

**SPECIAL FEATURE:  
HISTORICAL**

# Collision-induced Dissociation: Readings and Commentary

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**Collision-induced dissociation (CID), also known as collision-activated dissociation (CAD), is now central to the practice of mass spectrometry. The story of its discovery, fundamental basis, and its development as a technique applicable to different types of instruments has evolved over many decades. In this paper, these topics are explored by reference to and commentary on particular texts, chosen to represent milestones in the development of CID over the period 1910-1970.**

The origins of much of mass spectrometry lie in the work of the great English physicist, J. J. Thomson; the dissociation of molecular ions in the course of gaseous collisions is no exception. Writing in 1913, Thomson<sup>1</sup> made the observations quoted below in describing results obtained with an instrument in which the beam of accelerated ions was subject, in sequence, to deflections by an electric and a magnetic field arranged to produce orthogonal displacements. Ions of different velocity, but the same mass-to-charge ratio, fall along a parabola on a photographic plate detector in this instrument. Note that the photographic plate is an extremely sensitive detector in the kinetic energy range (tens of kiloelectron volts) used in these experiments and of course, it enjoys the Felgett advantage of continuous observation of all the signals all the time.

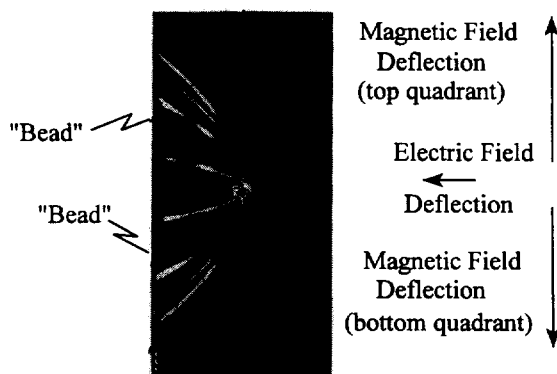
Thomson wrote<sup>1</sup> 'The photographs taken of the positive rays under electric and magnetic forces show also that in certain cases the velocities of the particles are grouped round certain values, for we find that some of the parabolas have a very decided beaded appearance: each bead corresponds to a group of particles moving with pretty nearly the same velocity. An example of this is shown in ...' (Fig. 1).

Thomson continues, 'It is remarkable that the parabola corresponding to the atom of hydrogen is often beaded in such a way that the velocity of the particles producing one bead is to that producing the other as  $\sqrt{2}:1$ . ... The occurrence of singly charged atoms of hydrogen with velocities in this proportion of  $\sqrt{2}$  to 1 might be accounted for in some such way as the following: the atoms with the larger velocity have been charged atoms during the whole of their career; they were atoms before they passed through the cathode and continue in this state after emerging from it; the atoms with the smaller velocity were part of a charged molecule before passing through the cathode; the molecule would only acquire a velocity  $1/\sqrt{2}$  that of the atom. After passing through the cathode and before being deflected by the electric and magnetic fields this charged

molecule breaks up into two atoms, one with a positive charge while the other is uncharged.'

Note that although Thomson did not explicitly claim that gaseous collisions were responsible for dissociation, it is hard to read his explanation in any other terms. Also, he proposed elsewhere that such high-energy collisions are responsible for charge exchange and charge stripping, two other ion/molecule collision processes evident in the parabola spectra. These continue, like collision-induced dissociation (CID), to be interesting and useful aspects of the modern subject!

Thomson's student F. W. Aston, who, like Thomson, was to be awarded a Nobel Prize, followed up his mentor's work on 'beading' in parabola mass spectra. He described the work to the Cambridge Philosophical Society in 1919,<sup>2</sup> placing it in context as follows: 'No one working with positive rays analysed by Sir J. J. Thomson's method can fail to notice the very remarkable intensity variation along the molecular and atomic parabolas described by him under the term "beading".'



