ELECTRONIC EXCITATION OF GROUND STATE ATOMS BY
COLLISION WITH HEAVY GAS PARTICLES

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INTRODUCTION

Most of the important chemical reactions which occur in the very high temperature air produced around space vehicles as they enter the atmosphere have been investigated both experimentally and theoretically, to some extent at least. One remaining reaction about which little is known, and which could be quite important at the extremely high temperatures that will be produced by the class of space vehicles now contemplated—such as the AOTV—is the excitation of bound electron states due to collisions between heavy gas particles. Rates of electronic excitation due to free electron collisions are known to be very rapid, but because these collisions quickly equilibrate the free and bound electron energy, the approach to full equilibrium with the heavy particle kinetic energy will depend primarily on the much slower process of bound electron excitation in heavy particle collisions and the subsequent rapid transfer to free electron energy. This may be the dominant mechanism leading to full equilibrium in the gas once the dissociation process has depleted the molecular states so the transfer between molecular vibrational energy and free electron energy is no longer available as a channel for equilibration of free electron and heavy particle kinetic energies.

Two mechanisms seem probable in electronic excitation by heavy particle impact. One of these is the collision excitation and deexcitation of higher electronic states which are Rydberg like. A report, entitled "Semi-Classical Theory of Electronic Excitation Rates", was submitted previously under Grant NAG 1-14211. This presented analytic expressions for the transition probabilities, assuming that the interaction potential is an exponential repulsion with a perturbation ripple due to the dipole-induced dipole effect in the case of neutral-neutral collisions, and to the ion-dipole interaction in the case of ion-neutral collisions.

However the above may be, there is little doubt that excitation of ground state species by collision occurs at the point where the initial and final potentials cross, or at least come very close. Therefore this mechanism would be applicable to the case where a gas is initially at very low temperature suddenly subjected to high energy heavy particle bombardment. This situation would model the measurement of excitation cross section by molecular beam techniques, for example. The purpose of this paper is to report values of cross sections and rate coefficients for collision excitation of ground state atoms estimated with the Landau-Zener
transition theory and to compare results with measurements of excitation cross sections for a beam of Hydrogen atoms impacting Argon atom targets. Some very dubious approximations are used, and the comparison with measurement is found less than ideal, but results are at least consistent within order of magnitude. The same model is then applied to the case of N-N atom collisions, even though the approximations then become even more doubtful. Still the rate coefficients obtained are at least plausible in both magnitude and functional form, and as far as I am aware these are the only estimates available for such rate coefficients.

The complete solution for electronic excitation rates will require modelling both the mechanisms mentioned above; the transitions from ground state to higher excited states and the transitions between upper electronic states. In addition, at very low gas densities, which will occur about modern space vehicles, the drain in excited state population by radiation will need to be taken into account simultaneously with collision transition rates.

EXPERIMENTAL H–Ar COLLISION EXCITATION CROSS SECTIONS

Cross sections for collision excitation of H atoms impacting Ar atoms have been measured by VanZyl, Neuman, Rothwell, and Amme for transitions to the 3s, 3d, 4s, and 4d states at collision energies from 25 to 2500 ev. Birely and McNeil measured some cross sections for 2s and 2p transitions at the higher energies. The results shown in Figure 1 are the cross sections with which theoretical estimates should compare.

H excitation by collision with other noble gas targets have been measured as well. The heavy partners Kr and Xe give quite similar results, but the lighter He and to some extent the Ne atom targets appear to provide some additional channels for excitation that complicate the interpretation. For present purposes, the Ar–H collision results will be used as the standard for comparison with the Landau-Zener method.

