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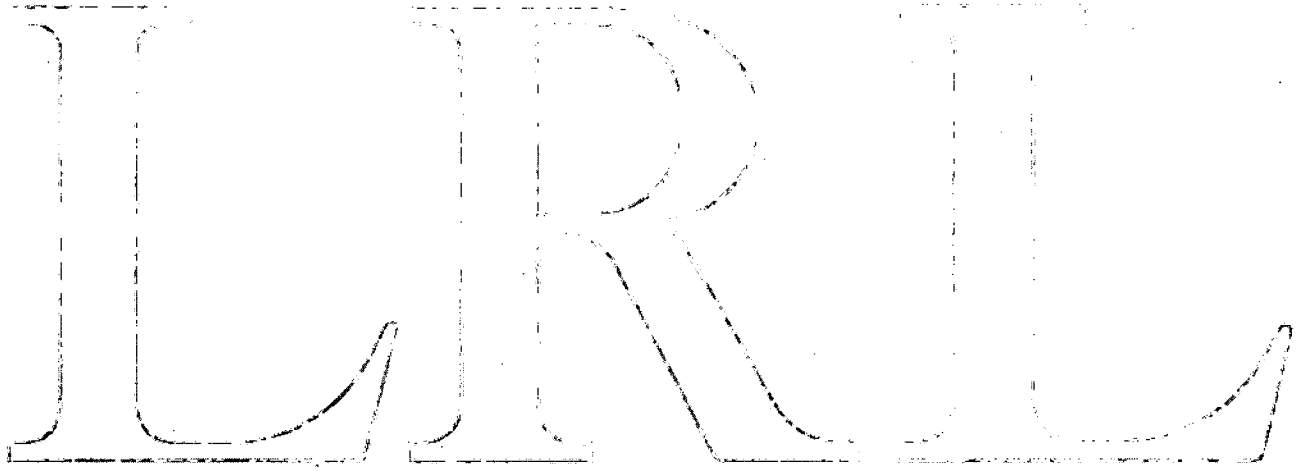

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The Chemistry of Gaseous Ions

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As we all know, the stoichiometry, energetics, equilibrium constant, and net rate of a reaction, while extremely useful to us, still do not constitute a complete description of a chemical process. Motivated by various needs and interests, we are always asking how chemical reactions occur, and regardless of the detail of the description given, we are rarely satisfied with it. It is the job of the chemical kineticist to supply these descriptions in various detail, and in some cases to reduce the phenomena of chemical reaction to a problem in molecular physics. Here I shall recount our efforts to elucidate the chemistry of gaseous ions through investigations of the energetics, rates, mechanisms, and molecular dynamics of their reactions.

Photochemical Ionization

It is well known that gaseous ions can be produced by the impact of energetic electrons and photons on molecules. In addition, however, ions and electrons can be produced by chemical reaction between particles of low kinetic energy. A particularly simple example, and one which we investigated a few years ago is the photosensitized ionization of gaseous alkali metals.[1] If cesium is photo-excited to one of its

electronic states with principal quantum number equal to 8 or greater, the following occurs

$$Cs\ (62) + h\nu \rightarrow Cs^*\ (np)$$

$$Cs^*(np) + Cs \rightarrow Cs_2^+ + e^- \qquad n \geq 8 \qquad (1)$$

$$Cs^*(np) + Cs \rightarrow Cs^+ + Cs^- \qquad n \geq 12 \qquad (2)$$

The energy of photon is insufficient to ionize the cesium atom, but the extra energy necessary for ionization can be supplied either by the bond energy of Cs_2^+ as in reaction (1), or by the electron affinity of Cs as in reaction (2). From a knowledge of the ionization energy of Cs, and the energy of the photon needed to initiate reaction (1), it is possible to deduce a lower limit for the bond energy of Cs_2^+. We did this for Cs_2^+, Rb_2^+, and K_2^+, and found that the one electron bonds in these molecules are at least 30 to 50% stronger than the corresponding two electron bonds in Cs_2, Rb_2, and K_2. The same thing has been found for the lithium and sodium systems by other workers who used different techniques. This apparently abnormal situation seems to be an electron correlation effect. The bonds are so weak (~1 eV) that extra bond energy one might expect to derive from two electrons is more than cancelled by electron-electron repulsion.

In a similar manner, one may deduce that the lower limits of the atomic electron affinities for Cs and Rb are 0.19 and 0.20 eV, respectively. There are no other measurements with which our values for Cs and Rb, respectively, can be compared, but these results are quite similar in magnitude to

the electron affinities which have been calculated for Li, Na, and K by apparently reliable techniques.