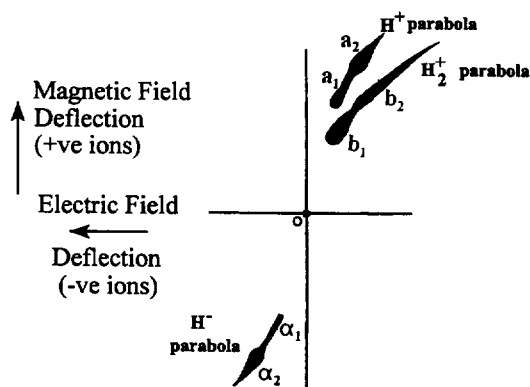
**Figure 1.** A parabola ion image recorded by Thomson showing 'beads' which represent the first evidence for the process of collision-induced dissociation. Note that the image was photographed twice, with magnetic field reversal, to more efficiently utilize the photoplate. Reproduced from Fig. 17, Plate I, in Ref. 1.

... Beadings at points corresponding to energy greater than the normal have been quite satisfactorily accounted for by multiple charges ... but the ones with which this paper is concerned have a smaller energy than the normal, actually half, and fractional charges are presumably impossible.'

Aston goes on to make a virtue of necessity as he describes an experiment in which he was forced to employ a willemite (phosphorescent zinc silicate) screen rather than the more sensitive and conventional photographic plate detector.<sup>2</sup> 'As no camera suitable for photographic recording was immediately available or necessary a willemite screen and visual observation was employed. This form has many obvious disadvantages ... however one notable advantage, namely that sudden and even momentary changes in intensity can be observed and *correlated in time* [original italics] with changes in the discharge or in the intensity of other lines.'

With this time-resolved capability, Aston was able to observe additional detail in the parabolas, and in particular to follow the behavior as a function of changing pressure.<sup>2</sup> 'At very low pressures with a potential of about 50,000 volt the parabolas are very faint but correspond to the general type, the primary streak  $a_1$  and spot  $b_1$  being much brighter than their satellites (doubtless due to few collisions). As the pressure rises the discharge becomes curiously unsteady ... then with absolute suddenness  $b_1$  flashes out intensely bright and with it appear *at the same instant* [original italics] its satellites  $a_2$  and  $\alpha_2$ .'

Aston's description of the phenomenon leading to the satellite patches, illustrated in Fig. 2 which is modified from his paper, is similar to that given by Thomson. He posits<sup>2</sup> that a collision of the molecular hydrogen cation may be associated with electron capture which might 'result in it splitting into two atoms one with a positive one with a negative charge. The energy of impact may be itself capable of causing this, if not some other cause,



**Figure 2.** Parabolas due to atomic and molecular hydrogen ions recorded by Aston. In reading these parabola ion images, left/right deflections are inversely proportional to kinetic energy-to-charge ratios and up/down deflections are inversely proportional to momentum-to-charge ratios. The spot at  $b_1$  is associated with the main beam of ionized molecular hydrogen and the collision-induced dissociation yields the bead at  $a_2$ , a proton of lower than usual kinetic energy;  $\alpha_2$  represents a hydrogen anion, with the same energy as the proton at  $a_2$ , and presumably formed by a dissociative charge inversion process. Reproduced, with modifications, from Ref. 2, Fig. 3.

e.g. radiation, may effect the dissociation. In any case it would give exactly the observed result, i.e. two bright patches lying symmetrically on the extension of the line joining the primary spot to the origin at twice its distance from the latter, corresponding to half the mass but the same velocity.'

Again, one does not quite recognize the modern CID phenomenon in these early analyses, and while a collision is involved there is uncertainty as to the need for an additional agent. The role ascribed to charge separation processes in the activated ion is also to be noted. In scrutinizing the parabola images, Aston saw (and perhaps misinterpreted) evidence for a process not recognized for another 70 years, and then not in the system he studied but in the unique  $C_{60}$  ion. He claimed that 'besides these forms of collision by which the velocity of the atom is practically unaffected there is distinct evidence that it [the high energy atomic hydrogen ion] may collide with and capture another hydrogen atom. If the atom struck ... is neutral ... the resulting positive ray will have the same momentum (the atom struck being relatively at rest) but double the mass so that it will strike the *molecular parabola* [original italics] at a point the same height above the X-axis as would the atom which generated it.' He ascribed the patch at  $b_2$  to this phenomenon. He went on to conclude that 'Should the above theory of collision with capture prove correct the formation of compound molecules by this means opens an extremely interesting field of chemical research.'<sup>2</sup> While the interpretation seems narrowly incorrect, the observation of helium atom capture in keV energy collisions of fullerene ions to produce endohedral complexes,<sup>3</sup> certainly bears out the broader prediction.

