other technological improvements which allow one to carry out conceptually simple experiments. Moreover, very often several potential energy surfaces are involved in the process and one wishes to know the efficiency of surface crossing and the region in configuration space where this occurs.


1. Ashfold, M. N. R. and Baggott, J. E. (eds), *Molecular Photodissociation Dynamics*, Royal Society of Chemistry, London, 1987.
2. Das, P. K., in *Reaction Dynamics: Recent Advances* (ed. Sathyamurthy, N), Narosa Publ. House, New Delhi, 1991, pp 62–100.
3. Houston, P. L., *J. Phys. Chem.*, 1987, **91**, 5388–5397.
4. Hall, G. E. and Houston, P. L., *Annu. Rev. Phys. Chem.*, 1989, **40**, 375–405.
5. Busch, G. E., Cornelius, J. F., Mahoney, R. T., Morse, R. I., Schlosser, D. W. and Wilson, K. R., *Rev. Sci. Instrum.*, 1970, **41**, 1066–1073.
6. Dzvonik, M. and Yang, S. C., *Rev. Sci. Instrum.*, 1974, **45**, 750–755.
7. Matsumi, Y., Das, P. K. and Kawasaki, M., *J. Chem. Phys.*, 1989, **92**, 1696–1701.
8. Zare, R. N. and Dagdigian, P. J., *Science*, 1974, **185**, 739–747.
9. Johnson, P. M., *Acc. Chem. Res.*, 1980, **13**, 20–26.
10. Bersohn, R., *Isr. J. Chem.*, 1973, **11**, 675–683.
11. Andresen, P., Ondrey, G. S., Titze, B. and Rothe, E. W., *J. Chem. Phys.*, 1984, **80**, 2548–2569.
12. Tatematsu, S., Kondow, T., Nakagawa, T. and Kuchitsu, K., *Bull. Chem. Soc. Jpn.*, 1977, **50**, 1056–1059.
13. Ashfold, M. N. R. and Simons, J. P., *J. Chem. Soc., Faraday Trans. 2*, 1978, **74**, 1263–1274.
14. Black, G., Sharpless, R. L. and Slanger, T. G., *J. Chem. Phys.*, 1976, **64**, 3985–3992.
15. Black, G. and Sharpless, R. L., *J. Chem. Phys.*, 1979, **70**, 5567–5570.
16. Kasper, J. V. V. and Pimental, G. C., *Appl. Phys. Lett.*, 1964, **5**, 231–233.
17. Zare, R. N., *Mol. Photochem.*, 1972, **4**, 1–37.
18. Yang, S.-C. and Bersohn, R., *J. Chem. Phys.*, 1974, **61**, 4400–4407.
19. Leone, S. R., *Adv. Chem. Phys.*, 1982, **50**, 255–324.
20. Kinsey, J. L., *Annu. Rev. Phys. Chem.*, 1977, **28**, 349–372.
21. Gerber, G. and Moller, R., *Phys. Rev. Lett.*, 1985, **55**, 814–817.
22. Guo, H. and Schatz, G. C., *J. Chem. Phys.*, 1990, **93**, 393–402.
23. Gedanken, A. and Rowe, M. D., *Chem. Phys. Lett.*, 1975, **34**, 39–43.
24. Riley, S. J. and Wilson, K. R., *Faraday Diss. Chem. Soc.*, 1972, **53**, 132–146.
25. Dzvonik, M. J., Yang, S. C. and Bersohn, R., *J. Chem. Phys.*, 1974, **61**, 4408–4421.
26. Sparks, R. K., Shobatake, K., Carlson, L. R. and Lee, Y. T., *J. Chem. Phys.*, 1981, **75**, 3838–3846.
27. Hermann, H. W. and Leone, S. R., *J. Chem. Phys.*, 1982, **76**, 4766–4774.
28. Shapiro, M. and Bersohn, R., *J. Chem. Phys.*, 1980, **73**, 3810–3817.
29. van Veen, G. N. A., Baller, T., De Vries, A. E. and van Veen, N. J. A., *Chem. Phys.*, 1984, **87**, 405–417.
30. Brewer, P., Das, P., Ondery, G. and Bersohn, R., *J. Chem. Phys.*, 1983, **79**, 720–723.
31. Barry, M. D. and Gorry, P. A., *Mol. Phys.*, 1984, **52**, 461–473.
32. Godwin, F. G., Gory, P. A., Hughes, P. M., Raybone, D., Watkinson, T. M. and Whitehead, J. C., *Chem. Phys. Lett.*, 1987, **135**, 163–169.
33. Ogorzalek Loo, R., Haerri, H. P., Hall, G. E. and Houston, P. L., *J. Chem. Phys.*, 1989, **90**, 4222–4236.
34. Felder, P., *Chem. Phys.*, 1991, **155**, 435–445.
35. Hwang, H. J. and El-Sayed, M. A., *J. Chem. Phys.*, 1991, **94**, 4877–4886.
36. Hwang, H. J. and El-Sayed, M. A., *J. Phys. Chem.*, 1992, **96**, 8728–8735.
37. van Veen, G. N. A., Baller, T., de Vries, A. E. and Shapiro, M., *Chem. Phys.*, 1985, **93**, 277–291.
38. Gedanken, A., *Chem. Phys. Lett.*, 1987, **137**, 462–466.


ACKNOWLEDGEMENTS. We thank the Department of Science & Technology and the Department of Atomic Energy, Govt. of India, for partly funding this research.