A striking feature of the cross sections shown on Fig.1 is the fact that the 3d and 4d transitions occur much more readily than the 3s and 4s transitions; the cross sections for excitation of the higher angular momentum states are both larger and occur at lower energies. Qualitatively this has been somewhat explained as follows. As the Ar(1S) and H(2S) atom approach, one of the Argon's electrons spends time near the Hydrogen in the H–(1S) configuration, leading to a strong ionic component in the diabatic wave function for the complex.

\[ \text{Ar}^{1S} + \text{H}^{2S} \rightarrow \text{Ar}^{+}(2P^0) + \text{H}^{1S} \]  \hspace{2cm} \text{Eq.}(1)
The complex \((\text{Ar}^{'\text{H}^-})\) can exist in two molecular configurations, \(2\Sigma^+\) or \(2\Pi\). The former is associated with two electrons in a bonding orbital about the positive ions and the latter in antibonding orbitals. At intermediate range the electron densities will maximize in a somewhat linear configuration with the ions.

\[
\text{Ar}^+ + \text{H}^- \longrightarrow \text{Ar}^{' +} + 2e + \text{H}' \\
\quad \longrightarrow e + \text{Ar}^{' +} + \text{H}' + e
\]  

Eq.(2)

When the two nuclei pull apart, the electrons either remain in the \(\text{Ar}^{' +} + \text{H}^-\) configuration or snap into the neutral states \(\text{Ar} + \text{H}\); in the latter case maximum overlap occurs with the \(\text{H}\) atom in the \((\text{nd})\) states, not in the \((\text{ns})\) states, and presumably the maximum overlap provides the maximum transition probability. VanZyl finds that the Balmer radiation emitted from the excited states is polarized just as one expects.

Although this concept seems direct enough that a simple model might be devised which would lead to reasonable approximations, VanZyl reports that his discussions with Alex Dalgarno about this possibility were discouraging. However that may be, the brash attempt is made here even though drastic approximations are involved, just to see what ensues.

**LANDAU-ZENER CROSS SECTION MODEL**

The Argon-Hydrogen collision potentials used in the calculations are shown in Figure 2. The repulsive potential between the ground state atoms is an estimate provided by Olson and Liu according to VanZyl et al:

\[
U = 200 e^{-1.678 r/a_o} \text{ ev.} \quad \text{Eq.}(3)
\]

where \(r\) is the distance between the collision pair and \(a_o\) is the Bohr radius. At some point the order of \(2a_o\) this potential crosses the Coulomb potential

\[
U = 15.00 - \frac{27.18}{r/a_o} \text{ ev.} \quad \text{Eq.}(4)
\]

which describes the attraction between \(\text{Ar}^+'\) and \(\text{H}'\) at large distances at least. The dashed curve represents the qualitative behavior that the diabatic \(\Sigma\) branch of this potential might take at close range. An uneducated guess is used that a crossing occurs at \(r_o\) about \(2a_o\) with the crossing potential \(U_o\) equal 6.5 ev. These numbers are in considerable doubt, and they could be varied to
change the magnitude of the cross sections and to some extent the energy where the peak cross section occurs. The relative comparisons between the different excited state cross sections will not depend on the transition to the ionic state as much as upon the intersections between the Coulomb potential and the interaction energy between Ar + H*, which fortunately are relatively well defined at the larger distances where the intersections occur. At 6a₀ and beyond, the Ar⁺ + H⁻ potential will be almost purely Coulomb, Eq.(4), while the neutral atom-atom potential is just a constant, the energy of the exited H atom in the nᵗʰ quantum level. The intersections occur where

\[
15.00 - \frac{27.18}{r/a₀} = 13.59 \left(1 - \frac{1}{n^2}\right)
\]

Eq.(5)

The Landau-Zener approximation⁹,¹⁰ for the probability of no transition at a potential crossing point is

\[
q = e^{-\gamma / \mu}, \quad \gamma = \frac{-2\pi}{\hbar} \frac{H_{12}^2}{u|\Delta \text{grad} H|}
\]

Eq.(6)

where \(H_{12}\) is the effective interaction energy between the two configurations at the crossing point, \(\mu\) is the velocity with which the system moves across that point, and \(\Delta \text{grad} H\) is the change in slope of the two potentials there. For the present case this is simply

\[
\Delta \text{grad} H = \frac{27.18}{a₀ (r/a₀)^2} \frac{e v}{\text{Bohr}}
\]

Eq.(7)

The probability of transition at the crossing is just \((1-q)\), of course. The cross section for transition after both an ingoing and outgoing transit of the crossing is

\[
S_o = 4\pi r_o^2 (1-U_o/E) \left[ E_3(\beta) - E_3(2\beta) \right]
\]

Eq.(8)

The factor \((1-U_o/E)\) accounts for the fraction of collisions with miss distance \(r_o\) which can reach the reaction surface due to conservation of angular momentum, and \(E_3(\beta)\) is an integral related to the exponential integral, which takes into account the fact that the crossing velocity \(\mu\) is a function of the miss distance, where \(\beta\) is the exponential factor given in Eq.(6).
The reduced mass for the collision is $\mu$, $E$ is the initial collision energy, and $U_0$ is the potential energy at the crossing point. Ref. 11 reviews the original Landau Zener theory and the derivation of these expressions.