So important was Aston's contribution to the understanding of CID, that, for many years, the common name for the resulting signals was 'Aston bands'. Summarizing much of his work in the 1942 edition of *Mass Spectra and Isotopes*, Aston first mentions that the velocity selection characteristic of his mass spectrograph 'virtually prevents effects of this kind by reducing them in general to a faint continuous background on the mass spectra produced.'<sup>4</sup> He then discusses experiments using this mass spectrograph which followed those using the parabola apparatus described above. He emphasizes the circumstances (poor vacuum) which enhance the observation of secondary bands and takes the opportunity when a new discharge bulb (ion source) gives strong signals, to study the phenomena. Aston even adds a third analyzing field to the instrument (the first three-analyzer mass spectrometer!) in order to demonstrate unequivocally that the reaction  $H_2^{+*} \rightarrow H^+ + H^-$  is indeed responsible for the beads such as  $a_2$  in Fig. 2.

The favorable signal levels also led to the discovery of a new band at apparent mass 5.18 atomic mass units/electronic charge and Aston goes on to assign the responsible transition.<sup>4</sup> 'Some years later during the preliminary running in of a new discharge bulb, which always results in abnormally strong beams of rays, a similar band effect was noticed on a photographed mass spectrum, this time in the region 5.2. The matter was further investigated and the band in region 0.5 was again observed. ... A special subsidiary electric deflect-

ing field was now attached to the camera and by observations with this it was demonstrated beyond any doubt that the particles causing the lighter band were protons, that is to say singly charged hydrogen atoms, with half normal energy. The presence of this type of secondary ray had already been suggested by the beading on the hydrogen parabolas and the explanation then suggested is doubtless correct.'

'The two bands are associated with the presence of two quite abnormally bright molecular lines due to the hydrogen molecule and the carbon monoxide molecule respectively. If a normal singly charged  $H_2$  molecule is dissociated after it leaves the electric field and one of the atoms formed retains the positive charge through the magnetic field it will simulate a normal primary ray of mass 0.5. If we suppose that the dissociations are caused by collisions, the particles will have impressed upon them a random change in velocity and direction and so tend to form a band and not a line.'

'Turning now to the case of the CO molecule here the atoms composing it have masses in the ratio 3 to 4 so that if the carbon atom retains the positive charge after the dissociation it will simulate a mass  $3/7 \times 12$ , that is 5.14. This is clearly the cause of the band observed. No effect could be seen at mass  $4/7 \times 16$  which leads to the very interesting conclusion that when  $CO^+$  is dissociated the positive charge remains with the atom of carbon rather than that of oxygen.'

Note Aston's recognition of the effects of collision as leading to a poorly focused signal. However, nothing quantitative was known regarding the width of the bands due to CID at the time of writing of this book in 1941. The interest so strongly displayed by Thomson in the chemical implications of his physics is evident in Aston's writing, as seen in the above quotation. The observation on which atom takes the charge in the dissociation of a diatomic ion is an early example of what was later generalized as Stevenson's rule;<sup>5</sup> carbon has a lower ionization energy than oxygen and hence appears as the charged fragment in this dissociation.

Much work in the 1920s and 1930s was done using mass spectrometers which employed  $180^\circ$  magnetic deflection and electrical detection and had greater sensi-

tivity than the earlier mass spectrographs. In this way H. D. Smyth<sup>6</sup> was able to observe an Aston band for hydrogen at apparent mass  $1/3$  as well as the well known band at  $1/2$ . He was driven, somewhat reluctantly, to the correct conclusion that these peaks are due to  $H^+$  ions generated through CID of  $H_2^+$  and  $H_3^+$ , respectively: '... it may seem absurd to suppose that ions can be disrupted by collision ... and yet retain their speed and direction. ...'

To confirm the conclusion he increased the pressure in the 'collision region' in the obvious way: 'As has already been mentioned the peaks at  $m/e = 1/2$  and  $m/e = 1/3$  are attributed to  $H^+$  ions resulting from  $H_2^+$  and  $H_3^+$  ions that have broken up ... after passing through the electric field... If this idea is correct, the intensity of these peaks relative to the  $H_2^+$  and  $H_3^+$  should be greater if the pressure ... could be increased without altering other conditions. This was actually done ... by stopping the pump. ...'

