ding section. In VIII the cyano C atom is sp hybridized and a π_z bond is formed between C atoms, but the N^+ and C^+ (isoelectronic with B) atoms have vacant $2p_z$ orbitals in VIIIa and VIIIb, respectively. Therefore cross-conjugation between the cyanide and carbonyl groups is particularly unfavorable, and hence the barrier to rotation about the amide N–C bond is predicted to be comparable with that for DMF. As the species $:C{\equiv}N:$ is stable, the limit resonance structure represented as III above may also be considered to contribute to the resonance hybrid for DMCN leading to an increased barrier to rotation. Thus it is seen that a simple valence-bond model is compatible with the observed $\Delta G^{\ddagger}$ value of 21.6 kcal mol^{-1}, being equal to or higher than that for DMF ($\Delta G^{\ddagger} = 21.0$ kcal mol^{-1}).

The halogen substituents X = F, Cl, and Br may also be considered in the resonance form II if it is assumed that these atoms are sp^2 hybridized with formal lone pair electrons in a $2p_z$, $3p_z$, or $4p_z$ atomic orbital, respectively. The degree of cross-conjugation (and hence the contribution from resonance structure II) is then determined by the overlap between these p_z orbitals and a C $2p_z$ orbital and the respective halogen orbital electronegativities.[42] Thus the barrier to rotation is predicted to decrease in the order F > Cl > Br, again as is observed experimentally. Detailed semiempirical SCF–LCAO–MO calculations in the CNDO/2 and INDO approximations, which include orbital overlap and two-electron interactions, will be reported elsewhere in an effort to develop a more sophisticated model for the C-substituted amide bonding systems initially studied here.

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Long-Lived States of Rare Gas Ions. An Ion Kinetic Energy Study

T. Ast,[1] J. H. Beynon, and R. G. Cooks*

Contribution from the Department of Chemistry,
Purdue University, Lafayette, Indiana 47907.
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Abstract: Collision-induced ionization of rare gas ions ($m^+ + N \rightarrow m^{2+} + N + e^-$) has been studied by ion kinetic energy spectroscopy. Kinetic energy loss spectra, taken using 8-keV reactant ions, provide direct information on the internal energies of the rare gas ions. Typically, reaction occurs from three energy states or groups of states. These are the ground state, a state with energy very close to the second ionization potential, and an intermediate state. The onset of each peak in the energy loss spectrum corresponds to adiabatic ionization, and this allowed fairly accurate determinations (±1 eV) of the energies of the reactant ionic states. A state of Ne^+ (energy 27.7 eV above the ground state) was observed, apparently for the first time, to be long-lived ($\gtrsim 10^{-5}$ sec). Experiments in which the ion accelerating voltage, collision gas pressure, and ionizing electron energy were varied confirmed the suggested major processes and provided further detail. For example, the highest energy state of the singly charged ions (probably due to high Rydberg levels) reacted both by a collision process and also by a unimolecular mechanism, the latter probably being pseudo-unimolecular and involving collisions with slit surfaces. Fine structure was sometimes observed in the kinetic energy loss spectra. In addition to the dominant 10/20 reaction, the 10/21 process was also observed.

The technique of ion kinetic energy spectroscopy (IKES)[2,3] has been applied to a wide range of problems in gaseous ion chemistry,[3] including studies on the structures and unimolecular reactions of ions, collision-induced reactions, the identification of isomeric compounds, and the determination of isotopic incorporation. The technique has proved particularly valuable in the study of multiply charged ions. Measurement of the kinetic energy (T) released in the fragmentations of doubly charged ions has been a key factor in allowing the proposal of structures for complex doubly charged ions, for studying isomerization in doubly charged ions, and in energetic studies on charge separation in simple doubly charged ions.[4]

Doubly charged ions formed in the ion chamber of a double-focusing mass spectrometer can undergo collision-induced charge exchange in the first field-free region of the instrument according to the general equation

$$m^{2+} + N \longrightarrow m^+ + N^+ \qquad (1)$$

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(1) On leave from Faculty of Technology and Metallurgy, University of Belgrade, Yugoslavia. This work was submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the School of Science, Purdue University.

(2) (a) J. H. Beynon, J. W. Amy, and W. E. Baitinger, *Chem. Commun.*, 723 (1968); (b) J. H. Beynon, R. M. Caprioli, W. E. Baitinger, and J. W. Amy, *Int. J. Mass Spectrom. Ion Phys.*, **3**, 313 (1969); (c) J. H. Beynon, W. E. Baitinger, and J. W. Amy, *ibid.*, **3**, 55 (1969).

(3) For general reviews, see (a) J. H. Beynon, *Anal. Chem.*, **42**, 97A (1970); (b) J. H. Beynon and R. G. Cooks, *Res./Develop.*, **22** (11), 26 (1971).

(4) (a) R. M. Caprioli, T. Ast, and J. H. Beynon, *Org. Mass Spectrom.*, **5**, 417 (1971); (b) J. H. Beynon, R. M. Caprioli, and J. W. Richardson, *J. Amer. Chem. Soc.*, **93**, 1852 (1971); (c) T. Ast and J. H. Beynon, paper presented at 19th Annual Conference on Mass Spectrometry and Allied Topics, ASMS, Atlanta, Ga., May, 1971.

where N is a collision gas molecule or atom. It has been shown[5] that ion kinetic energy spectroscopy provides an extremely suitable method for studying these processes and for separating the energetically unique product ion, m^+, from the other ions which make up the normal mass spectrum.

More recently,[6] we have found IKES to be a valuable method for the study of collision-induced ionization reactions (also referred to as charge-stripping) of the type shown in eq 2. Complex organic compounds can

$$m^+ + N \longrightarrow m^{2+} + N + e^- \qquad (2)$$

be characterized by a mass spectrum (which can be obtained with excellent sensitivity) consisting of only those doubly charged ions which result from the above (10/20) type reaction.[7] Furthermore, the small amount (Q') of kinetic energy, which is lost *by the reactant ion*,[8] can be measured by IKES. Thus, for example, studies[6] on nitric oxide have shown the existence of two states of the reactant NO^+ ion, both of which can be ionized to give ground-state NO^{2+}.

Other previous studies on the transformation $m^+ \rightarrow m^{2+}$ have largely been concentrated on the rare gases. Indeed, we are aware of only two instances in which mass spectrometric studies of this type were made on polyatomic ions. By adding collision gas to the second field-free region of a double-focusing mass spectrometer, Jennings[9] was able to observe very weak signals which he attributed to reaction 2, the reactants being the molecular ions of toluene and fluorobenzene. Seibl[10] has reported the occurrence in complex organic ions of the autoionization process, $m^+ \rightarrow m^{2+} + e^-$. Both the above experiments were severely hampered by the weak signals attainable.

This paper is concerned with the study of reaction 2 in rare gases, *i.e.*, with the charge-stripping process $G^+ \rightarrow G^{2+}$, where G^+ is a rare gas ion. Attention is concentrated on the problem of energy balance in this reaction, the mechanism(s) of the process, and the possibility that several states of the ion can react in this way. Earlier work, employing ion kinetic energies in the keV range, has revealed the operation of three distinct mechanisms. These are (i) autoionization of G^+ from a state of energy greater than the second ionization potential (IP)[11] of G, (ii) a pseudo-unimolecular process in which resonance ionization of highly excited G^+ occurs on interaction with a metal surface (in practice a slit), and (iii) formation of G^{2+} following collision with a gas molecule or atom. The autoionization mechanism (i) was first observed by Daly[12] and confirmed by later workers.[13] It is believed that it occurs from a state or states with an energy not much greater than the second ionization potential of the rare gas in question. The pseudo-unimolecular process (ii) involving interaction with a solid surface has been proven to occur.[14] It does not involve detectable kinetic energy loss and occurs from states which also lie near the second IP but which are different from the autoionizing states. Newton and coworkers conclude that high Rydberg states are involved.[14a] The collision-induced process (iii) has been shown, in the argon case, also to involve the higher Rydberg levels.[15]

The studies just noted leave unanswered a number of important questions. Among them are the following: is process iii limited to the long-lived Rydberg states, or, can the true metastable states (as distinguished from those which are merely long-lived) of the rare gas ions take part? Is energy transferred to the target molecule in process iii and, if so, in what form? Is any kinetic energy loss detectable in process ii? All the experiments quoted were done with poor energy resolution. IKES should therefore introduce a new dimension into the study of this type of reaction with the possibility of measurements of Q' values in combination with the previously employed pressure and electron energy variations.[16] The sensitivity of the IKES method is also several orders of magnitude better than that achieved in most of the above studies.