Received 4 February 1993; revised accepted 28 April 1993

# Probing interatomic potentials using low-energy ion beams

**D. Mathur**

Atomic and Molecular Sciences Laboratory, Tata Institute of Fundamental Research, Homi Bhabha Road, Bombay 400 005, India

**An overview is provided of the utility of a new ion collision technique, translational energy spectrometry (TES), in probing molecular potential energy surfaces. TES is a gas-phase collisional technique in which the analysis of the changes in the kinetic energy of a projectile ion which has undergone collision with a neutral atom/molecule furnishes information about the interaction potential between the projectile and the target. An advantage this technique offers over conventional spectroscopic and laser-based methods is relatively easy access to intrinsically unstable species such as singly charged radicals and multiply charged molecular ions.**

QUANTITATIVE insight into interatomic potentials which govern the dynamics of chemical transformation processes continues to elude physicists and chemists even though sophisticated quantum mechanical methodologies and powerful laser techniques have enabled increasingly detailed studies to be carried out of atomic

and molecular species, theoretically, at levels well beyond Hartree–Fock and, experimentally, over the entire spectral range from the microwave to the X-ray region. Despite the astounding strides that have been made in development of laser-based experimental techniques in the last decade, an active need continues to be felt to develop new methodologies for investigating the *dynamical* aspects of chemical transformation processes on a microscopic level, *collision by collision*. Ion translational energy spectrometry (TES) is an example of one such recent non-laser-based development.

TES is a gas-phase collisional technique in which the analysis of the changes in the kinetic energy of a projectile ion which has undergone collision with a neutral target atom or molecule furnishes information about the interaction potential between the projectile and the target. As the projectile is a charged species, ion-neutral reactions can be investigated whose dynamics are dominated by interactions which occur at large internuclear distances. In other words, only the long range part of the overall potential energy surface on which a given reaction occurs need be considered in concomitant theoretical studies. This provides a distinct advantage insofar as quantitative understanding of reaction dynamics needs theoretical information of only a subset of the entire complex interatomic potential surface; conversely, experimental results forthcoming from TES measurements of ion-neutral reaction phenomena provide a stringent test of the effectiveness of contemporary quantal techniques of generating molecular potential energy surfaces.

This brief account attempts to provide an overview of this new ion collision technique for probing molecular potential energy surfaces. Collision processes leading to single and multiple electron capture, charge stripping and dissociation, are examples of ion-neutral reactions which occur readily at large internuclear separations of reactant species; these are topics which have been extensively studied in experiments carried out at the author's laboratory in the last ten years (see refs. 1, 2 for recent reviews and compilation of pertinent literature).

## Long-range interactions

Consider the simplest of molecular dynamics problems, that involving the interaction of one hydrogen atom with a single hydrogen molecule:

$$H_a + (H_b - H_c) \rightarrow (H_a - H_b) + H_c \qquad (1)$$

In attempting to gain information on exactly how this simple hydrogen transfer reaction proceeds on a microscopic level, recourse has to be made to an approximate treatment.

The first approximation to be made is of a theoretical nature: one constructs a three-dimensional potential energy surface by considering only those reactions which proceed when the reactant H atom approaches $H_2$ collinearly (along the $H_b$–$H_c$ axis). In such a case, only two parameters suffice to construct an appropriate potential energy surface in which energy changes can be plotted as a function of $H_a$–$H_b$ distance and $H_b$–$H_c$ distance. It turns out that, in this particular case, such an approximation is extremely good, because the lowest energy pathway happens to be that which results from a collinear collision. Furthermore, high level *ab initio* quantum-chemical calculations of the energy surfaces of the H–$H_2$ system can be carried out reasonably accurately. On the other hand, for most other chemical transformation processes the calculation of energy surfaces continues to be a formidable task. If we consider a chemical reaction in which the reactants and products are considered as a dynamic system comprising $n_e$ electrons and $n_n$ nuclei, the combined motion of all the particles requires solution of a nonseparable Schrödinger equation of $3(n_e + n_n - 1)$ variables. This requires a multidimensional configuration space. Moreover, it is also clear that analytical solutions for such an equation will not be forthcoming; even purely numerical methods, requiring 'reasonable' computational effort, are ruled out in all but a very few cases. It is therefore advantageous to attempt to tackle 'real' problems in a piecewise fashion, by employing techniques which are appropriate only in a given subset of the total configuration space. This necessitates the making of a second approximation, one which is of an *experimental* nature.

We can choose our reactants in such fashion that transformation processes of interest occur with high probability in only a part of an overall complex, multidimensional energy surface. Collisions in which one of the reactants is an ion provide the major example of this approach. Here, those transformation processes can be studied which occur as a result of relatively long-range interactions between reactant species. In such cases asymptotic approximations to complex energy surfaces are often sufficient to explain, and lend substance to, experimental information. An additional advantage of focusing on ion-neutral reactions is that, in many cases, simplifying straight line trajectory approximations, such as the impact parameter method, yield satisfactory results.

## Experimental hardware

The probing of long-range interatomic interactions by means of ion-neutral collisions can, in principle, be carried out in a variety of ways. A conceptual diagram of the experimental hardware necessary for such studies is shown in Figure 1. An ion beam is a prerequisite; in

