II. Theory of Electron Capture

Low energy ion-atom collisions can be described theoretically with very simple models, but there is a great range in the complexity and detail of more sophisticated models. First, a simple physical picture will be used to set up a framework for later discussion. With respect to electron capture for low energy collisions, the motion of the nucleus of the projectile is slow compared to the motion of the electrons bound on the target. In such slow collisions, the electrons have time to adjust to the changing inter-atomic fields that the projectile and target atom present, essentially forming quasi-molecules. Similar to **Equation 1.1**, we can more generally describe a typical collision system by

$$A^{+q} + B \rightarrow A^{+(q-k)} + B^{+k} + Q \qquad \textbf{(Eq. 2.1)}$$

where k is the number of transferred electrons.

Figure 2.1 illustrates typical molecular potential energy curves associated with single electron capture. The incident channel, A^{+q} + B, is essentially flat at large inter-nuclear distances, dips a little at intermediate distances due to the polarization of the target atom, and then rises sharply at small inter-nuclear distances as the Coulomb potential starts to dominate. Once an electron has been captured by a multiply charged projectile, both the projectile and the target are positively charged, so every exit channel, $A^{+(q-k)}$ + B^{+k}, will be repulsive due to the Coulomb interaction.

At an inter-nuclear distance, R_c (referred to as the crossing radius, since the potential curves cross at this point) there is an enhanced probability of charge

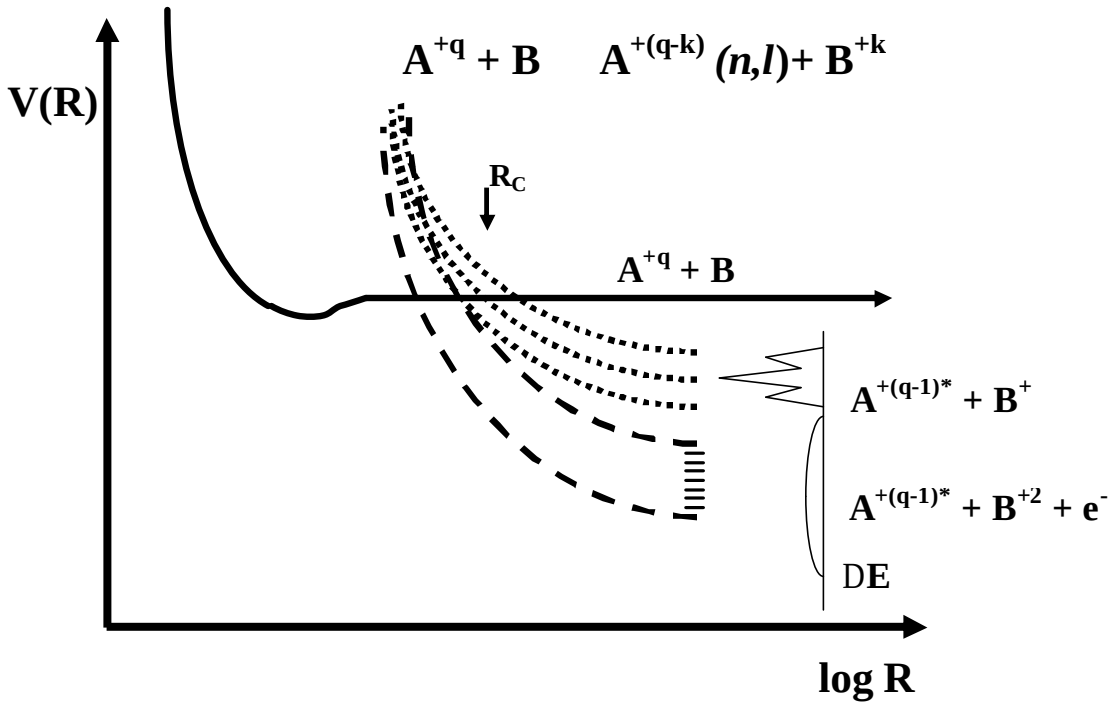

Figure 2.1 Illustration of the molecular potential energy curves V(R) versus log (R), associated with single electron capture (R is the inter-nuclear separation). The short dashed lines represent single electron capture, and the longer dashed lines represent double electron capture followed by transfer ionization (T.I.).

transfer. For highly charged projectile ions, the number of curve crossings can become large, and many final states can be populated. The Q-value is, essentially, the asymptotic difference in the energy of the incoming and outgoing channels, and can be expressed as

$$Q = V_i (R_c) - V_e (R_c). \qquad \textbf{(Eq. 2.2)}$$

After electron capture has occurred, the Q-value is shared as kinetic energy between the target and the projectile ion.

