High-Energy Collisional Activation Studied via Angle-Resolved Translational Energy Spectra of Survivor Ions*

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Angle-resolved translational energy spectroscopy has been applied to Cs_4I_3^+ ions that survived 8 keV collisions with a range of collision gas targets, including inert gases and deuterium. The experimental data comprise values of the translational energy loss ΔT_R as a function of the (laboratory-frame) scattering angle θ_R for each collision gas under conditions such that single-collision events dominated the scattering. The values of ΔT_R increase with θ_R , in accordance with very general expectations. However, for any value of θ_R , the values of ΔT_R for helium and deuterium as targets were almost indistinguishable from one another but were at least five to six times larger than those for neon and all other collision gases. These data have been shown to be consistent with theoretical considerations based upon conservation of energy and linear momentum. Theoretical approaches include the simple "elastic-limit" model, which makes no mechanistic assumptions, and a particular "binary-model" theory, which excludes electronic excitation as a possibility. Both theories are consistent with the experimental data and interpret the surprisingly large values of ΔT_R for low-mass targets in terms of large recoil energies of the target required to ensure conservation of momentum. The most likely alternative candidate as sink for ΔT_R is internal excitation of the target, but this possibility was excluded in the present work by choosing ΔT_R values less than the lowest excitation energies of the inert gas targets. Moreover, such an interpretation cannot explain the similar results obtained using helium and deuterium, which were markedly different from those obtained for all other collision gases. (*J Am Soc Mass Spectrom* 1993, 4, 835-844)

The phenomenon of collision-induced dissociation (CID) of ions has been of practical and theoretical interest for some time. In particular, CID arising from collisions between reactant ions and thermal target gas atoms (or molecules), at energies in the kiloelectronvolt range, has been characterized as proceeding via two well-separated steps, that is, a fast collisional-activation (CA) step followed by the dissociation itself on a slower time scale. Although this distinction between the CA step and the overall CID process is not universally made, it is important for the present work in which the two steps are separated experimentally.

Seminal work on understanding the CA processes involved in CID of small ions (few atoms only) was due to Durup [1]; this work was updated and extended by Los and Govers [2], with particular reference to diatomic reactant ions. Subsequent work on the

CA process at kiloelectronvolt energies has attempted to apply to larger ions the understanding achieved by these fundamental studies [1, 2]. The elegant work of Futrell and co-workers [3-5] is notable in this respect and has extended the earlier fundamental work on diatomic ions to systems of chemical interest. Parallel with these physical chemistry studies, attempts have been made to relate the principles thus established to CID experiments using analytical mass spectrometers. For example, the interpretation of the data [6] on variation of kinetic energy release, in CID of organic ions (< 200 Da) with scattering angle, relied upon the insights from earlier CID work [1, 2]. Recent work by Cooks and co-workers [7-9], on ions of similar size, has further extended the understanding of CID of ions of chemical interest. An excellent review of current understanding of the CA process has been published by McLuckey [10].

Among the studies of the CA process in analytical mass spectrometers, certain observations concerning the CID of larger organic ions have been of practical and theoretical interest [11-17]. These observations, initially published by Derrick and co-workers [11, 12, 15, 16], concern the CID of large organic reactant ions as studied by mass-analyzed ion kinetic energy spec-

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trometry (MIKES). The fragment ions appeared at values of the electric sector field E much lower than those predicted by eq 1, which assumes negligible fractional transformation of translational to internal energy in the CA step and also ignores any translational energy release to the products of the dissociation:

$$E_P = E_R \times (m_P/m_R) \quad (1)$$

where subscripts R and P denote reactant and product ions, respectively, and E (bold type) denotes the electric sector field strength as distinct from the symbol E , which denotes the physical object (electric sector) itself. Large discrepancies between experimental values of E_P and those predicted by eq 1 imply correspondingly large losses of translational energy [11-17] in the CA process.

Of course, the basic concept of the CA method involves increasing the internal energy ϵ_R at the expense of translational energy T_R , so that some discrepancy between predicted and observed E_P values must in principle exist. It has been the surprisingly large magnitude of the translational energy losses ΔT_R of the reactant ions, up to 50 eV and even higher, that has aroused interest [11-17]. The most obvious interpretation of such observations involves an assumption that most of ΔT_R is transformed into ϵ_R to meet large requirements of internal energy (kinetic shift) over and above the dissociation threshold. Such kinetic shifts are required to permit the dissociation rate constants k_d to rise to values (of the order of 10^6 s^{-1}) that match the experimental time scale, which in turn is determined solely by the physical dimensions of the apparatus used and by the speed with which the ions traverse it. For larger organic ions (frequently protonated peptides [11-17]), the large number of effective vibrational modes demands a correspondingly large value of ϵ_R in order that k_d can attain values demanded by the observational time window. These large values of ϵ_R can be provided only by conversion of T_R by the CA step or from precollision internal energy ϵ_R^0 deposited in the reactant ions by the ionization process itself.