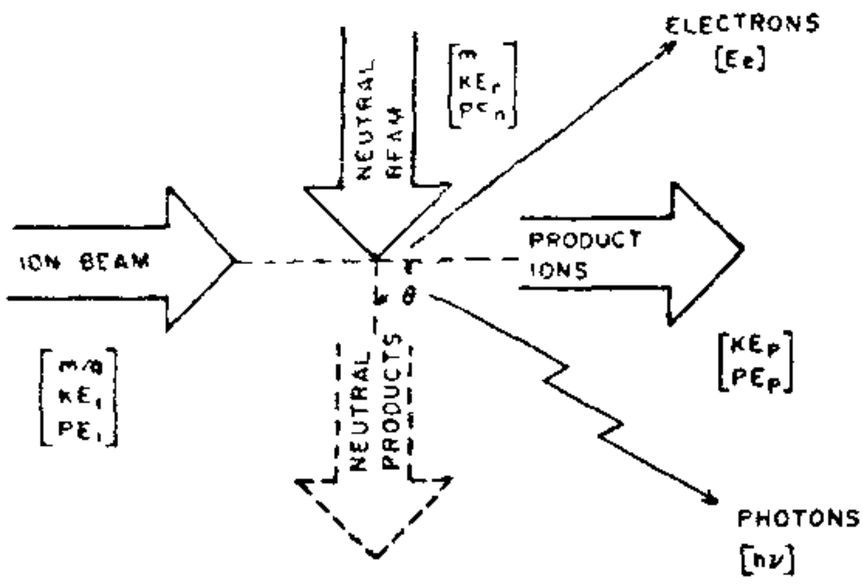


**Figure 1.** Schematic representation of an ion-neutral collision process.

an ideal experiment, the ion projectiles should have a well-defined mass-to-charge ratio ($m/q$) and initial kinetic energy ($KE_i$), and with a quantum-mechanical description which is well established (in other words, a well-defined potential energy $-PE_i$). These ions are transported in such a manner as to be incident, at an angle, $\theta$, on a neutral beam which also ought to be well-defined in terms of $m$, KE and PE. A high-vacuum environment is mandatory to ensure that the classical mean-free path for ion collisions with molecules other than those present in the target beam is very much larger than the overall dimensions of the apparatus; typical base pressures in the $10^{-8}$–$10^{-7}$ Torr range are used.

Ion-neutral interactions will, in general, give rise to a variety of possible signals which can be detected: neutral products in excited electronic states, electrons with specific energy, $E_e$, photons of energy $h\nu$, or product ions with kinetic energy $KE_p$ and a modified quantal description given by potential energy $PE_p$. A practical translational energy spectrometer[3], one of four such in operation today, is shown schematically in Figure 2. The product ion signal is the parameter that is monitored in this apparatus; it comprises a high pressure ion source in which positively or negatively charged ions can be produced by electron impact under conditions in which all electronically and vibrationally excited states are collisionally de-excited very efficiently within the source region. The ions are extracted out of the source and accelerated by an electrostatic potential into a region of cylindrically symmetric electric fields which help to collimate the beam into a pencil shape. This spatially well-defined beam is then passed first through a region of crossed electric and magnetic fields (Wien filter) where $m/q$ selection occurs, and then through an electrostatic energy monochromator. The ion beam emerging from the monochromator possesses a well-defined spatial geometry, kinetic energy and potential energy, the latter by virtue of being in the ground state.

Collisions between the ion beam and the neutral beam occur in a spatially well-defined field-free region; both beams are of 1–2 mm cross sectional diameter. Ions entering the post-collision region are energy analysed by a second electrostatic analyser and are detected by a high-gain particle (channel electron) multiplier. The methodology adopted for different types of experiments on such an apparatus is as follows.