When more than one electron is captured by the projectile, it is often the case that more than one excited state of the ion is populated. As mentioned in the last chapter,

these multiply excited states will primarily decay by emitting photons or by ejecting one of the electrons. The case when two electrons are captured, and one of them is ejected is referred to as transfer ionization (T.I.). In **Figure 2.1** several potential energy curves leading to T.I are shown. An ion that captures two electrons into excited states can also decay by photon emission, which results in "true" double capture to the projectile ion.

A. Classical Over-Barrier Model

The basic classical over-barrier model is a fairly simple approach for describing low energy collisions between multiply charged ions and light atoms, but is quite useful in qualitatively estimating which reaction channels will be most strongly populated. Therefore, a brief overview of this model will be discussed. Consider a particle of charge Z colliding with a hydrogen atom. The energy, E, of the electron (assuming its in the ground state of the H atom) can be expressed as

$$E = -\frac{1}{2} - \frac{Z}{R}, \qquad \textbf{(Eq. 2.3)}$$

where R is the inter-nuclear separation. (Unless otherwise sited, atomic units will be used throughout.) At a point y from the target nucleus, along the inter-nuclear axis the total potential energy is

$$V(y) = -\frac{1}{y} - \frac{Z}{R-y}. \qquad \textbf{(Eq. 2.4)}$$

The two potential wells have a saddle point, where V(y) has a maximum value, $V(y_m)$ along the inter-nuclear line. The value of y at which the saddle is located along the inter-nuclear axis can be found by solving for where the derivative of the potential is zero. For this condition,

$$\frac{dV(y)}{dy} = 0, \qquad \textbf{(Eq. 2.5)}$$

we can solve for y = y_m,

$$y_m = \frac{1}{\sqrt{Z}+1} R. \qquad \textbf{(Eq. 2.6)}$$

The height of the barrier at y = y_m is

$$V(y_m) = -\frac{1}{R}(\sqrt{Z}+1)^2. \qquad \textbf{(Eq. 2.7)}$$

When the effective energy of the electron in the target is equal to the energy that it would have in the nth shell of the projectile we have

$$-\frac{1}{2} - \frac{Z}{R} = -\frac{Z^2}{2n^2} - \frac{1}{R}. \qquad \textbf{(Eq. 2.8)}$$

The condition for electron capture to occur is that only when the effective energy is greater, or "over" the saddle point potential energy, or "barrier" can electron capture occur. The active electron will be transferred at the inter-nuclear separation where it has enough energy to overcome the potential barrier given by the superposition of the Coulomb potentials of the projectile and target. This is expressed as

$$-\frac{1}{2} - \frac{Z}{R} > V(y_m) = -\frac{1}{R}(\sqrt{Z}+1)^2. \qquad \textbf{(Eq. 2.9)}$$

Equation 2.8 and **Equation 2.9** can be used to solve for n_p to give

$$n_p = \sqrt{Z^2 \frac{(2(\sqrt{Z}+1)}{Z+2\sqrt{Z}}}. \qquad \textbf{(Eq. 2.10)}$$

Equation 2.10 will most likely not yield an integer number, so the greatest integer *n* that is less than n_p is the level on the projectile ion that the electron will be captured into. Also, from **Equation 2.8**, the crossing radius can be solved for

$$R_C = \frac{Z-1}{\frac{1}{2}\left(\frac{Z^2}{n^2}-1\right)}, \qquad \textbf{(Eq. 2.11)}$$

and calculated now that *n* is known. The electron capture cross section can be expressed as

$$s = \frac{1}{2} p R_C^2, \qquad \textbf{(Eq. 2.12)}$$

with the assumption that the probability for sharing the electron is equal after the barrier has been crossed. Reaction channels that have crossing radii in the region around this inter-nuclear separation will be most strongly populated. Since the potential well of the projectile ion is much deeper than that of the target, the energy levels of the projectile ion that match the energy level of the electron on the target will be excited states. Therefore, electron-capture will preferentially be to excited states of the projectile.

