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Scattering angular distributions in collisionally activated dissociation of some high mass ions: Analysis of mass-analyzed ion kinetic energy peak shapes

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A method has been developed to determine scattering angular distribution in collisionally activated dissociation (CAD) of high mass ions by analyzing translational energy spectra recorded by mass-analyzed ion kinetic energy spectrometry. Scattering angular distributions have been obtained for CAD of C$_2$F$_4$I$^+$, Cr(CH$_3$COCHCOCH$_3$)$_3$$^+$, and Cs$_3$I$_5$ with He. Large energy losses observed in the translational energy spectra are attributed to the elastic energy transfer to the collision gas accompanying collisional deflection. Deflections of the parent ions get larger as the translational energy for relative motion in the center-of-mass coordinate system decreases. This has been explained by the reactive line-of-centers model. Either vibrational excitation via momentum transfer or vibronic excitation via nonadiabatic interaction is compatible with the experimental data. On the other hand, electronic excitation via the Franck–Condon process is not a feasible mechanism to explain the excitation process in CAD of high mass ions at keV translational energy. © 1995 American Institute of Physics.

INTRODUCTION

Collisionally activated dissociation (CAD) of polyatomic ions at superthermal energy (10–10000 eV) is an important technique in mass spectrometry which is used to induce ion fragmentation. In fact, this forms the basis for tandem mass spectrometry$^{6,7}$ which observes the fragment (daughter) ions generated from a selected precursor (parent) ion. Usefulness of tandem mass spectrometry in mechanistic studies is obvious. Recently, the technique has been adopted as a useful structural probe for large polyatomic ions such as high mass ions generated from proteins, oligosaccharides, etc.$^{8–10}$

The current understanding of CAD of polyatomic ions has been derived mostly from earlier investigations on CAD of diatomic ions which are summarized in several review articles.$^{1–3}$ It is widely accepted that CAD occurs in two successive steps, namely, the collisional excitation step and the dissociation step

$$m_1^+ + N \rightarrow m_1^+*, \quad (1)$$
$$m_1^+* \rightarrow m_2^+ + m_3. \quad (2)$$

Here, $m_1^+$ and $N$ are the parent ion (projectile) and the collision gas (target) and $m_2^+$ and $m_3$ are the fragment ion and neutral, respectively. $m_1^+*$ represents the parent ion excited by collision. Large difference between collision time and dissociation time is thought to be responsible for the validity of the above two step model. Many years ago, Durup proposed several limiting mechanisms to categorize the excitation step.$^{11}$ Among these, pure electronic excitation via Franck–Condon transitions ("process 1"), rovibrational excitation via momentum transfer ("process 2"), and "oblique electronic transition" (process 1–2) may be important under the mass spectrometric conditions considered here.

In the case of CAD of polyatomic ions, it is generally assumed that the dissociation of a collisionally activated parent ion would be well described by statistical theories such as Rice–Ramsperger–Kassel–Marcus (RRKM) theory.$^{12,13}$ However, fundamental understanding of the excitation step has not been satisfactory yet due to the inherent experimental and theoretical difficulties in the investigation. Recently, Futrell and co-workers have begun to investigate the collision dynamics in CAD of small polyatomic ions utilizing angle- and energy-resolved cross-beam tandem mass spectrometry.$^{14–18}$ Ability to plot the CAD probability as a two-dimensional contour map has been especially useful to elucidate the nature of the excitation process. In particular, it has been found that the electronic excitation is much more prevalent even at modest collision energy than was previously thought. Also important is the fact that the energy transfer collision is impulsive in nature, resulting in significant angular scattering. This means that the prevailing concepts about CAD, e.g., vibrational excitation dominating at low collision energy and electronic excitation at high collision energy,$^{1–5,19}$ do not apply. Also, pure electronic excitation via Franck–Condon processes (process 1) is no longer acceptable as a limiting model for intermediate energy.