The principal unknown is the effective interaction $H_2$ between the two states at the crossing point. Olson, Smith, and Bauer developed an empirical relation for $H_2$ which provides a fair approximation for the relation between $H_2$ and $r_0$. This is given in terms of the ionization potentials $I_1$ and $I_2$ for the colliding species (in this case 15.00 ev for Argon and 13.59 ev for Hydrogen) in order to account for deviations from Hydrogen like states.

$$R_0^* = \frac{r_0}{2} [(2I_1)^{1/2} + (2I_2)^{1/2}], \quad H_{12} = (I_1 I_2)^{1/2} R_0^* e^{-0.86 R_0^*} \text{ Eq. (9)}$$

Values of $H_{12}$ given by Eq.(9) are within a factor 3 of values that duplicate experimental rates for a wide variety of ion-ion recombination reactions such as considered here.

The somewhat complex form of the cross section given by Eq.(8), which accounts for the variation in crossing velocity $u$ with miss distance, is not necessary for the subsequent transitions to the excited H states. Crossing distances are so large that collisions close enough to make the transition to the Coulomb like potential, either on the incoming or the outgoing leg of the collision trajectory, have essentially the crossing velocity for head on collisions. Then the cross section for production of the $n^{th}$ quantum state is

$$S_n = S_o e^{-\sum (\beta_n + \beta_{n+1})} (1-e^{-\beta_n}) \text{ Eq.(10)}$$

where $S_o$ is the cross section of Eq.(8) for the initial transition to the Coulomb like potential, and the factors $\beta_i$ are given by Eq.(8a) for escape from this potential to the $i^{th}$ quantum level of Hydrogen.

Excitation cross sections which result from these bold approximations are shown on Figure(3). The Landau-Zener method provides no preference for escape to the higher angular momentum
states, so it is not surprising that this feature of the experimental results is missing. The most that can be said for the calculated cross sections is that they seem to represent a sort of average for the degenerate states with different angular momentum. For example, the calculated cross sections for transitions to the 3rd and 4th quantum levels peak at about 250 ev collision energy, whereas the experimental cross sections peak in the vicinity of 100 ev for the nd transitions and about 800 ev for the ns transitions. The calculated cross sections have a broader half width than observed. Finally, the calculated peak cross sections fall off more rapidly than they should, decreasing about a factor of 8 going from n = 3 to 4, while the observed cross sections decrease about a factor of 3 or 4. Also the calculated cross sections are about an order of magnitude less than observed. However some of the discrepancies could be adjusted by reasonable variations in doubtful parameters. For example $r_o$ could easily be as much as 3a_o for the initial transition to the Coulomb like potential, which would increase the cross sections by about 5. Values of $H_{12}$ are uncertain by at least a factor of 3, which can shift the energy where the cross section maximizes by a factor of 10. Notwithstanding the discrepancies, a rough functional similarity remains which is also quantitative to about an order of magnitude.

The upper dashed curve on Figure(3) represents the cross section for all transitions to the H'Ar configuration, while the lower dashed curve represents the cross section for collisions which remain in that configuration after essentially all the escapes to neutral atoms.

