Probing interatomic potentials by ion translational energy spectrometry: A new crossed molecular beams apparatus

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Abstract. This report presents details of the development of a new crossed molecular beams apparatus designed and fabricated to carry out high sensitivity ion translational energy spectrometric investigations of the potential energy surfaces of small molecular species. The translational energy spectrometer is used to carry out experimental studies of ion-neutral reactions resulting in charge stripping of CS$^+$ radicals and dissociation of metastable CO$^{2+}$ dications. These results are interpreted in the light of high-level ab initio molecular orbital calculations of the pertinent molecular potential energy functions. New results for the double ionisation energy of CS and the kinetic energy released upon dissociation of specific electronic states of CO$^{2+}$ are presented.

Keywords. Crossed molecular beams; small molecular species; ion translational energy spectrometer; interatomic potentials.

1. Introduction

Experimental developments over the last two to three decades have made feasible detailed studies on the structure and spectroscopy of molecular ions, and a substantial body of information now exists on positively-charged diatomic and polyatomic molecules covering the spectral region from the microwave to the infrared. However, despite the fact that molecular ions have been the subject of spectroscopic studies for close to six decades, there continues to be an active interest in developing techniques and methodologies for ever more sophisticated investigations, particularly those which aim to probe the dynamical aspects of chemical transformation processes on a microscopic level, collision by collision. Ion translational energy spectrometry is an example of one such recent development in gas-phase ion chemistry.

Translational energy spectrometry 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 to

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the extent that quantitative understanding of reaction dynamics needs theoretical information of only a subset of the entire complex interatomic potential surface.

The experimental technique can be summarised as follows: a fast, monoenergetic beam of a particular ionic species is made to collide with a second, thermal energy beam of neutral atoms or molecules, the number densities of the collidants being kept low enough to ensure that the likelihood of more than a single collision occurring is negligible. The change in the potential energy of the projectile-target system as a reaction occurs manifests itself as a variation in the kinetic energy of the projectile. At keV collision energies, and small scattering angles, these measured energy changes in the kinetic energy can be related to changes in the internal (potential) energy accompanying a whole gamut of possible ionic reactions.

Translational energy spectrometers (TES) have been used to study the collisional properties of atomic and molecular gas-phase ions in only a few laboratories (Kobayashi 1982; Mathur et al 1985; Giese et al 1986; O’Keefe et al 1988; Hamdan and Brenton 1991). In the earliest development of TES, the machine developed in our laboratory was amongst the first to be used for experimental studies of quantum state-diagnosed electron capture reactions in ion-neutral collisions and studies of metastable multiply charged molecular ions (Mathur et al 1985, 1986, 1988). In this report we present details of the development of a new crossed molecular beams apparatus designed and fabricated to carry out high sensitivity ion translational energy spectrometric investigations of the potential energy surfaces of small molecular species and to augment the on-going programme of investigations in the broad area of chemical dynamics and experimental studies of interatomic potentials in our laboratory. The details of the apparatus are presented in the following section, and a description of some ion-neutral reactions that can be studied using this apparatus is presented in § 3. Sample results are also presented which indicate the manner in which experimental information gained from our ion translational energy spectrometry experiments is related to contemporary, high-level ab initio calculations of molecular potential energy functions.

2. Crossed molecular beams translational energy spectrometer

Figure 1 shows a schematic diagram of our ion translational energy spectrometer. Positively charged ions, formed when gas is introduced into a low-voltage arc type electron impact ion source, are electrostatically extracted by an accelerating potential in the range 2–5 kV. These ions are collimated and focussed by a three-element electrostatic lens into a spatially well-defined beam which impinges on the entrance plane of a Wien filter. This is a region of crossed electric and magnetic fields where dispersion of the incident beam occurs on the basis of ion velocities. As all ions emerging from the ion source are accelerated through the same potential, an ion velocity spectrum corresponds to a spectrum of mass-to-charge ratios. Mass-selected ions are then passed through a region in which interaction with a second atomic or molecular beam can occur in a 90° crossed geometry. In the post-collision region, the scattered ions are energy monochromated by a large electrostatic parallel-plate energy analyser whose overall energy resolution is generally of the order of 0.08%. The monoenergetic ion beam passes through another region in which interaction can occur with a neutral atomic or molecular beam, again in a 90° crossed beam geometry. The reaction products which are scattered in the forward direction are energy analysed by a
second parallel plate electrostatic energy analyser. Final ion detection is by means of a channel electron multiplier (model Phillips X-919 AL) operating in the particle counting mode, coupled to conventional pulse counting electronics which is interfaced to a laboratory microcomputer which carries out data acquisition and control of some experimental parameters in an on-line mode.