Although this kinetic-shift effect must indeed be operative, it appears that it cannot on its own account for all of the relevant experimental observations. For example, the values of ΔT_R (measured as ΔT_P and converted via eq 1) observed in all cases studied [11-17] are much larger for light collision targets (H_2 , D_2 , He) than for all others (Ne, Ar, Kr, Xe, N_2) in the same apparatus. This observation can be rationalized in terms of $\Delta \epsilon_R$ (kinetic shift), as the predominant sink for ΔT_R , only if CA by the light targets yields a significant fraction of activated ions in an isolated state which cannot undergo the dissociation reactions monitored. However, $\text{Cs}_{n+1}\text{I}_n^+$ ions, of masses comparable to those of the large organic ions of interest but with fewer atoms (e.g., 21 vibrational modes for Cs_5I_4^+ compared with approximately 500 for a peptide ion of similar mass) and presumably very different electronic

states, display comparable losses of translational energy ΔT_R in CID-MIKES experiments. Finally, the peak shapes observed in CID-MIKES experiments are also strongly dependent on the nature of the target gas. Highly asymmetric peaks, with extensive tailing on the low-energy side, are observed for He, H_2 , and D_2 , while much more narrow and symmetric peaks are observed when other target gases are used [17].

Two different approaches have been proposed to account for the surprisingly large values of ΔT_R , and for their dependence upon the nature of the target gas. That suggested by Bricker and Russell [13] proposes that those CA collisions that lead to observable CID products are necessarily accompanied by excitation (possibly including ionization) of the target. On the other hand, Derrick and co-workers [11, 12, 15, 16] and ourselves [17] have accounted for the experimental observations on the assumption that recoil translational energy of the target is a major sink for ΔT_R .

The present work has attempted to clarify this problem by making observations on reactant ions that survived the CA process sufficiently long (25 μs or longer) so that their translational energies could be measured. In the companion article, the delayed dissociation spectra of these survivor ions, selected via their ΔT_R values, are used to estimate their internal energies. This approach represents an extension of earlier work by Cerny and co-workers [18, 19], who studied the low-energy tails on MIKES peaks corresponding to reactant ions that survived the CA process; preliminary accounts of these delayed dissociation studies have been published [20, 21]. (It is worthwhile to note that the low-energy tails of interest here [18-21] differ from those studied by Ballard and Gaskell [22], which apply to MIKE spectra for both CID and spontaneous dissociations of reactant ions formed by fast-atom bombardment only, and concerns background signals as low as $0.5 \times E_R$.)

This article reports measurements of translational energies of reactant ions that survived CA as a function of scattering angle. Previous investigations, using the MIKES technique, of the angular dependence of kiloelectronvolt collisions without immediate chemical consequences have involved electronic excitation and ionization (charge stripping) of simple monatomic and diatomic reactant ions [23]. This work demonstrated the necessity for ion-beam collimation both before and after the collision in order to cleanly separate the collisional deflection from the energy dispersion by the electric sector, and thus adequately specify the angle. Because such collimation dramatically reduces the intensity of the reactant ion beam, it was necessary to choose a reactant ion available at high yield, and the Cs_4I_3^+ ion fulfilled this requirement. In addition, there is no possibility that this reactant ion will produce fragment ions via losses of a few Da (e.g., losses of hydrogen atoms), thus avoiding ambiguities in the identification of ions observed at a few electronvolts below the unscattered reactant peak in the MIKE spec-

trum. Finally, since the Cs_4I_3^+ ions were produced by bombardment of a "dry" CsI sample, the problems associated with collisional desolvation of ions sputtered from liquid matrices [22] were avoided.