The TES technique utilizes the fact that collision-

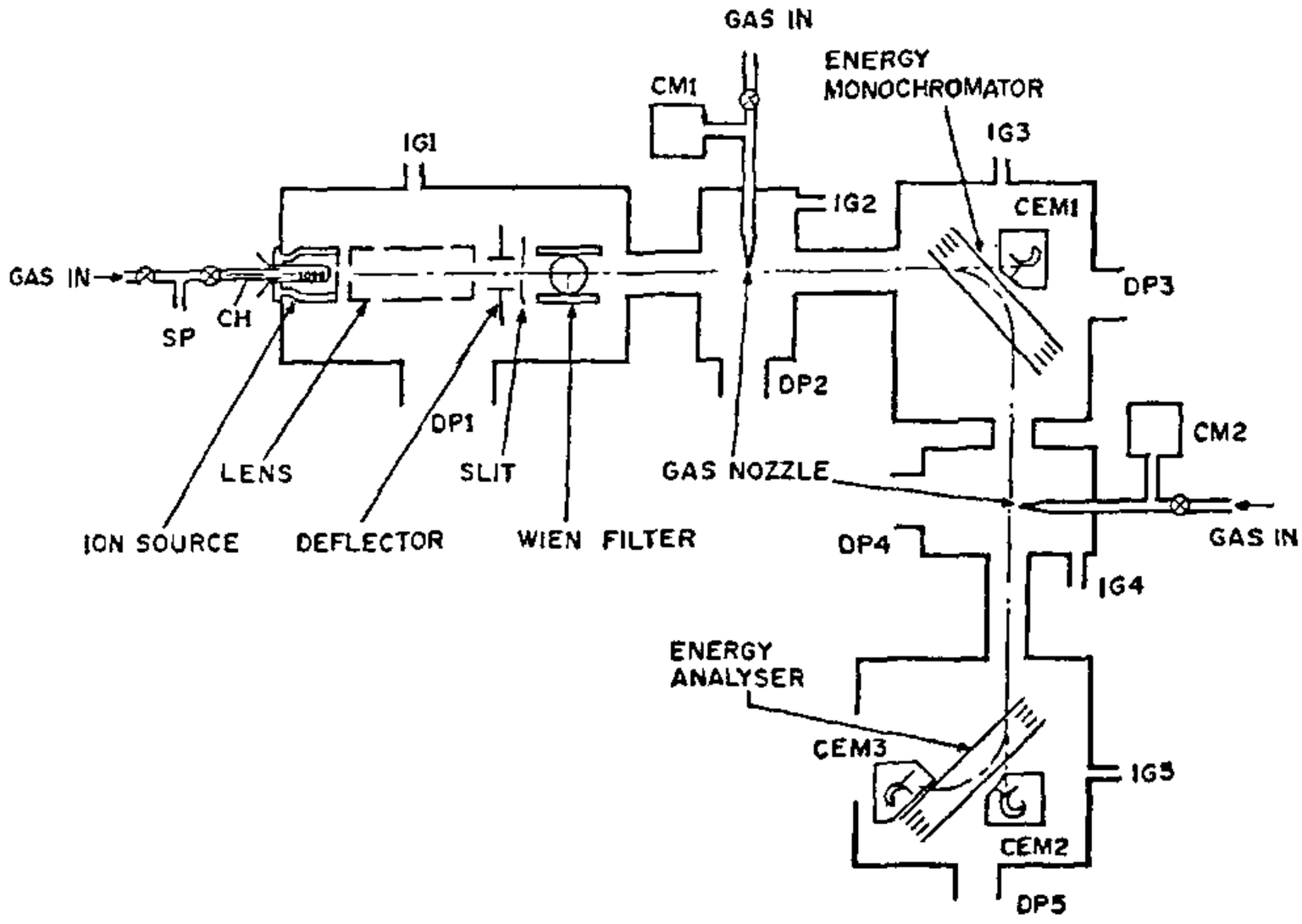


**Figure 2.** Translational energy spectrometer developed at TIFR, Bombay (see text for description).

induced transitions between the various energy levels of the incident ion and/or the neutral target manifest themselves as discrete changes in the translational energy of the incident ion. At keV impact energies, and small scattering angles, these measured energy changes can be related to excitation and de-excitation amongst the low-lying electronic states of the collision partners. Conversion of the projectile ion's kinetic energy into internal (potential) energy in the target, or in the projectile itself, makes it possible for an entire gamut of reactions to occur. Amongst the ion-neutral processes of much contemporary interest are those in which conversion of kinetic energy into potential energy leads to:

a) further ionization of singly charged projectile ions, resulting in formation of doubly charged species which may be metastable to the extent of making possible their subsequent detection. This process is known as charge stripping;

b) double ionization of a neutral target following capture of two electrons by an incident singly charged ion. This process is referred to as double electron capture;

c) dissociation of metastable doubly charged projectile molecular ions;

d) collisional excitation and de-excitation of excited ions, and

e) electron capture by multiply charged ions.

Measurement of the fraction of kinetic energy that is converted into internal energy renders amenable experimental studies of all the above processes on a quantitative basis and provides tests for theoretically derived potential energy surfaces upon which these reactions occur. In order to provide a flavour of the type of information than can be accessed by TES, we present below some sample results which pertain to classes of molecules which are not readily amenable to conventional spectroscopic and laser investigations: multiply charged molecules and radical species. Isolated multiply charged molecular ions constitute a class of molecular entity which dissociate much less rapidly than would be expected from conventional perturbative single-particle theories of molecular structure. Studies of such species has developed into a subject of considerable contemporary interest[2]. Studies of radical diatomic and triatomic ions, on the other hand, have assumed much importance in recent years because of their significance in applied areas such as combustion chemistry, astrochemistry and materials processing in the electronics industry.

## Some experimental results

### *Excitation/de-excitation of molecular ions*

TES has recently been applied to studies of collisional excitation and de-excitation processes in multiply charged molecular ions[1,2]. Consider the following ion-neutral collisions:

$$XY^{2+} + M \rightarrow XY^{2+*} + M - \Delta E \quad (1)$$

$$XY^{2+*} + M \rightarrow XY^{2+} + M + \Delta E \quad (2)$$

The first collision is an inelastic process in which the projectile ion's translational energy is converted into internal excitation energy of $XY^{2+}$, giving rise to an overall endoergicity (negative value of energy defect). The second collision, on the other hand, is a superelastic one in which the internal excitation energy of the projectile ion, $XY^{2+*}$, is converted to translational energy, giving rise to an overall exoergicity (positive value of energy defect). It is assumed here that the target $M$ remains a spectator; in practice, use of rare gas targets is an extremely good approximation to this idealized situation because, for such species, collisional excitation and ionization are precluded by cross sections which are considerably lower than those for processes involving other species.

Measurement of the overall energy defects for the above inelastic collisions enables spectroscopic information to be obtained for ionic species which cannot be readily studied by conventional optical spectroscopic techniques. Figure 3 shows an example of an ion translational energy spectrum[4] of collisional excitation of $NO^{2+}$ states; the measured spectrum is correlated with potential energy curves of the three lowest states of $NO^{2+}$ calculated using multiconfiguration self-consistent-field techniques[5]. The potential energy curves show the vertical energy difference between the minima of the $X^2\Sigma^+$ and $B^2\Sigma^+$ states at an internuclear distance of 1.2 Å to be 4.96 eV. The curves also show that the three lowest electronic states are deep enough to support a number of vibrational levels; the vibrational spacing for the first six vibrational levels of