It is possible that mass spectrometrists have always possessed a degree of fecklessness when it comes to handling the instrumentation, and this quality is evident when one 'stops the pump' in order to introduce collision gas into a particular region. In his study on discharges in hydrogen, Smyth recorded the spectrum shown here as Fig. 3. In addition to the two peaks due to CID, the very abundant ion/molecule reaction product  $H_3^+$  is to be noted. This ion was first observed and commented on by Thomson and although its origin was explored in some detail by Smyth, various candidate reactions were considered, but the responsible reaction was not identified.

In dealing with this ion in a typically thorough section in his 1913 book, Thomson<sup>7</sup> first carefully excludes the possibility that the signal at mass/charge 3 can be due to  $C^{4+}$  then he shows that it must be due to  $H_3^+$ . His comments on chemical bonding are far-sighted: 'These results seem to me to point to the conclusion that  $X_3$  is tri-atomic hydrogen  $H_3$ . If this is so, its properties are very interesting. Unlike  $O_3$  its existence cannot be reconciled with the ordinary views about valency. If, however, we regard an atom of hydrogen as consisting of a positive nucleus and one negative

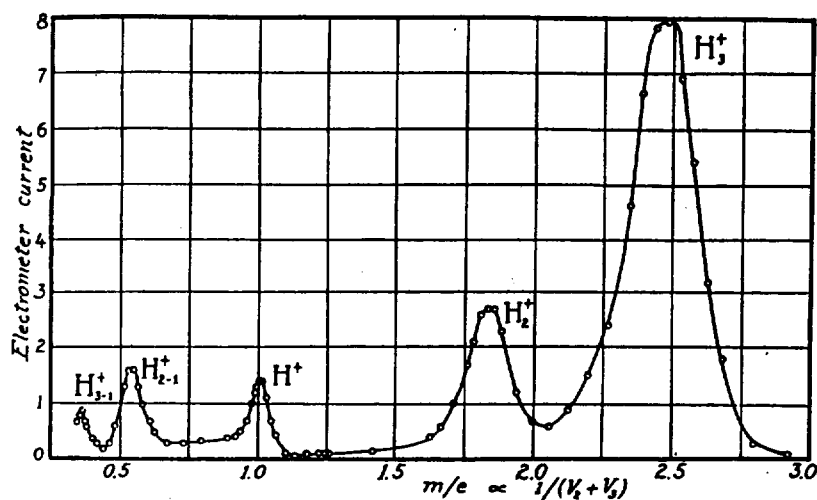


Figure 3. Mass spectrum of hydrogen showing ion/molecule reaction product at  $m/e$  3 and CID products at  $m/e$  0.3 and 0.5. Reprinted from Ref. 6 with permission from The American Physical Society.

corpuscle [i.e. an electron], it will not exert forces analogous to those excited by a magnet and I can see no reason why a group of three of these arranged so that their axes form a closed ring should not form a stable arrangement.'

Bainbridge and Jordan,<sup>8</sup> apparently for the first time, introduced a 'scattering gas' into the region between the electrostatic and magnetic sectors of a double focusing mass spectrometer in work reported in 1937. Using stable ions to serve as internal mass calibrants, they measured the apparent mass/charge ratio of the peak for  $C^+$  generated by CID of  $CO^+$  as  $5.145 \pm 0.002$ , compared to the expected value in the absence of energy loss of 5.145(7). Within experimental error, the peak occurred at the expected position for the transition  $28^+ \rightarrow 12^+ + 16$ . However, they explicitly recognized that translational energy might be lost to internal energy in the collision process.

A closely related phenomenon to CID is the spontaneous dissociation of previously activated molecular ions, discovered in 1945.<sup>9</sup> A short excursion into this closely related topic is therefore necessary. Ions which are neither stable, nor unstable, on the time scale of the mass spectrometer can fragment en route through the instrument. Like the products of CID, such metastable ions give rise to more or less well-focussed peaks if the dissociation occurs in the field-free region prior to the magnetic sector of a sector-field mass spectrometer.