Simple considerations of energy conservation for the CA step yield the expression given in eq 2 for the translational energy loss $\Delta T_R (= T_R^0 - T_R)$:

$$\Delta T_R = [(\epsilon_R - \epsilon_R^0) + (\epsilon_G - \epsilon_G^0) + h\nu] + \Delta T_G = Q + \Delta T_G \quad (2)$$

where superscript 0 denotes a precollision value, $\Delta T_G (= T_G - T_G^0)$ the translational energy gained by G in the collision, and Q the total inelasticity. Little is known about the radiation $h\nu$ emitted by larger ions of chemical interest during or immediately following kiloelectronvolt collisions. Experiments on extremely low yields of UV-visible emission from small ions, in collision with gases or electrons, have been reported [24-28]. It has been suggested [27, 28] that most of this UV radiation may originate from excited neutral molecules formed by electron transfer from the target gas. In cases where this electron transfer is exothermic, it is possible to observe radiation from the target gas also. However, it must be emphasized that the intensity of this radiation is generally extremely low (close to the limits of detection [29]), consistent with earlier considerations [25, 30] of a low probability that emission in this frequency range can compete with internal conversion to the electronic ground state in all but a small number of exceptional cases. Infrared emission from vibrationally excited ions has been studied by Dunbar and co-workers [30-33] and shown to occur on a time scale of several seconds. Further, in the present context, the fact that the energy discrepancies of interest (several electronvolts) are comparable for reactant ions, which are very different chemically but have similar masses (e.g., $\text{Cs}_{n+1}\text{I}_n^+$ and protonated peptides), makes it highly unlikely that the large ΔT_R values could be accounted for in terms of emitted photons. For all these reasons, it will be assumed here that radiation does not play a significant role in the energy balance expressed in eq 2.

By choosing inert gas targets G, the values of $(\epsilon_G - \epsilon_G^0)$ become the well-known excitation energies of these atomic species, so that target excitation [13] can be removed from consideration in the present work by restricting experimental values of ΔT_R to be less than the appropriate first excitation energies (Table 1). (A few experiments involving diatomic targets will be reported here for purposes of comparison.) All quantities in eq 2, other than ϵ_G for inert gas targets G, are to be understood as most-probable values representative of appropriate distributions.

Experimental

Experiments were conducted using a VG Analytical ZAB-EQ tandem hybrid instrument (BEqQ configura-

Table 1. Lowest excitation energies ($^2P_{3/2}$ for all except helium, 3S_1), and ionization energies, for the inert gases

Gas	Energy (eV), 1st excited state	Ionization energy (eV)
D ₂	11.37	15.43
He	19.819	24.580
Ne	16.619	21.559
Ar	11.548	15.755
Kr	9.915	13.996
Xe	8.315	12.127

From C. E. Moore, *Atomic Energy Levels as Derived from the Analyses of Optical Spectra*, U.S. National Bureau of Standards, NSRDS-NBS 35, 1971. Values for D₂ are from G. Herzberg, *Spectra of Diatomic Molecules*, Van Nostrand, New York, 1950.

tion), but in the experiments reported here, the tandem quadrupole assembly was not employed. The CsI sample was used as a dry powder, deposited on the probe in solution; the primary beam was 30 keV Cs^+ . In collision experiments, the collision gas was used at as low a pressure as possible, consistent with adequate signal/noise ratios in the resulting spectra. These pressures were such that reactant beam intensities were attenuated by about 15-20%. Using the approach of Kim [34], it was estimated that under these experimental conditions, approximately 90% of the attenuation was due to single-collision events. Experiments using helium, with attenuations in the range 15-85%, showed no significant variation in ΔT_R versus θ_R (see below) up to 50% attenuation.

The BEqQ instrument used here has all the same features as those described previously [35] for a related instrument but, in addition, has a high-field magnet with extended mass-range optics and a VG 11-250J datasystem for instrument control and data acquisition. In particular, facilities for beam collimation and angular selection, similar to those described previously [23, 35], were added to the standard ZAB-EQ instrument. Prior to the collision cell, z-collimation was achieved using the standard z-restrictor between ion source and magnet, plus an additional special z-restrictor at the point of intermediate focus between B and E; y-collimation was achieved by a combination of the variable α -slit, located between source and B, and a special extra slit located about 10 cm before the slit at the intermediate focal point between B and E. In this way, observations were restricted as far as possible to events occurring in the xz-plane via y-collimation. (The main optical axis is defined here as the x-axis, so the focusing and dispersion occur in the xy-plane.) The angular dependence of the scattered intensity was investigated by using a 1-mm-high aperture that could be moved in the z-direction (slit-height direction) at the double-focus point (image slit of the electric sector E). At its maximum displacement of 5 mm from the central axis, this aperture lay on a linear trajectory, originating at the collision cell, at an angle of $0.29 \pm 0.03^\circ$ to the main axis (x-axis). This method of defining

scattering angles has been used previously [6, 17, 23] on instruments similar to that used here. Use of an electrically floated collision cell, to more narrowly specify the location of the scattering events and thus the magnitude of the laboratory-frame scattering angle θ_R , is applicable [17] to fragment ions but not to reactants.