Ion Mobility

When gaseous ions are subjected to an electric field they are accelerated. If collisions between the ions and surrounding neutrals occur, the individual ion velocities do not increase indefinitely, but instead fluctuate about a mean or drift velocity which characterizes the progress of the group of ions through the gas. The drift velocity per unit field strength is called the ion mobility, and the value of the mobility is a measure of the effectiveness of ion-molecule collisions in inhibiting ion transport. The nice thing about the ion mobility κ is that it is directly related to the ion-molecule interaction potential, which in the simplest case is determined principally by the polarizability α of the neutral molecule. The low temperature, low field strength limiting relation is

$$\kappa = 35.9/(\alpha\mu)^{1/2} \quad \text{cm}^2/\text{volt sec}$$

where μ is the ion-neutral reduced mass in amu, and α is in atomic units. The relation is simple because the ion-molecule collisions which occur most frequently and which dominate the mobility are grazing collisions in which the ion and neutrals pass at a distance of 8-10 Å. At these internuclear separations the ion-molecule interaction potential is closely represented by the ion-induced dipole term $V = -\alpha e^2/2r^4$, where e is the

fundamental charge, and r is the separation. By measuring the mobilities of Cs_2^+ in Cs, and Rb_2^+ in Rb, we found the polarizabilities of Cs and Rb to be 53 $Å^3$ and 40 $Å^3$, respectively. These enormous polarizabilities are in agreement with results of recent measurements by a totally different technique. They reflect the very large volume occupied with high probability by the valence electron in these atoms. Other more complicated potential functions can be tested by ion mobility measurements, and we can expect to see much more of this work in the immediate future.

Charge Transfer

When a fast beam of ions impinges on a slow moving target beam of the parent neutrals, so-called resonant charge exchange occurs with little momentum exchange:

$$Cs^+ \text{ (fast)} + Cs \text{ (slow)} \rightarrow Cs \text{ (fast)} + Cs^+ \text{ (slow)}$$

The effectiveness of this charge exchange process can be measured by the attenuation of the ion beam, which follows the Beer's Law expression

$$I = I_o \exp(-n \sigma \ell)$$

where I and I_o are the final and initial ion projectile beam currents, and n and ℓ are respectively the concentration of atoms in, and the thickness of, the neutral beam. The proportionality constant σ is the cross section for the charge transfer process, and is a function of the relative energy of the colliding particles. If the measured value of σ is multiplied by

$2/\pi$ and the square root taken, the result is a distance which is in a broad sense the distance to which the particles must approach in order for the probability of electron transfer in a collision to become equal to one-half. We have found that this effective electron transfer distance is 12 Å, and 9 Å for the Cs^+-Cs, Rb^+-Rb, and K^+-K systems, respectively, at 15 eV relative energy. In general, these distances increase with decreasing relative energy.

The cross section for this resonant charge transfer process may be expressed fairly rigorously in terms of the difference in energy between the bonding and antibonding states of the molecule ion. Thus we were able with our measured cross sections to test the accuracy of certain approximate methods for calculating the bonding-antibonding energy difference for large internuclear distance. The simple LCAO method fails at large internuclear separations, but when the proper approach is used, even with nodeless atomic wave functions, good agreement between experimental and calculated cross sections is obtained.

Ion-Neutral Associations

It is well known, of course, that ions in solution are often strongly attached to solvent molecules. Something of the nature of this solvation can be learned from gas phase studies. By photoionizing ammonia-helium mixtures at total pressures of from 1 to 10 torr and sampling the ions with a mass spectrometer, it is possible to measure the equilibrium constants of the reactions

$$NH_4^+(NH_3)_{n-1} + NH_3 = NH_4^+(NH_3)_n$$

where n ranges from 2 to 4. We have found,[4] as had Kebarle[5] in earlier work, that the equilibrium constant for adding the fifth ammonia is smaller by a factor of 1000 than the equilibrium constants for adding the fourth ammonia molecule. Similarly, we have been able to show that after two dimethyl amine molecules have added to the dimethyl ammonium ion, the equilibrium constant for further solvation reactions drops by a factor of approximately 500 at 20°C. Other of our studies with methyl and trimethyl amine have revealed analogous behavior which demonstrates that the first solvation sphere is completed when the maximum possible number of hydrogen bonds between nitrogen atoms have formed. The temperature dependence of the equilibrium constants indicate that the bond or association energy in the first coordination sphere is about 15 kcal, and about 5 kcal in the second sphere. As studies of this type are perfected, accurate single ion thermodynamic quantities will be forthcoming.