In their preliminary report on the discovery of metastable ions in 1945, Hipple and Condon<sup>9</sup> noted that the product ions due to spontaneous dissociation will occur on the mass/charge scale at positions given by  $(m_2)^2/m_1$ , where  $m_1$  is the mass of the parent ion and  $m_2$  is that of

the product. These ions have substantially lower kinetic energies than normal fragment ions (by a factor  $m_2/m_1$ ) and Hipple and Condon simply used electrostatic retardation to reject ions with lower than full kinetic energy. The result of this experiment is shown in Fig. 4 for the case of n-butane (the influence of petroleum analysis already being strongly felt in research in mass spectrometry, and the authors being employed by the mass spectrometer manufacturer Westinghouse). The improved quality of the mass spectrum in the absence of the metastable peaks led to the fitting of 'metastable suppressors' on mass spectrometers. Twenty years later, metastable ions were a principal interest of many mass spectroscopists and CID was being suppressed.

In their full paper on metastable ions, Hipple, Fox and Condon<sup>10</sup> took care to distinguish the phenomenon they were reporting from CID. This was necessary because CID was sufficiently well known to be the obvious explanation for any diffuse peaks observed at non-integral masses in mass spectra.

The high quality of CID experiments being performed in the 1950s is prominently in evidence in a series of experiments reported by the group of White at the General Electric company (another erstwhile mass spectrometer manufacturer) in a 1959 paper entitled 'Charge permutation and dissociation of molecular ions by impact with neutral molecules'.<sup>11</sup> Working with a triple-sector mass spectrometer (an instrument repopularized two decades later) and using very high-energy mass-selected primary ions, this group performed collision-activated dissociation (CAD) by placing either a gas-filled collision chamber or a very thin (500 Å) nickel foil at the focal point between the second and

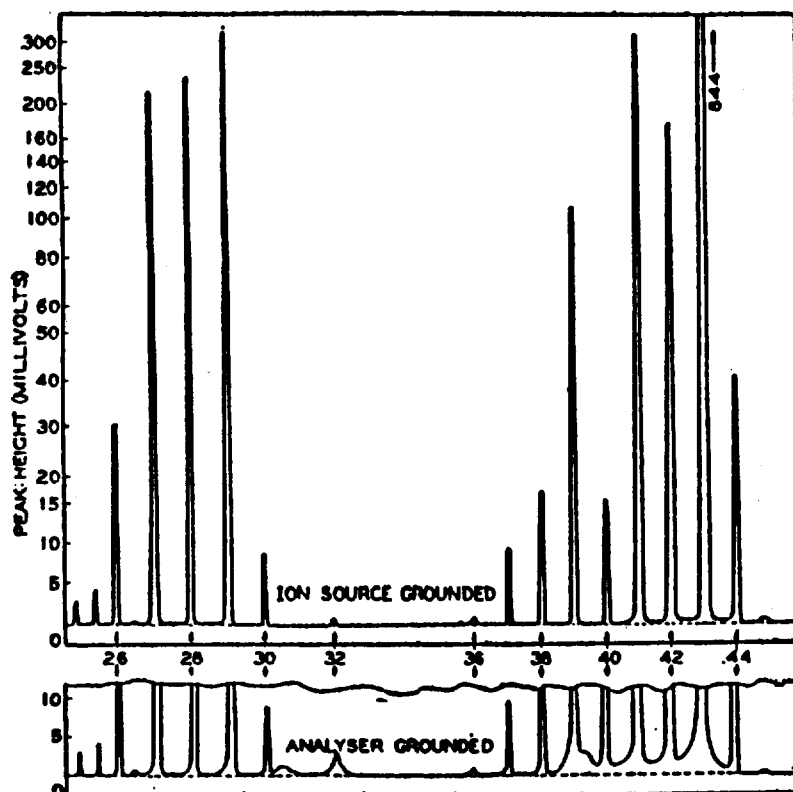


Figure 4. Mass spectrum of n-butane, with (above) and without (below) suppressing low kinetic energy (metastable) ions. Reprinted from Ref. 9 with permission from the American Physical Society.

third sectors. They observed structure in 'Aston bands'. Figure 5 illustrates the case of  $O^{+}$  generated from  $CO^{++}$  in high-energy collisions, showing the characteristic triple peak in the kinetic energy scale. It was assumed that the (more or less) symmetrical side peaks were due to a single process: 'Thus, the supposition was made that the side peaks are caused by a fairly discrete amount of kinetic energy being given to the ions during dissociation immediately following the collision.'