Another interesting development in this area in recent years has been the observation by Derrick and co-workers of huge translational energy losses in CAD of large polyatomic ions such as polypeptide ions when helium was used as the collision gas.$^{20–24}$ Even though a theory based on a binary collision model has been proposed by the above investigators to account for the huge energy losses, a more detailed dynamical study is desirable.$^{25}$

Recently, we have derived an accurate mathematical expression for the translational energy profile of a daughter ion in CAD analyzed by conventional mass-analyzed ion kinetic
energy spectrometry (MIKES). Good sensitivity of a MIKE peak profile and its center to the scattering angle of the parent ion means that angular information in the collisional excitation step may be available from this method. Accordingly, we utilize this method here to investigate the following CAD reactions in an attempt to elucidate the collision dynamics of large polyatomic projectiles:

\[ C_6F_5I^+ \rightarrow C_6F_5^+ + I \]  \hspace{1cm} (3)

\[ m/z \ 293.9 \quad m/z \ 167.0, \]

\[ Cr(CH_3COCHCOCH_3)^+ \rightarrow Cr(CH_3COCHCOCH_3)_2^+ \]

\[ m/z \ 349.1 \quad m/z \ 250.0, \]  \hspace{1cm} (4)

\[ + CH_3COCHCOCH_3 \]

\[ Cs_4I_4^+ \rightarrow Cs_4I_3^+ + CsI \]  \hspace{1cm} (5)

\[ m/z \ 1172.1 \quad m/z \ 912.3. \]

**EXPERIMENT**

A double focusing mass spectrometer with reversed geometry (VG analytical, model ZAB-E) was used in this work. Pentafluoroiodobenzene \( C_6F_5I \) and chromium(II-III)acetylacetonate \( [Cr(CH_3COCHCOCH_3)_3] \) were introduced to the ion source via septum inlet and direct probe, respectively, and ionized by electron ionization. 15 eV of electron energy was used to reduce the contribution from metastable ion decomposition (MID). Cesium iodide cluster ions were generated by fast atom bombardment using an 8 keV xenon atom beam. Ions generated were accelerated to 1–8 keV translational energy. The parent ions were selected by the magnetic sector. The translational energy spectra of daughter ions generated by unimolecular dissociation of the parent ions, namely, MID, or by CAD occurring in the second field-free region of the instrument were obtained by scanning the voltages applied to the electric sector. This is the so-called mass-analyzed ion kinetic energy spectrometry (MIKES).

Energy resolution \( (E/\Delta E) \) of the electric sector was 2000 or higher as estimated from the full width at half maximum of the MIKE profile of the parent ions. To induce CAD, collision gas was introduced into the collision cell located near the intermediate focal point of the instrument. The collision cell was electrically floated at high voltage to reduce further contribution from MID. The remaining MID signal was subtracted numerically. Floating the collision cell was also useful to reduce the parent ion translational energy to less than 1 keV when needed. Collision gas pressure was adjusted to give 10%–15% attenuation of the parent ion beam. Peak distortion from multiple collisions was not important under this condition as confirmed by experiments at lower attenuations. The translational energy scale (abscissa) of a CAD-MIKE profile was calibrated by utilizing the peak position of the same daughter ion in the corresponding MID-MIKE spectrum. When this was not possible, several MID-MIKE peak positions from other samples were used for the calibration. He, Ar, and Xe were used as collision gases. The purities of the gases purchased were better than 99.995% and gas purifiers were used to remove water as much as possible.

**RESULTS**

In MIKE spectrometry of a unimolecular reaction or metastable ion decomposition (MID), the average laboratory translational energy \( K_2 \) of the daughter ion, \( m_2^+ \), produced from the parent ion, \( m_1^+ \), is very well approximated by

\[ K_2 = (m_2/m_1) K_1. \]  \hspace{1cm} (6)

Here, \( K_1 \) is the initial laboratory translational energy of \( m_1^+ \) and \( m_1 \) and \( m_2 \) are the masses of \( m_1^+ \) and \( m_2^+ \), respectively. Since a certain amount of the internal energy of \( m_1^+ \) or its distribution is released as the relative translational kinetic energy of fragments, the laboratory translational energy, \( K_2 \), tends to show a distribution centered at \( K_2 \). In particular, when dissociation occurs isotropically in the center-of-mass coordinate system with a unique kinetic energy release, \( T \), the MIKE peak profile in the absence of instrumental discrimination is well approximated by a rectangle with the width \( \Delta \)

\[ \Delta = 4(K_2 T m_2/m_1)^{1/2}. \]  \hspace{1cm} (7)