Reactions of Electrons

What happens to the electrons in an ionized gas? If only weak electric fields are applied, they fairly rapidly come to thermal equilibrium with the surrounding gas, and undergo neutralization and attachment reactions. If the ion concentration is fairly high, above 10^7 ions/cc, then ion-electron dissociative recombination occurs. An example is

$$e^- + NO^+ \rightarrow N + O \qquad k = 4.1 \times 10^{-7} \text{ cc/ion sec}$$

which is an important reaction in the upper atmosphere. We were able some years ago to make one of the first crude measurements of the rate constant of this reaction, which we see is about 10^3 times larger than even the rate constants of "fast" reactions between neutral molecules which proceed at "every collision." More recent and refined work of Gunton and Shaw, Weller and Biondi, and others has provided precise values of this rate constant over an extended temperature range.

The reason dissociative recombination rates can be so large is indicated in Fig. 1. Reaction corresponds to "switching" from a state of the free electron plus molecular ion to a dissociative state of the neutral molecule. This can occur when the "free" electron approaches to within several angstroms, let us say 5 Å, of the ion. The collision cross section for this approach is large--of the order of $25\ \pi$ Å^2 multiplied by $e^2/r_o\ kT$, the ratio of the Coulomb potential energy at 5 Å to the thermal energy kT. This latter factor is of order 100, so the reaction cross section is approximately 8×10^3 Å^2!

It is more common, however, for slow electrons to undergo attachment to electronegative species. The possibilities are nicely illustrated by

$$e^- + SF_6 \rightarrow (SF_6^-)^* \xrightarrow{M} SF_6 \qquad (3a)$$

$$\rightarrow SF_5^- + F \qquad (3b)$$

$$\rightarrow SF_5 + F^- \qquad (3c)$$

Process 3a is called electron capture, and the attachment energy must be removed by the inert third molecule M, just as in atom recombination. The processes 3b and 3c are examples of dissociative attachment reactions. They are in effect atom abstraction reactions by the simplest of free radicals, the electron. Many analogous reactions are now known.

By measuring the time dependent electrical conductivity of an ionized gas at microwave frequencies it is possible to follow electron concentration variations. Using this technique, we found[6] that the rate constant for the overall disappearance of electrons was 3.1×10^{-7} cc/sec, again a very fast reaction. As a matter of fact, for low energy particles there is a fairly well defined quantum mechanical limit to the size of a rate constant which is imposed by the De Broglie wavelength, and this reaction is very nearly as fast as the limit allows. Other attachment reactions are not as fast, but nevertheless relatively small amounts of electronegative gases will convert thermal electrons to negative ions very rapidly.

Ion Recombination

Given a collection of positive and negative gaseous ions, by what means and how fast do they recombine, or neutralize

each other? We have been able to show[7] that there are parallel bimolecular and termolecular neutralization processes. For example,

$$NO^+ + NO_2^- \rightarrow \text{neutrals } (NO^+,\ N,\ O,\ NO_2) \qquad (4)$$

$$NO^+ + NO_2^- \rightleftarrows (NO^+\ NO_2^-)^* \qquad (5)$$

$$(NO^+\ NO_2^-)^* + M \rightarrow NO^+\ NO_2^- + M \rightarrow \text{neutrals} \qquad (6)$$

In reaction 4, two ions come close enough so that the electron can be transferred back to the positive ion to form an electronically excited neutral. The rate constants that we have measured for such reactions are large ($\sim 2 \times 10^{-7}$ cc/ion sec), and show that electron transfer can occur when the ions approach to within 10-20 Å of each other. This rather large electron transfer distance is entirely consistent with the idea that electron transfer occurs when the Coulomb potential energy of the ions becomes equal to the energy of the neutrals when one of them is in a highly excited electronic state. The large characteristic radius for electron motion in these states ($r = 0.53\ n^2$ by the Bohr formula) is what makes the transition matrix element large even at large distances.

Recently, measurements of some bimolecular ion neutralization rates have been made by Aberth and Peterson at Stanford Research Institute by using mergered beams of ions. Although the systems are different, their results are generally consistent with our own.

If rapid bimolecular neutralization can occur, how can the higher order termolecular process contribute significantly to ion recombination? The answer lies in the extreme range of the Coulomb potential. Even when ions are separated by approximately 100 Å and electron transfer cannot occur, the ions are still interacting with an attractive Coulomb potential energy which is of the order of kT or greater. Consequently, collisions with neutrals can remove some of the relative energy of an ion pair, and cause them to become weakly bound. Eventually the bound pair will come close enough to undergo electron transfer. The number of ion-ion collisions that bring ions close enough to become bound by a third body encounter is much greater than the number that allow direct electron transfer. Consequently, the "three-body" process described by reactions 5 and 6 contributes to the recombination rate, and is the dominant path as soon as the gas pressure is greater than 10 torr at room temperature.