Typical gas pressures in our apparatus are generally of the order of $10^{-1}$ Torr within the ion source, and $5 \times 10^{-7}$ Torr immediately outside the ion source and in the mass analysis region. The pressure is maintained at such low values by using an oil diffusion pump of pumping speed 1500 ls$^{-1}$. The pressure in the energy monochromation and energy analysis plus detection region is maintained at $1 \times 10^{-7}$ Torr with the help of similar pumps of 2500 ls$^{-1}$ pumping speed. The interaction region has a base pressure of $3 \times 10^{-8}$ Torr. The number densities in the region where the projectile and reactant beams interact are maintained such that they are equivalent to pressures of the order of $10^{-4}$ Torr. The diameter of the gas nozzle is 1 mm; atomic (molecular) beams emanating from it present an interaction volume of 1 mm$^3$. Fast pumping (1500 ls$^{-1}$) ensures that pressures are nearly three orders of magnitude lower in the region immediately outside the interaction zone.

A feature which distinguishes our TES apparatus is the unusually high angular resolution (0.001$^\circ$) with which post-collision reaction products are energy analysed and detected. The significance of this feature will be discussed in the context of the molecular dissociation results presented in §3.
2.1 Ion source

A low-voltage plasma is utilised to produce ionic species in our apparatus. The majority of the ions produced by our high pressure ion source are in their electronic and vibrational ground state with very few in the excited state. Due to the high pressure inside the ion source, in the range 0.1–1.0 Torr (as determined by a thermocouple gauge coupled to the gas-feed line) the excited ions, even if they are produced, will collisionally de-excite and, hence, the projectile ion beam will comprise mainly ground state ions. This important feature of the projectile ions makes the present TES apparatus unique and somewhat simplifies the analysis of collisional data since projectile ions do not comprise any excited states. This is the major advantage of a high pressure, low voltage type ion source compared to the conventional low pressure electron impact ion sources, where the projectile ions are in the ground as well as in excited states.

The ion source follows the original design of Menzinger and Wahlin (1969) and is based on the following principle: in a gaseous dc arc discharge, a sharp potential drop (the so-called “cathode fall”) occurs in the neighbourhood of the cathode, while a plasma (the “positive column”), within which the potential is nearly constant, exists in the vicinity of the anode. By generating such a plasma condition and by extracting the ions from the plasma through a small hole in the anode, one can produce ion beams with a small energy spread nearly identical to the thermal energy spread of the plasma. The plasma density is increased by confining the discharge within a small spatial region, which results in high source efficiency. This is achieved by having an alumina washer before the anode, thereby leaving only a small circular portion of the anode at the front end exposed to the cathode. A schematic diagram is shown in figure 2. The plasma is formed in a restricted region near the anode, and the sheath thickness (or Debye length) has been shown by Raheja et al (1983) to be smaller than the anode orifice.

Ion extraction from our source can occur under one of three possible conditions (see figure 3):

(a) If an extremely low extraction potential is employed, field penetration from within the plasma into the extraction region can severely distort ionic trajectories.

(b) Similarly, if the extraction potential $E_x$ is very high, significant field penetration into the plasma region occurs and the ionisation conditions in the vicinity of the orifice can become distorted in an unpredictable fashion. In both conditions the extracted ions have to traverse the electric field gradient of the sheath.