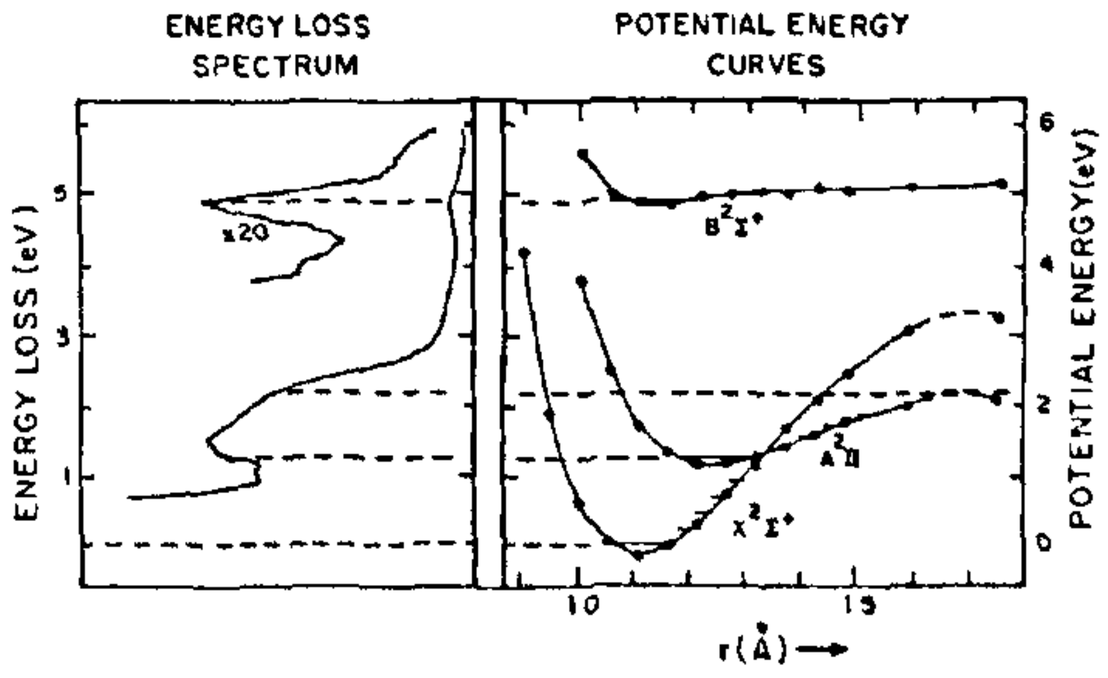


**Figure 3.** Translational energy spectrum of excitation of $NO^{2+}$ in 6 keV collisions with He and associated potential energy curves calculated using the MCSCF technique

$X^2\Sigma^+$ has been calculated[5] to be 0.24 eV, while the average vibrational spacing for the first five vibrational levels of $B^2\Sigma^+$ was found to be 0.16 eV. These high-level calculations were followed by two high resolution TES investigations[6]. In both experiments, the following scattering processes were investigated:

$$NO^{2+} + He \rightarrow NO^{2+*} + He - \Delta E, \quad (3)$$

$$NO^{2+*} + He \rightarrow NO^{2+} + He + \Delta E, \quad (4)$$

$$NO^{2+}(NO^{2+*}) + He \rightarrow NO^{2+}(NO^{2+*}) + He\ (\Delta E = 0). \quad (5)$$

In the correlation diagram shown in Figure 3, the elastically scattered $NO^{2+}$ projectile ion beam coincides with the zeroth vibrational level of the calculated $NO^{2+}(X^2\Sigma^+)$ ground state. The onset of the first broad peak confirms the calculated energy for a Franck–Condon transition from $X^2\Sigma^+$, $v=0$ to $A^2\Pi$, $v=0$, whereas the sharp cut-off point of the same peak corresponds to a vertical transition of the dissociative threshold of the $A^2\Pi$ upper electronic state. The energy of the transition, which is centered at 4.9 eV, and its unusual sharpness, indicate that the excitation is between $X^2\Sigma^+$, $v=0$ and $B^2\Sigma^+$, $v=0$. This deduction is in accord with the shallow potential energy well calculated for the $B^2\Sigma^+$ state which is not expected to support more than one bound vibrational level.

A translational energy spectrum for $CS_2^{2+}$-He collisions at 6 keV impact energy[7] is shown in Figure 4.