Here, \( m_3 \) is the mass of the neutral fragment. Dishing of the rectangle may occur because of the instrumental discrimination. An accurate, even though complicated, analytical expression for the dished MIKE profile at a unique kinetic energy release, \( B(K_2; T) \), has been reported already. Then, taking into account the kinetic energy release distribution \( [K_{\text{ERD}}, n(T)] \), the overall MIKE profile can be expressed as

\[ F(K_2) = \int n(T) B(K_2; T) dT. \]  \hspace{1cm} (8)

An efficient and accurate algorithm to evaluate the KERD from its MID-MIKE profile is available. When the same dissociation reaction occurs by CAD, namely, via reactions (1) and (2), some of the initial laboratory translational energy of \( m_1^+ \) is lost elastically and/or inelastically in reaction (1). Even though excitation of both \( m_1^+ \) and \( N \) can contribute to the inelastic energy loss, \( Q \), excitation of \( m_1^+ \) has often been neglected when inert gases are used as targets because the energy gaps between the ground and the first excited electronic states of inert gases are large. In CAD requiring a highly endoergic collision, simultaneous excitation of projectile and target, especially such as Xe, often contributes a satellite band at lower energy than the CAD-MIKE peak generated without target excitation. It is to be noted that \( Q \) cannot be larger than the translational energy for relative motion in the center-of-mass coordinate system, \( K_1^3 \)

\[ K_{\text{rel}} = -N / (m_1^+ + N), \]  \hspace{1cm} (9)

Considering the above energy losses, conservation of energy in the laboratory coordinate system is given by

\[ K_1 = K_1^1 + K_N + Q. \]  \hspace{1cm} (10)

Here, \( K_1^1 \) and \( K_N \) are post-collision translational energy of \( m_1^+ \) and \( N \), respectively. Then, the center of the MIKE peak of \( m_2^+ \) will be located at
K'_1 = (m_2/m_1)K_1'

and the peak will be broadened by kinetic energy release. Distributions in K'_1 and Q further result in asymmetric tails on the lower translational energy side of a MIKE profile. It will become clear later that such tails arise mostly from CAD of projectiles which have undergone significant collisional deflection in the center-of-mass frame, even toward the complete backward direction.

The collision kinematics of CAD can be more easily understood in the center-of-mass frame of the collision event. Figure 1 shows the Newton diagram for ion-beam/stationary-target collision. Taking v_1 as the precollision laboratory velocity of m_1^+, the laboratory velocity (v) of the center of mass is given by

v = \frac{m_1}{m_1 + N} v_1.

(12)

v_1 is related to the precollision kinetic energy (K_1) of m_1^+:

v_1 = (2K_1/m_1)^{1/2}.

(13)

The precollision velocities of m_1^+(\omega_1) and N(\omega_N) in the center-of-mass coordinate system are

\omega_1 = \frac{N}{m_1 + N} v_1,

\omega_N = -\frac{m_1}{m_1 + N} v_1.

(14)

In the beam/gas collision investigated in the present work, target atoms are not stationary but move with thermal velocity. For example, the average speed of the target is as large as 7.6% of v_1 in the worst case [reaction (5)] with He target at K_1 of 2 keV. Since the target motion is isotropic, however, Eqs. (12), (14), and (15) provide a decent average description.

In elastic scattering, the magnitudes of the post-collision velocities of m_1^+ (\omega_1') and N (\omega_N') are the same as the precollision values, respectively. Hence, \omega_1' lies on a circle of radius |\omega_1| as shown in Fig. 1, which is usually called the elastic scattering circle (ESC). In endoergic collisions leading to CAD [reaction (1)], \omega_1' lies within ESC. In elastic collisions, scattering angles in the laboratory frame, \Theta_s, and in the center-of-mass frame, \theta_s, are related as follows:

\tan \Theta_s = \frac{\sin \theta_s}{\cos \theta_s + m_1/N}.

