schematic diagram of the potential energy curves of He_2, He_2^+, and He_2^{2+}. (Reproduced with permission, [31].)

factors and the instrument line shape (Lorentzian with a 60-meV half width) gives good agreement with the measured TES spectrum (Fig. 8b). The agreement between experiment and theory is reasonable, although further improvement to the signal-to-noise ratio would be beneficial.

3.5.3. High-resolution TES of homonuclear diatomic molecules by H^+ and H_2^+ impact

In 1994, another energy-loss spectrometer was constructed in our laboratory [18] using the knowledge we had gained from the previous instrument. Its sensitivity was higher, and the ultimate resolution was ~0.02 eV for a translational energy of 3 keV. Our early study focused on diatomic systems, and the detail observed in the TES spectra was considerably improved over our previous work. Data from this instrument helped us make many new conclusions on ion/molecule collisions.

A schematic of the new instrument has been shown elsewhere in detail [18]. Briefly, two 70° (956-mm radius) electrostatic analyzers (ESA) are symmetrically positioned, and a gas collision cell is placed in the middle of the drift region between the ESAs. It was shown [18] that the energy-resolving power, $E/\Delta E$, could be defined in terms of the forward-direction energy dispersion, A_δ^{2F} of ESA2:

$$\frac{E}{\Delta E} = \frac{A_\delta^{2F}}{w_o + w_i + \Delta},$$

where E is the translational energy of the ion beam of width ΔE, w_o the object slit, w_i the image-slit width, and Δ the total image aberrations, including collisional aberrations when collision gas is introduced into the collision cell. In the design adopted, $A_\delta^{2F} = 1017$ mm, approximately the radius of the analyzer. However, it was shown [18] that the forward dispersion can be increased considerably and is dependent on the ion optical geometry. The reader might assume that improved performance is being obtained

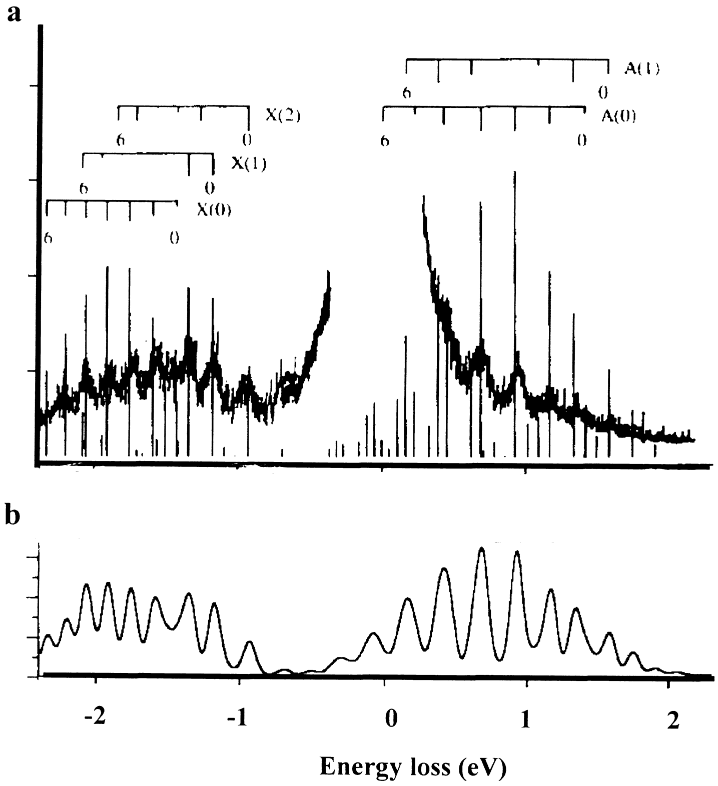

Fig. 8. (*a*) Energy-loss spectrum NO^{2+} on He. The initial state is given by X(i), and A(i), respectively. The final vibrational state is indicated along the horizontal bar; (*b*) simulated spectrum taking the Franck-Condon factors, that is, sticks in upper panel, and convoluting with a 60-meV apparatus function. (Reproduced with permission, [37].)

at no extra cost. This is partly true, as the main cost is an increased intermediate image width that is formed in the middle of the collision cell, where no slit needs to be placed. However, there is a practical limit on this image because of the size of the collision cell opening and the size of aberrations generated by the collision process itself (which increase as a function of the intermediate image dimensions). A full discussion of the ion optics in circumstances of collisional scattering has been given elsewhere [38].

