Electron transfer between multicharged ions and neutral species

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A reduced coupling matrix-element formula has been developed for application to the class of reactions $A^{+z} + B \rightarrow A^{+z-1} + B^+$, where $4 \le z \le 54$. The reduced coupling matrix elements have been combined with an absorbing-sphere model based on the Landau-Zener method to obtain a relatively simple formalism for obtaining the electron transfer total cross sections. The method assumes a large number of final product channels available for reaction and is applicable for relative velocities $v_{rel} \le 1 \times 10^8$ cm/sec. For such electron transfer reactions, the cross sections at a given velocity are dependent primarily on the charge state of the incident ion and the ionization potential of the target atom; also, for a given colliding pair, the cross section is found to be almost independent of the relative velocity. Cross sections have been calculated for H, He, Ne, Ar, Kr, Xe, and H₂ targets. For the cases of H₂ and Ar there are experimental data available; the comparison between theory and experiment is quite favorable.

I. INTRODUCTION

The study of electron transfer between partially and fully stripped ions colliding with neutral species is a topic of much current research activity. Some of the early motivation arose because of the possibility of using the reaction

$$A^{+z} + B \to A^{+z-1} + B^+ \tag{1}$$

as the basis for an x-ray laser,¹ since the cross sections are large and $A^{*e^{-1}}$ is predominately produced in highly excited Rydberg states which radiate in the vuv and x-ray region. Further interest has been stimulated by the tokamak research program where charge-exchange collisions of stripped ion impurities with deuterium atoms in the fusion plasma can lead to significant radiation cooling losses.²

In the collision velocity region of interest to the above problems, $v \leq 1 \times 10^8$ cm/sec, very little theoretical or experimental research has been conducted. Experimental programs have been severely hampered by the difficulty of producing ions in high-charge states at low collision velocities, while theoretical work has been limited by the inadequate knowledge of the potential energy curves and coupling matrix elements for reactions of the type (1).

Recently, we have used the Landau-Zener theory modified for application to multicrossing systems to calculate electron-capture cross sections for a number of fully-stripped-ion-hydrogen-atom collision systems.^{3,4} For these one-electron diatomic molecule (OEDM) systems, reasonably accurate values of the relevant radial coupling matrix elements could be quickly and easily obtained. For many purposes, one can approximate the more general collision systems represented in Reaction (1) as one-electron systems in which an active electron can move between relatively inert centers of charges +1 and +z, respectively. This is justifiable because of the long-range nature of the capture process for these multicharged ions.

We have taken advantage of this concept in the development of an approximate theory that can be used to predict cross sections for Reaction (1) with reasonable accuracy. In order to accomplish this, we have computed a large number of the OEDM coupling matrix elements which were then parameterized in terms of the charge z of the initial ion and the internuclear distance at which they were evaluated. By using these matrix elements and an extension of the Landau-Zener method applied to the case where there is a large number of curve crossings (absorbing sphere model), we find it is possible to evaluate the cross sections rapidly for large classes of colliding systems. Because of the approximations made, the method is most applicable to electron exchange reactions where z is large $(z \ge 10)$ or to cases at lower z where there are a large number of A^{+z-1} excited levels available for reaction.

II. THEORY

In order to explain the collision mechanism for Reaction (1), a schematic of the interacting potential energy curves is shown in Fig. 1. The initial channel, that of $A^{*x} + B$, is slightly attractive at large internuclear distances owing to a polarization interaction between the ion and atom, and has a repulsive wall located at small internuclear distances. The product channels of $A^{*z-1} + B^*$, in turn, have very repulsive Coulomb forms (z - 1)/R, and cross the initial state. Strong coupling occurs at these curve crossings which leads to the elec-



FIG. 1. Schematic diagram for the potential curves of the electron transfer reaction: $A^{+z} + B \rightarrow A^{+z-1} + B^+$.

tron transfer. Moreover, for sufficiently high z, the number of curve crossing becomes very large because of the great number of $A^{*z-1*} + B^*$ states that cross the $A^{*z} + B$ potential curve.