Our study of this "termolecular" ion recombination process taught us that even though third order, it is not termolecular at all! Instead of undergoing just one collision with a neutral to produce a permanently bound state, an ion pair experiences many collisions in which small amounts of energy are removed from and added to them in a random fashion. The result is a collision induced "diffusion" of the ion pair in energy space which leads the ions eventually to a permanently bound state.[8,9] It is likely that this many body deactivation actually occurs in many other recombination

processes that are thought to be termolecular.

Ion-molecule Reactions

Now we turn to the matter of metathetical ion-molecule reactions. There is already a vast chemistry here, and it is rapidly becoming more extensive. Because of the devices readily available to focus, mass- and energy-select and detect ions, these reactions are excellent for detailed studies of reaction dynamics. As examples, we have extensively investigated the reactions

$$Ar^+ + D_2 \rightarrow ArD^+ + D \qquad k = 1.40 \times 10^{-9} \text{ cc/sec} \qquad (7)$$

$$N_2^+ + D_2 \rightarrow N_2D^+ + D \qquad k = 1.8 \times 10^{-9} \text{ cc/sec} \qquad (8)$$

The rate constants of these reactions are large at thermal energies, and in pretty good agreement with the collision rate calculated using the ion-induced dipole potential. On this basis, the reactions appear to be very similar. However, use of molecular beam techniques to study the reactions over a wide energy range shows that while in some respects the similarities persist, in other respects the reactions are totally and unexpectedly different.

In order to see the basis of these ion beam experiments, consider Fig. 2, which shows what the trajectories of a projectile ion would look like if it were scattered from a target molecule fixed in space. The important thing to note is

that grazing collisions which sample only the weak part of the intermolecular potential produce small deflections ("forward scattering") of the projectile, while more nearly head on collisions give small distances of closest approach, strong interactions and large deflections of the projectile ("backward scattering").

This connection between scattering angle and type of collision persists even in reactive collisions so long as the interaction time between projectile and target is short compared to a rotational period. We[10,11] and others[12,13] have found that both reactions (7) and (8), as well as other exothermic hydrogen abstraction reactions, proceed by this short lifetime or "direct interaction" mechanism. However, for the more complex reaction

$$CH_3^+ + CH_4 \rightarrow C_2H_5^+ + H_2$$

Z. Hermann and R. Wolfgang found clear evidence that "sticky" collisions occur in which the collision complex lasts several rotational periods. In such cases the correlation between scattering angle and type of collision is largely lost.

Figure 3 shows some of our experimental results for the Ar^+-D_2 reaction. This is a contour map of the intensity of ArD^+ plotted as a function of its speed relative to the center of mass of the Ar^+-D_2 system, and the angle through which the product has been scattered relative to the original direction of the Ar^+ projectile. The very high intensity peak near zero scattering angle shows that most of the ArD^+ is formed

in grazing collisions in which little or no impulse is imparted to the freed D atom. This remarkable type of process is called spectator stripping, since the freed D atom appears merely to stand and watch while its partner is stripped away.

Figure 3 does show, however, that there is a detectable amount of scattering of products through angles as large as 180°. Thus, head-on collisions also give the ArD^+ product, but in low intensity because head-on collisions occur much more rarely than grazing collisions. It appears then that if there is a long range interaction that permits atom transfer in grazing collisions to occur with high probability, forward scattering will dominate, and the reaction cross section and rate constant will be large.

Besides intensity, there is another important difference between products formed by head-on and grazing collisions. Measurement of the product kinetic energy and use of the energy and momentum conservation laws shows that ArD^+ formed by grazing collisions is highly excited internally--very nearly to its dissociation limit. The ArD^+ formed by head-on collisions is also internally excited, but to a significantly lesser degree--about half of its dissociation limit. Apparently the strong interaction between all particles which occurs in head-on collisions allows the incipient ArD^+ convert some of its internal energy to relative translational energy as ArD^+ and D start to leave the scene of the collision. We have found the same difference in internal excitation energy of

the forward and back scattered products of the N_2^+-D_2 reaction.

Still another difference between grazing and head-on collisions is revealed by isotope effects. In the N_2^+-HD reaction, N_2H^+ is favored by factors as large as 20 in grazing collisions, but for head-on collisions, N_2D^+ is favored by a factor as large as 2. As yet, there is no complete, detailed explanation for these isotope effects.