As an illustration of part of this study, Fig. 9 shows the TES spectra for H^+ and $H_2{}^+$ on N_2 [22]. Interpretation of the vibrational bans is given in Table 5. Without entering into a detailed discussion of these data and those on H_2, N_2, and O_2 [22,39], a brief summary of the main findings follows: (1) spin was found to be strongly conserved; (2) orbital angular momentum and total angular momentum were not conserved; (3) g↔g and u↔u selection rules for homonuclear diatomics were allowed; 4) Σ^+–Σ^- symmetry transitions were not observed out of 20 possibilities [40], although one instance may exist at a small energy defect; (5) for $H_2{}^+$ projectiles, excitation to triplet states was strongly favored over excitation to singlet states by a factor of four; and (6) Rydberg excitation, and to a lesser extent target ionization, are either absent or hidden below the other signals present. The data for H^+ and $H_2{}^+$ collisions with CO above ~10 eV excitation show there are several processes not corresponding to Rydberg excitation and not corresponding to known processes cited in the literature [18]. There is a need for further theoretical work to account for these highly excited processes seen on the new spectrometer.

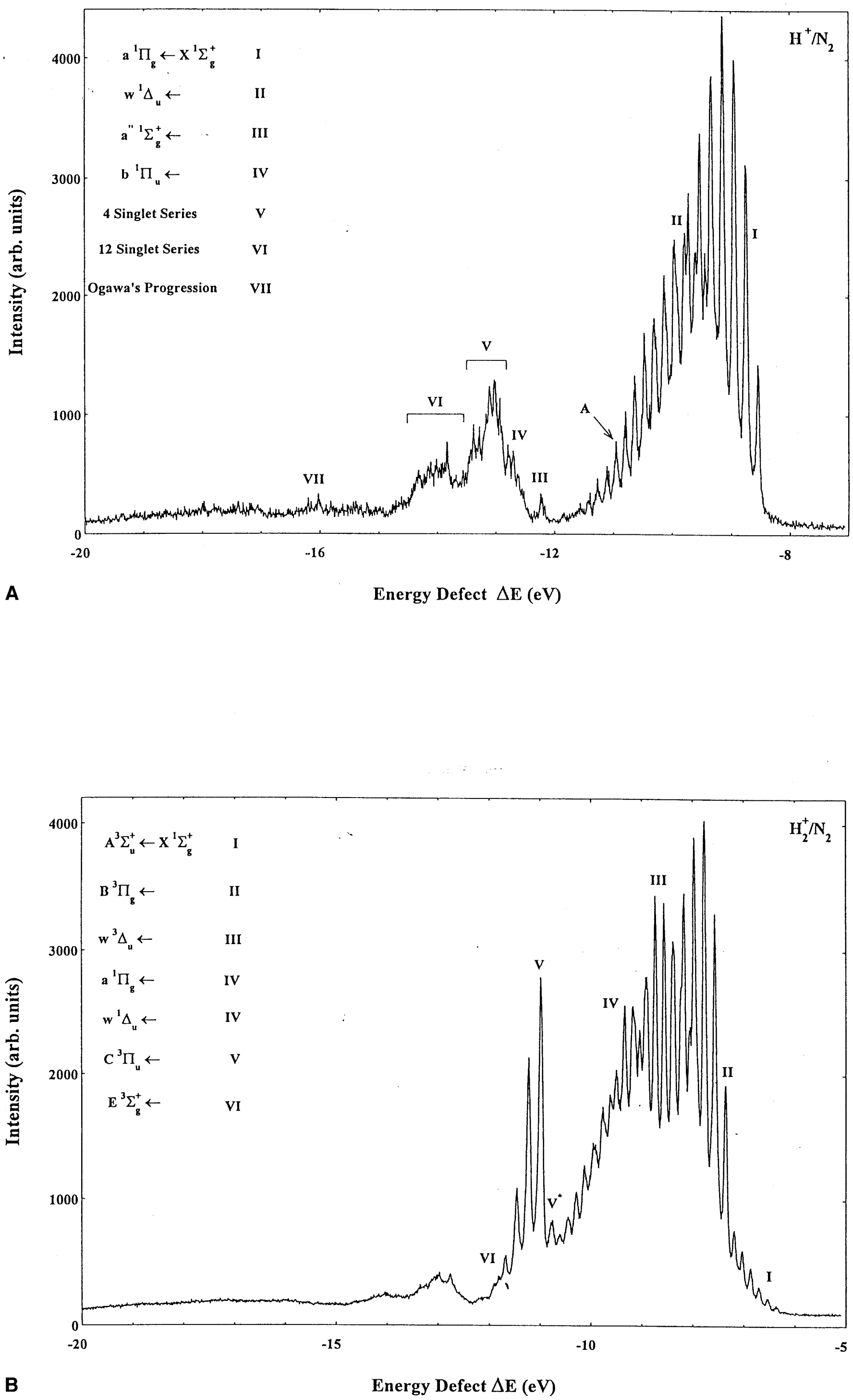

Fig. 9. TES spectra of 3-keV H^+ and $H_2{}^+$ projectile ions scattered off molecular nitrogen over the energy-loss ranges (*a*) H^+/N_2 (−7 to −20 eV) and (*b*) $H_2{}^+/N_2$ (−5 to −20 eV). The energy resolution was set to 0.015 eV. (Reproduced with permission, [22].)