The large number of curve crossings allows us to make certain simplifying assumptions on how to calculate the cross sections. As a starting point, we can look at the Landau-Zener transition probability that the colliding particles will remain on the $A^{*z} + B$ potential curve at a curve crossing. The formula is given by

$$p = \exp(-2\pi H_{12}^2 / \Delta F v_{\rm rad}), \qquad (2)$$

where H_{12} is one half the adiabatic splitting at the curve crossing R_x , ΔF is the difference in slopes of the diabatic potential energy curves at R_x , and v_{rad} is the radial velocity at R_x . From numerical work on electron transfer for ion-ion mutual neutralization (an analogous process in that the initial state is an attractive Coulomb potential that is crossed by the relatively flat potential curves of the neutral products), we have found that for a system where there are a large number of crossing states, an absorbing-sphere model can be accurately employed.⁵ That is, we assume unit probability for reaction inside some critical distance R_c determined by the crossing parameters. The chargeexchange cross section is then simply given by

$$Q = \pi R_c^2 \,. \tag{3}$$

From the previous numerical work,⁵ we know that the conditions for obtaining R_c are given by

$$0.15 = 2\pi H_{12}^2(R_c) / \Delta F(R_c) v_0, \qquad (4)$$

where v_0 is the incident velocity. Since the region of strong interaction occurs at large internuclear distances, it is reasonable to represent ΔF of Eq. (4) by

$$\Delta F = (z - 1)/R^2 , \qquad (5)$$

where it is assumed that the dominant potential forms are a constant interaction for the initial state and a repulsive Coulomb form for the product states.

As always, the most difficult problem is in developing a formulation for the coupling matrix elements that can be easily applied from case to case. The first step was to obtain the H_{12} 's for a large number of stripped-ion-atomic-hydrogen systems. These were determined, in an extension of previous calculations,^{3,4} from an analysis of the pseudocrossings observed in the exact adiabatic potential curves derived for each system using the OEDM program of Power.⁶ The range of z in these computations was from 4 to 54. The next step was to find a suitable functional form for these parameters. Recognizing that the matrix elements must decrease exponentially, we arrived, after much trial and error, at the reduced parameters

$$H_{12}^* = z^{1/2} H_{12}$$

and

$$R_x^* = R_x / z^{1/2} , (6)$$

where all quantities are in a.u. A semilog plot of these quantities is shown in Fig. 2. The average error from the derived functional form

$$H_{12}^* = 9.13 \exp(-1.324R_x^*) \tag{7}$$

is only 17%. For systems where the target is not atomic hydrogen, it seems reasonable to multiply the exponential portion of Eq. (7) by

$$\alpha = [I_t(eV)/13.6]^{1/2}, \qquad (8)$$

where I_t is the ionization potential of the target atom.^{7,8} For molecular targets, a further modification is to multiply Eq. (7) by the square root of the Franck-Condon factor q for the specific transition between vibrational levels.⁹ Thus, a generalized functional form for the coupling matrix element is

$$H_{12}^* = 9.13q^{1/2}e^{-1.324\alpha R_x^*}.$$
 (9)

We may combine Eqs. (4), (5), and (9) to derive the relation from which R_c may be determined:

$$R_c^2 e^{-2.648 \alpha R_c/z^{1/2}} = 2.864 \times 10^{-4} z (z-1) v_0/q .$$
(10)

The cross section can then be easily obtained from Eq. (3) provided that there are a large number of curve crossings at the internuclear separation around R_c . If this condition does not hold at the calculated value of R_c , one can still obtain practical estimates of the cross section by a slight modification of the procedure. In this case, one substitutes a smaller value for R_c in the evaluation of Q, usually corresponding to an appropriate inner crossing close to a localized group of cross-



FIG. 2. Reduced radial coupling matrix plot $(z^{1/2}H_{12})$ vs $R_x/z^{1/2}$ for fully stripped ions colliding with atomic hydrogen. The matrix elements were obtained from an analysis of the pseudocrossings observed in the adiabatic curves for each system (Ref. 6). The charge state range covered is from z = 4 to 54. H_{12} and R_x are in a. u.

ings. The probable error in the computed cross sections must increase significantly in such cases. Even for systems involving stripped ions of low zcolliding with atomic hydrogen, where the additional symmetry for two-center Coulomb problems reduces considerably the number of interacting crossings, application of the present model can lead to useful results. In this case, one substitutes for the value of $R_{\rm o}$ calculated from Eq. (10), the nearest innercrossing radius. One would expect the cross section obtained with this absorbing-sphere model to be considerably higher than the previously obtained Landau-Zener results.³ However, the approach is not unreasonable when one considers that the Landau-Zener method with its neglect of quantum tunneling and transitions due to rotational coupling, actually gives a lower limit cross section.