White and his collaborators also derived a relationship between the width of the CID peak and the energy released as translational energy. They went on to calculate the kinetic energy released as 5.9 eV and to account for its magnitude in terms of a mechanism involving fragmentation from the doubly charged ion. 'The mechanism for this dissociation is probably that involving ... a potential barrier separating the ground state of the doubly charged ion from the two separated ions and having a height above both. The difference between the height of this barrier and the sum of the potential energies of the two separated ions would then be the kinetic energy of the dissociation.'

A second mechanism was proposed to explain the central narrow peak: 'Probably the simplest mechanism ... would be transformation of a very small fraction of the available kinetic energy into vibrational energy sufficient to dissociate the ion.'

These ideas of (i) addition of sufficient vibrational excitation to an already vibrationally 'hot' ion to cause dissociation, and (ii) electronic excitation directly to a repulsive electronic surface, still sound decidedly modern. The work of White and co-workers is outstanding for its technical prowess and for its contributions to the kinematics of ion dissociation.

CID involves conversion of translational to internal energy in the activation step, and this is recognizable, at

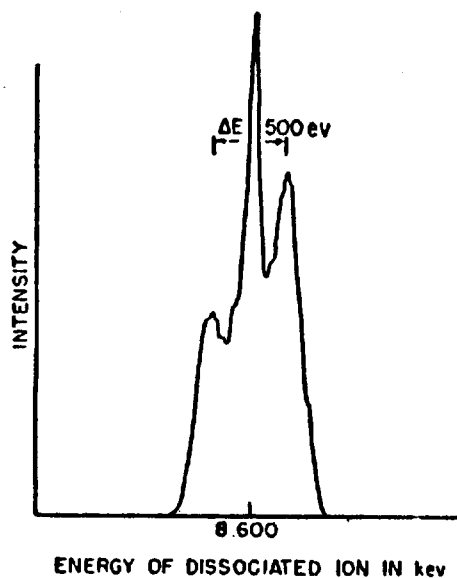


Figure 5. Structure in the CID peak for dissociation of  $CO^{++}$  to give  $O^{+}$ . The data show two processes: one gives rise to the central peak and the other, due to fragmentation from the nascent doubly charged ion generated in the collision, gives rise to the second peak which is associated with a large kinetic energy release. Discrimination effects mean that only the 'wings' of this peak are observable. Reprinted from Ref. 11 with permission from the American Physical Society.

least in principle, by a small shift in the kinetic energy of the product ions from the value expected from equipartitioning of energy in proportion to the masses of the ionic and neutral fragments. As just noted, it also involves conversion of internal energy into translational energy of separation of the two fragments (kinetic energy release) and this is by far the more important factor responsible for the large range of kinetic energies observed in the fragment ions. The measurement of both kinetic energy loss and kinetic energy release was apparently reported only as recently as 1963, by McGowan and Kerwin.<sup>12</sup> For an elegant treatment of the subject of flat-topped metastable peaks and a derivation of the relationship between peak width and kinetic energy release, the reader is referred to a 1965 paper of Beynon, Saunders and Williams,<sup>13</sup> conveniently reprinted in the *Journal of Mass Spectrometry*.<sup>14</sup>

A remarkable series of papers on CID was produced by Kupriyanov and co-workers in the USSR in the 1960s using a tandem magnetic sector instrument.<sup>15</sup> These studies were cited in the Western literature of the time but are now largely forgotten, even by workers active in the area of CID. This research group concentrated on the metastable and CID behavior of polyatomic ions and made contributions which included the measurement of the cross-section for CID (total as well as those for individual product ions). These measurements were made as a function of the collision energy and the nature of the target gas. Presciently, this group also explored the effects of the initial excitation of the projectile ion by varying the ionizing electron energy, and they emphasized the similarity between the product spectra recorded as a result of CID and conventional electron impact spectra. The value of CID as a method of ion characterization was recognized and the method was used to compare ions generated from different precursors. In considering the mechanism of activation, the suggestion was made that direct electron excitation predominates at higher collision energies while vibrational excitation is more important at lower energies, a view that is still accepted.