Table 5

		TES Data	Vibrational Transition	Spectroscopic Data[b,c]		
Reaction	Band[a]	$\Delta E_{v'v''}$ (eV)	(v′v″)	$\Delta E_{v'v''}$ (eV)	ω_e (eV)	r_e (A)
H^+/N_2 a $^1\Pi_g \leftarrow$ X $^1\Sigma_g^+$	I	−8.55	0–0	−8.55	0.210	1.220
		−8.76	1–0	−8.76		
		−8.96	2–0	−8.96		
		−9.15	3–0	−9.16		
		−9.35	4–0	−9.36		
		−9.53	5–0	−9.55		
		−9.74	6–0[d]	−9.74		
$w^1\ \Delta_u \leftarrow$	Π	−[e]	0–0	−8.89	0.193	1.268
		−[e]	1–0	−9.08		
		−[e]	2–0	−9.27		
		−9.44	3–0	−9.45		
		−9.60	4–0	−9.63		
		−9.80	5–0	−9.81		
		−9.97	6–0	−9.99		
		−10.12	7–0	−10.16		
		−10.30	8–0	−10.33		
		−10.48	9–0	−10.50		
		−10.63	10–0	−10.66		
		−10.79	11–0	−10.83		
		−10.95	12–0	−10.99		
		−11.11	13–0	−11.14		
		−11.27	14–0	−11.29		
		−11.42	15–0	−11.44		
$a''^1\ \Sigma_g^+ \leftarrow$	III	−12.20	0–0	−12.3		1.12
b $^1\Pi_u \leftarrow$	IV	−12.52	0–0	−12.5	0.079	1.284
		−12.56	1–0	−12.57		
		−12.63	2–0	−12.64		
		−12.70	3–0	−12.70		
		−12.78	4–0	−12.76		
$b'\ ^1\Sigma_u^+ \leftarrow$	V[d,f]	−12.9 to −13.6	0–0	−12.86	0.094	1.444
$c_3\ ^1\Pi_u \leftarrow$	V	−12.9 to −13.6	0–0	−12.94	0.272	1.116
$c_4'\ ^1\Sigma_u^+ \leftarrow$	V	−12.9 to −13.6	0–0	−12.95	0.273	1.108
$o_3\ ^1\Pi_u \leftarrow$	V	−12.9 to −13.6	0–0	−13.10	0.246	1.178
12 possible states ←	VI	−12.7 to −13.8				
Ogawa’s Progression	VII	−16.05		−16.0		
N_2^+ $(X^2\Sigma_g^+ \leftarrow N_2\ (X^1\Sigma_g^+)$		[e]		−15.58		

Note. Spectroscopic assignment of the TES spectrum of H_2^+/N_2 (refer to Fig. 9).

[a] Refer to Fig. 10.

[b] Spectroscopic data taken from [39].