B. Landau-Zener Model

Landau **[2.1]** and Zener **[2.2]** independently derived a formula for predicting the probability of a transition occurring at a molecular curve crossing. By treating the multi-channel charge transfer process as a series of couplings between two states, and making a couple of assumptions that simplify treatment of the problem, approximate solutions of the two state coupled channels problem can be derived, leading to analytical expressions for the transition probabilities.

Since the charge transfer process can be broken down into a series of two state systems, and it's easiest to first describe the model by considering a two state system. The first assumption made is that the coupling matrix element, H_{12}, at the crossing radius

is much less than the relative kinetic energy of the ion-atom system. This allows the system to be treated semi-classically, where the nuclear motion of the ion is treated classically, and the electron is treated quantum mechanically with the wave function of the electron given as

$$\Phi(r,t) = \sum_{k=1}^{N} c_k(t) f_k(r,t), \qquad \textbf{(Eq. 2.13)}$$

where c_k are the wave function coefficients, and N is the number of states included (N=2 for a two state system). This allows r(t) to be calculated classically. The second assumption is that the transition between the states occurs in a localized region around R_C which is small enough that the potential energy curves, $|f_1\rangle$ and $|f_2\rangle$, can be approximated by tangents in this region.

The wave functions and the coupling matrix elements are assumed to be constant in the crossing region, and equal to their values at R_C in this region. This is expressed as

$$\dot{H}_{12} = |\dot{f}_1 > = |\dot{f}_2 > = 0$$

and **(Eq. 2.14)**

$$H_{12}(R) = H_{12}(R_C).$$

This allows the two-state coupled channels problem to be defined by

$$\dot{c}_1 = c_2 H_{12} e^{-i\int_{-\infty}^{t}(E_1 - E_2)dt'}$$

and **(Eq. 2.15)**

$$\dot{c}_2 = c_1 H_{12} e^{i\int_{-\infty}^{t}(E_1 - E_2)dt'},$$

where E_1 and E_2 correspond to the energy levels of the two states.

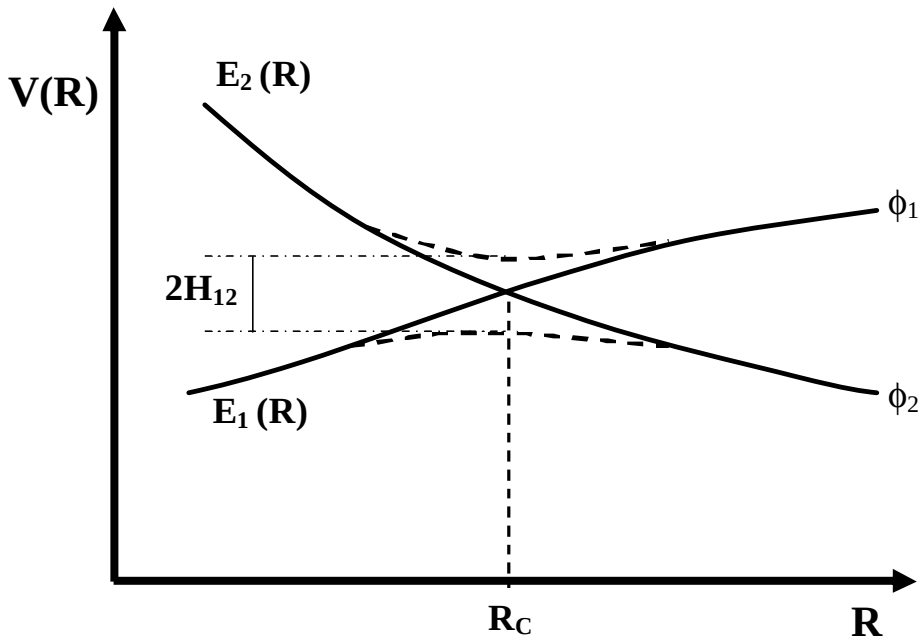

Figure 2.2 A plot of potential energy, V(R), versus the inter-nuclear separation, R, where two potential curves cross at the radius R_C. The coupling matrix element, H_{12}, is half the adiabatic splitting at the crossing radius.