(16)

Hence, \Theta_s increases rapidly with the target mass at a given \theta_s. For example, the center-of-mass scattering angle of 90° in the collision of a projectile m/\zeta 1000 with He corresponds to laboratory angle of 0.2°, while these are 2.3° and 7.5° with Ar and Xe, respectively. This means that a large fraction of the high mass projectiles which have suffered collision with He or their dissociation products can be collected with conventional MIKE spectrometers.

Recently, we have developed an accurate and efficient algorithm to calculate a CAD-MIKE profile when scattering occurs along (\theta_s, \phi_s) direction with the inelastic energy transfer of Q and when dissociation occurs with the release of kinetic energy T. This was called a \theta_s, \phi_s, QT CAD-MIKE profile. Here, \theta_s and \phi_s are the scattering polar angles in the center-of-mass coordinate system for the collision partners. Various instrumental effects and discriminations were accounted for in the derivation. Accuracy of the algorithm was checked by comparing with rigorous but very time-consuming ion-optical trajectory calculations. In relation to the present work, it is to be mentioned that the position and shape of a \theta_s, \phi_s, QT CAD-MIKE profile are mostly determined by \theta_1 and T. Also, instrumental discrimination is not significant in CAD of high mass ions with light target such as He even at a large scattering angle (\theta_s ~ 90°).

Even though the above profiles can be calculated easily now, extraction of angular information from experimental data requires further knowledge about the CAD processes which are not generally available experimentally at the moment. This necessitates adoption of some simplifying assumptions. The two step model mentioned previously is one of such assumptions, which has been incorporated already in the calculation of the profiles. Even though exceptions have been reported, the two step model is known to be a good description of CAD processes. In the present work, the main difficulty lies in the fact that knowledge on Q and T, especially their angular dependences, is not available. According to the RRKM picture of unimolecular reaction and the actual measurements of breakdown graphs for various molecular ions, a given fragment ion tends to be produced over a limited internal energy range of the parent ion. Hence, even though the range of the inelastic energy transfer in a collision depends on various factors, the post-collision internal energy of m_1^+ which actually dissociates along a particular channel is likely to be rather narrowly distributed.

The above kinetic consideration has led us to assume that the
post-collision internal energy distribution and also the $Q$ distribution for $m^+_1$ dissociating along a particular channel are the same regardless of the scattering angle and the collision gas. Then, the kinetic energy release distribution, $n(T)$, in the dissociation will also be independent of the scattering angle and the collision gas. The above assumption about $Q$ is not critical to the data analysis because a calculated $\theta_s \phi_s QT$ CAD-MIKE profile is rather insensitive to $Q$. On the other hand, the assumption of constant $n(T)$ which has been made because of lack of detailed information can be critical to the final outcome (to be discussed).

Figure 2 shows CAD-MIKE profiles for reaction (3) obtained at the parent ion translational energy of 7, 3, and 1.5 keV using He and Xe as collision gases. Since the MIKE peak broadening arising from kinetic energy release is proportional to $K^{-1/2}_1$ [see Eq. (7)], overall peak width gets narrower as the incident energy is lowered. To compare the CAD-MIKE profiles obtained at different translational energy more easily, the $x$ scales of the presented spectra have been taken to be inversely proportional to $K^{-1/2}_1$. In the case of MID, MIKE profiles obtained at different translational energy nearly coincide when such $x$-scale adjustments are made when $n(T)$ is invariant with the translational energy. It is to be noted that the CAD-MIKE profiles obtained at three different translational energy with Xe collision gas look nearly the same after the $x$-scale adjustment. Also, the energy shift at the peak top, namely, the translational energy difference between the expected MID peak center and the CAD peak top, remains nearly constant at around 2 eV regardless of the incident energy $K_1$. A conventional MIKE spectrometer has a small collection angle, the maximum being $\sim 0.3^\circ$ for the present instrument. Dependence of the elastic energy transfer, $K_N$, on $\Theta_s$, $m_1$, and $N$ is well known. For reaction (3) with Xe at $\Theta_s$ of $0.2^\circ$, the elastic energy loss results in the energy shift of 0.1, 0.05, and 0.03 eV in the daughter ion peak at 7, 3, and 1.5 keV of the incident energy. This means that the observed energy shift at the peak top must result mainly from parent ion excitation in CAD with Xe (see below for more detailed treatment). The CAD-MIKE profile obtained with Ar nearly coincides with the Xe case.