Experimental Section

All measurements were made using a Perkin-Elmer Hitachi RMH-2 mass spectrometer,[18] modified as previously described so as to allow IKES[2] and also to allow collision gases to be admitted to the first field-free region[19] (Figure 1). The pressure in this region was read by means of an ionization gauge attached directly to the collision chamber. Except for pumping by the gauge itself and losses through the slits on either side of the field-free region, pressures were read under static conditions.

A typical experimental procedure for studying the reaction $G^+ \rightarrow G^{2+}$ was as follows. A value of V, the ion accelerating voltage, was chosen and the electric sector voltage was adjusted to a value E which transmitted the main beam of singly charged ions formed in the source. These ions were either collected at the β-multiplier (placed just behind the plane of the energy resolving β-slit), or the particular ions G^+ were selected by mass analysis and detected at the final collector. Both procedures gave identical V/E ratios. The voltage on the electric sector was then halved, *i.e.*, set to a new value $E_1 = E/2$, and the magnet current adjusted to pass ions of apparent mass G/4 (referred to the mass scale appropriate to settings V and E). At this stage the signal recorded on the final collector was due to G^{2+} ions formed from G^+ ions which had lost no energy in the charge-stripping reaction 2. The electric sector value had to be halved since these doubly charged ions have half the kinetic energy acquired by normal doubly charged ions formed in the source; similarly, the normal mass scale position of G^{2+} ions (G/2) changed to G/4. As the final step in the experiment the accelerating voltage was increased over a narrow range; this resulted in the

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(5) (a) J. H. Beynon, A. Mathias, and A. E. Williams, *Org. Mass Spectrom.*, 5, 303 (1971); (b) T. Ast, J. H. Beynon, and R. G. Cooks, *J. Amer. Chem. Soc.*, 94, 1834 (1972); (c) T. Ast, J. H. Beynon, and R. G. Cooks, *Org. Mass Spectrom.*, 6, 749 (1972).

(6) R. G. Cooks, J. H. Beynon, and T. Ast, *J. Amer. Chem. Soc.*, 94, 1004 (1972).

(7) An analogous reaction is the 10/21 process in which products m^{2+}, N^+ and e^- are formed. This is discussed later.

(8) It is emphasized that Q' refers only to the kinetic energy lost by the reactant ion irrespective of the form in which it appears in the products. It therefore differs from Q, the net kinetic energy converted to internal energy; see Q. C. Kessel and E. Everhart, *Phys. Rev.*, 146, 16 (1966).

(9) K. R. Jennings, *Int. J. Mass Spectrom. Ion Phys.*, 1, 227 (1968).

(10) J. Seibl, *Org. Mass Spectrom.*, 2, 1033 (1969).

(11) The second ionization potential refers to formation of the doubly charged ion throughout this paper, not to ionization of an excited neutral.

(12) N. R. Daly, *Proc. Phys. Soc., London*, 85, 897 (1965).

(13) A. S. Newton, A. F. Sciamanna, and R. Clampitt, *J. Chem. Phys.*, 47, 4843 (1967).

(14) (a) A. S. Newton, A. F. Sciamanna, and R. Clampitt, *ibid.*, 47, 1779 (1967); (b) K. Okuno, Y. Kaneko, and I. Kanomata, *Recent Develop. Mass Spectrosc., Proc. Int. Conf. Mass Spectrosc., 1969*, 830 (1970).

(15) J. W. McGowan and L. Kerwin, *Can. J. Phys.*, 41, 1535 (1963).

(16) Kinetic energy loss measurements can also be made by the coincidence techniques of Everhart and others.[17] These techniques have, however, been applied almost exclusively to higher energy reactant ions and hence to larger scattering angles and to multiple electron loss collisions.

(17) H. Ewald and W. Seibt, *Recent Develop. Mass Spectrosc., Proc. Int. Conf. Mass Spectrosc., 1969*, 39 (1970), and references therein.

(18) J. H. Beynon, W. E. Baitinger, J. W. Amy, and T. Komatsu, *Int. J. Mass Spectrom. Ion Phys.*, 3, 47 (1969).

(19) J. H. Beynon, R. M. Caprioli, and T. Ast, *ibid.*, 7, 88 (1971).

Table I. Kinetic Energy Loss Spectra of Rare Gas Ions[a]

Rare gas	1st IP[c]	2nd IP[d]	ΔIP[e]	Loss of kinetic energy, $Q'_{\min}$[b]		
				Peak A	Peak B	Peak C
He[f]	24.6	78.9	54.3	0[g]		54.5 ± 2
Ne[h]	21.6	62.6	41.0	0	13.3 ± 1.0	42.2 ± 2
Ar	15.9	43.4	27.5	0	8.9 ± 0.8[i]	27.5 ± 0.6[i]
Kr	14.7	38.5	23.8	0	7.6 ± 0.5	24.1 ± 1
Xe	13.4	33.3	19.9	0	6.9 ± 0.5	19.5 ± 1

[a] All results in this table are for experiments in which air was used as collision gas. All values are in eV. [b] $Q'_{\min}$ values refer to the peak onset, as obtained by extrapolation to the base line, corrected for the main ion beam width. The limits given represent probable errors. [c] Refers to the higher energy state ($^2P_{1/2}$) when the ground state of the rare gas atom is a doublet since the higher state is what should correlate with $Q'_{\min}$. Values are taken from J. L. Franklin, J. G. Dillard, H. M. Rosenstock, J. T. Herron, K. Draxl, and F. H. Field, "Ionization Potentials, Appearance Potentials and Heats and Formation of Gaseous Positive Ions," NSRDS-NBS 26, U. S. Government Printing Office, Washington, D. C., 1969. [d] These values give the total energy required to produce a doubly charged ion from the neutral species. Values taken from the above reference except that for He; see R. W. Kiser, "Introduction to Mass Spectrometry," Prentice-Hall, Englewood Cliffs, N. J., 1965, p 303. [e] These values are the differences of the values in columns 3 and 2. [f] Electron ionizing energy 120 eV. [g] The values in this column are in each case zero, within 0.3 eV. [h] Electron ionizing energy 100 eV. [i] Average for eight different collision gases.

collection of products of the charge-stripping reaction in which the reactant ion had suffered kinetic energy loss (eq 2). The spectrum obtained by this accelerating voltage scan provides a distribution of Q' values; *i.e.*, it constitutes a kinetic energy loss spectrum which is specific to ions undergoing charge-stripping. The accelerating voltage had to be increased to compensate for the amount of kinetic energy lost before the product ions could be transmitted.

Standard conditions used for recording the kinetic energy spectra of the reacting rare gas ions were: electron energy 70 eV (unless otherwise specified), electron emission current 1 mA, ion accelerating voltage 8 or 10 keV, source pressure 1×10^{-5} Torr, collision gas pressure 5×10^{-5} torr (air unless specified).

Kinetic energy loss spectra were also recorded at the β-multiplier (see Figure 1), *i.e.*, without mass analysis. However, since there is always some leakage of the collision gas back into the source, serious interference can arise. For example, with air as collision gas, the products of reactions 3 and 4 will be transmitted and recorded

$$N_2\cdot^{+} \longrightarrow N^{+} + N\cdot \tag{3}$$

$$O_2\cdot^{+} \longrightarrow O^{+} + O\cdot \tag{4}$$

at the β-detector under the same experimental conditions as the products of reaction 2. This procedure was therefore limited to cases where the reactant and collision gases were identical, *e.g.*, Ar^+ upon Ar. Either the accelerating voltage or the electric sector voltage[20] could be scanned in these experiments which gave essentially the same results as those obtained using mass analysis. Of the various methods for plotting the kinetic energy loss spectra of product ions of reaction 2, that in which the accelerating voltage is scanned and the ions are monitored at the final collector is most suitable. All the experiments reported below have been obtained by this procedure.