In connection with the above, one should note that although the present model is based essentially on a radial coupling mechanism, contributions due to rotational coupling are also implicitly included in the cross-section calculations. In fact, one would expect that a significant portion of the unit probability for a reaction within R_c would be due to product states being formed via the rotational coupling mechanism. However, since the rotational L_y matrix element is directly related to the overlap integral between molecular states of the same symmetry, it seems improbable that significant rotational coupling would occur at internuclear distances greater than R_c where the overlap becomes negligible.

For fully stripped ions colliding with an atomic hydrogen or deuterium target, the crossing distances may be simply evaluated for a given excitation level n of the one-electron ion formed by the use of

$$R_x = \frac{2(z-1)}{(z/n)^2 - 1} \quad . \tag{11}$$

In Eq. (11), the same assumptions were made as were utilized in Eq. (5). For cases where the reactant ion is partially stripped, it is necessary to resort to the use of tabulated energy levels.¹⁰

III. CROSS-SECTION CALCULATIONS

The formulas presented in Sec. II can be applied to a variety of collision systems. Unfortunately, however, experimental data are not presently available for what are probably the most interesting systems, those of multicharged ions colliding with atomic-hydrogen or deuterium targets. Therefore, besides calculating cross sections for atomic hydrogen targets, we have also calculated cross sections for H_2 , He, Ne, Ar, Kr, and Xe targets where data are becoming available. Thus, in the near future it will be possible to make a critical comparison between theory and experiment.

A. Atomic-hydrogen target

Although there are no experimental data, the atomic-hydrogen target cross sections are probably of most interest. Since much of this interest is concerned with fully stripped ions where the one-electron ions, resulting from the charge transfer, have relatively widely separately energy levels, especially for the low z ions, it is essential to first construct an R_c -vs-z plot. The curve crossings for the various excited product states are then calculated to ascertain whether a high density of curve crossings is available for reaction at internuclear distances in the vicinity of R_c . If this is not the case, then an estimate of the cross section may be obtained by choosing a reduced value of R_c that is consistent with the curve-crossing information.

A plot of R_c vs z for an atomic hydrogen or deuterium target at a relative velocity of 7×10^7



FIG. 3. Absorbing-sphere radius R_c vs z for an atomic-hydrogen target at a relative velocity of 7×10^7 cm/sec.

cm/sec is shown in Fig. 3. It is interesting to note that electron capture can be expected to occur at reasonably large internuclear distances, being on the order of 10 a_0 for collisions of multicharged ions with a z of 7 and increasing to $20a_0$ for a z of 50, where a_0 is the Bohr radius. R_c vs z can be conveniently converted to Q_{\max} vs z using Eq. (3) in order to obtain an idea of the possible magnitudes of the cross sections (Fig. 4). It is seen that the cross sections can be large, and will normally be on the order of 10^{-14} cm² for $z \ge 10$. For specific cases, particularly low-z ions, the actual cross sections will vary below the values given, but for the high-z ions, the condition that a large density of product crossing states be present is satisfied, so that the Q_{\max} values of Fig. 4 should correspond closely to the actual cross sections. If should be noted that the cross-section dependence on z predicted by us for high-z ions will be approximately linear with z, instead of z^2 as predicted by Presnyakov and Ulantsev¹¹ or as is found for charge transfer at high velocities,¹² $v \ge 3 \times 10^8$ cm/sec, by binary encounter methods.