Results and Discussion

Experimental Investigations

In these experiments, for which the beam collimation and angular selection facilities of the instrument were used, the reactant ion beam was collimated to the maximum possible extent consistent with adequate signal/noise ratios. The ideal condition [23], in which observations are restricted to scattering events occurring in the xz-plane, could not be satisfied fully, as discussed below.

The translational energy spectra shown in Figures 1 and 2 for Cs_4I_3^+ reactant ions in collision with helium and neon, respectively, were obtained using an effec-

Figure 1. Translational energy spectra of Cs_4I_3^+ reactant ions (m/z 912) after collision with helium, at different displacements of a 1-mm moveable z-aperture; a 1-mm displacement corresponds to an angle with the principal optical axis of 0.06° at the collision cell, so the z-displacements correspond to angles of $0.00 \pm 0.03^\circ$, $0.14 \pm 0.03^\circ$, and $0.26 \pm 0.03^\circ$. Initial translational energy was 7936.0 eV, with a full-beam width at half height of 3 eV. Peak B corresponds to ions of types (1) and (2) (see text, unscattered and elastically scattered ions), while Peak C corresponds to inelastically scattered ions (type (3)).

Figure 2. Translational energy spectra of Cs_4I_3^+ reactant ions (m/z 912) after collision with neon, at different displacements of a 1-mm moveable z-aperture; a 1-mm displacement corresponds to an angle with the principal optical axis of 0.06° at the collision cell, so the z-displacements correspond to angles of $0.00 \pm 0.03^\circ$, $0.14 \pm 0.03^\circ$, and $0.26 \pm 0.03^\circ$. Initial translational energy was 7936.0 eV, with a full-beam width at half height of 3 eV. Peak B corresponds to ions of types (1) and (2) (see text, unscattered and elastically scattered ions), while Peak C corresponds to inelastically scattered ions (type (3)).

tive angular resolution of approximately $\pm 0.03^\circ$. Similar results were obtained for several collision gases, and the results are summarized in Figure 3. Note the similarity between the results for He and D_2 (essentially indistinguishable from one another, although the values of ΔT_R for He are consistently slightly larger than for D_2), and the marked separation between these results and those for all other collision gases. The important property of the collision target in these experiments, therefore, appears to be its mass, or possibly some other property closely correlated with mass; excitation and ionization energies (Table 1) do not correlate well with the observations summarized in Figures 1-3. It is true that one of the crucial comparisons (He with D_2) involves a monatomic and a diatomic target, but no other option is available for this particular comparison.

The trends evident in Figures 1-3 can be understood qualitatively in terms of three kinds of ions arriving at the slit at the double-focus point:

1. Ions that have undergone no collisions whatsoever;
2. Ions that have experienced elastic collisions ($Q = 0$); and

Figure 3. Most probable values of translational energy loss $\Delta T_R = (T_R^0 - T_R)$ for Cs_4I_3^+ ions, for different collision targets, as a function of scattering angle (inelastically scattered ions, type (3)). A displacement of the movable z-aperture by 1 mm corresponds to an angle of $0.06 \pm 0.03^\circ$ at the collision cell. Experimental uncertainties for D_2 and for He are standard deviations for pooled experiments conducted on two occasions.

3. Ions that have undergone inelastic collisions ($Q > 0$) involving significant internuclear momentum transfer (and thus necessarily involving rotational/vibrational excitation, but not necessarily excluding simultaneous electronic excitation [1]).

Ions in categories 1 and 2 are expected to dominate the translational energy spectra at low scattering angles, and to correspond to values of ΔT_R that are zero (type 1) or small (type 2). Those ions falling into category 3, however, should become of greater relative intensities, and show increasing values of ΔT_R , at larger angles. These predictions are borne out by Figures 1 and 2, in which the ions of types 1 plus 2 (peak B) have been successfully resolved from those of type 3 (peak C). The survival of peak B at the larger z-displacements, evident in some of these spectra, reflects residual cross talk between energy dispersion and angular selection; restriction (via beam collimation) to events in the xz-plane has been shown [23] to be a necessary condition for complete elimination of such cross talk in apparatus of the kind used here. This condition could not be strictly fulfilled in the present work because of beam intensity limitations.

Another striking trend evident from Figures 1-3 concerns the much larger values of ΔT_R , at a given z-displacement (scattering angle θ_R), observed for helium compared with those for neon and all heavier target gases. This trend with target mass is also evident in CID-MIKES experiments [11-17] and in previous experiments of the present kind [18, 19] but without angular selection, that is, integrated over the full

instrumental range for z (and thus for θ_R). A similar dependence on target mass was also noted [36] in measurements of excess translational energy of ionized target atoms produced by 4 keV collisions with neutral projectiles, as discussed further below.