Results

The experimental conditions just outlined allow the detection of G^+ ions which are converted to G^{2+} ions in the first field-free region of a double-focusing mass spectrometer whether they undergo kinetic energy loss or not. It must still be established that no other ions interfere with those due to the collision-induced ionization reaction 2. The only other ions which could be collected under these experimental conditions are the daughter ions G^{2+} formed from the diatomic rare gas ions $G_2{}^{2+}$ according to the reaction

$$G_2{}^{2+} \longrightarrow G^{2+} + G \tag{5}$$

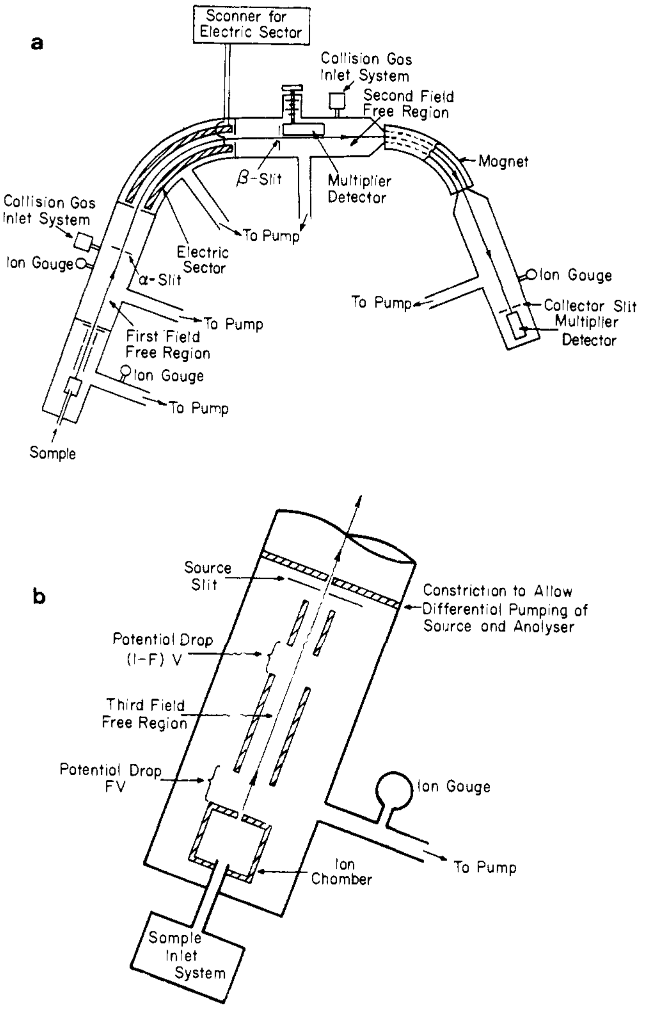

Figure 1. Modified Hitachi RMH-2 mass spectrometer: (a) overall view, (b) detail of ion source region.

Since $G_2{}^{2+}$ must result from an ion–molecule reaction occurring in the source, its abundance should show at least a square law dependence upon source pressure. In experiments with the rare gases at different source pressures, using air as collision gas, all peaks in the kinetic energy loss spectra retained the same relative abundances. This rules out the possibility that the ion source reaction 5 makes any significant contributions to the recorded spectra for any collision gas.

Generally, three peaks or groups of peaks (A–C) were evident in the kinetic energy loss spectra of rare gas ions undergoing the charge-stripping reaction 2. Figure 2 shows the spectra for each of the rare gas ions using air as collision gas. Figure 3 shows the changes in the argon spectrum which occur with different

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(20) Electric sector voltage scans could not be employed when using the final collector because a simultaneous magnet scan would have been necessary to transmit the product ions.

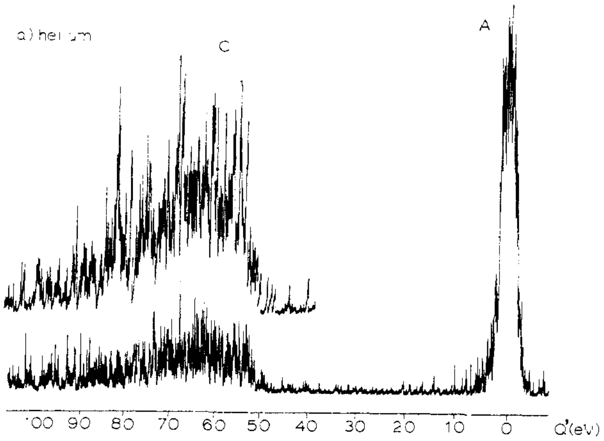

Figure 2a. Ion kinetic energy loss spectrum for the charge-stripping reaction of helium.

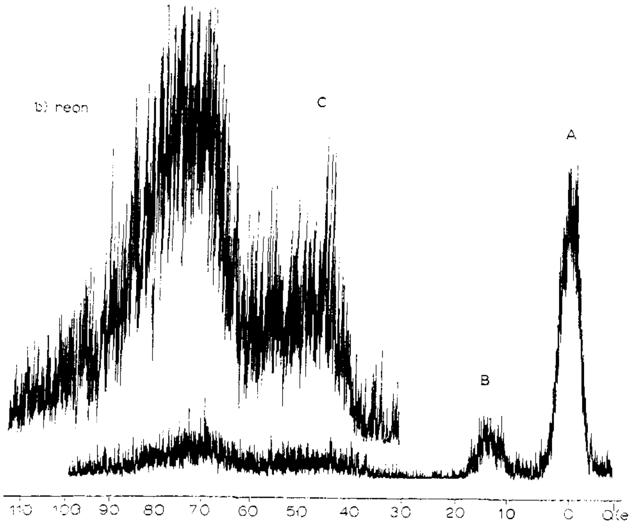

Figure 2b. Ion kinetic energy loss spectrum for the charge-stripping reaction of neon.

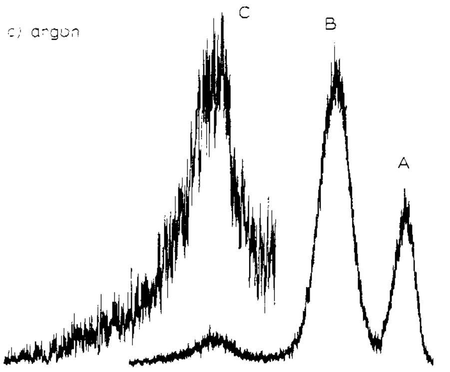

Figure 2c. Ion kinetic energy loss spectrum for the charge-stripping reaction of argon.

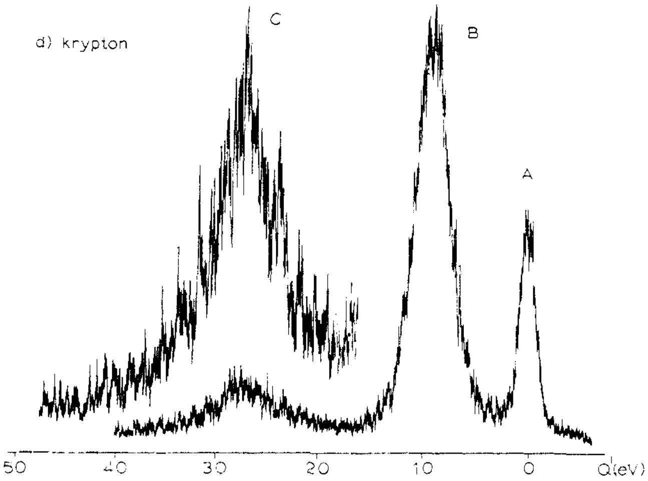

Figure 2d. Ion kinetic energy loss spectrum for the charge-stripping reaction of krypton.

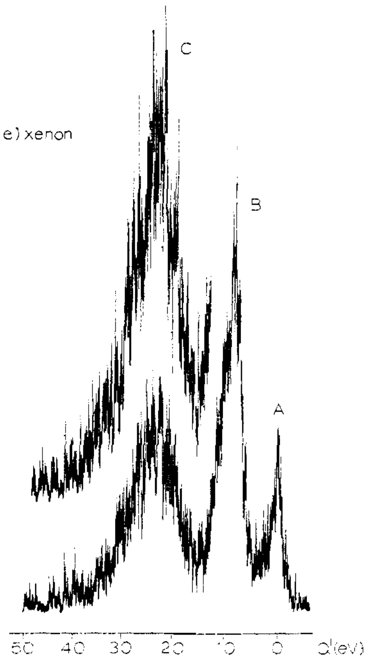

Figure 2e. Ion kinetic energy loss spectrum for the charge-stripping reaction of xenon.

collision gases. In both Figures 2 and 3 the rather low abundance peaks (C) corresponding to greatest Q' values have been replotted at greater sensitivity to show their detailed shapes. Figure 4 shows the effect of variation of electron energy E_{el} upon the $Ar^+ \rightarrow Ar^{2+}$ ion kinetic energy loss spectrum using air as collision gas. Figure 5 illustrates the structure sometimes seen in peak C.