The modern era in CID can be traced to the work of Jennings<sup>16</sup> in 1968, which was recently recognized with the 1995 ASMS Research Award and the contemporary work of McLafferty. Jennings had been interested in the properties of metastable ions and the use of 'defocusing' techniques to separate them from the main beams of stable ions (the inverse of the 'metastable ion suppressor' noted above). This was first achieved by Barber and Elliot<sup>17</sup> in a technique in which the accelerating voltage of a sector mass spectrometer was scanned to resupply the ionic product of a metastable ion fragmentation with the missing kinetic energy carried away by its neutral partner. Hence the method allowed the full sensitivity of the mass spectrometer to be devoted to metastable ions fragmentations while the masses of the product and precursor ions were deduced from the value of the accelerating voltage needed to transmit the product. Jennings worked with Barber and Wolstenholme<sup>18</sup> on this topic and then sought to extend the method to CID, not being unknowledgeable of the considerable history of that technique as laid out in this article.

By gently baking the instrument during operation,

sufficient gas was released to degrade the vacuum to the point where CID occurred (Fig. 6). The fact that this work was done on a commercial mass spectrometer lent it added interest to other investigators. In addition, Jennings cleverly chose to work with aromatic compounds and to use low-energy electron ionization so that the only precursor ion generated was the molecular ion itself. Under these conditions, the CID products could all be uniquely assigned to one parent ion. The CID spectrum was found to correspond quite closely to the conventional 50 eV electron impact mass spectrum.

At about the same time, Futrell and Tiernan<sup>19</sup> were undertaking a research program in low-energy ion/molecule collisions of mass-selected ions in the Wright Patterson Airforce Base Laboratories. This work is noteworthy for the fact that a four-sector instrument was employed and a carefully designed deceleration system allowed access to very low collision energies. Hence ion/molecule reactions could be performed on mass-selected ions. The subject of ion/molecule reactions is outside the scope of this article, but the instrumentation used for low-energy CID and ion/molecule reactions increasingly overlaps. (One only has to note the present-day dual use of Fourier transform and quadrupole ion traps for these purposes to realize this.)

Also in the 1960s, McLafferty began his initial investigations of the structures (connectivities) of polyatomic ions, using CID to distinguish between isomers. The fact that CID processes are relatively insensitive to the internal energies of the ions (a fact which is assisted by the relatively narrow range of energies normally represented in an ion beam that is examined some microseconds after ionization) made this a powerful procedure for fingerprinting ions. Typical of the detailed enquiry into ion chemistry which was undertaken by the collisional activation technique is a study by McLafferty and co-workers<sup>20</sup> entitled 'collisional activation spectra of organic ions'; this paper has been reprinted in its entirety in the *Journal of Mass Spectrometry*.<sup>21</sup>

The success of attempts to decouple the products of metastable ion dissociation and CID from the normal ions observed in a mass spectrum, exemplified by the accelerating voltage scan method,<sup>17</sup> led to a search for improved procedures. The key to completely unambiguous examination of dissociation processes, be they metastable or collision-induced, is to employ two

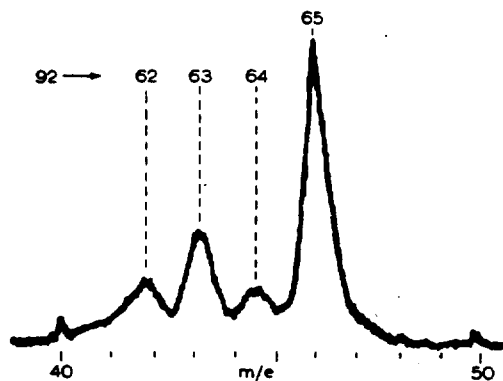


Figure 6. Part of the CID spectrum of the molecular ion of toluene ( $m/z$  92) recorded by Jennings using a commercial mass spectrometer. Reprinted from Ref 16 with permission from the *Int. J. Mass Spectrom. Ion Phys.*, 1, 227 (1968). © 1968 Elsevier Science.

separate and uncoupled mass analyzers. Reverse geometry instruments allow this to be achieved and new instruments were constructed in which precursor and product ions were separately mass-analyzed. This was done by McLafferty and co-workers for the study of collisional activation<sup>22</sup> and by Beynon *et al.* for the study of metastable ion fragmentations.<sup>23</sup> The subsequent development of soft ionization methods allowed the generation of relatively simple CID spectra of molecular ions representative of the individual molecular components of complex mixtures. The combination of CID with soft ionization methods,<sup>24</sup> (first, chemical ionization, later, the desorption ionization methods, and still later, electrospray and laser desorption) represented the beginning of the subject of tandem mass spectrometry (MS/MS) for direct mixture analysis.