Since the multicharged ions that can be produced and used in an experiment at velocities $v \le 1 \times 10^8$ cm/sec are limited to $z \le 10$ for the near future, we have also evaluated some cross sections for



FIG. 4. Maximum cross section Q_{max} vs z for an atomic-hydrogen target at a relative velocity of 7×10^7 cm/sec.

partially to fully stripped C, N, and O colliding with atomic hydrogen. The results are given in Table I for a collision velocity of 7×10^7 cm/sec. The cross sections are found to be large, $Q > 10^{-15}$ cm^2 , but do not follow any simple *z*-scaling rule. For these low-z cases, particularly for fully stripped ion collisions, the cross sections are highly dependent on the molecular structure of the colliding pair since a high density of curve crossings is not available. In order to construct Table I, it was necessary for the partially stripped ions to resort to the atomic-energy levels of Moore¹⁰ and the R_c information given by Fig. 3. The Q_{max} values shown in Fig. 4 for these cases do not represent the actual cross sections but only indicate upper limit cross sections for the various zstates. The estimated error limits shown in Table I are based primarily on the available density of crossing product states.

As expected, referring to our previous discussion, the present results for low-z fully stripped ions, particularly C⁺⁶ and O⁺⁸, are considerably larger than the previously obtained Landau-Zener cross sections.³ A related observation is that the low- $z z^{3/2}$ dependence seen in the Landau-Zener cross sections does not appear

TABLE I. One-electron transfer cross sections at $v = 7 \times 10^7$ cm/sec for C^{+z}, N^{+z}, and O^{+z} + H collisions. Error limits are estimated to be ±40% for the partially stripped ions and may be slightly larger for the fully stripped cases where there are only one or two curve crossings available for reaction.

z	$Q(C^{+z})$ (10 ⁻¹⁵ cm ²)	$Q(N^{+z}) (10^{-15} \text{ cm}^2)$	$Q(O^{+z}) (10^{-15} \text{ cm}^2)$
4	4.4	3.8	2.6
5	1.8	1.6	6.6
6	5.7	5.8	5.3
7	•••	3.0	3.0
8	•••		7.0

in the absorbing-sphere results. On the other hand, as was noted previously, the absorbingsphere model predicts an approximately linear dependence on z in the high-z region where it is expected to be most accurate.

B. Molecular-hydrogen target

Molecular hydrogen is an interesting target gas for a number of reasons. Reliable experimental information is now becoming available for these systems¹³ thus providing a reasonable test of the theoretical approach. Comparison of the molecular-hydrogen calculations with the cross sections for atomic hydrogen illustrates the differences to be expected between atomic and molecular targets of the same species. Interestingly enough, the condition that there be a high density of crossings, which is a requirement for application of the absorbing-sphere model, is better satisfied for molecular hydrogen than for atomic hydrogen. In the former case, not only will there be a distribution of quantum levels available for the product high-z ion but also a distribution of vibrational levels for the resulting H_2^+ .

The H₂ calculations are given at one velocity, $v = 7 \times 10^7$ cm/sec, but since the calculated cross sections are only larger by 12% at 5×10^7 cm/sec and smaller by 12% at 10×10^7 cm/sec, these values are appropriate for the velocity range of 5–10 $\times 10^7$ cm/sec. The molecular target calculations are complicated by the fact that the target Franck-Condon factors and the various associated ionization potentials must be included in the calculations, and that a proper average must be taken over the vibrational levels of the final state. Thus the computational work involved is considerably greater than for atomic target gases.

The results for ions of z = 4-25 are shown in Fig. 5 along with some data of Crandall¹³ for C^{*z}, N^{*z}, and O^{*z} colliding with H₂. The remarkably good agreement observed gives us confidence in our theoretical method. We should note that, in our calculations, we have assumed that the H₂ target gas is in its ground vibrational state, an assumption which is valid at room temperature. We do find, because of the more favorable Franck-Condon factors, that the H₂⁺ ions produced are preferentially populated in the v = 1-4 vibrational levels.

The H_2 calculations (Fig. 5) may be compared to the atomic H calculations (Fig. 4 and Table I) to give some idea of the possible differences between an atomic and molecular target of the same species. For hydrogen, the molecular target yields cross sections that are generally much smaller than those for the atomic target, especially at z \geq 10. This results from two factors that reduce the magnitude of the coupling matrix element [Eq. (9)]. The first is the greater ionization potential of H₂ relative to H, and the second is the presence of the Franck-Condon factors in the molecular matrix element. Thus, electron transfer cannot occur at as large an internuclear separation for the molecular target as it can for the atomic target. This trend will be valid for other atomic and molecular species for $z \ge 10$, as long as the ionization potential of the molecular target is greater than the ionization potential of the atomic target. If it is less, it will be necessary to perform more detailed calculations before a prediction can be made.