Theoretical Considerations

The present experimental investigations of angular dependence of CA events demand a theoretical treatment that includes scattering via momentum transfer. The present work is thus very different from that described by Los and Govers [2] in which the nature of excited-state potential curves of diatomic reactant ions was deduced from translational energy spectra of the product ions, using the explicit assumption that the CA step involves only long-range electronic excitation with negligible internuclear momentum transfer. Two versions of the momentum-transfer model of CA were used in the present work.

The elastic-limit model does not pretend to calculate values of the total inelasticity Q . Rather, these must be evaluated or assumed separately and supplied as input to the calculations. This model then evaluates the value of (T_R/T_R^0) for selected values of laboratory-frame scattering angle θ_R of the reactant ion, and for assumed values of (Q/T_R^0) . No assumptions are made concerning the disposition of Q among internal modes of reactant ion and target, and emitted radiation (eq 2). The model is a simple consequence of the conservation of energy (eq 2) and of linear momentum in the two orthogonal directions defining the plane of the collision [23]. However, the momentum conservation equations, considered in this model, involve the precollision and postcollision momenta of the entire reactant ion (and also of the entire target gas molecule, in the event that this is not monatomic). These momentum conservation equations must, of course, be satisfied in any event, but it is the omission of details of all intermediate steps that results in Q being undetermined by the model and its consequent appearance as an input parameter for the calculation. On the other hand, this disadvantage of the elastic-limit model is balanced by its flexibility in accounting for any and all contributions to Q , including electronic as well as rotational/vibrational excitation, or a combination thereof. The result of these considerations leads [23] to the following relationship:

$$\begin{aligned}
 & [1 + (m_G/m_R)]^2 (T_R/T_R^0) \\
 &= \left\{ \cos \theta_R \pm [\cos^2 \theta_R - (1 - m_G^2/m_R^2) \right. \\
 &\quad \left. - (m_G/m_R)(1 + m_G/m_R)(Q/T_R^0)]^{1/2} \right\}^2 \quad (3)
 \end{aligned}$$

where all quantities are defined in a laboratory-fixed reference frame. Derivation of eq 3 also assumes [23] that T_G^0 is negligible, so that ΔT_G (eq 2) is approximately T_G , which is valid for the present example of 8

keV ions colliding with thermal target atoms. The choice of sign for the second term on the right side of eq 3 corresponds to the "soft-hard collision" dichotomy discussed previously [23]. In the present work, the hard collisions (positive sign in eq 3) are not considered, since they are predicted to correspond to ΔT_R values of up to several hundreds of electronvolts and are believed [37, 38] to have much lower cross sections than their soft counterparts.

In contrast to the elastic-limit model summarized by eq 3, the so-called binary limit of the momentum-transfer model of CA considers a polyatomic reactant ion to be composed of two parts, an "impact" portion that interacts (exchanges momentum) with the target while the other is assumed to remain as a "spectator" for the duration of the collision. Such an interaction leads to rotational/vibrational excitation of the ion (but does not necessarily exclude simultaneous electronic excitation). Early applications [39-41] of this model to CID of simple ions (predominantly H_2^+) included estimates of dissociation cross sections. However, the most common use of the binary-limit concept has involved comparison of the predicted values of ΔT_R with those predicted by elastic-limit calculations. Examples of such applications include scattering of N_2^+ on Ar [42] and of Ar^+ on N_2 [43]. The mathematical expressions for ΔT_R as a function of θ_R have been conveniently summarized [23]. More recently, Uggerud and Derrick et al. [44, 45] have succeeded in deriving expressions for Q (as well as for ΔT_R) within the binary limit, under the restriction that only vibrational/rotational excitation is considered. This represents a considerable advance, although there remains a requirement to assume how the reactant mass is to be divided between impact and spectator portions. Uggerud and Derrick et al. [44, 45] stated that their impact portions were assumed to be single constituent atoms of the reactant ion, but their treatment is more generally applicable.