It is apparent from Figures 2–5 that the kinetic energy loss peaks typically have rather sharp onsets and that peaks B and C show more tailing on the high Q' side. Moreover, the onset is relatively unaffected by collision gas pressure and nature, whereas the tailing is very much affected. We have therefore adopted a procedure for measuring peak positions which involves extrapolation of the leading edge to the base line. Because of the effects of discrimination upon peak shapes (see later), deconvolution procedures do not appear to be warranted. Further justification of the adopted procedure, which bears some relation to the earliest methods of treating ionization efficiency curves, is made herein. In reporting peak positions the onset is corrected for the finite width of the main beam of stable ions which leaves the source with the same ki-

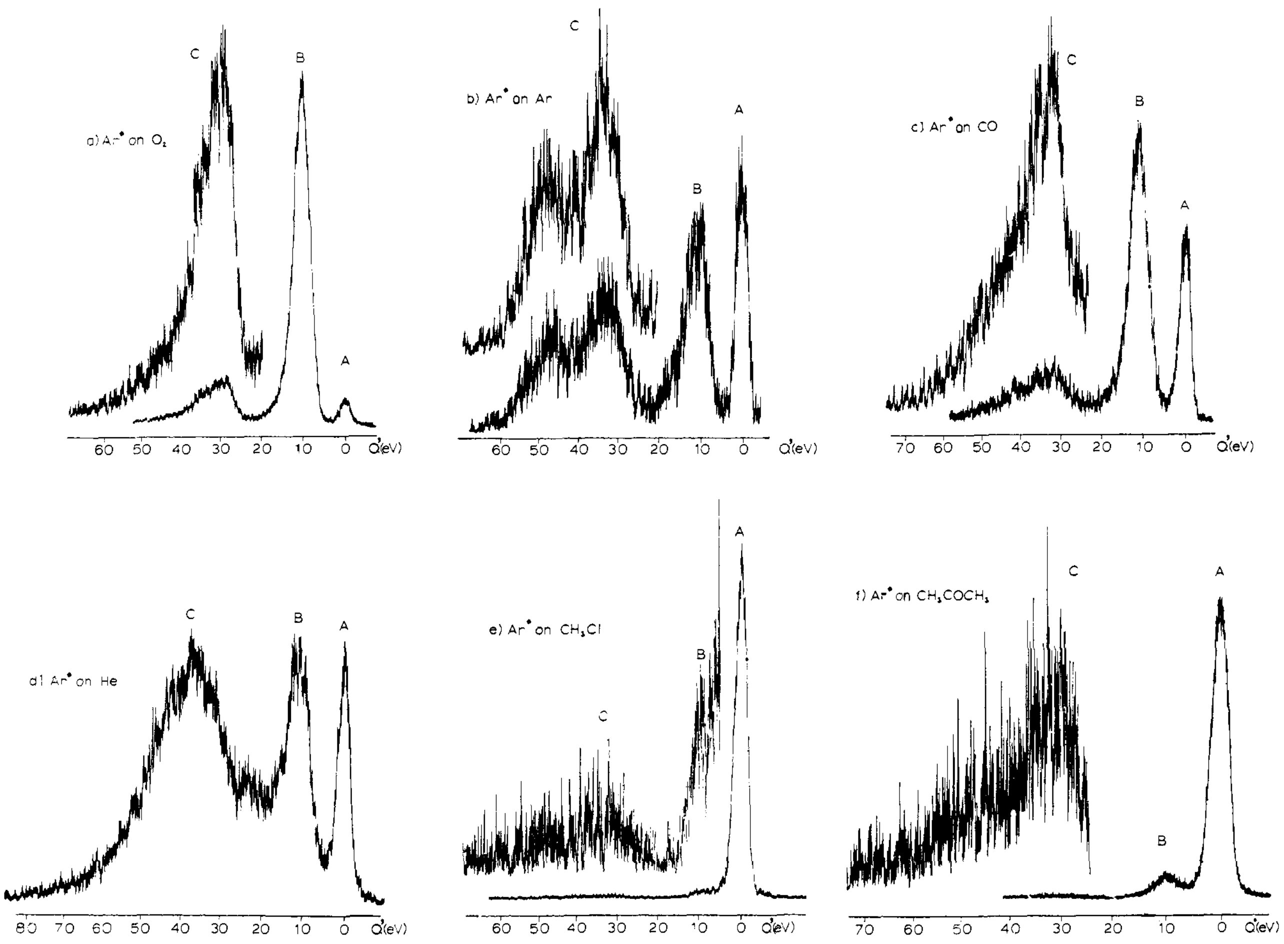

Figure 3. Ion kinetic energy loss spectra of Ar^+ ions undergoing the charge-stripping reaction with various collision gases.

netic energy V, but does not suffer reactive collisions. (This correction procedure is analogous to that employed in determining T, the kinetic energy release in unimolecular fragmentations.[21]) In practice, the width of peak A was very similar to the main beam width, and its center corresponded, within experimental error, to zero kinetic energy loss. Hence this peak served as an internal reference of peak width and position. Its use in this way gave results for peaks B and C which were indistinguishable from those found using the main beam standard.

Table I reports $Q'_{\min}$ values ($Q'_{\min}$ is defined as the Q' value of the peak onset corrected for the half main beam width at base line) for peaks A, B, and C for all rare gases using air as collision gas. Table II provides the same data for argon ions using several different collision gases, and it also provides data on peak widths. Tables III and IV illustrate the effects of collision gas pressure and accelerating voltage upon the relative intensities of peaks A–C. Table V traces the collision gas pressure dependence of peaks A, B, and C individually over a wide pressure range in a typical case.

The accuracy and reproducibility of the kinetic energy loss measurements were largely determined by the accuracy with which the accelerating voltage could be measured, the stability of this voltage, and the energy resolution available. A stability of better than 100 ppm as measured on a differential voltmeter was usual in the course of an experiment lasting several hours. Short-term stability was better than 10 ppm. Reproducibility of kinetic energy loss measurements was better than 1 eV, even when measurements were made on different occasions.

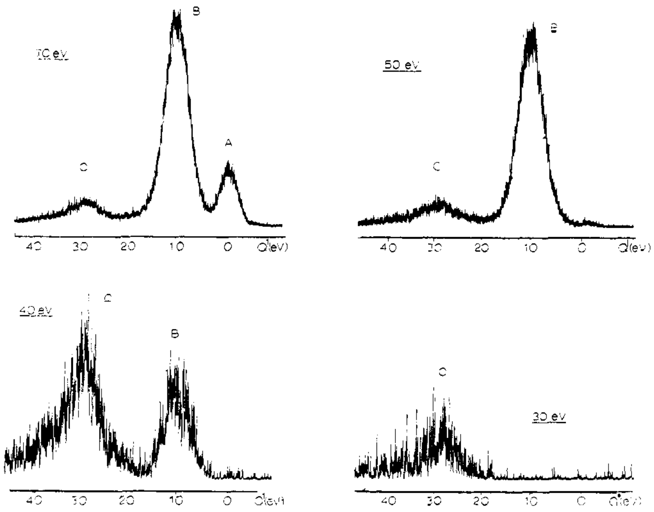

Figure 4. Ion kinetic energy loss spectrum of Ar^+ ions obtained at various ionizing electron energies using air as collision gas.

The sensitivity of the measurements is best seen from the signal-to-noise characteristics of Figures 2–5. In most cases these spectra were not taken at maximum

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(21) J. H. Beynon, R. M. Caprioli, and T. Ast, *Org. Mass Spectrom.*, **5**, 229 (1971).