With He as the collision gas, the energy shift at the peak top is larger than that with Xe and gets larger as the incident energy is lowered ($\sim 6.5$ eV at 7 keV and $\sim 12$ eV at 1.5 keV). Also, the peak is broader with He than with Xe. As was mentioned previously, a particular daughter ion is usually produced over a limited internal energy range of the parent polyatomic ion. This leads one to conclude that the substantial energy shift observed with He compared with Xe cannot be explained by inelastic energy transfer. In addition, the observation that the downward energy shift increases with decreasing $K_N$ in He CAD cannot be rationalized by inelastic energy loss.

Insofar as peak distortion resulting from the energy loss distribution is not significant, the average energy loss and $n(T)$ can be calculated easily using an algorithm developed previously. For this purpose, we analyzed the profiles obtained with Xe or Ar because the center-of-mass scattering angles sampled for these collision gases are small. Data are virtually identical for these gases and only the Xe data will be presented for reaction (3). The average values of $Q$, 3.9 ± 0.4 eV, obtained by treating the Xe CAD-MIKE profiles in Fig. 2 were essentially the same regardless of the incident energy. The kinetic energy release distributions evaluated by the above mentioned algorithm at these different incident energies were also nearly the same, as shown in Fig. 3. Results from numerical analysis were used to regenerate the CAD-MIKE profiles as a check. One of these calculated profiles is shown in Fig. 2(a) as circles. Since thermochemical

![Image: Graph showing CAD-MIKE profiles for reaction (3) with Xe at different incident energies.]

FIG. 2. CAD-MIKE profiles for reaction (3) at the parent ion translational energy of (a) 7 keV ($V=8$ kV, $V'=1$ kV), (b) 3 keV ($V=4$ kV, $V'=1$ kV), and (c) 1.5 keV ($V=2$ kV, $V'=0.5$ kV). $V$ is the accelerating voltage in the ion source. $V'$ is the voltage applied to the collision cell. Collision gases are He (dotted line) and Xe (solid line). Origin of the $x$ (energy) coordinate is taken at the MID-MIKE peak position, $x$ scale is taken to be inversely proportional to $K^{-1/2}_1$ (see the text). Peak heights are normalized. Open circles represent recalculated Xe CAD-MIKE profile (see the text). The long tails with nearly constant intensity observed at lower energy sides of Xe CAD-MIKE profile are due to the dissociation between the cell and the grounded exit slit.
data for reaction (3) are not available, one cannot judge whether the average $Q$ obtained above is reasonable. Comparing the energy thresholds for halogen loss from $C_6H_5X^+$ (X=Cl, Br, I)\(^{39-41}\) with those from $C_6F_5X^+$ (X=Cl, Br),\(^{42}\) the threshold energy of 4–5 eV is expected for reaction (3), giving some credence to the above analysis. As a matter of fact, such a small difference in $Q$ does not affect the $\theta_s \phi_s QT$ CAD-MIKE profile noticeably.

$\theta_s \phi_s QT$ CAD-MIKE profiles with He collision gas were calculated using the average $Q$ and convoluted with $n(T)$ obtained above. The results were then summed over the scattering volume and $\phi_s$. In the summation over the scattering volume, distribution of the parent ion beam intensity along the Z direction was measured to consider instrumental discrimination more rigorously.\(^{32}\) Scattering probability along different $\phi_s$ was assumed to be equal. The peak shape thus calculated corresponds to a CAD-MIKE profile at scattering angle $\theta_s$, which is the angle between the precollision and post-collision velocities of the parent ion in the center-of-mass coordinate system. This will be called the basis function $C(K_2; \theta_s)$. Samples of these functions calculated for reaction (3) at 1.5 keV incident energy at various center-of-mass scattering angles are shown in Fig. 4 together with the experimental CAD-MIKE profile. It is to be noted that even the daughter ions generated by $\sim 90^\circ$ scattering in the center of mass have decent probability to be detected when He is used as the collision gas. This probability increases further as the parent ion mass increases, eventually arriving at the situation of equal probability at every $\theta_s$. Fitting the experimental CAD-MIKE profile, $F(K_2)$, with these basis functions, the scattering angular distribution is obtained