![Schematic diagram of the high pressure plasma ion source.](image)
probing interatomic potentials using molecular beams

\begin{figure}
\centering
\includegraphics[width=0.8\textwidth]{figure3}
\caption{Ion extraction conditions as a function of applied extraction field $E_2$ and the mean electric field within the ion source $E_1$. Our operating conditions induce the plasma sheath to collapse, as indicated in case (c).
}
\end{figure}

(c) The third possibility is one where the diameter of the extraction orifice is larger than the sheath thickness whereupon the sheath collapses and ions can be extracted from the equipotential region of the plasma bulk, thus avoiding the complications associated with the other two configurations. As a result, ions are extracted from an approximately equipotential region and possess a relatively narrow energy distribution.

Penetration of the extraction potential into the plasma region will, as mentioned above, create distortions in the ionisation conditions in the vicinity of the anode aperture. This will manifest itself as a variation in the plasma voltage or plasma current. Both these quantities are monitored in our apparatus. Since no such variation is observed on the application of the extraction potential, we conclude that field penetration into the plasma region is negligible. The sheath thickness has been determined to be of the order of 0.03 mm. This is certainly much smaller than the anode aperture (0.5 mm). On the basis of these observations it is clear that in our ion source the plasma is best described by case (c).

2.2 Ion extraction and beam formation system

Extraction of ions is by means of a three-element electrostatic lens assembly which is mounted coaxially between the ion source and Wien filter inside the same vacuum chamber where the ion source is housed. Mounting the lens assembly and Wien filter on the same stainless steel rods after the ion source reduces the chances of axial misalignment. Ions are extracted from the ion source by raising the ion source to a positive accelerating voltage (typically in the range 1–3 kV), such that the rest of the apparatus can be maintained at ground potential. Thus, only the positive ions are extracted out of the ion source with an energy essentially equal to the accelerating potential and the quanta of charge on the ion.

2.3 Mass analysing system

The Wien filter used for analysis of ion velocities has a simple on-line geometry; it utilises crossed electric and magnetic fields as compared to the conventional mass analysers using magnetic sectors. As all ions emerging from the ion source are accelerated through the same potential an ion velocity spectrum corresponds to a
spectrum of mass-to-charge ratios. The filter consists of an electromagnet and a pair of electrostatic deflection plates. The plates are mounted between the magnet poles to produce an electric field \( E \) perpendicular to the magnetic field \( B \). The deflector plates, 76 cm long, are made from stainless steel, and the magnet pole tips are the same length as the deflector plates. The electromagnet develops a maximum magnetic field of 1000 gauss.

The filter's ability to disperse masses makes it a superior tool for analysis of mass-to-charge ratios; some of its main features of importance in our apparatus are:

a) straight-line system;
b) adjustable dispersion;
c) small size, upto 50 times smaller in weight and size compared to a conventional sector magnet analyser.

Dispersion properties which can be altered simply by changing the magnetic field afford much convenience and are of importance in TES studies of small molecular systems. The versatility provided by our filter is illustrated which reference to the mass spectra of methane measured with two different settings of magnetic field \( B \) (figure 4).

(a) The first mass spectrum (bottom panel) is acquired with \( B = 84 \) gauss and the mass scan is obtained by varying the electric field \( E \). It is observed that mass 16 (\( \text{CH}_4^+ \)) and mass 15 (\( \text{CH}_3^+ \)) are not clearly resolved.

![CH4 Mass Spectrum](image)

**Figure 4.** Mass spectrum of \( \text{CH}_4 \) obtained under two different magnetic fields in the Wien filter.
(b) By just increasing the magnetic field from 84 to 144 gauss, the effect of variable dispersion of the filter is clearly observed (top panel). The two peaks of mass 16 and 15 for \( \text{CH}_2^+ \) and \( \text{CH}_3^+ \) respectively are well resolved, with a distinct 90% valley between the two peaks.

2.4 Atomic/molecular beam target

The neutral atomic or molecular beams are essentially of thermal energy and are produced by a long (20–25 cm) stainless steel tube of 1 mm internal diameter which is connected to a high pressure gas reservoir. The length of the tube and the gas pressure within it (ca. 10–100 Torr) ensures that the neutral beam emerging possesses mainly those velocity vectors which are aligned parallel to the axis of the tube. The pressure immediately outside the tube is maintained in the \( 10^{-7} \) Torr range. Supplementary experiments carried out on an electron-scattering apparatus in our laboratory have shown that the atomic or molecular beam emerging from such an arrangement maintains a diameter of 1 mm for distances up to 3 mm from the tip of the tube under our pumping conditions.