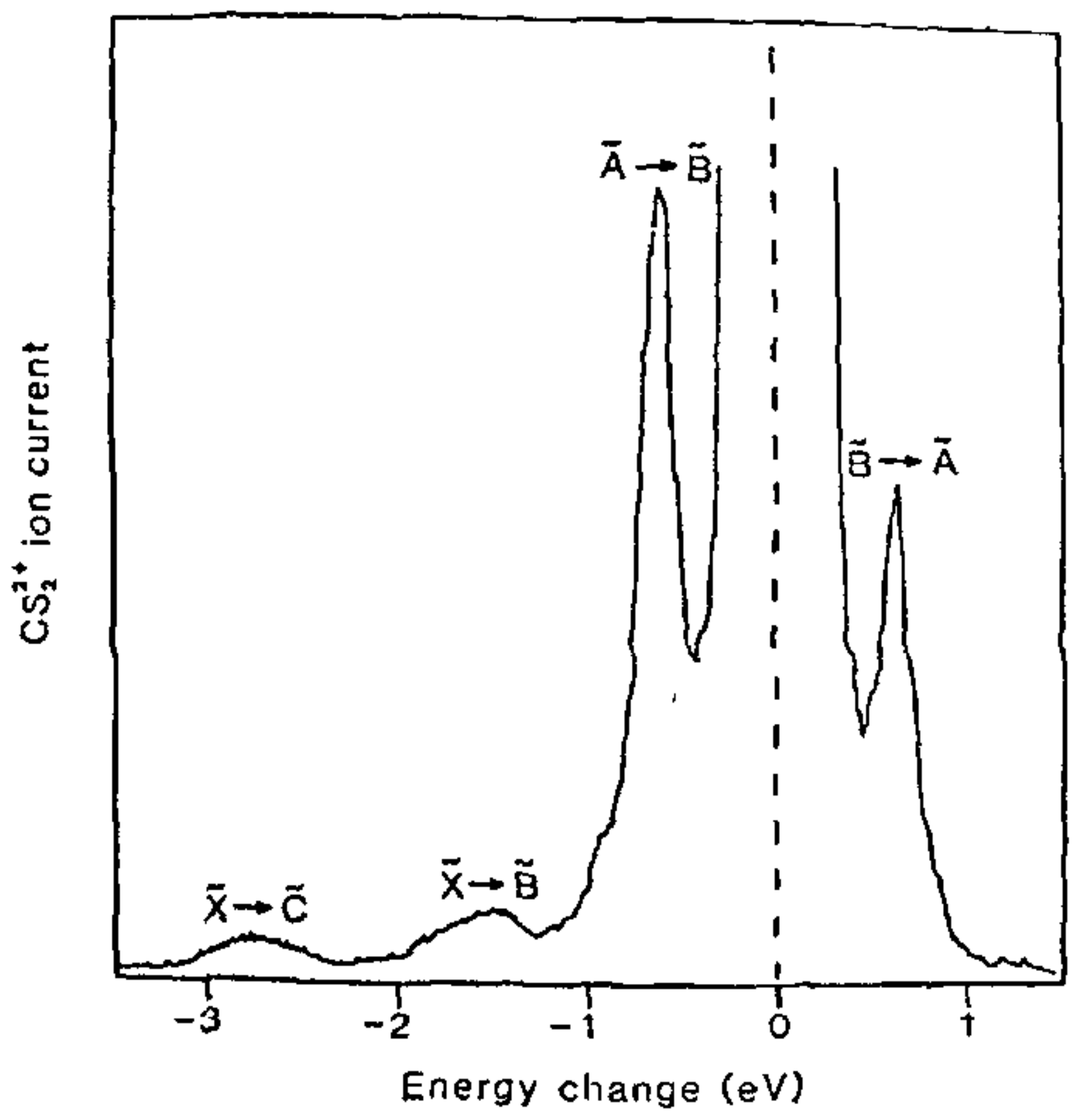


**Figure 4.** Translational energy spectrum for $CS_2^{2+}$-He collisions at 6 keV impact energy. (Adapted from ref. 7).

It illustrates a major advantage TES possesses over conventional spectroscopic methods in that dipole forbidden transitions are also accessible using TES. The dominant inelastic peaks in the spectrum correspond to a translational energy change of $\pm 0.6$ eV and represent excitation and de-excitation transitions between the $A^1\Delta_g$ and $B^1\Sigma_g^+$ states of the dication. Weaker energy loss peaks at $-1.5$ eV and $-2.7$ eV are due to spin-forbidden transitions from the ground $X^3\Sigma_g^-$ state to the $B^1\Sigma_g^+$ and $C^1\Sigma_u^-$ states, respectively. The measured energy changes provide a good test for the theoretical calculations of excitation energies using large-scale configuration interaction procedures[8]. The lowest energy spin-forbidden transition, predicted by calculations to be $X^3\Sigma_g^- \rightarrow A^1\Delta$ is not observed in the spectrum, possibly due to inadequate energy resolution and the proximity of a strong spin-allowed $A \rightarrow B$ transition.

Considerably higher values of energy resolution have recently been achieved; vibrational excitation of $CO_2^+$ (ref. 9) and fine-structure transitions in rare gas ions[1] have been observed in TES experiments.

### *Electron capture by doubly and triply charged molecules*

An important category of inelastic ion-neutral collisions is that which leads to electron capture:

$$XY^{2+} + M \rightarrow XY^+ + M^+ \pm \Delta E \quad (6)$$

where $\Delta E$ represents the overall energy defect for the process. The energy budget for such processes can be expressed in terms of $\Delta E$ as

$$\Delta E \approx [IE_2(XY) + \mathbf{E}_{exc}(XY^{2+})] - [IE_1(XY) + \mathbf{E}_{exc}(XY^+) + IE_1(M) + \mathbf{E}_{exc}(M^+)], \quad (7)$$

where $IE_1$, $IE_2$ represent the single and double ionization energies, respectively, and $\mathbf{E}_{exc}$ is the excitation energy pertaining to a specific electronic state. A small part of the total energy released in the electron capture process is carried away by the recoiling target. However, it is possible to estimate this component by assuming that there is negligible scattering in the incoming channel and that only Coulomb scattering exists in the outgoing channel.

The methodology adopted for measuring $\Delta E$ in TES experiments is as follows. If $\mathbf{V}$ is the energy analyser voltage at which the elastically scattered $XY^{2+}$ projectiles are transmitted, then $(2\mathbf{V} - \Delta V)$ will be the voltage at which the singly charged electron capture product, $XY^+$, will be detected. $\Delta V$ is related to the

energy defect $\Delta E$ simply by the energy analyser's geometrical factor. Experimental determination of $\Delta E$ also makes it possible to deduce the internal excitation energies of the projectile and product ions, thus facilitating quantum-state-diagnosed studies of the electron capture process[10].

Figure 5 shows a high resolution translational energy spectrum of $CO^+$ ions formed in electron capture reactions of $CO^{2+}$ colliding with Ne at a collision energy of 6 keV (ref. 1) and calculated potential energy (PE) curves of the three lowest-energy electronic states of $CO^+$ and $CO^{2+}$. Considering the shapes and positions of the PE curves it is possible to deduce that if the projectile $CO^{2+}$ ions are produced in the $v=4$ level of the $^1\Sigma^+$ state (as would be the case for a vertical transition from the $v=0$ level of the $^1\Sigma^+$ state of neutral CO), then electron capture into the $X^2\Sigma^+$ state of $CO^+$ will populate a range of vibrational levels from $v=0$ to $v=10$, with largest Franck–Condon overlaps for the highest vibrational levels. Capture into the $A^2\Pi$ state of $CO^+$, on the other hand, will predominantly populate the $v=0$ level. The manifestation of this in the energy defect spectrum would be a relatively sharp peak for the latter transition and a broader, structured one for the former. On the other hand, if $CO^{2+}$ is formed within the ion source in the $v=0$ level of the $^1\Sigma^+$ state, then capture into the $X^2\Sigma^+$ state of $CO^+$ will be into a narrower distribution of vibrational levels ($v=3$–6, with largest Franck–Condon factors for the $v=4$, 5 levels). Capture into the $A^2\Pi$ state of $CO^+$ will again produce a narrow energy defect peak, with only the $v=0$ level being populated. The excellent correlation between the measured energy spectrum and the expectations from calculated PE curves lends much credence to the quantal calculations.