[c] $r_e = 0.989$ Å for the X $^1\Sigma_g^+$ ground state of N_2.

[d] Vibrational transitions beyond this are either weak or overlap other electronic states.

[e] Not observed.

[f] Band V is a mixture of several states, whilst individual components can be identified only ν_{00}, ω_e and r_e values are given for reference.

3.6. Los et al. (FOM Institute, Amsterdam)

In 1982, de Bruijn and Los developed a time- and position-sensitive detector to study the dissociative charge exchange of H_2^+ on gaseous and alkali metal targets [16,41]. The ingenuity of the method is its relative simplicity and compactness. The principle of their detection method is shown in Fig. 10, where a primary ion beam (2.5–10 keV) is allowed to undergo collision-induced dissociation. Both fragments resulting from charge exchange fall on the multi-anode detector, which measures the arrival time and radial

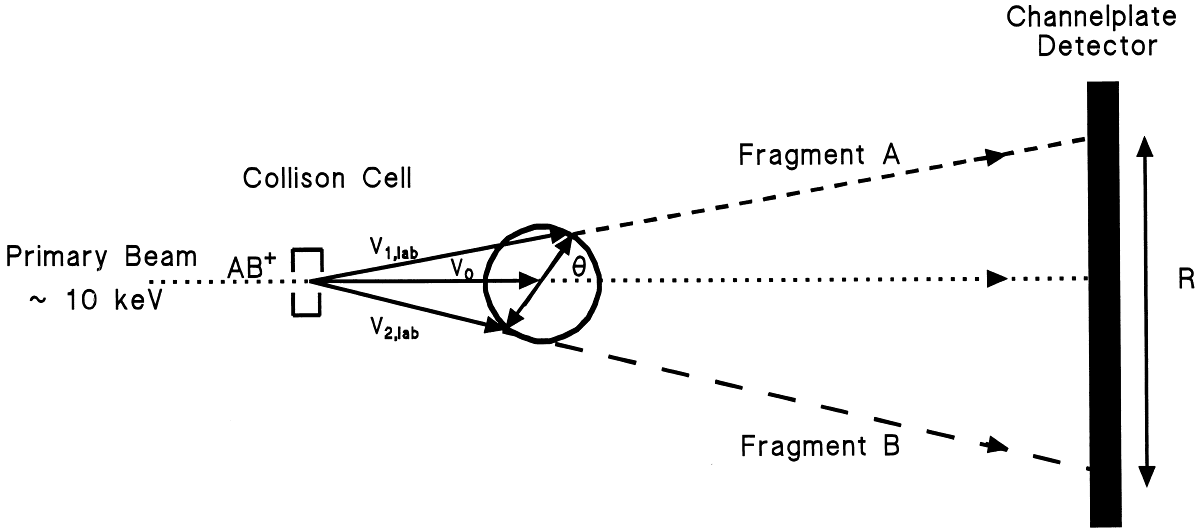

Fig. 10. Illustration of the time- and position-sensitive detector developed in the FOM Institute. (Reproduced with permission, [16].)

position of each fragment. High resolution in position (100 μm) and time (0.5 ns) were achieved, allowing the kinetic energy release and direction of the associated momentums to be directly determined. The method is considerably more sensitive than a translational-energy spectrometer, as just described. However, this does not supercede the earlier-described TES method, as the information and applicability of each technique is different. Their early landmark experiment is the charge exchange of H_2^+ on Mg populating the $H_2^*(C^3\Pi_u)$ excited state, which subsequently predissociates via the repulse $b^3\Sigma_u^+$ curve of H_2. Fig. 11a shows the reaction path over the potential energy curves leading to the two fragments H+H. The energy-release distribution shows vibrational predissociation up to v=16, (see Fig. 11b). Moreover, the technique allows the energy-release distribution as a function of the center-of-mass scattering angle to be