It is helpful to examine the distribution of Ar^+ scattered by D_2 without reaction. A contour map of this nonreactive scattering is shown in Fig. 4. The most remarkable feature is the intensity at 180°, which represents Ar^+ which has made a head-on collision with D_2 and failed to react. By comparing Figs. 3 and 4 we can see that the numbers of reactive and non-reactive collision are quite comparable. This finding refutes the idea so often applied to all exothermic ion-molecule reactions, which is that reaction occurs "upon every close collision." Even though the Ar^+-D_2 reaction is exothermic and has no activation energy barrier, violent head-on collisions with very close approach of Ar^+ and D_2 give no reaction in a large number of cases. Actually, as the relative translational energy is lowered, a greater fraction of collisions are reactive, which is contrary to one's intuition. In the N_2^+-D_2 system, however, we find the expected behavior: head-on collisions almost always lead to reaction regardless of the energy.

Finally, I would like to point out that while the contributions that the study of gaseous ion phenomena can make to our understanding of intermolecular forces and reaction dynamics are clear, the eventual application of this work to synthetic chemistry should not be ignored. Discharge tubes and plasma jets have already been used to effect desired syntheses, but in only rather crude ways. As our understanding of the generation, neutralization, and reactions of ions increases, it may be possible to use discharges, afterflows, and ion beams as special tools for the specific synthesis of new compounds.

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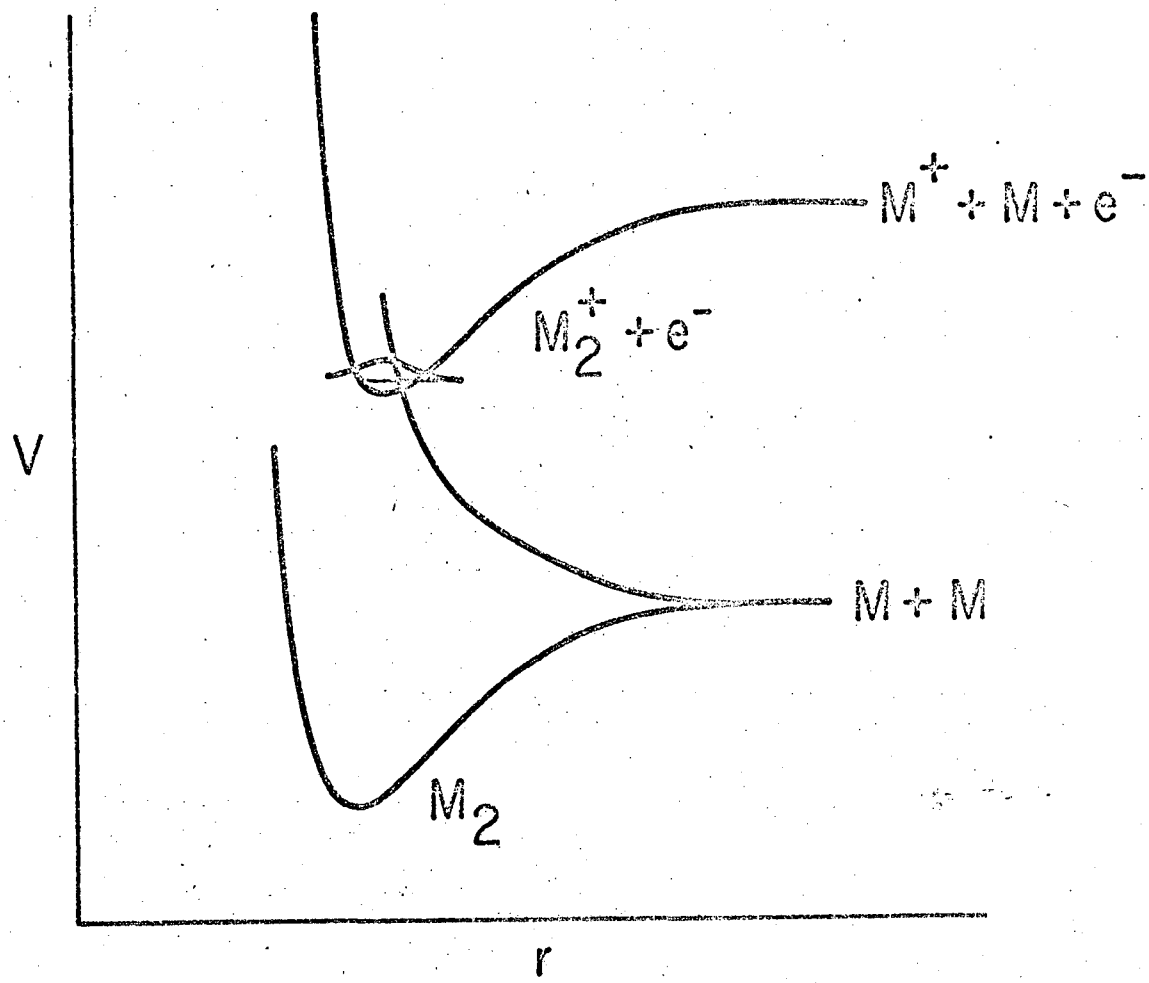