Of the relationships thus deduced by Uggerud and Derrick et al. [44, 45], the most useful for the present work are:

$$\Delta T_R/T_R^0 = (2/\mu^2) \times \left\{ (\mu - \cos^2\theta_R) \pm \left[(\mu - \cos^2\theta_R)^2 - \mu^2(1 - \cos^2\theta_R) \right]^{1/2} \right\} \quad (4)$$

$$Q/\Delta T_R = \mu/2\epsilon \quad (5)$$

$$\epsilon = [1 + (m_a/m_C)]/[2 \times [1 - (m_a/m_R)]] \quad (6)$$

$$\mu = [1 + (m_a/m_C)]/[1 + (m_a/m_C) - (m_a/m_R)] \quad (7)$$

where m_R and m_C are written as m_{ion} and m_g , respectively, in the original work [44, 45], and m_a denotes the mass of the impact portion (originally assumed [44] to be a single atom) of the reactant ion. Equations

4, 5, and 7 correspond respectively to eqs 41, 42, and 39 of the original work [44], reexpressed for convenience in terms of dimensionless mass ratios, while eq 6 is the correct expression for ϵ , given as eq 2 in the follow-up work [45], which corrected errors in the original [44]. In this model, Q is determined as a fixed fraction of ΔT_R (eq 5) and is not an input parameter. The hard-soft collision dichotomy (see eq 3) appears also in eq 4.

It is important to emphasize a fundamental limitation of all relationships derived from only considerations of conservation of energy and momentum. No attempt is made in such derivations to specify the $R^+ - G$ interaction potential, so that the equations of motion are not considered in any way and thus no information is available concerning relative cross sections for competing outcomes. For example, eq 3 permits, within the elastic-limit approximation, calculation of $\Delta T_R^{(1)}$ for R^+ scattered through angle $\theta_R^{(1)}$ with inelasticity $Q^{(1)}$, and also of $\Delta T_R^{(2)}$ for R^+ scattered through $\theta_R^{(2)}$ with inelasticity $Q^{(2)}$. However, such a calculation provides no information concerning the relative probabilities of these two events. The only caveat to this conclusion concerns cases in which the specifications of the collision are inconsistent with the conservation requirements, a condition signaled by a negative value for the expression within square brackets (in either eq 3 or eq 4) whose square root must be evaluated; in such cases, of course, the cross section is zero. The limiting case of eq 3, in which this expression in square brackets is exactly zero and in addition θ_R is zero (head-on collision), corresponds to the conventional calculation of the center-of-mass collision energy (T_{COM}), the maximum translational energy available for conversion into internal energy:

$$Q_{max}/T_R^0 = T_{COM}/T_R^0 = m_G/(m_R + m_G) \quad (8)$$

Again, eq 8 contains no information concerning the probability of such an occurrence.

To compare the two models with respect to interpretation of the experimental data summarized in Figures 1-3, it is necessary to estimate appropriate values of Q for input into the elastic-limit model (eq 3). The ions of interest are $Cs_4I_3^+$ ions that survived the collisions for the 25 μs flight time through the energy analyzer to the detector. The dissociation channel of lowest critical energy, as judged from the unimolecular fragment spectrum, is that forming $Cs_3I_2^+$ by expulsion of a neutral CsI fragment. It is possible to estimate ΔE_0 , the thermodynamic zero-point energy difference for this reaction, from theoretical calculations [46] of the binding energies (relative to ionic dissociation limits) of the two ions, together with experimental [47] and theoretical [48] values of the dissociation energy of CsI (again relative to ionic dissociation limits). The resulting value for ΔE_0 of 1.46 eV is subject to an uncertainty of some ± 0.02 eV arising from errors in reading values from Figure 6 of ref 46. This thermodynamic quantity for the reaction is related to the kinetic

parameter Q_{CID} , the magnitude of internal energy deposited in R^+ by CA events leading to dissociation on the experimental time scale, via eq 9:

$$Q_{CID} = \Delta E_o + T + \epsilon_p - \epsilon_R^o \quad (9)$$

where T is the kinetic-energy release value for the dissociation and ϵ_p is the combined internal energy of the dissociation products. All quantities in eq 9, with the exception of ΔE_o , are understood to represent mean values. The value of T for the reaction of interest has been measured [49, 50] as 0.17 eV. The internal energies of the dissociation products are controlled by the detailed dynamics of the unimolecular fragmentation, and no quantitative information concerning ϵ_p is available. The values of ϵ_R^o are controlled by energy deposition during the sputtering process and by preferential depletion of ions with higher values of ϵ_R^o due to dissociation during flight between the ion source and the collision cell. In view of the intense metastable peak observed for this reaction, the population of reactant ions must include some with values of $\epsilon_R^o \geq (\Delta E_o + T)$, corresponding to values of Q_{CID} (eq 9) close to zero. At the other extreme, the sputtering process presumably produces some ions with ϵ_R^o close to zero, and such ions will require (eq 9) $Q_{CID} = (1.46 + 0.17 + \epsilon_p)$ eV to lead to observable dissociation. The present experiments are concerned with survivor ions that do not undergo CID (i.e., ions with $Q < Q_{CID}$). In view of these energetic considerations, the elastic-limit cal-

culations were conducted for Q values of 1 eV and 3 eV to ensure that the relevant range was covered.