The pressure in the gas reservoir feeding the 1 mm tube is monitored by a capacitance manometer. To avoid oil vapour contamination in the gas line, where the majority of the gases used are of research grade (99-999% pure), sorption pumps are used to evacuate the gas line instead of mechanical pumps. Sorption pumps contain molecular sieves which, when cooled to liquid nitrogen temperature, adsorb air, thus creating a hydrocarbon-free vacuum of \( 10^{-4} \) Torr in the gas line. The gas flow to the interaction region is controlled by a needle valve which is capable of sustaining a constant flow-rate throughout the duration of the experiment.

2.5 Energy monochromation and analysis

Electrostatic energy analysers work on the principle that the path traversed by a charged particle in an electric field is dependent on its kinetic energy. Those within a narrow range of energies, which means a narrow range of deflections, are selected by a slit and allowed to pass. We have chosen to use one of the simplest analysers, consisting of two parallel plates as shown in figure 5, held at different potentials, thereby creating a uniform electric field between the two plates. The charged particles that enter this field at 45° at the entrance slit follow a parabolic path and are refocussed at the exit slit of the analyser (Harrower 1955). The slit widths in our design are chosen so as to give an energy resolution of 0.1%, but in practice, a value of 0.08% could be routinely obtained.

During initial charge stripping experiments, the energy analyser was made only from two parallel plates shown in figure 5; on many occasions, a low energy peak at half the deflecting voltage of the elastically scattered peak was observed. This peak was found to be due to the reflection of low energy ions from the copper surface, as indicated by trajectory 2 in figure 5a. These reflections were subsequently eliminated by adding three intermediate plates between the two end plates, with equal spacing (1.5 cm for this design) between each of them. Trajectory calculations were carried out to determine the ions path under the influence of the electric field, so as to make apertures at the right places in each of these intermediate plates (figure 5b). Each of the intermediate plates was connected by a resistance chain so as to provide a linear voltage gradient and thus create a uniform electric field.
2.6 Data acquisition and control of experimental parameters

On-line data collection is by means of a microprocessor controlled multichannel analyser (MCA) having an interface to a voltage ramp generator. The ramp produces 0 to +5 volts staircase output which controls the programmable power supply connected to the parallel plate analyser.

During measurements of ion kinetic energy spectra, the analyser voltage is scanned and the output pulses of the channel electron multiplier are synchronously stored in different memory locations on a multiple scanning basis. After scanning the analyser voltage a sufficient number of times to yield an adequate signal-to-noise ratio, data are transferred via a RS-232/C serial link and stored in a computer for off-line analysis.

3. Applications of ion translational energy spectrometry and results

3.1 Charge stripping reactions in ion-neutral collisions

One of the major applications of ion translational energy spectrometry to gas-phase ion chemistry has been in studies of charge stripping reactions occurring in ion-neutral collisions. TES has been the major technique used to study the formation energetics of a new class of molecular species – doubly charged molecular ions possessing lifetimes much longer than expected on the basis of Coulomb’s law applied to, say, a diatomic molecule with two positive charges (for a review, see Mathur (1988), Marathe and Mathur (1991), and references therein).

In a charge stripping reaction of the type

\[ A^+ + B \rightarrow A^{2+} + B + e - \Delta E \]  

(1)

studied at a scattering angle of \( 0 \pm 0.001^\circ \), the difference between the kinetic energies of \( A^+ \) and \( A^{2+} \) is given by the endoergic energy defect, \( \Delta E \), which is related directly to the double ionisation energy of \( A \) in the following manner

\[ \Delta E = IE_{2n}(A) - IE_1(A) + E_b - E_{el} - E_a \]  

(2)

where \( IE_{2n}(A) \) and \( IE_1(A) \) are the double and single ionisation energies, respectively, of
the projectile, \( E_s \) is the total energy (kinetic plus potential energy) acquired by the target, \( E_{el} \) is the kinetic energy of the ejected electron and \( E_i \) is the internal energy of the projectile (\( A^+ \)).