Table II. Effect of Various Collision Gases on $Q'_{\min}$ and Peak Width in Argon[a]

Collision gas	Peak A		Peak B		Peak C	
	$Q'_{\min}$	Width[b]	$Q'_{\min}$[c]	Width[b]	$Q'_{\min}$[c]	Width[b]
N_2	0[d]	2.9	9.1 ± 0.8	4.2	28.1 ± 1	12.0
O_2	0	3.0	8.9 ± 0.8	4.6	26.9 ± 1	10.1
Ar	0	3.2	9.3 ± 0.8	6.0	27.7 ± 1	9.9
CO	0	3.0	8.9 ± 0.8	5.2	27.5 ± 1	14.7
CO_2	0	3.0	9.3 ± 0.8	5.8	27.1 ± 1	15.2
He	0	3.2	8.5 ± 0.8	*e*	27.1 ± 1	20.5
CH_3Cl	0	3.3	*f*	*f*	*f*	*f*
1-Butanol	0	3.0	8.2 ± 0.8	5.7	*f*	*f*
Acetone	0	3.3	8.1 ± 0.8	5.3	27.9 ± 1	10.3
CCl_4	0	3.3	8.5 ± 0.8	4.6	27.5 ± 1	*e*

[a] All data are given in eV. [b] Measured at half-height and not corrected for the main beam width. Probable errors are 0.3 eV for peaks A and B and 2 eV for peak C. [c] The $Q_{\min}$ values have probable errors of 0.8 eV (peak B) and 1.0 eV (peak C). [d] The values in this column are in each case zero within ±0.3 eV. [e] Peak overlap occurred. [f] Signal too weak to allow measurement.

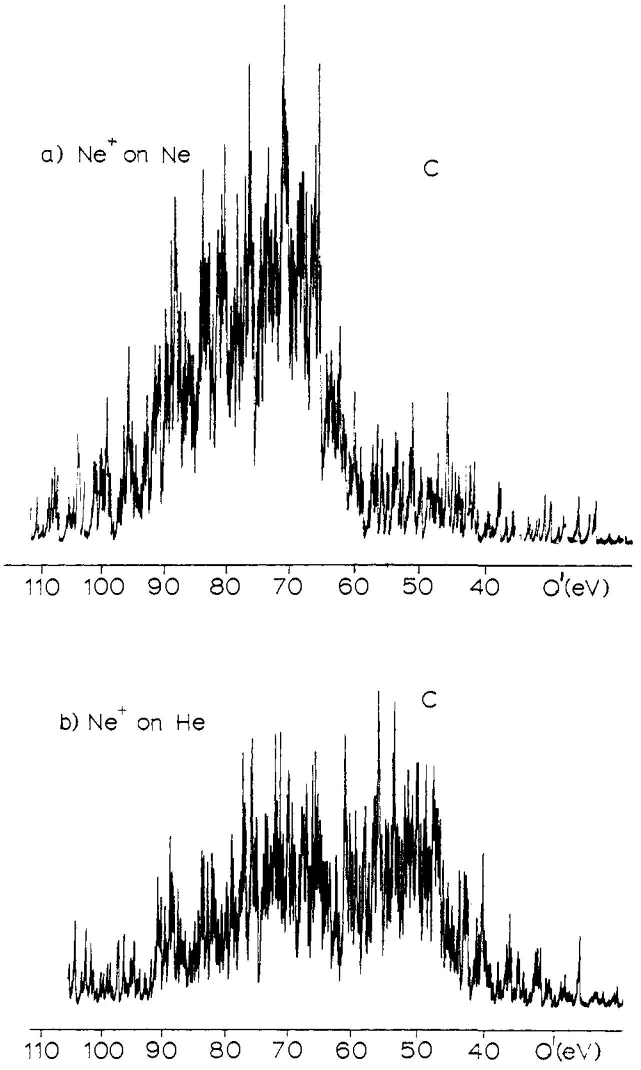


Figure 5. Partial ion kinetic energy loss spectra of Ne^+ ions showing the occurrence of collision gas ionization $Ne^+ + Ne \rightarrow Ne^{2+} + Ne^+ + 2e^-$.

Table III. Collision Gas[a] Pressure Dependence of Relative Abundances of Peaks A, B, and C in Krypton

Pressure, Torr	Relative abundances A:B:C
4×10^{-7}	100: *b*: *b*
9×10^{-7}	100: *b*: *b*
3×10^{-6}	55:40: 5
7×10^{-6}	40:54: 6
3×10^{-5}	28:64: 8
6×10^{-5}	23:67:10
1×10^{-4}	23:66:11

[a] Air was used as collision gas. [b] No measurable signal obtained.

Table IV. Accelerating Voltage Dependence of Relative Abundances of Peaks A, B, and C in Krypton[a]

Accelerating voltage, keV	Relative abundances A:B:C
8	28:64:8
6	41:56:3
4	61:39:*b*

[a] Air was used as collision gas. [b] No measurable signal obtained.

Table V. Collision Gas[a] Pressure Dependence of Abundances of Peaks A, B, and C in Krypton

Pressure, Torr	Abundances (arbitrary units) A	B	C
4×10^{-7}	36	*b*	*b*
9×10^{-7}	38	*b*	*b*
3×10^{-6}	45	12	5
7×10^{-6}	59	27	14
3×10^{-5}	100	86	96
6×10^{-5}	90	100	100
1×10^{-4}	83	76	100

[a] Air was used as collision gas. [b] No measurable signal obtained.

instrument sensitivity. The total ion current due to products of the charge-stripping reaction was, at optimum pressures, typically about 10^{-5} of the signal due to nonreacting singly charged rare gas ions.

Discussion

Peak Shapes. First, one must examine the meaning of peak positions and peak widths in the kinetic energy loss spectra. The basic process under consideration, conversion of kinetic to internal energy, is the reverse of that normally studied in unimolecular and collision-induced ionic fragmentations in the field-free region. Peak positions measure directly the kinetic energy lost by the reactant ions or, more accurately, the exact kinetic energy which must be supplied to these ions to make up for the impending loss and so permit passage through the electric sector. If the reactant ions suffer small deflections on collision, their energies are still accurately measured by the electric sector.

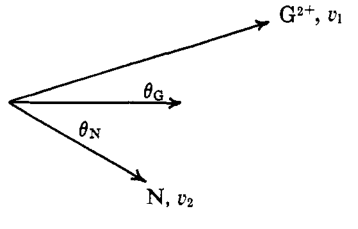
What peak widths should result if a single sharply defined kinetic energy were lost in a charge-stripping reaction? The nonreactant ion beam has a finite kinetic energy spread as it emerges from the source, and the peak due to this nonreacting beam is further broadened by elastic collisions in the field-free region. Hence the ions G^+, which are formed in the source, accelerated through voltage V, and traverse the instrument in the presence of a given collision gas at a given pressure, provide a standard for the intrinsic peak width. The validity of this argument is demonstrated by the fact that all the rare gases showed a peak (A) due to ions undergoing the charge-stripping reaction with essentially no kinetic energy loss, and this peak had essentially the same width and shape as that due to the nonreactive G^+ ions.

Given that we have a measure of the intrinsic peak width we must inquire into the origin of broadening and the possible operation of discrimination against ions which suffer large kinetic energy losses and angular deflections. The kinetic energy (Q') lost by G^+ ions, in excess of that required to form double ionized G^{2+}, may appear as kinetic energy of N, kinetic energy of the electron, or internal energy of N or of G^{2+} ions. In the general case there will be several processes occurring, separately or together, and a rather complex distribution of Q' values can be expected. The distribution is expected to be broader for processes which have large Q'_{min} values, and, in addition, the cross sections for such processes are expected to be smaller than those for cases in which Q'_{min} is smaller.

Turning from the actual distribution of Q' values to the measured distribution, one confronts the question of instrumental discrimination. This depends largely upon the kinetic energy acquired by the collision partner, since this is the factor which largely determines the angular deflection of G^+ after ionization to G^{2+}.

Consider the situation before collision,

After an inelastic collision, we have



assuming N and G^+ are point masses and ignoring the ejected electron as irrelevant in a discussion of momenta. Now, applying the law of conservation of momentum at right angles to the direction of motion of the center of mass

$$\begin{gathered} 0 = m_G v_1 \sin\theta_G - m_N v_2 \sin\theta_N \\ v_2/v_1 = (m_G/m_N)(\sin\theta_G/\sin\theta_N) \end{gathered} \tag{6}$$

The value of θ_G, and hence the instrumental discrimination, is therefore dependent upon the ratio m_G/m_N.