The initial conditions are

$$|c_1(-\infty)| = 1 \quad \text{and} \quad |c_2(-\infty)| = 0 . \qquad \textbf{(Eq. 2.16)}$$

From these conditions, the probability for an adiabatic, or non-crossing transition is given by

$$P_{11} = |c_1(\infty)|^2 . \qquad \textbf{(Eq. 2.17)}$$

This can be analytically solved to give

$$P_{11} = e^{-2pg} \qquad \textbf{(Eq. 2.18)}$$

where

$$g = \frac{[H_{12}(R_C)]^2}{\left|\frac{d}{dt}(E_1 - E_2)\right|}. \qquad \textbf{(Eq. 2.19)}$$

By defining ΔF as the difference in the slopes, the denominator of **Equation 2.19** can be expressed more simply, as

$$\frac{d}{dt}(E_1 - E_2) = \frac{dR}{dt}\frac{d}{dR}(E_1 - E_2) = v_r \Delta F \qquad \textbf{(Eq. 2.20)}$$

where v_r is the radial velocity. Now it is possible to write the Landau-Zener probability for an adiabatic transition in the form

$$p = P_{11} = e^{\frac{-2p[H_{12}(R_C)]^2}{v_r \Delta F}}, \qquad \textbf{(Eq. 2.21)}$$

and the probability of an diabatic transition is just, $(1-p)$. There are two ways that the electron can transfer. The electron can have a diabatic transition at the crossing radius for that particular transition, as the inter-nuclear separation decreases and the ion is approaching the atom, followed by an adiabatic transition as the inter-nuclear separation increases, when the ion passes the atom. This is one scenario leading to electron capture, but the opposite order, that is, an adiabatic transition on the incoming path, and a diabatic transition on the exit path will also have the end result of electron capture. Since there are two ways this can happen, we can express the total probability of the electron transferring at a given impact parameter as

$$P = 2p(1-p) \qquad \textbf{(Eq. 2.22)}$$

The cross section for the two level case is then given by

$$s = 2p\int_0^{R_C} bPdb \qquad \textbf{(Eq. 2.23)}$$

where b is the impact parameter.

The basic two level charge exchange concept can be extended to a multi-level system, if the transition regions are well separated from one another. In an N level system, with N-1 crossing radii, the probability of a transition to a particular state can be found by adding the probabilities for transitions along all the possible paths which lead to a transition to the final state.

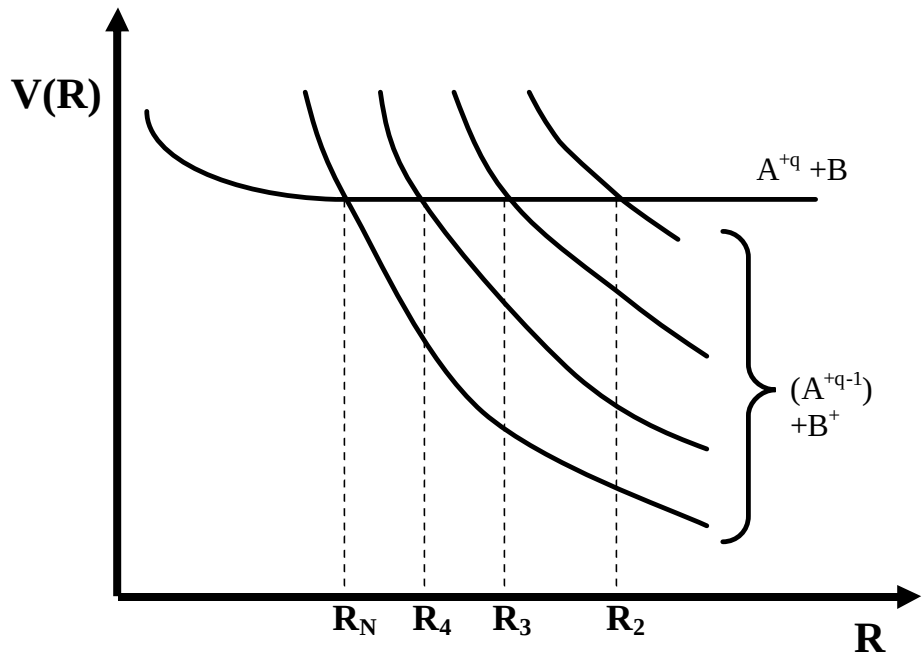

Figure 2.3 A diagram plotting V(R) versus R, to illustrate several potential curves with different crossing radii.