*Dissociation dynamics*

Collision-induced dissociation of multiply charged molecules is an important subset of the overall class of energy transfer reactions that are readily amenable to investigation by energy spectrometric methods in which the momentum or energy distributions of fragment ions can be monitored. By conducting experiments at collision energies of a few keV, kinetic energy releases of a few eV in the centre-of-mass frame become amplified in the laboratory frame[1,2]. If **E** is the kinetic energy of a projectile homonuclear diatomic molecule and $\varepsilon_{cm}$ is the kinetic energy released (in the centre-of-mass) upon dissociation, the measured energy in the laboratory frame, $\varepsilon_{lab}$, can be deduced simply by addition of collision velocities

$$\varepsilon_{lab} = \mathbf{E}/2 \pm (\varepsilon_{cm}\,\mathbf{E})^{1/2} + \varepsilon_{cm}/2. \qquad (8)$$

The amplification of $\varepsilon_{cm}$ in the laboratory frame can be demonstrated most easily by considering a typical kinetic energy release of 5 eV following dissociation of a homonuclear diatomic doubly charged molecule. For an incident molecular ion energy of 3 keV, fragment ions possessing this value of kinetic energy release will be detected as two peaks in the translational energy spectrum centred around 1500 eV energy, each separated from the other by 490 eV (corresponding to fragment ions which are forward and backward scattered). This energy 'amplification' makes it possible to study dissociation processes even in instruments possessing relatively modest energy resolution capabilities. Measurement of $\varepsilon_{cm}$ provides a quantitative check on the shapes of calculated PE curves. Detailed correlations have recently been made of TES measurements with *ab initio* quantal calculations of molecular potential energy

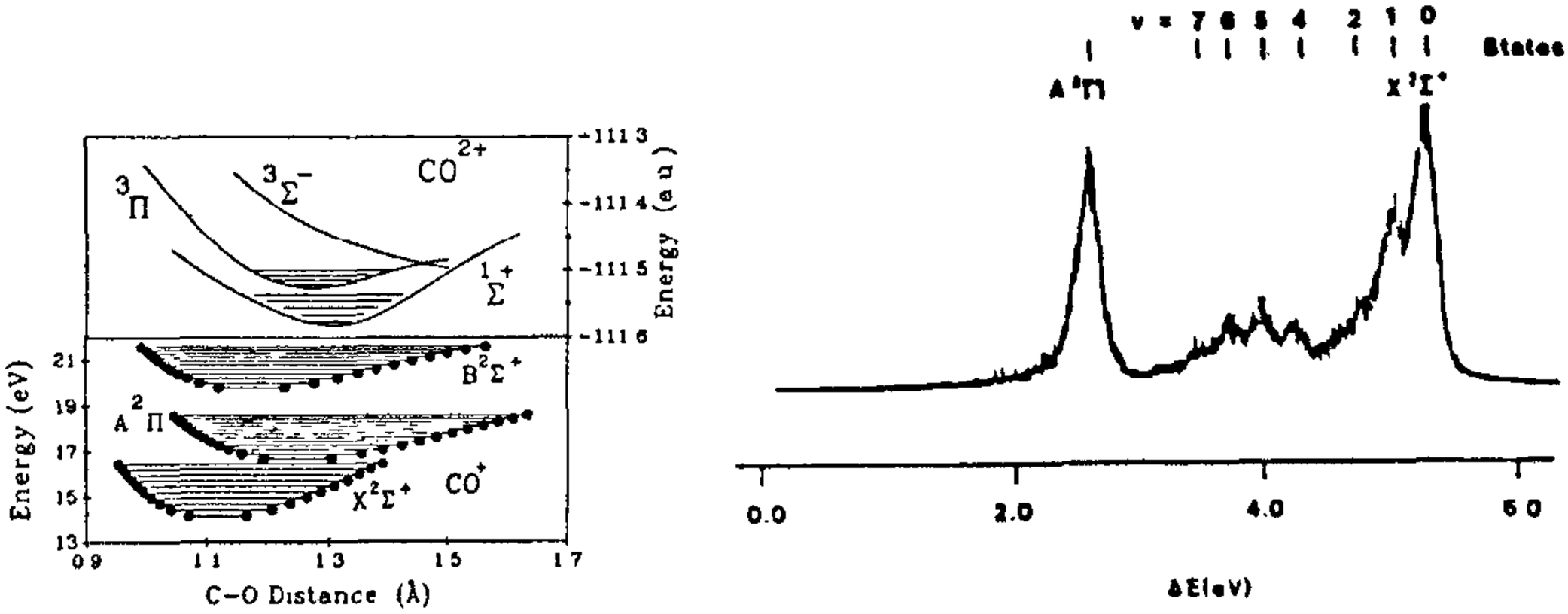


**Figure 5.** Potential energy curves of low-lying states of $CO^+$ and $CO^{2+}$ and a translational energy spectrum of $CO^+$ products (in the $X^2\Sigma^+$, $v=0-7$ and $A^2\Pi$ states) of electron capture by metastable $CO^{2+}$ ions colliding at 6 keV with Ne

functions of several radical sulphur-containing singly and doubly charged ions of astrophysical and quantum chemical interest[11].