In our experiment, the values of \( E_s \) and \( E_i \) are equated to zero. Previous experience with our high pressure ion source indicates that projectile ions would be produced predominantly in their ground electronic and rovibronic state. \( E_b \) is assumed to be zero for the following reasons. Firstly, electronic excitation of the target can be considered to be absent since no corresponding peak is observed at an energy loss of \( \approx 6 \) eV in the translational energy spectrum of the projectile ion. Regarding momentum transfer to the target ion, simple kinematics applied to our zero degree scattering situation indicates that the recoil imparted to the target is negligible (\( \leq 0.1 \) eV) in the present measurements, mainly as a result of the extremely high value of angular resolution in our apparatus.

By determining the minimum value of the energy defect of the charge stripping reaction, that is, by determining the threshold for formation of \( A^{2+} \), \( E_{tr} \) is reduced to zero. The double ionisation energy of the projectile can now be related to the measured value of the energy defect of the reaction by

\[
\Delta E = IE_{tr}(A) - IE_{i}(A). \tag{3}
\]

Experimentally, charge stripping measurements are carried out in the following fashion. If \( V \) is the energy analyser voltage at which the elastically scattered singly charged \( A^+ \) peak is transmitted, then \( 0.5V - \Delta V \) will be the voltage at which the analyser transmits the doubly charged product ions. The minimum value of \( \Delta V \), which is related to the minimum energy defect, \( \Delta E_{\text{min}} \), of the charge stripping reaction by the energy analyser's geometrical factor, is the measured quantity which enables deduction to be made of the ionisation energy of the singly charged ion.

Charge stripping peaks usually exhibit relatively sharp and well-defined onsets, which enable determination of values of \( \Delta E_{\text{min}} \) with greater accuracy than is generally possible in the analogous threshold extrapolation procedure adopted in conventional electron impact ionisation efficiency curve measurements for doubly charged ions. In actual practice, the value of \( \Delta E_{\text{min}} \) is obtained from the high energy side of the charge stripping peak (by extrapolation to the baseline); measurement of the peak onset in this way eliminates additional translational energy loss from any other inelastic process which may interfere.

The charge stripping technique yields only differences between the single and double ionisation energies and, consequently, accepted values of the single ionisation energy of a molecular species must be available in order to deduce a value for the double ionisation energy. Furthermore, the singly ionised projectile must be assumed to be, or ensured as being, in its ground electronic state. It has been discovered that one of the major advantages of this method of measuring double ionisation energies is the ability of charge stripping reactions to yield information even for doubly charged molecular species which cannot be formed in conventional ion sources.

A typical single scan of the charge stripping spectrum of \( \text{CS}^+ \) radical ions, measured at a collision energy of 3 keV with \( \text{N}_2 \) in the interaction region, is shown in figure 6(a). Calibration of the energy scale is carried out with reference to the charge stripping of atomic \( \text{C}^+ \) ions (figure 6b).

\[
\text{C}^+ + \text{N}_2 \rightarrow \text{C}^{2+} + \text{N}_2 + e + \Delta E_1, \tag{4}
\]
where spectroscopically known values of the single and double ionisation energies of C are used to determine the energy defect (Moore 1958). The error associated with the calibration procedure is estimated to be less than ±0.2 eV. From the spectrum shown in figure 6a, the ionisation energy of the CS$^+$ ion is determined to be 22.0 ± 0.9 eV. The first vertical ionisation energy of neutral CS has been measured in photoelectron spectroscopy experiments to be 11.3 ± 0.2 eV (Jonathan et al. 1971). The first determination of the double ionisation energy of the CS molecule is thus found by us to be 33.3 ± 1.1 eV.

The vertical double ionisation energy of CS can be theoretically deduced by calculating the potential energy curves of neutral and doubly charged CS. Our TES results indicate that the CS$^{2+}$ electronic state accessed in our experiments possesses a potential well which is deep enough (≈ 1.6 eV) to account for a lifetime of at least 3 μs against spontaneous dissociation into C$^+$ + S$^+$ fragments. Clearly, the experimental information provides a very stringent test for contemporary quantum chemical methods of generating accurate potential energy surfaces for hitherto little explored species such as CS radicals.