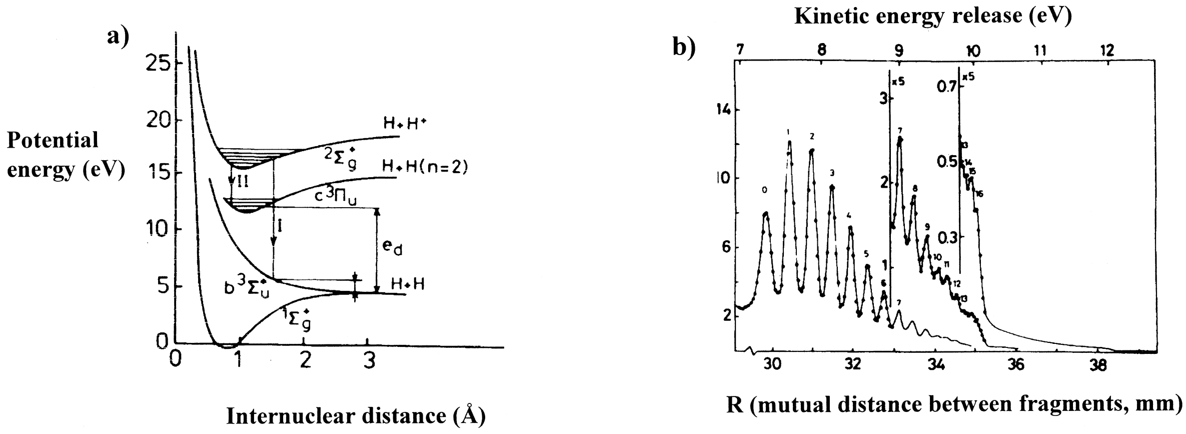

Fig. 11. (*a*) Potential energy curves of H_2^+ and the higher states of H_2 taking part in the charge transfer and predissociation mechanism; (*b*) part of the so-called R-spectrum exhibiting the kinetic energy release distribution for the charge transfer of H_2^+ on Mg. (Reproduced with permission, [16].)

determined, allowing a very complete picture of the collision process to be gleaned.

Since the pioneering experiments of Los, the technique has been refined at the FOM by van der Zande and his colleagues [42]. Challenging spectroscopy is being tackled using this apparatus, which has been demonstrated to measure a range of information: kinetic energy release distributions, state-selected cross sections, lifetimes of states, and rotational distributions in ions.

5. Concluding remarks

Translational-energy spectroscopy (TES) is a relatively specialized area of research, which overlaps the interests of physicists and physical chemists. Some of the outcomes can be applied to areas in mass spectrometry (e.g., exploring the fragmentation mechanism of ions and, hence, increasing the quality and quantity of structural information offered by MS/MS). At a fundamental level, it is a true spectroscopic technique, exemplified by the landmark applications that have come thorough the work at the FOM. It is not a technique for broadly surveying unknown molecules. Other methods overlap with TES, and it has found a role in conjunction with these, filling gaps in our knowledge. It can, however, compete and improve on other methods; NO^{2+} was a case in point, where photofragment spectroscopy failed, probably becase of the low abundance of the molecular dication. TES has been widely applied to study less abundant species, for example, multiply charged ions, where it has been proven to be a powerful tool.

There is a sizable physics community that measures absolute cross sections for state-selected charge exchange in multiply charged ions, and that as yet are not taking full advantage of some the methods discussed above. TES is very powerful for the measurement of fractional populations of excited states. High-resolution TES can be applied to very weak signals, estimated at $\sim 10^4$ to 10^5 ions s^{-1}. It is ideally suited to the measurement of state-selected cross sections and may be unique in many applications. Depending on the TES method adopted, one should be cautious about the accuracy of cross-section measurements. TES performs well for excited state studies of ions, and considerable thermochemical data has been gathered [43]. The applicability of quantum selection rules to collisional systems is now better understood. Many examples can be cited of states that are not observed by other techniques being accessible to TES. Our own recent work for H^+ and $H_2{}^+$ impact on CO for highly excited CO [18], shows processes not observed by electron or photon studies. These experiments indicate that fast ion impact is different than electron or photon impact for higher excitation energies. Isomeric compounds have very recently been studied, and TES can distinguish these compounds. TES spectra were found to be similar to published UV spectra but with very different intensity patterns and with some additional individual bands, possibly because of-spin related phenomena. The development of TES has been vigorous over the last 30 yr, and a considerable body of work is in the literature and textbooks. I am sure TES will still be curiosity driven, but I do feel the level of activity will be reduced because of the demands placed on scientists from applied areas in this postgenomic age.

Acknowledgements

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