$$F(K_2) = \sum P(\theta_s)C(K_2; \theta_s)d\theta_s,$$

Here, $P(\theta_s)$ is the normalized polar differential cross section satisfying

$$\int P(\theta_s)d\theta_s = 1.$$
the energy shift at the peak top is nearly constant at \( \sim 3.2 \text{ eV} \) at three values of the incident energy. For this reaction, reliable thermochemical data are also not available to estimate the threshold energy for reaction. According to literature data, \(^{42,43}\) it can be anywhere in the range 3–6 eV. The average \( Q \) of 4.6±0.3 eV obtained by analyzing the Xe CAD-MIKE profiles using the method mentioned previously is not unrealistic in this regard. With He collision gas, development of the peak tail at the lower energy side becomes distinct, especially at low incident energy [Fig. 6(b)]. The peak shifts further to the lower energy side at 0.7 keV translational energy [Fig. 6(c)], similar to reaction (3). The angular distributions deduced for reaction (4) with He collision gas are shown in Fig. 7. It is obvious that deflection of the parent ion increases as the incident energy decreases. In particular, backward scattering is significant for 0.7 keV CAD. To highlight this point, the energy positions corresponding to 180° scattering in He CAD are marked by vertical arrows in the MIKE spectra (Fig. 6). At 7 keV [Fig. 6(a)], the corresponding position is not shown because it lies well outside of the spectral range shown (\(-221.5 \text{ eV} \) from the origin). As \( K_{\text{rel}} \) decreases, the peak top shifts gradually toward backward scattering.

To see the effect of the parent ion mass, we investigated CAD of Cs\(_2\)I\(_4\), namely, reaction (5). Figure 8 shows the CAD-MIKE profiles obtained at 7, 3, and 2 keV incident energy using He and Xe collision gases. With Xe, the bands look almost symmetric with nearly the same energy shift at the peak top (\( \sim 1.4 \text{ eV} \)) regardless of the incident energy. Average \( Q \) of 2.2±0.2 eV obtained by analyzing the Xe CAD-MIKE profiles compares well with the theoretically predicted critical energy of 1.5 eV.\(^{44}\) With He, however, peak tailing is distinct even at 7 keV incident energy for this reaction. Scattering angular distributions in Fig. 9 show that deflection of the parent ion is more significant in this case than in reactions (3) and (4). Deflection increases as incident energy is lowered, just as in the previous cases. Backward scattering dominates forward scattering at 2 keV incident energy. The fact that the backward scattering is significant is evident from comparison of the positions of the peak tops and arrows (180° scattering marker) in Fig. 8. That signal intensity is substantial below this marker in Fig. 8 can be attributed to kinetic energy release broadening in backward scattering when the bandwidth of the corresponding Xe CAD-MIKE profile is considered. All the observed signal arises from scattering within the ESC and the scattering shifts gradually toward the backward direction as the incident energy decreases. This supports the kinematics picture described earlier.