The experimental results show that the width of peak C, and to a smaller extent peak B, is dependent upon the m_G/m_N ratio. For example, in Figure 3, Ar^+ with He as collision gas ($m_G/m_N = 10$) shows a substantially broader peak C and hence less discrimination than is found for Ar^+ using other collision gases (m_G/m_N 0.5–2). Again, Figure 2 shows that using air as collision gas the heavier rare gases, with larger m_G/m_N ratios, give a broader peak C. The same principles are also seen to operate in experiments in which the accelerating voltage was varied. At low ion kinetic energies discrimination, if present, should become more apparent leading to narrower peaks, which, indeed, was observed. One must therefore conclude that the shape of peak C is subject to appreciable discrimination effects resulting from kinetic energy transfer to the collision partner, N.

We have so far discussed the effect of the ratio m_G/m_N upon the discrimination against the products G^{2+}, *i.e.*, the effect upon θ_G (eq 6). We can now consider the effects of v_2 upon the angular deflections θ_G and θ_N. As the kinetic energy acquired by the collision partner, N, tends to zero, so v_2 tends to zero, and θ_G tends to zero. Hence, since the instrumental geometry fixes the maximum θ_G which can give observable G^{2+} ions, instrumental discrimination decreases as the kinetic energy acquired by the collision partner, N, decreases. By contrast, internal energy acquired by N does not contribute to v_2 and therefore does not cause discrimination.

In summary, the peak broadening observed on the high energy side of all the peaks is due to the collection of ions formed in collisions in which N, e^-, or G^{2+} has received excess energy. Among these processes, those in which N receives kinetic energy are discriminated against, and the experimental results suggest that this process is an important contributor to the reactions in which excess energy is involved. The relative abundances of peaks A, B, and C do not therefore represent the relative number of ions undergoing each reaction and only at the onset for each process ($Q' = Q'_{\text{min}}$) can one be sure that discrimination is absent.

Finally, in this discussion of peak shapes, some comments on the extrapolation procedure for determining Q'_{min} are appropriate. The determination of Q'_{min} is a threshold measurement and therefore subject to well-known inaccuracies. It is satisfying, however, to see (*vide infra*) the measure of agreement between theory and experiment achieved using this procedure, and it must be noted that the quality of the data does not at this junction seem to justify more complex treatments of the onset values. The agreement achieved (Table II) when the same reaction was studied using different collision gases, which sometimes caused appreciable changes in peak shapes, is also satisfactory. One of the major reasons why this simple treatment works so well is that the signal usually rises very sharply from onset and the difference between Q'_{min} and the most probable Q value is frequently small.

Major Features of the Spectra. The major feature of all rare gas ion kinetic energy loss spectra is that they show three peaks (A–C) for all collision gases, except that He gives no observable peak B. The relative abundances and shapes of these peaks (especially that of peak C) vary with collision gas pressure, nature of the collision gas, accelerating voltage, and ionizing electron energy. On the other hand, the value of Q'_{min} for each peak shows very little variation with changes in these parameters. Indeed, the observed variations are often of the same order as the experimental uncertainty, and the question of whether or not real differences occur will be taken up in the detailed discussions which follow.

The variations in peak widths and shapes with the nature of the collision gas are most marked for peak C. Some of the reasons for this variation have already been mentioned; further discussion follows later. The variations in relative peak intensities accompanying changes in collision gas pressure or ion accelerating voltage (Tables III and IV) can be accounted for as manifestations of a single phenomenon, *viz.*, those reactions in which larger energy losses occur require stronger interactions with the collision gas and *vice versa*. (A strong interaction can be looked on as involving a closer approach of the two species. Note that strong is used here only in a relative sense.) Hence, as the collision pressure is increased, large energy loss (*e.g.*, peak C) should be favored over smaller losses (*e.g.*, peak B) which in turn should be favored over process A which seems to require only a very weak collision. This is exactly what is observed.

Given that peak C requires a stronger collision than B or A, it should be favored by an increase in accelerating voltage relative to the other peaks. Again this is what is observed; the abundance of peak C is far more sensitive to ion accelerating voltage than is that of either A or B. Indeed, even the relatively small change from 8 to 6 keV has an appreciable effect on the abundance of the product ions due to this process (Table IV).

The behavior of the individual peaks, A–C, with changes in collision gas pressure, shown in Table V, suggests that the processes leading to peaks B and C are bimolecular. Peak A, on the other hand, saturates earlier and appears to have an order somewhere between bi- and unimolecular. Later results bear this out well.

A final point in this outline of the main features of the processes under study concerns the effects of varying electron energy. The existence of three separate peaks in the rare gas spectra point to three well-defined energy states (or groups of states) of the reactant ions. It should therefore be possible to change the population of these states and to eliminate some entirely by lowering the energy of the ionizing electrons. Moreover, the largest energy losses should correspond to the most stable reactant ions; thus peak C should increase in abundance relative to B and A as the ionizing energy is lowered. This is shown to be so in the case of argon by the results of Figure 4, and the same behavior was observed in other rare gases.

Peak A: $Q'_{\mathrm{min}} \approx 0$. The fact that no energy loss apparently occurs when doubly charged ions are formed is the most striking feature of the process or processes which give rise to this peak. The reactant state or states of the singly charged ion must therefore have internal energies very close to the second ionization potential of the rare gas in question and they must also have lifetimes of 5×10^{-6} sec or more.[18]

Peak A could always be observed at background first field-free region pressures (4×10^{-7} Torr at *ca.* 1×10^{-5} sample pressure). Moreover, with most collision gases, only a moderate increase was seen (Table V) as this pressure was raised to 5×10^{-5} Torr (at higher pressures the signal decreased, presumably due to scattering). Thus, for a 100-fold pressure increase, the Kr^+ upon air signal increased by a facor of 3, while the Ar^+ upon air signal increased by a factor of 8. Hence, it seems that both a unimolecular and a collision-induced reaction is involved in generating peak A, with the latter the less important.

Support for this hypothesis came from studies in which polar collision molecules were used. In these cases, *e.g.*, Ar^+ on methyl chloride, peak A showed a near-linear increase with pressure, and at optimum pressures it was approximately ten times more abundant than, for example, in the case of Ar^+ upon Ar (see Figure 3e where peak A completely dominates the spectrum). It seems that polar target molecules are particularly effective in producing the perturbation needed for collision-induced ionization and can be used to obtain a spectrum in which the bimolecular process is dominant. It is significant that Q'_{min} under these conditions was indistinguishable from Q'_{min} under unimolecular conditions, pointing to the fact that both reactions occur from states of identical or near-identical energies. Furthermore, the width of peak A under conditions favoring the unimolecular reaction was nearly identical with that under conditions in which the gas-phase collision was dominant (see Table II).

Complementing the evidence, taken from the Q' values, that peak A is due to reactions of states of the singly charged ions having energies very close to the second ionization potential, are data on the effects of varying the ionizing electron energy. Thus, peak A is only seen in helium spectra when the energy of the ionizing electrons is in excess of $\sim$80 eV. For neon, the peak disappears at energies below 70 eV, but for xenon it is pronounced even at 40 eV. In the case of argon (Fig. 4) peak A decreases sharply in intensity below an ionizing voltage of 50 eV (the theoretical threshold is 43.4 eV). All of these results are in agreement with expectation based on the values of the second ionization potentials of the rare gases (Table I).

It is possible to arrive at a fairly complete interpretation of the above results in terms of the three mechanisms (i–iii), noted in the introductory section. First, the autoionization process should give $Q'_{\mathrm{min}} = 0$. The pseudo-unimolecular slit-interaction mechanism (ii) and the collision-induced process (iii) both represent instances in which only very slight perturbations are required to cause a reaction. If, as has been suggested, these reactions do occur from Rydberg levels, then the energy which must be supplied will be at most a few tenths of an electron volt.[22] Thus for both these processes, $Q'_{\mathrm{min}} \approx 0$. Both these processes, which we consider mechanistically to be essentially identical, could be accompanied by some peak broadening due to energy transfer to the target. The results (Table II) suggest that any such effect is too small to be measured. The transition from G^+ to G^{2+} therefore involves a vanishingly small perturbation, brought about by either a gaseous or a solid target.