Figure 1. Potential energy as a function of internuclear distance for the diatomic molecule M_2, and its ion M_2^+ plus a free electron. Dissociative ion-electron recombination occurs when the approach of an electron causes a transfer of the system from the stable M_2^+ curve to the dissociating state of M_2.

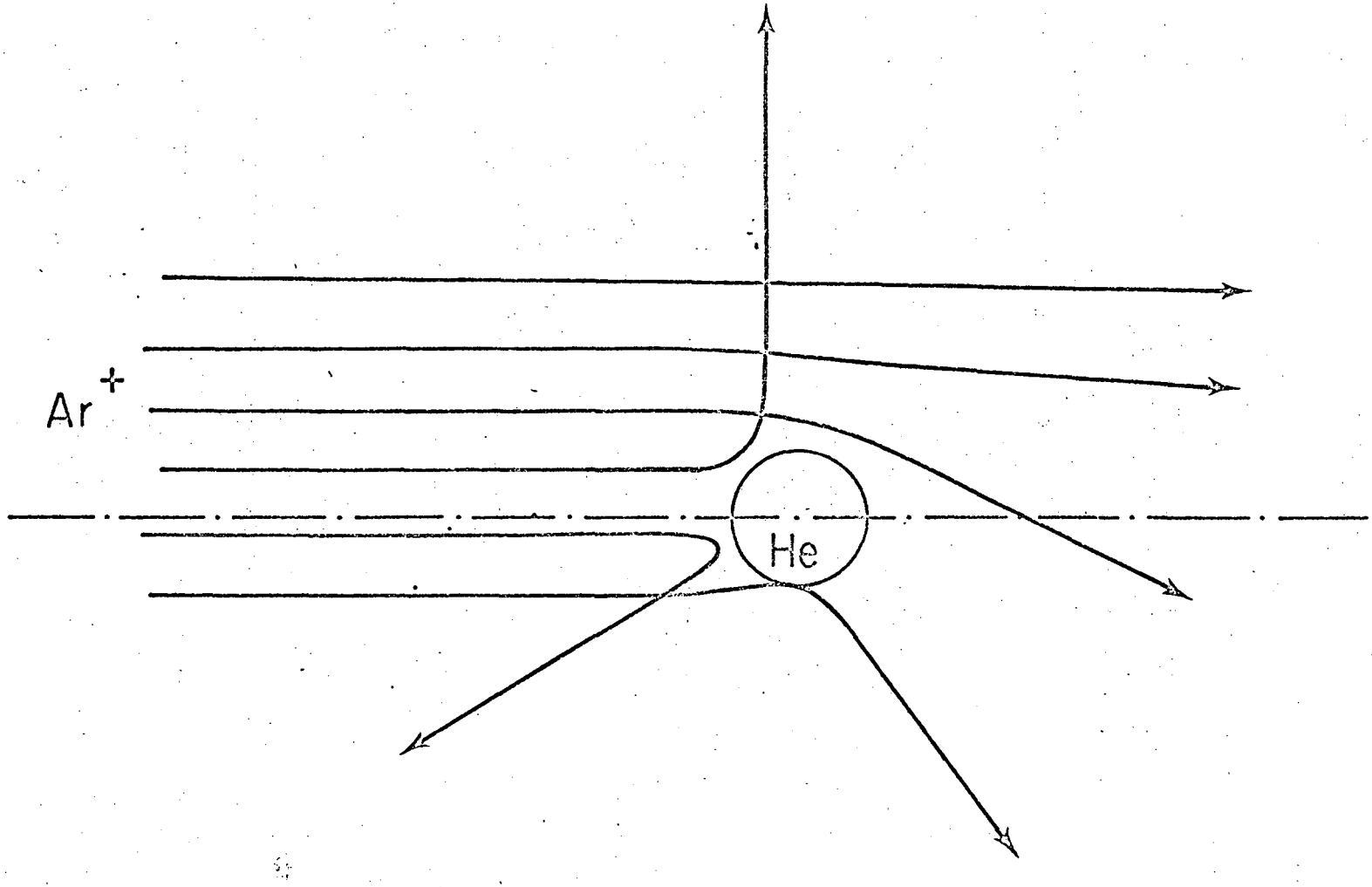

Figure 2. A few trajectories for high energy collisons between an Ar^+ projectile and a fix He target. Grazing collisions lead to small angle scattering, and head-on collisions to large angle scattering of the projectile.