If $R_2 > R_3 > \ldots R_{N-1} > R_N >$ are the crossing radii, and p_i (i = 2, 3, …, N) is the two state transition probability for a crossing at R_i, the general expression for capture into the final state is given by Salop and Olson **[2.3]** as

$$P_i = p_2\, p_3 \ldots p_i\,(1- p_i)[1+(p_{i+1}\, p_{i+2} \ldots p_N)^2$$
$$+(p_{i+1}\, p_{i+2} \ldots p_{N-1})^2(1- p_N)^2 \qquad \textbf{(Eq. 2.24)}$$
$$+(p_{i+1}\, p_{i+2} \ldots p_{N-2})^2(1- p_{N-1})^2$$
$$+ \ldots +(p_{i+1})^2(1- p_{i+2})^2 + (1- p_{i+1})^2].$$

One of the important elements of the Landau-Zener model is the coupling matrix element, H_{12}. A widely used universal formula for H_{12} was developed by Olson and Salop **[2.4, 2.5]**, as

$$H_{12} = \frac{9.13}{\sqrt{q}} e^{\left(-1.32 R_C / \sqrt{q}\right)} \qquad \textbf{(Eq. 2.25)}$$

where q is the effective projectile charge. This is a quite simple expression, but has been quite successful at predicting approximate values of capture cross sections (typically within better than a factor of two).

Another feature of this model is that it helps to explain why, when there are many possible final states that can be populated, only a few of these states actually contribute to the capture cross section. The concept of a 'reaction window' is useful in understanding the state-selective nature of low energy charge capture. Potential crossings at very large and very small crossing radii both yield electron capture probabilities that are low. Only for intermediate crossing radii, where the probability is maximal, is the contribution to capture appreciable. By examining how the Landau-Zener probability depends on the quantities that define it, it becomes clear why this is true. The radial velocity, v_r, is given as

$$v_r = v\sqrt{1-(b/R_C)^2} \qquad \textbf{(Eq. 2.26)}$$

where b is the impact parameter, and v is the relative collision velocity. Also, the difference in the slopes of the adiabatic potential curves (neglecting the polarization of the incident channel), ΔF, is

$$\Delta F = (q-1)/R^2 \qquad \textbf{(Eq. 2.27)}$$

where q is the charge of the incident projectile ion. **Equation 2.26** and **Equation 2.27** can be used to express the probability of an adiabatic transition, given in **Equation 2.21**, as

$$p = e^{\left(\frac{-2p\sqrt{q}R_C[H_{12}(R_C)]^2}{v\sqrt{1-(b/R_C)^2}(q-1)}\right)}. \qquad \textbf{(Eq. 2.28)}$$

Keeping in mind that the probability of capture is, P = 2p(1-p), we can examine how the probability behaves for small, intermediate, and large crossing radii for a two level system. For very large crossing radii, since the coupling between the initial and final states is weak, the matrix coupling term, H_{12} goes to zero, and the adiabatic transition probability goes to a value of 1. Therefore, the capture probability goes to zero. For very small crossing radii, the coupling between the two states is very strong, and H_{12} becomes large, so the adiabatic transition probability goes to zero (becomes diabatic). The capture probability goes to zero in this scenario as well. At intermediate crossing radii, where p = 0.5, the probability for capture is at a maximum.