The relevant range of values for ϵ_R (and thus Q) is defined by the physical dimensions of the apparatus via the corresponding time windows and dissociation rate constants, and in particular is independent of the nature of the collision gas. It is thus pertinent to compare values of ΔT_R calculated for different targets G , at the same angle θ_R and for the same value of Q . The results of such calculations based on the elastic-limit model (eq 3) are shown in Figure 4. The difference between ΔT_R and Q corresponds (eq 2) to ΔT_G when ϵ_G is zero, and is much larger for helium than for neon. For yet heavier targets, the predicted difference between ΔT_R and Q is even smaller than for neon, but these calculations have been omitted from Figure 4 in the interests of clarity. The physical reason underlying this consequence of eq 3 is simply the relationship between translational energy ($\propto v^2$) and momentum ($\propto v$), where v is the magnitude of the velocity. For two collision gases G_1 and G_2 at fixed values of Q and of θ_R , a small ratio (m_{G1}/m_{G2}) requires a correspondingly large ratio (v_{G1}/v_{G2}) for momentum conservation to be satisfied, and this implies an even larger difference when the v^2 ratio is considered.

It is also possible to interpret Figure 4 in a fashion directly related to the experimental peak widths exemplified in Figures 1-3. The experimental uncertainty in θ_R ($\pm 0.03^\circ$) implies that a corresponding range of values of ΔT_R should be considered. For example, for

Figure 4. Values of translational energy loss ΔT_R , calculated using the elastic-limit model (eq 3), for reactant ions R^+ of mass 912 Da and translational energy 8 keV in collision with thermal target atoms G of mass 4 Da (He) or 20 Da (Ne), as a function of scattering angle θ_R . Representative values of the inelasticity Q were estimated (see text) to yield dissociation rate constants sufficiently small ($\leq 10^5 \text{ s}^{-1}$) that the activated ions would survive the 25 μs flight time from collision cell to detector. In the present experiments, θ_R could be specified to within $\pm 0.03^\circ$, and ΔT_R to within ± 2 eV.

an experimentally defined angle θ_R of $0.15 \pm 0.03^\circ$, and for Q in the range 1–3 eV, Figure 4 predicts ranges for ΔT_R of 10–26 eV and 4–10.5 eV for He and Ne, respectively, as collision gases for Cs_4I_3^+ at 8 keV. These calculated ranges correspond closely to those defined by the experimental peaks in Figures 1b and 2b, measured at 25% of peak height. This degree of quantitative agreement between experiment and elastic-limit model calculations (eq 3) should probably be regarded as fortuitous; however, it is reassuring that the experimental trends are reproduced by the theory.

Calculations based upon the Uggerud–Derrick theory (eqs 4–7) are summarized in Figure 5. In this case, Q is calculated as a result of the theory rather than treated as an adjustable parameter. However, it is necessary to choose a value for m_a , the mass of the “impact portion” of the reactant ion. For the present calculations, m_a was chosen to be 130 Da, representative of the atomic masses of Cs and I. The marked separation between the curve for helium and those for all other rare gas targets is still evident (Figure 5), but now there is a greater distinction among the curves for all collision gases other than helium. Real-valued solutions to eq 4 do not exist for $\theta_R > \arcsin(\mu - 1)$, reflecting the impossibility of conserving momentum for larger scattering angles when the discrepancy between

masses of the ion and the target is too large. For $m_a = 130$ Da and $m_R = 912$ Da, these limiting values for θ_R are 0.245° for helium and 1.21° for neon, relative to the instrumental limit of 0.29° . In this regard, note the extremely weak signals observed for He at $0.26 \pm 0.03^\circ$ (very close to the limit) in Figure 1c, compared with those for Ne in Figure 2c. Thus, according to the Uggerud–Derrick model with m_a chosen to be 130 Da, the maximum energy that can be deposited in an 8 keV Cs_4I_3^+ ion via collision with helium corresponds to this limit, evaluated as 1.8 eV at a laboratory scattering angle of 0.245° . At the experimental limit for θ_R of 0.29° , the theory predicts values of Q of 1.3 eV for each of Ne, Ar, and Xe. These values for Q lie well within the range estimated above based upon independent information on the energetics of $\text{Cs}_{n+1}\text{I}_n^+$ ions, and are therefore consistent with the present observations (Figures 1–3) that Cs_4I_3^+ can be scattered through such angles and survive for 25 μs without dissociation.