C. He, Ne, Ar, Kr, and Xe targets

Rare-gas targets have also been included in our calculations since data are becoming available from Salzborn's group.^{14,15} For the rare-gas targets, there is, however, one major complication. It is that there is a high probability for more than one electron to be transferred or ejected during the collision. In fact, for Ar^{+z} -Ar collisions, four-electron transfer cross sections have been observed with magnitudes of $Q \gtrsim 10^{-16}$ cm².

In our model, we cannot differentiate between one- and multielectron transfer processes other than to say that the multielectron transfer for systems where there is a large density of curve



FIG. 5. Electron transfer cross sections vs z for a molecular-hydrogen target at a relative velocity of 7×10^7 cm/sec. The data shown are from the work of Crandall (Ref. 13) for the incident ions: C^{+z} , solid squares; N^{+z} , solid circles; and O^{+z} , solid triangles.

crossings will be a subset of our calculated cross section. This assumption is based on the fact that the coupling matrix elements are much smaller for multielectron exchange processes than for singleelectron exchange.¹⁶ Since we have also assumed unit probability for electron transfer within some critical distance R_c , conservation of unitarity of the S matrix requires that our calculated cross section can only be compared to the sum of all the electron-loss processes.

With the above clarification in mind, total electron transfer cross sections for high-z ions (z = 4-25) colliding with rare-gas targets are shown in Fig. 6. The trend for the heavier rare gases to have larger cross sections than the lighter rare gases is just reflected in the dependence of the coupling matrix elements on the ionization potential of the target [Eq. (9)]. The higher the ionization potential, the smaller the coupling matrix element is at a given internuclear separation and the more difficult it is to remove the electron from the target. The energy dependence of the calculated cross sections is again slight, with the cross sections being only 12% higher at 3.5×10^7 cm/sec and 12% lower at 8.5×10^7 cm/sec than the values shown in Fig. 6 at $v = 5.4 \times 10^7$ cm/sec.

The data shown for the Ar system are taken from the work of Klinger *et al.*¹⁴ and were subsequently readjusted by Salzborn¹⁵ to reflect a more accurate determination of the target scattering length. These data are the sum of the singleand multielectron cross sections. The agreement is quite reasonable as was found for the H_2 systems.

IV. CONCLUDING REMARKS

A theoretical method has been developed to calculate the electron transfer cross sections for highly charged ions, $z \ge 4$, colliding with neutral species at velocities $v \le 1 \times 10^8$ cm/sec. The applicability of the theory is contingent upon there being available a high density of curve crossings in the internuclear range around a critical distance R_c , which is easily calculated. Because of this requirement, the model is most applicable to highly charged ions, $z \ge 10$, although useful estimates of the cross sections can be made for many lower-z collisions. According to this theory, for systems where the above requirement is met, the capture cross sections are, at a given velocity, dependent primarily on the charge state of the incident ion (roughly linear with z in the high-zrange) and on the ionization potential of the target.



FIG. 6. Electron transfer cross sections vs z for He, Ne, Ar, Kr, and Xe targets at a relative velocity of 5.4×10^7 cm/sec. The data shown (closed circles) are the renormalized cross sections of Salzborn *et al*. (Refs. 14 and 15) for Ar^{+z} colliding with Ar, where we have summed over the single- and multielectron transfer cross sections.

The cross sections show very little dependence upon collision velocity, at least in the 10^7 -cm/sec range.

We estimate that for ions of $z \ge 10$, the cross sections will have an accuracy of $\pm 40\%$. In some cases where lower-z projectiles are involved, the error will be considerably larger because of the lack of sufficient curve crossings. However, the specific systems where problems will arise can be easily predicted in advance by calculating R_c vs z from the graphs shown. The value of R_c can then be compared to the curve crossings R_{\star} quickly calculated from energy-level information to ascertain whether the product states are available for reaction. If not, the cross sections obtained will be too large and a modified approach must be followed as explained previously. So far, from the limited amount of experimental data available, our calculations have been shown to be very reasonable estimates of the cross sections.

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