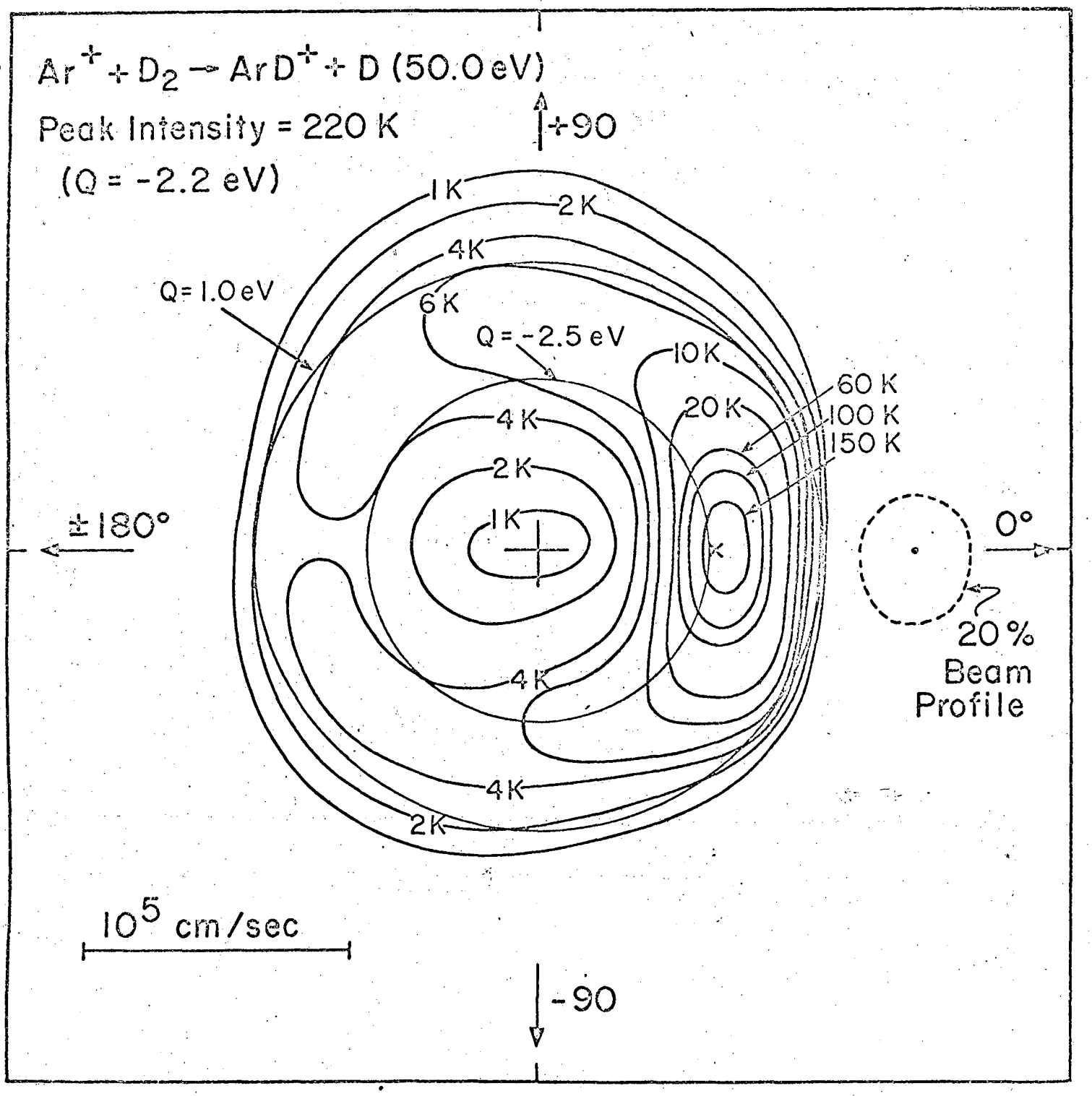

Figure 3. A contour map of the intensity of ArD^+ product from the Ar^+, D_2 reaction plotted in the center of mass coordinate system. The direction of the Ar^+ is taken to define zero degrees. The quantity Q is the relative kinetic energy of products minus that of reactants.