The processes underlying CID continue to be understood with increasing precision. Some of the authors already mentioned made significant contributions in this respect. Perhaps the clearest summary of the mechanisms of CID was that provided by Durup in 1970.<sup>25</sup> This author distinguished four limiting-case mechanisms:

'Process 1 is a pure electronic excitation of  $AB^+$  to  $AB^{+*}$  through a vertical transition (i.e. obeying Franck-Condon principle) with or without an excitation of the target M and with essentially no deflection of the c.o.m. of  $AB^+$  (i.e. with little momentum transfer perpendicularly to the incident flight direction). The excited  $AB^{+*}$  ion dissociates into  $A^+ + B$  after the collision.

Process 1 is predominant at high incident energies ( $> 10^3$  eV).

Process 2 is an elastic scattering of one or several of the atoms composing the incident ion, resulting in vibrational and/or rotational excitation of  $AB^+$  above the dissociation limit of its initial electronic state; the momentum transfer vector is essentially perpendicular to the incident flight direction, and the c.o.m. of  $AB^+$  is usually significantly deflected.

Process 2, which is a purely adiabatic process, is likely to predominate at incident energies of about  $10^2$  to  $10^3$  eV.

Process 3 is a completely inelastic collision between  $AB^+$  and M, i.e., a process where the whole relative translational energy of the collision partners is converted into internal energy of a more or less long-lived ( $AB^+$ , M) complex which later dissociates into  $A^+ + B + M$ .

Process 3 is predominant at very low incident energies, close to the energetic threshold for  $AB^+$  dissociation (a few eV).

Process 4 is a radiationless transition of  $AB^+$  to a dissociative state of the same energy (i.e., a predissociation of  $AB^+$ ) induced by a vanishingly small perturbation brought about by the target.

Process 4 is likely to occur at low incident energies ( $10^1$  to  $10^4$  eV).

This remarkable achievement of synthesis, made by considering a bewildering array of experimental data, has hardly been improved on since. A modern summary would be likely to consider the relative velocities of the collision partners rather than their energies because the

mass of the ion can no longer be assumed to be in the range of  $10^2$  dalton. Note, however, that Durup gives due weight to impulsive collisions, a mechanism that was largely ignored until elaborated by Uggerud and Derrick.<sup>26</sup> For a readable modern account of the mechanisms of CID, the review of McLuckey is recommended.<sup>27</sup>

This treatment breaks off about 25 years ago—a safe distance from the present. It therefore omits the development of low-energy CID, in many ways a simpler and more powerful experiment than high-energy (keV range) CID. This experiment is now the principal implementation of CID, being carried out in triple quadrupoles,<sup>28</sup> quadrupole ion traps<sup>29</sup> and ion cyclotron resonance mass spectrometers.<sup>30</sup> The treatment given above also omits the growing number of experiments which use surfaces as collision partners, an experiment known as surface-induced dissociation (SID).<sup>31</sup> It also omits the fascinating new information on the mechanisms of CID being obtained by making observations over a range of scattering angles.<sup>32</sup>

In considering the development of CID one cannot

avoid three impressions: first, the slowness with which the essential features of the experiment were assembled after the fast start early in the century; second, the way in which key advances were predicated on novel instrumentation rather than great insights; third, the surprises that have occurred, one of the more recent being the observation that  $C_{60}^{+}$  ions can capture helium atoms in the course of collisions in the keV energy range.<sup>3</sup> No other observation so neatly confounds the CID experiment—notwithstanding Aston's early surmise quoted above on the possibility of such processes—or so intertwines the two great areas of mass spectrometry, ion/molecule reactivity and fragmentation.

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