Thus mechanism iii definitely occurs and is dominant if a polar collision gas is used at pressures $>10^{-5}$ Torr. In the absence of a polar collision gas mechanism iii is

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(22) Compare the life-time calculation for Rydberg levels in He^+ given by Hagstrum.[23]

(23) H. D. Hagstrum, *Phys. Rev.*, **104**, 309 (1956).

less important. Under our experimental conditions, the autoionization process i is expected to give results which are indistinguishable from those for process ii.

While we have interpreted our results on the gas-phase collision reaction as supporting the idea that Rydberg states are involved, the suggestion[15] that (for Ne^+ at least) other states in the energy vicinity of the second IP may be involved cannot be excluded. The fact that Rydberg levels are the only possibility for helium[14a] and the close similarities in behavior of all the rare gases prompt our partiality toward this explanation.

Peak B: Q'_{min} 7–13 eV. This peak occurs in all the rare gases except helium. In neon it is of significantly lower abundance (relative to peak A, which presumably has the same mechanism(s) in the different gases) than in the heavier gases. The experiments in which electron energy, ion accelerating voltage, and collision gas pressure were varied, all showed the behavior of peak B to be intermediate between those of peaks A and C. This suggests that the peak arises from reaction of an excited state of the singly charged ion which has lower energy than that of the states which give rise to peak A. These experiments also make it unlikely that the reaction involves the Rydberg states accompanied by ionization of the collision gas. Indeed, this alternative is untenable since Q'_{min} is approximately constant when different collision gases are employed (Table II).

While the minimum energy loss is apparently independent of the nature of the collision gas, the distribution of Q' is not; hence there is some variation in the widths and shapes of peaks B (this is even more pronounced for peak C). It is probable that Q' values greater than Q'_{min} are not due in any large measure to the formation of doubly charged ions in higher energy states. Certainly, the formation of excited doubly charged ions is not detectable in process A and there is evidence (next section) that they contribute little, if at all, to process C. Hence kinetic energy transfer to the target gas or the electron or excitation of the target is indicated.

If Q'_{min} corresponds to reaction without any product excitation, then it provides a direct measurement of the energy of the reactant state of the singly charged ion. Ar^+, Kr^+, and Xe^+ have well-characterized long-lived states whose energies match very well those determined from Q'_{min}. These states ($^4D_{7/2}$, $^4F_{9/2}$, $^4F_{7/2}$, and $^2F_{7/2}$) have energies[23] of 32.16, 33.38, 33.45, and 34.25 eV, respectively, in Ar^+. The ionization energies of these states are therefore 11.22, 10.00, 9.93, and 9.13 eV. If all four states were involved in reaction 2, a quartet of peaks would be observed in the energy loss spectrum. In practice, only a single peak is seen (discussed further in the section on fine structure, below), its onset (8.9 eV) corresponding closely with that predicted (9.13 eV) for the first peak in the quartet. In Kr^+ and Xe^+ the same four states are also long-lived and closely spaced. The highest energy state in this group in Kr^+ ($^2F_{7/2}$, 30.32 eV) leads to an expected Q'_{min} of 8.24 eV (found 7.6 eV); in Xe^+ the same state should give Q'_{min} 6.97 eV and the observed value was 6.9 eV.

The occurrence of peak B in neon, when none was expected on the basis of the known metastable states of Ne^+, is significant. Although relatively weak, the peak could be seen clearly with several collision gases. If the assumption of no excess energy transfer to products at Q'_{min} is correct in this case, the state has an energy relative to the ground state of the atom, of 49.3 ± 1 eV (27.7 ± 1 eV relative to the ground state of the ion). Using air as collision gas and varying the ionizing electron energy gave an onset of ~50 eV. We must therefore conclude that this peak does indeed represent a new long-lived state of Ne^+ with an average lifetime $\geq 5 \times 10^{-6}$ sec. All the states of Ne^+ in this energy region are known,[24] and the only ones which could be metastable are the $^4P_{5/2}$ and $^4P_{1/2}$ states at 27.16 and 27.26 eV, in good agreement with the observed value of 27.7 ± 1 eV. We might also note that Hagstrum's failure to observe this state was probably only due to sensitivity considerations, since his other observations are in good agreement with ours although he used an entirely different experimental technique.[23]

The good agreement between theory and experiment defines the states involved in the Ne^+, Ar^+, Kr^+, and Xe^+ reactions and also indicates that reaction without any product excitation or (because of experimental uncertainty) with very little such excitation has a high probability. This is in accord with the widely held view[25] that collision may involve interaction of the electrons of the two species with little momentum transfer to the nucleus of the collision partner.

The above discussion accounts for the behavior of the heavier rare gas ions, but He^+ seems to be exceptional. It does possess a metastable state ($2^2S_{1/2}$; energy 65.38 eV referred to the ground state of the atom)[21] in the defined energy range, but it gave no detectable peak B with any of the collision gases used in this experiment (air, oxygen, benzene, helium). Two possible reasons may be considered. First, this state is susceptible to Stark quenching and has a lifetime given by $t = (1.6 \times 10^{-2})E^{-2}$ sec, where E is field strength in volts/centimeter.[26] For this effect to reduce the lifetime to the order of 5×10^{-6} sec, a field strength of about 60 V/cm would be required. Under our experimental conditions the field strength in the accelerating region is about 5000 V/cm leading to $t \approx 10^{-9}$ sec. The ions spend far more time than this in this region hence Stark quenching will be complete. Second, this metastable state is formed with lower efficiencies than are those in the heavier rare gases. This was one reason why Hagstrum, in an Auger electron emission experiment,[24] could not detect this state while he could study the metastable states in Ar^+, Kr^+, and Xe^+.

Peak C: $Q'_{min} > 20$ eV. The Q'_{min} values for peak C (Table I) are in excellent agreement with the difference between the first and second ionization potentials of the rare gases. Thus ground-state rare gas ions react to form ground-state doubly charged ions, and there is often a high probability that this reaction will occur with essentially no energy transfer to the collision gas or to the ejected electron. This lack of energy transfer is analogous to the situation observed for process B, discussed above. Thus, as expected, it

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(24) W. Persson, *Phys. Scr.*, 3, 133 (1971).

(25) (a) H. M. Rosenstock and C. E. Melton, *J. Chem. Phys.*, 26, 314 (1957). Compare also Q. C. Kessel, Abstracts, Sixth International Conference on the Physics of Electronic and Atomic Collisions, Cambridge, Mass., 1968, p 751; (b) J. Durup, *Recent Develop. Mass Spectrosc., Proc. Int. Conf. Mass Spectrosc., 1969*, 921 (1970).

(26) W. E. Lamb and M. Skinner, *Phys. Rev.*, 78, 539 (1950).

was found that change in the nature of the collision gas did not affect the $Q'_{\min}$ value (Table II).

On the other hand, many collisions are accompanied by kinetic energy transfer to the products or by excitation of the collision gas, and changes in the shape of peak C in argon with different collision gases (Figure 3) reflect variations in this excess energy. The differences in distributions of Q' values, as measured by the peak width at half-height, are given in Table II. It is noteworthy that peak C in helium shows no pronounced differences in shape from that in the other rare gases, an indication that excitation of the doubly charged product ion (impossible for He^{2+}) is not an important part of the excess energy loss.

A particularly interesting feature of peak C in argon was the appearance of a distinct second maximum shifted upwards in energy by some 16 eV.[27] This peak was clearly defined only when argon itself was used as collision gas (Figure 3b). It was shown, by detailed studies on the corresponding neon reaction, to be the result of ionization of the collision gas, as expressed in the general reaction 7. The occurrence of the 10/21

$$G^+ + N \longrightarrow G^{2+} + N^+ + 2e^- \qquad (7)$$

reaction 7 should not be surprising since it is in a sense merely a generalization of 10/20 reaction 2 in which N is formed in a particular excited state.