It is of interest to note that Krishnamurthi et al. (1992) have recently completed a detailed experimental and theoretical study of singly and doubly charged CS radicals; their calculated value for the double ionisation energy of CS is found to be in good accord with the results indicated above.

3.2 TES studies of the dissociation of molecular dications

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 (Marathe and Mathur 1992). 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:

\[
\varepsilon_{lab} = \frac{E}{2} \pm \left( \frac{\varepsilon_{cm} E}{2} \right)^{1/2} + \varepsilon_{cm}^{1/2}
\]

(5)

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, the fragment ion possessing this value of kinetic energy release appears in the laboratory frame at 1500 \pm 245 eV; in practice two peaks are seen in the translational energy spectrum around 1500 eV, 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.

Such energy amplification 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 \( E = m v^2/2 \), 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.

Multiply charged molecules may also dissociate into charged fragments in a collisionless (unimolecular) fashion. Consider the spontaneous process:

\[
M_1^{++} \rightarrow M_2^{++} + M_3^{+}
\]

(6)

where \( x, y \) and \( z \) represent the charge states on \( M_1, M_2 \) and \( M_3 \), respectively. The kinetic energy, \( \varepsilon \), that is spontaneously released in such a process can be deduced from the translational energy spectrum of \( M_2^{++} \) and \( M_3^{+} \) (Marathe and Mathur 1991):

\[
\varepsilon = \frac{y^2 z^2 M_2^2 4 e V_{acel}(\Delta V_{anal})^2}{16xM_2 M_3 V_{el}^2},
\]

(7)

where \( V_{acel} \) is the voltage with which the incident ion beam was accelerated, \( \Delta V_{anal} \) is the width of the fragment ion peak, measured in terms of analyser voltage, that is observed in the translational energy spectrum and \( V_{el} \) is the analyser voltage at which elastically scattered stable ions are transmitted.

Dissociation of doubly charged molecules can also occur by collision processes of the type:

\[
XY^{2+} + M \rightarrow XY^{++} + M^+ \rightarrow X^+ + Y^+ + M^+,
\]

(8)

in which electron capture in a highly excited (dissociative) electronic state of the singly charged species, XY', precedes fragmentation. In the case of homonuclear diatomic projectiles such a process gives rise to translational energy peaks which coincide with the elastically scattered XY^2+ peak; additional peaks with larger kinetic energy releases may also be obtained as symmetrical structures on both the low energy as well as the high energy side.
Figure 7. Translational energy spectrum showing the fragment ions resulting from dissociation of metastable CO$_2^+$ (see text).

The CO$_2^+$ ion has been the subject of a number of experimental and theoretical investigations in the past few years (for a recent compilation of pertinent references, see Krishnamurthi et al 1991). We present an example of the application of TES to studies of the dissociation of this dication.

A typical raw 0° translational energy spectrum of CO$_2^+$ ions colliding with He at an impact energy of 5 keV is shown in figure 7. In the spectrum shown in figure 7A, the central peak a is the elastic scattering peak. Peaks b$_1$ and b$_2$ are due to C$^+$ dissociation fragments. In the first approximation the dissociation products are produced in a variety of centre-of-mass angles; the rigid constraint on ion detection imposed by the angular resolution in our apparatus ensures that only those fragment ions are detected which are scattered such that their velocity vectors are either in the same or the opposite direction as the incoming CO$_2^+$ beam velocity (forward or 0° scattering and backward or 180° scattering, respectively). Clearly, in the former case the velocity vectors of the fragment ions and the projectile CO$_2^+$ ions would add whereas in the latter case there would be subtraction. In the spectrum shown in figure 7, peak b$_2$ corresponds to forward scattered C$^+$ ions and peak b$_1$ is due to the backward scattered component. Similarly, peaks c$_2$ and c$_1$ correspond to forward and backward scattered O$^+$ fragments.