**DISCUSSION**

The most critical assumption made in the previous section to evaluate a scattering angular distribution from an ex-
Experimental CAD-MIKE profile is that $Q$ and $n(T)$ (especially the latter) of a given dissociation channel be invariant with incident energy, the collision gas, and scattering angle. CAD-MIKE profiles obtained at various incident energies with Xe and Ar collision gases comply with this assumption. However, this does not prove the assumption because the center-of-mass angle sampled by the instrument is confined mostly to the forward direction with Xe and Ar. Information on the angular dependence of $n(T)$ or its invariance may be obtained with angle-resolved mass spectrometry (ARMS). ARMS was developed initially as a method to observe dissociation of polyatomic ions with large internal energy prepared via violent collisions. It was reported that relative intensities of fragment ions requiring larger endoergicity increase with the scattering angle. This indicates that the post-collision internal energy distribution for a parent ion shifts toward higher energy with scattering angle. Hence, it is likely that the internal energy distribution for parent ions which actually dissociate also shifts upward with scattering angle. It should also be noted that small differences in internal energy can result in noticeable differences in kinetic energy release. In fact, Beynon and co-workers reported as much as 100% increase in the average kinetic energy release as the scattering angle increased. However, their analysis did not take into account certain ion-optical considerations. Intermixed influence of the kinetic energy release distribution and the angular distribution has not been resolved in the contour map obtained even with angle- and energy-resolved cross-beam tandem mass spectrometry by Futrell and co-workers. Further development of this beam method may provide valuable information on the angular dependence of $n(T)$ which is essential for the progress in the present technique. Until reliable information on angular dependence of $n(T)$ is available, it may be ignored as assumed in the present work. In the meantime, we have checked the influence of angular dependence of $n(T)$ by analyzing data with basis functions which broadened (larger kinetic energy release) monotonically with the scattering angle. Use of such basis functions resulted in quantitative changes in the angular distributions obtained, as expected. However, the general trend mentioned in the previous section was not affected.

The kinematic variables most strongly varied in this study are the total available energy, $K_{\text{rel}}$, and the range of center-of-mass scattering angles sampled experimentally. The latter can be estimated with Eq. (16) from the instrumentally defined maximum scattering angles of $\sim 0.3^\circ$ and $\sim 0.8^\circ$ in the Z and Y directions, respectively. In the case of scattering by Ar or Xe, the sampling of the center-of-mass scattering angle is restricted to forward and backward directions. CAD’s originating from the backward scatterings, which would appear at much lower translational energies in the MIKE spectra than the forward scattering peaks, were hardly observed.
detectable. On the other hand, all the center-of-mass scattering angles can be sampled in scattering with He, even though with some instrumental discrimination. To investigate the influence of $K_{\text{rel}}$ on CAD dynamics, $K_1$, $m_1$, and $N$ in Eq. (9) were varied. With He, $K_{\text{rel}}$ was less than 100 eV and was even as small as 6.8 eV for Cs$_i$I$_4$/He at 2 keV, while an order of magnitude larger with Ar or Xe. Such a substantial difference in $K_{\text{rel}}$ with different collision gases might have provided useful information on the influence of $K_{\text{rel}}$ and the nature of the target species on CAD. It is unfortunate in this regard that only forward scattering could be observed with Ar or Xe. However, it is interesting to note that the angular distributions for reaction (3) with He at 3 keV and for reaction (5) with He at 7 keV are similar. $K_{\text{rel}}$'s for these reactions, 20 and 24 eV, respectively, are very similar. This indicates that $K_{\text{rel}}$ exerts the major influence on the collision dynamics in CAD of high mass ions. As was mentioned earlier, we investigated reaction (4) to see if a large number of vibrational degrees of freedom of a projectile would exhibit any noticeable influence on the collision process. The fact that the angular distribution for this reaction looks qualitatively similar to the other two cases indicates that the general trend in the collision process is governed more by the projectile mass and the available total energy than by the detailed projectile structure.

The facts that substantial deflection of the parent ion occurs in CAD and that the deflection gets larger as the incident energy is lowered are in almost complete agreement with the results from angle-resolved tandem mass spectrometric study of smaller polyatomic ions by Futrell and co-workers. According to these investigators, deflection of the parent ion in CAD can be rationalized qualitatively by the reactive line-of-centers model assuming that the colliding species are hard spheres. In this model, the line-of-center energy ($E_{lc}$) or the radial kinetic energy which is effective for excitation is expressed as a function of impact parameter, $b$

$$E_{lc} = K_{\text{rel}}(1 - b^2/d^2).$$

(19)

$K_{\text{rel}}$ was defined in Eq. (9) and $d$ is the hard sphere diameter. For a reaction with critical energy $E_0$, the maximum value of impact parameter, $b_{\text{max}}$, for an effective collision is given by

$$b_{\text{max}} = d(1 - E_0/K_{\text{rel}})^{1/2}.$$

(20)