Evidence for the occurrence of reaction 7 in the neon spectrum is as follows. When neon is used as collision gas, a second maximum appears in peak C, but it dominates the peak and the signal due to reaction 2 is only seen at high sensitivity (Figure 5a). Furthermore the new peak itself shows a steep onset, is fairly broad, and is shifted some 20 eV from the normal peak C. Thus, the total loss in kinetic energy represented by the threshold of this peak is ~60 eV, which is in agreement with the energy requirements for the reaction

$$Ne^+ + Ne \longrightarrow Ne^{2+} + Ne^+ + 2e^- \qquad (8)$$

It is interesting to note that reaction 8 has such a large cross section that it was observed with good sensitivity even when other collision gases were employed. Leakage of neon from the source into the first field-free region was enough to cause a significant signal resulting from reaction 8. As can be seen from Figure 5b, this signal is about equal in intensity with the normal peak C arising from reaction 2. To check the assignment that the second part pf peak C was indeed due to reaction 8, the neon source pressure was gradually decreased in an experiment where air was used as collision gas. This resulted in a decrease of the second part of peak C relative to its first part.

The cross section for collision-gas ionization accompanying charge-stripping was large only when the same rare gas was used as reactant ion and as collision gas. Apparently some element of resonance is involved in reaction 8. This may be related to the enhanced propensity for ionization of the collision partner to occur when the two species have similar masses.[28] It is also significant that reaction 7 was dominant in neon and the corresponding reaction was important in argon but difficult to distinguish for the other rare gases. The high first ionization potential of helium coupled with the large energy requirement for the process $He^+ \rightarrow He^{2+}$ may partly explain why this case is exceptional, but other factors must be operative to account for the krypton and xenon results. This may be related to the superior ability of lighter elements to cause greater energy transfers in adiabatic collisional excitation processes.[29]

Fine Structure in Energy Loss Spectra. Only the major features of the distributions of Q' values have been discussed above. In addition to peaks A–C, very low intensity peaks at intermediate positions appeared occasionally in some spectra. For example, when Ar^+ reactions with He collision gas were studied (Figure 3d), a weak peak could be observed between peaks B and C. It has not, however, proved possible to study these features at the available signal strength.

Careful examination of some of the peaks A–C reveals details in their appearance which we believe to represent fine structure. This is especially true for peaks C, and, to some extent, peak B.

Consider, for example, peak C in xenon (Figure 2e). As already discussed, this peak represents the transition in which ground-state Xe^+ ions lose an electron upon collision to become Xe^{2+} ions. However, the ground state of Xe^+ is a doublet designated $^2P_{1/2}$ and $^2P_{3/2}$. The energy difference between these two states is 1.3 eV; this difference should be reflected in the amount of energy required to produce Xe^{2+} ions in reaction 2, and, consequently, should be observable in the kinetic energy loss spectrum of Xe^+. Indeed, peak C in xenon shows two sharp onsets, separated by approximately 1.8 eV. This difference is very difficult to determine with any degree of confidence at our present level of energy resolution; therefore, we hesitate to postulate the above assignment conclusively. The two corresponding ground states of Kr^+ are separated by 0.7 eV; Figure 2d shows the fine structure observed in that case. For Ar^+ the energy difference between the two ground states becomes too small to distinguish.

Besides the two main features of peak C in Ar^+ upon argon (Figure 3b), there seems to be an intermediate peak, shifted by approximately 11.5 eV from the onset of peak C. We believe that it is due to the reaction

$$Ar^+ + Ar \longrightarrow Ar^{2+} + Ar^* + e^- \qquad (9)$$

where the value of ~11.5 eV represents the formation of the doublet $^3P_0$ and $^3P_2$ excited state of neutral argon (11.6 eV).

Further indications of fine structure are presented by the shape of peak B in some spectra (see, for example, Figure 2e). As discussed above, this peak represents the transition to the doubly charged ion from a collection of four closely spaced (1.4–2.4 eV) states of the singly charged ions, and the onset of peak B is in very good agreement with the transition from the highest level of the group. Structure on the high-energy side of B could represent transitions from other states within this group, but accurate measurements and assignments, again, were not possible.

Conclusions

The value of ion kinetic energy spectrometry as applied to the study of charge-stripping reactions

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(27) The onset of this peak was more difficult to establish than usual because of overlap from the peak due to reaction 2.

(28) H. S. W. Massey and E. H. S. Burhop, "Electronic and Ionic Impact Phenomena," Oxford University Press, London, 1952, p 532.

(29) J.-C. Houver, J. Baudon, M. Abignoli, M. Barat, P. Fournier, and J. Durup, *Int. J. Mass Spectrom. Ion Phys.*, **4**, 137 (9170).

resides largely in two features: (i) the energies of long-lived ionic states can be defined; (ii) mechanistic detail, including that involved in the conversion of kinetic to internal energy, is made available for study. As applied in the present study, IKES has produced a much more complete knowledge of the rare gas charge-stripping reactions than previously possessed, particularly by separating the reactions of the different forms of the rare gas ions. It has also led to the identification of a previously undetected long-lived state of Ne^+.

Our experimental method is, however, relatively simple and is limited particularly by the fact that only processes leading to small scattering angles can be studied. Although this feature obviates any quantitative cross-section work, discrimination does not affect those processes in which the target receives no kinetic energy, and the onset measurements therefore provide reliable data on the internal energies of the reactant ions.

The advantage of the present technique over high resolution electron spectrometry is that we select only long-lived states for study. There are many applications of ion beams in which the composition at times of the order of microseconds is important.

It is worth emphasizing that the energy loss spectra (Q' distributions) obtained in the present study reflect energy states of the reactant ion (with the exception of the 10/21 component of peak C). Energy loss spectra (Q distributions) obtained by coincidence techniques[8,17] can also show multiple peaks, but in all the cases studied to date these peaks are associated with different energy levels of the *product*, not the reactant species.

We find that singly charged rare gas ions exist in three states (or groups of closely spaced states) which are long-lived and which can undergo charge-stripping on interaction with a neutral species to give the doubly charged rare gas ions. The states involved are the ground state, a group of states of energy 7–13 eV less than the second ionization potential, and a group of states with energies very similar to the second IP. This last group reacts by at least two mechanisms. One, collision with a gaseous species, is thought to involve the higher Rydberg states and is analogous to the reactions leading to peaks B and C. The other is a unimolecular or quasi-unimolecular process in which interaction of the Rydberg states with metal (slit) surfaces is assumed. Possibly the autoionization process observed by others[12,13] for states with energies slightly in excess of the second ionization potential also contributes to this process.

The sharp onsets normally observed for each peak in the kinetic energy loss spectrum also indicate that the reactant ion exists in a single state or a set of closely spaced states. The good agreement between the measured energies of the states and literature data indicates that charge-stripping can occur with very little energy transfer to the collision gas or the ejected electron. At the same time, other collisions leading to charge-stripping are accompanied by extensive energy transfer and even by ionization of the collision gas. The prediction that Q' values in excess of $Q'_{\min}$ would tend to be associated with large $Q'_{\min}$ values is borne out by the fact that peak widths increase in the order $A < B < C$.

Our results appear to be consistent with the theory of Massey and Hasted on inelastic collisions.[30] In particular, our observation that $Q'_{\min}$ values for peaks B and C correspond to adiabatic or near-adiabatic transitions is expected for ion energies in the low keV range, since for the large Q' values involved, maximum cross-sections should occur at $Q' = Q'_{\min}$.

Supplementary measurements which helped establish the reaction mechanisms and energies of the reactant ions were ionizing electron energy variation, changes in source and field-free region pressures, changes in ion accelerating voltage, and finally changes in the nature of the collision gas. Although the ionizing electron energy measurements were not very accurate, they gave results which agreed well with the ion internal energies established from the energy loss spectra. Changes in collision gas produced two observations which have not been explained. First, reaction of the Rydberg states is apparently favored by a polar collision gas; second, reaction of the intermediate energy states ($^4D_{7/2}$, $^4F_{9/2}$, $^4F_{7/2}$, $^2F_{7/2}$) in Ar^+, Kr^+, and Xe^+, and the new state in Ne^+ is favored by oxygen as collision gas.

Acknowledgment. We thank the National Science Foundation (GP-16743) for support, and Dr. E. G. Jones and Dr. M. Bertrand for helpful discussions.

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(30) (a) H. S. W. Massey, *Rep. Progr. Phys.*, **12**, 248 (1949); (b) J. B. Hasted, *Proc. Roy. Soc. Ser. A*, **212**, 235 (1952). Compare also N. F. Mott and H. S. W. Massey, "The Theory of Atomic Collisions," 3rd ed, Oxford University Press, London, 1965, p 685.