Figure 8 shows a comparison between the kinetic energy spectrum of O$^+$ fragments resulting from dissociation of CO$_2^+$ at two different collision gas pressures. The shapes of the peaks are observed to be different at the two pressures, and these differences are amenable to interpretation in terms of the opening of different dissociation channels (involving different electronic states of the dication). For lower gas pressures (figure 8a) the extreme ends of the peaks exhibit sharp onsets, indicating the existence of a single valued kinetic energy release of 5.7 eV, in good agreement with the recent
Figure 8. Translational energy spectrum of O$^+$ fragments resulting from dissociation of metastable CO at He collision gas pressures of $1 \times 10^{-6}$ Torr (upper panel) and $1 \times 10^{-5}$ Torr (lower panel).

measurements of Hamdan and Brenton (1989). At higher collision gas pressures, the spectrum shown in figure 8b shows the presence of a higher KER component, having a value of 8 eV. These two KER values are amenable to interpretation in terms of the ab initio potential energy curves of CO$_2^+$ recently reported by Krishnamurthi et al (1991) and Larsson et al (1989).

The spectrum may be interpreted in terms of collisional excitation of low-lying metastable CO$_2^+$ states to higher electronic states which dissociate within very short lifetimes. If the projectile beam is assumed to comprise ions in both the $^1\Sigma$ and the $^3\Pi$ state, then the following two excitation channels can be considered.

\[ \text{CO}_2^+ (^3\Pi) + \text{He} \rightarrow \text{CO}_2^+ (^3\Sigma^-) \]  \hspace{1cm} (9)

and

\[ \text{CO}_2^+ (^1\Sigma) + \text{He} \rightarrow \text{CO}_2^+ (^1\Pi) \]  \hspace{1cm} (10)

The dissociation limits corresponding to these two states are the same; that of C$^+ (^2P) + O^+ (^2D)$, lying roughly 3.3 eV above the ground state dissociation limit of C$^+ (^2P) + O^+ (^4S)$. The $^1\Pi$ state will predissociate via the $^3\Sigma^-$ state (Larsson et al 1989) to the ground state dissociation limit, releasing about 6 eV energy in the process. The $^1\Sigma$ state, on the other hand, is seen, on the basis of our computations, to predissociate via a
curve crossing with the $^5\Sigma$ state with an associated KER of 8.2 eV. These two values are in good agreement with the experimentally obtained values of 5.7 eV and 8 eV.

Additional peaks, marked $d_1$ and $d_2$, correspond, respectively, to $C^+$ and $O^+$ fragments which are formed as a result of the collision-induced dissociation of $CO^{2+}$ via an electron capture channel involving an intermediate highly excited (dissociative) state of $CO^{++}$. The energy defects for these electron capture induced dissociation (ECID) reactions indicate an overall exothermicity; the measured values were $4.5 \pm 1.0$ eV and $11 \pm 1.5$ eV for formation of $C^+$ and $O^+$ fragments, respectively. The kinetic energy released in the case of $C^+$ products of the ECID reaction was measured to be $\approx 0.3$ eV.

A noteworthy feature of the spectra of figure 8 is the pronounced enhancement of the ECID contribution to the $O^+$ dissociation channel as the pressure increases. As discussed above, quantitative assessment of this information is precluded by the acute paucity of theoretical information on the pertinent potential energy functions.

In order to interpret the ECID spectrum it is necessary to have information on the energies of various electronic states of $CO^{++}$ ions which are populated in the intermediate electron capture stage of the dissociation process. The excited states of $CO^+$ which are of interest are those which will spontaneously dissociate into either $C^+ + O$ or $C + O^+$ fragments. Clearly this means that only those $CO^{++}$ states in which vibrational levels lying very close to the dissociation limit are populated in a vertical transition from the original $CO^{2+}$ state, and others, which are either purely repulsive or which undergo rapid predissociation, by a curve crossing with a purely repulsive state. Information about such states from conventional UV emission spectroscopy and photoelectron spectroscopy is extremely scarce and recourse has to be made to theoretical calculations of hitherto unavailable potential energy functions of highly excited states of $CO^+$ (see Krishnamurthi et al 1991).

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