As $K_{\text{rel}}$ decreases, $b_{\text{max}}$ also decreases, resulting in larger deflection. Compared to the systems investigated by Futrell and co-workers, the masses of the parent ions studied in this work are heavier by an order of magnitude. Center-of-mass translational energy is comparable or slightly larger. For example, $K_{\text{rel}}$ is 7 eV for collision of 2 keV Cs$_i$I$_4$ with He. Hence, the impulsive mechanism for the collisional excitation process postulated from the studies on light polyatomic ions seems to be valid also for CAD of heavy polyatomic ions investigated here. Extrapolating the above argument, one expects to observe nearly completely buck scattering as $K_{\text{rel}}$ approaches the threshold energy. Very poor signal-to-noise ratio made it difficult to acquire such data in the present cases.

The substantial deflections of the parent ions observed in He CAD excludes the pure electronic excitation via Franck–Condon processes as a viable mechanism for CAD of heavy polyatomic ions at keV laboratory translational energy. Of the two remaining mechanisms mentioned in a previous section, rovibrational excitation via momentum transfer presumed to occur adiabatically on the ground state surface is one possibility. Alternatively, "oblique electronic transition," which is a vibronic excitation which arises from nonadiabatic effects is also a possibility. Recently, Lorquet and co-workers reported a quantum mechanical study on the mechanism of energy transfer in CAD of H$_4^+$ by He. A complete configuration interaction calculation was carried out to obtain adiabatic potential energy curves along a collision trajectory. In the adiabatic representation, a succession of avoided crossings and conical intersections was found along the reaction path. In particular, a strong nonadiabatic interaction involving the ground state was found to occur whenever He was in the neighborhood of the origin which was fixed at the middle of a H–H bond. For CAD of polyatomic systems studied here, there are many more electronically excited states near the ground state than that for H$_3^+$+He system. Consequently, electronic excitation via nonadiabatic interactions in a small impact parameter collision is quite feasible. Further multiple crossings via nonadiabatic interactions can also result in vibrational excitation. To summarize, the scattering angular distributions in CAD of heavy polyatomic ions obtained in this work can be rationalized by vibrational excitation via momentum transfer and with the vibronic excitation via nonadiabatic interaction. The observed magnitudes of energy shifts are more consistent with electronic transitions.

CONCLUSION

We have obtained the scattering angular distributions in CAD of heavy polyatomic ions with He collision gas. Even though a similar but crude attempt was reported previously, the present result is expected to be superior because various factors affecting the MIKES profiles have been taken into account. Analysis has been made possible with the use of an accurate and efficient algorithm which was developed with the present purpose in mind. Since the extent of information available from the present method is limited compared to angle-resolved tandem mass spectrometry developed by Futrell and co-workers, an additional assumption was needed for data analysis along with the two step model. Namely, accepting the statistical picture for the dissociation step, the post-collision internal energy distribution for the parent ions which actually dissociate along a particular channel and $n(T)$ were assumed to be independent of both scattering angle and collision gas. An extensive investigation on the angular dependence of $n(T)$ with angle-resolved tandem mass spectrometry will be very helpful for the development of the present technique. Compared to the angle-resolved tandem mass spectrometry, the advantage of the present method is its ability to investigate CAD of heavy polyatomic ions using the conventional MIKES technique.

For all the reactions investigated, large deflections of the parent ions were observed which increased as the translational energy was lowered. Hence, one of the previously accepted models for CAD, namely, electronic excitation...
via Franck–Condon process, is not applicable in the present cases. Such a conclusion is in agreement with the experimental and theoretical investigations on smaller polyatomic ions by Futrell and co-workers\textsuperscript{14--18} and by Lorquet and co-workers,\textsuperscript{54} respectively. Either vibrational excitation or momentum transfer or vibronic excitation via nonadiabatic interaction are likely candidates to explain the excitation step. Although it is not possible at the moment to determine which of the two models is mainly responsible for CAD of heavy polyatomic ions, the magnitude of $Q$ favors vibronic excitation. Accurate determination and analysis of other relevant properties such as relative cross sections and KERDs may be useful for this purpose. This possibility is being explored.

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