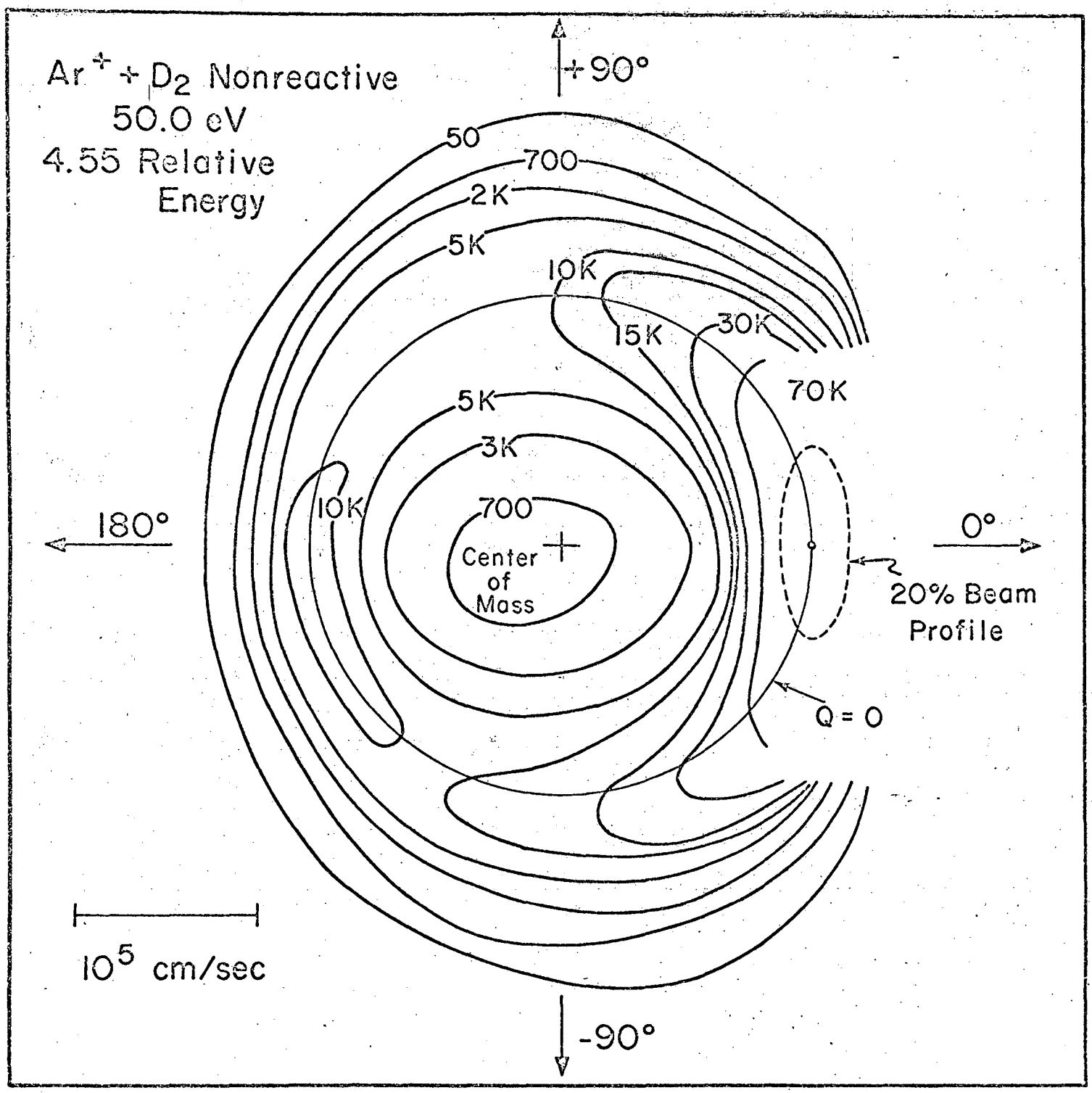

Figure 4. A contour map of the intensity of Ar^+ scattered from D_2 plotted in the center of mass coordinate system. The direction of the projectile beam defines the zero of angle. The circle labelled Q = 0 corresponds to elastic scattering of Ar^+ by D_2. Note that the intensity of nonreactive scattering at 180° is greater than that of the corresponding reactive scattering shown in Fig. 3.

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