C. Absorbing sphere model

The absorbing sphere model is an alternate version of the Landau-Zener model, and was developed by Olson and Salop **[2.4]**. Since part of the body of experimental data presented in this dissertation, and experimental data taken by others, have used this

theory for comparing experimental data to theoretical calculations, a brief overview of the absorbing sphere model is presented. The main argument of this theory is, that for highly charged ions incident on a target atom, as the inter-nuclear separation becomes small, and the reaction window is reached, the density of states on the ion is so large that essentially all the reaction flux goes into capture. For any impact parameters that are equal to the reaction window radius or smaller, electron capture will occur, and the system acts as an absorbing sphere. If we take R_C as the radius of the sphere, where the charge transfer probability inside this radius is assumed to be unity, the charge-transfer cross section is approximated as

$$s = pR_C^2 . \qquad \textbf{(Eq. 2.29)}$$

The semi-empirical expression used to determine the value of R_C is

$$R_C^2 e^{\left(-2.648 R_C a / \sqrt{q}\right)} = 2.864 \times 10^{-4} q(q-1) v_0 / f , \qquad \textbf{(Eq. 2.30)}$$

where the value, $a = \sqrt{I/13.6}$, and I is the ionization potential in units of electron volts. Also, v_0 is the incident velocity of the projectile, and f is the Franck-Condon factor for specific vibrational transitions (for a molecular target). In this model, the trajectory of the projectile is approximated as linear, and the attractive induced-dipole polarization is neglected.

D. Müller and Salzborn's Scaling Law

An empirical scaling law **[2.6]** was developed by Müller and Salzborn to calculate charge-transfer cross sections, using 107 data points for single-electron transfer, and 77 data points for double-electron transfer, for collision energies ranging from 10-100 keV for various collision systems. It was believed that the capture cross sections would have little energy dependence in the range of collision energies for which the scaling law was derived. This is reflected in the equation for the cross section,

$$s_{MS} = Aq^{a} I^{b}, \qquad \textbf{(Eq. 2.31)}$$

where q is the charge of the ion, I is the ionization potential of the target (in eV). A, a, and b are fitting parameters with values of $(1.43 \pm 0.76) \times 10^{-12}$ cm^2, 1.17 ± 0.09, and -2.76 ± 0.19, respectively, for single capture. For double capture, the fitting parameters A, a, and b are $(1.08 \pm 0.95) \times 10^{-12}$ cm^2, 0.71 ± 0.14, and -2.80 ± 0.32, respectively.

E. The Langevin cross section

The models discussed in this chapter up to this point have neglected the attractive polarization potential. In very low energy collisions this polarization is expected to become a more influential effect in capture process since the electron cloud will have a relatively longer amount of time to adjust to the field presented by the ion as the ion comes into the vicinity of the target. In this model, it is presumed that the projectile ion will follow a spiraling orbit toward the target atom, due to the polarization potential whenever the impact parameter is less than a critical value. The critical value for the impact parameter is

$$b_0 = \left(\frac{4q^2 a_D}{m v_r^2} \right)^{1/4} . \qquad \textbf{(Eq. 2.32)}$$

Here, v_r is the relative velocity of the collision, m is the reduced mass of the collision system, and a_D is the dipole polarizability.

The polarization potential is defined as

$$V_p = -a_D q^2 / 2R^4 , \qquad \textbf{(Eq. 2.33)}$$

where, again, q is the charge of the projectile ion, and R is the inter-nuclear separation. If there is a crossing between diabatic potential-energy curves at an inter-nuclear separation that is less than this critical impact parameter, the probability of charge transfer is high. An upper limit of the charge-transfer cross section, know as the Langevin cross section **[2.7]**, is

$$s_L = p b_0^2 . \qquad \textbf{(Eq. 2.34)}$$

One of the limitations of this model is that it is assumed that the charge-transfer cross-section is zero for impact parameters greater than the critical impact parameter. If there is a crossing at an inter-nuclear separation greater than b_0 the Langevin cross section, s_L may not be an upper limit. Also, if a molecule is used as a target, instead of an atom, dipole and quadrupole moments with even longer range potentials exist that depend on the orientation of the molecule. This would generally pose an added complication to computing cross sections, since these moments would be more important in low energy collisions. However, the only molecule used as a target for cross sections measured for this dissertation was H_2, which has a zero dipole moment and a small quadrupole moment. Also, since the dipole and quadrupole moments depend on q, and the polarization potential depends on q^2, and most of the data measured was for fairly

large q values, it is expected that any dipole or quadrupole moments would not be important except at extremely low collision energies **[2.8]**.