The energy amplification referred to above also offers the possibility of obtaining sub-Doppler resolution which occurs due to the narrowing down of the velocity distribution of an ion beam when it is accelerated, a notion known as kinematic compression. If an ion beam possessing an energy spread given by $\Delta E$ is extracted from an ion source and accelerated to an energy E, the intrinsic energy spread is maintained at $\Delta E$ no matter what the value of E. However, since $E = mv^2/2$, the velocity spread of the accelerated beam is substantially reduced from its value prior to acceleration. For example, if an ion beam with an energy spread of 1 eV is accelerated to 3 keV laboratory energy, the velocity spread in the fast beam corresponds to an ion temperature of less than 1 K! Such 'kinematic compression' that TES affords has been utilized to gain information on molecular dissociation via rotational resonances in species such as $CH_4^{2+}$ and $CS^+$ (ref. 12). For rotationally hot diatomic molecules, the addition of the extra centrifugal energy term

$$V_{rot}(r) = \hbar^2 J(J+1)/2\mu r^2 \qquad (9)$$

to the rotationless ground state potential energy function gives rise to an *effective* potential energy curve with a rotational barrier at large values of internuclear separation, $r$. For a range of values of the rotational quantum number $J$, there will exist vibrational levels in the effective potential energy curve which lie *above* the ground state dissociation limit. These quasibound rotational resonance states decay by tunnelling through the potential barrier, their lifetimes being determined by the barrier shape and the reduced mass of the quasibound system[11]. Such states are normally inaccessible in conventional spectroscopic techniques but their studies are of considerable importance in determining the energy budget in many astrophysical environments.

## Concluding remarks

Translational energy spectrometry is a relative newcomer in the contemporary arsenal of experimental techniques used for probing molecular potential energy functions. It offers important advantages of conceptual simplicity and the access it affords to hitherto-difficult-to access molecular entities. However, practical implementation is far from straightforward. No commercial instruments exist for TES studies and considerable in-house development is mandatory for a useful instrument to become functional. This latter aspect can be turned to advantage in terms of the opportunities and challenges the development of a TES instrument offers to young researchers.

The best energy resolution that has been achieved in the author's laboratory is of the order of 500 meV, a figure which is more than adequate for on-going experimental studies on spin-selected excitation processes in ion-molecule collisions[13]; in the case of dissociation studies, effective centre-of-mass energy resolution values as low as a few tens of meV have been attained[12]. There continues to be scope for further improvement in these figures. Future incorporation into TES of tunable laser beams for state selection of projectile ions (or, indeed, target molecules) holds much promise. Incorporation of a third energy analyser offers the possibility of conducting sequential studies of state-selected reactions on a microscopic level, collision by collision. Efforts in both these direction are under way in the author's laboratory.


1. Mathur, D., *Physics of Ion Impact Phenomena*, Springer-Verlag, Berlin, 1991.
2. Mathur, D., *Phys. Rep.*, 1993, **225**, 193–272.
3. Mathur, D., Rajgara, F. A. and Krishnamurthi, V., *Proc. Indian Acad. Sci. (Chem. Sci.)*, 1991, **104**, 509–523.
4. Jonathan, P., Herman, Z., Hamdan, M. and Brenton, A. G., *Chem. Phys. Lett.*, 1987, **141**, 511–522.
5. Cooper, D. L., *Chem. Phys. Lett.*, 1986, **132**, 377–382.
6. Hamdan, M. and Brenton, A. G., *Chem. Phys. Lett.*, 1989, **155**, 321–327.
7. Jonathan, P., Hamdan, M., Brenton, A. G. and Willett, G. D., *Chem. Phys.*, 1988, **119**, 159–173.
8. Millie, P., Nenner, I., Archirel, P., Lablanquie, P., Fournier, P. and Eland, J. H. D., *J. Chem. Phys.*, 1986, **84**, 1259–1271.
9. Mathur, D., Wilkins, A. C. R. and Brenton, A. G., *Rapid Commun. Mass Spectrom.*, 1992, **6**, 479–483.
10. Mathur, D. and Rajgara, F. A., *Phys. Rev.*, 1990, **A41**, 4824–4830; Mathur, D., Kingston, R. G., Harris, F. M. and Beynon, J. H., *J. Phys.*, 1986, **B19**, L575–580; Pedersen, J. O. K. and Hvelplund, P., *J. Phys.*, 1987, **B20**, L317–322; Hamdan, M. and Brenton, A. G., *J Phys*, 1989, **B22**, L45–50.
11. Krishnamurthi, V., Krishnamurthy, M., Marathe, V. R. and Mathur, D., *J. Phys.*, 1992. **B25**, 5149–5162; Nagesha, K., Marathe, V. R. and Mathur, D., *Chem. Phys.*, 1991, **154**, 125–134; Mathur, D., Nagesha, K. and Marathe, V. R., *Chem. Phys. Lett.*, 1992, **200**. 394–398.
12. Krishnamurthi, V., Mathur, D. and Evans, G. T., *Rapid Commun. Mass Spectrom.*, 1991, **5**, 557–564, Kumar, G. R., Menon, L. and Mathur, D., *Phys. Rev.*, 1993.
13. Krishnamurthy, M., Raheja, U. T. and Mathur, D., *Pramana—J. Phys.*, 1993 (in press).


ACKNOWLEDGEMENTS. It is a pleasure to acknowledge the contributions that my colleagues F. A. Rajgara, U. T. Raheja, C. Badrinathan and V. Krishnamurthi have made towards the development of translational energy spectrometry.

Received 19 March 1993, revised accepted 19 April 1993