Alternative proposals [13] that attribute variations in ΔT_R to obligatory excitation of the different targets cannot be tested by the theoretical models employed here. The most relevant experimental evidence involves the indistinguishable data obtained (Figure 3) for D_2 and for He as collision gases. The excitation and ionization energies of these two gases are very different (Table 1), which presents a serious problem for the interpretation [13] in terms of target excitation as the major sink for ΔT_R . Further, the great majority of the present experimental data (Figure 3) for inert gas targets correspond to measured values of ΔT_R that are less than the lowest excitation energies (Table 1). The present interpretation in terms of target translational energy T_C can accommodate both of these facts, although the helium–deuterium comparison does face a minor ambiguity in that it involves a monatomic and a diatomic collision gas. It would clearly be preferable to have a direct experimental test that could detect large translational energies for the scattered target gas atoms.

It does not seem possible to devise an experiment to detect such fast atoms in apparatus of the kind used in the present work. A crossed-beam experiment, employing coincident detection of scattered ions and target atoms, could in principle provide such evidence, and such experiments have been reported [51] for atomic ions scattered off atomic targets. The closest experimental analogy to the present work appears to be that of Morgan et al. [36], who measured excess translational energies (analogous to ΔT_C) of target gas ions formed in 4 keV collisions with neutral projectiles. The cross sections for these ionizing collisions were invariably low for neutral inert gas projectiles, and were zero for organic projectiles with helium as the collision target [36]. On the other hand, these workers [36] found the excess translational energies of the ionized target gas to be large (up to 10 eV) for heavy projectiles (e.g., Xe^0) in collision with light targets (e.g., H_2), but these excess energies decreased to much smaller values as the mass ratio approached unity. The

Figure 5. Values of translational energy loss ΔT_R , calculated using the theory of Uggerud and Derrick et al. [44, 45] (eqs 4–7), for reactant ions R^+ of mass 912 Da and translational energy 8 keV in collision with inert gas targets, as a function of scattering angle θ_R . The value of m_a , the impact portion of the projectile ion, was taken to be 130 Da. The values of $Q/\Delta T_R$ calculated from eq 5 are: He, 0.026; Ne, 0.127; Ar, 0.209; Xe, 0.462.

simple elastic-limit collision theory (eq 3) was invoked to interpret these data, although not all aspects of the phenomenon could be accounted for.

Increasing values of ΔT_R (most probable values measured at peak maximum) and an increasing extent of the low-energy tails of MIKES peaks for CA survivor ions, as the mass of the target is decreased, were observed [18, 19] in experiments in which beam collimation was not applied. These observations reflect the theoretical requirement that the range of ΔT_R values corresponding to the instrument-defined range for θ_R is much larger in the case of a low-mass target (Figures 3 and 5). Thus, integration over θ_R implies superposition of R^+ survivor ions with a wider range of ΔT_R values in the case of the low-mass targets, accounting qualitatively for these observations. Because nothing is known about the $R^+ - G$ interaction potential, no predictions can be made concerning the relative probabilities for the various (ΔT_R , θ_R) combinations, and thus no detailed quantitative interpretations of the peak shapes can be made using either of the theoretical approaches employed here.

Conclusions

The present experimental data on variation of translational energy spectra of CA survivor ions, with scattering angle and with nature of the collision gas, have been shown to be consistent with simple theoretical expressions derived from considerations of conservation of energy and linear momentum. The elastic-limit theory makes no mechanistic assumptions but requires that the total inelasticity Q be estimated independently as an adjustable parameter. The particular expression of "binary-model" collision theory, derived by Ungerud and Derrick et al. [44, 45], assumes that electronic excitation is not involved and calculates Q as a defined fraction of ΔT_R . Both of these theoretical approaches can account qualitatively and semiquantitatively for all of the present observations, and both interpret the difference ($\Delta T_R - Q$) as T_G , the recoil energy of the target. The alternative interpretation proposed by Bricker and Russell [13], in which this difference is attributed to obligatory excitation (or possibly ionization) of the target, is not applicable to the majority of the present observations for which the values of ΔT_R were chosen to be less than the lowest excitation energies of the appropriate rare gas targets. Further, this proposal [13] cannot account for the observation that use of helium and deuterium yielded almost indistinguishable results, which differed markedly from those obtained using all other collision gases. Although the present results strongly support the recoil-energy interpretation, some ambiguities remain. For example, only one reactant ion was examined in this work; it was not possible to find a large organic ion at sufficient intensity that beam collimation was feasible. Further, the possibility that internal energy of the reactant ion provides a major sink for ΔT_R

has not been ruled out definitively by the present experiments alone. A complementary approach, which attempts to assess the internal energies of the survivor ions, is described in an accompanying article [52].

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