N ATOM EXCITATION IN N-N COLLISIONS

Although there is doubt that N is bound strongly enough to permit a similar mechanism, and the assumptions become more uncertain than for H-Ar collisions, the preceding charge transfer and recombination mechanism is assumed for excitation in neutral N atom collisions as well, just to see whether the results make any sense at all. Figure(4) shows the interaction potentials used for the N-N collisions. Because of the low lying N('D^0) and N('P^0) states of atomic N, a much larger multiplicity of states occurs. Moreover, the range of atom interaction is larger so that crossings occur within distances where the potentials have split into a fan of attractive and repulsive branches. For example, the four well known potentials for ground state collisions diverge within 6a_o and the higher state potentials fan out at somewhat greater distances. The multiplicities of levels are 4,6,4,30,18, and 12 for the 6 lowest lying configurations with transitions in zero point energies from 0 to 7.14 ev. Although the electron affinity for the N atom is in doubt, Gilmore suggests that a Coulomb like N+N^- potential may lead into the observed bound state b^1Sigma_u^+ of N_. This would be consistent with N('P) having an electron affinity about 0.29ev. The potential at long range between N' and N^- is
Faced with this horrible multiplicity of unknown potentials and unknown crossing points, we brashly assume that one of the intermediate potentials that is level until very short range will give a sort of average transition probability for the entire fan of attractive and repulsive potentials. The $^5\Sigma_g^+$ potential for two ground state N atoms is an example that is relatively flat until closer than 3$a_o$. Accordingly the effective crossing point is taken to be where the product state energy level equals the Coulomb potential of Eq.(11). This no doubt underestimates the distances where many crossings actually occur, which will result in overestimating the effective interaction energies $H_{12}$. On the other hand, the most repulsive potentials have the greater probability in collision due to their higher degeneracy, with larger values of the potential gradient change at the intersection, which may somewhat compensate for the crude averaging. The first effective crossing is assumed to be between the $^5\Sigma_g^+$ potential and the ionic potential at 4.4ev, and that crossings between the ionic potential and the two lowest states at 2.38 and 3.57ev are relatively ineffective.

Cross sections which follow from the above are shown in Figure(5). In this case there are no experimental data with which to compare. All that can be said is that the size of the cross sections are reasonable, with maxima at about $10^{-16}$ cm$^2$ at 250 ev collision energy for the lowest states and decreasing to about $10^{-19}$ cm$^2$ around 3000 ev for the higher states considered. Transitions to the higher states would probably occur primarily in multiple collisions involving the perturbations of Rydberg like states in collision, such as analyzed in the previous report\textsuperscript{1}, provided that densities are high enough that collision induced transitions are not negligible compared with radiation losses.

HEAVY PARTICLE COLLISION EXCITATION RATE COEFFICIENTS

Once the collision cross sections are estimated, the rate coefficients are just an integral over a Boltzmann distribution of collision energies\textsuperscript{11}.

\[ U = (14.54 - .29) - \frac{29.18}{r/a_o} \text{ ev} \quad \text{Eq.(11)} \]
\[ k(T) = \bar{u} e^{-x_0} \int_0^\infty S(x) (x_0+x) e^{-x} \, dx \]  
Eq. (12)

where \( \bar{u} \) is the mean collision velocity \((8kT/\pi m)^{1/2} \), \( x \) is the dimensionless collision energy above the activation threshold \((E-U_o)/kT\), and \( x_0 \) is the dimensionless threshold energy \( U_o/kT \). These integrals could be evaluated numerically for each temperature desired, but in view of the uncertainties in the cross sections it seems adequate and more convenient to use an approximate analytic expression in terms of the cross section parameters. Both the observed and calculated cross sections have a somewhat similar shape that can be fit around the maximum with a function of collision energy \( E \) having the form

\[ S = 4 S_m e^{-\beta (1-e^{-\beta})}, \quad \beta = [E_c/(E-U_o)]^n \]  
Eq. (13)

This function fits the threshold at \( U_o \) and the maximum cross section \( S_m \). The parameters \( E_c \) and \( n \) are chosen to fit the cross section at another value, such as the half maximum.

\[ Q_m = 0.5 = e^{-[E_c/(E_m-U_o)]^n} \]

\[ E_c = (-\ln 0.5)^{1/n} (E_m-U_o) = (0.69315)^{1/n} (E_m-U_o) \]  
Eq. (14)

\[ Q_{1/2} = 0.14645 = e^{-[E_c/(E_2-U_o)]^{1/2}} \]

\[ E_c = (-\ln 0.14645)^{1/n} (E_2-U_o) = (1.92108)^{1/n} (E_2-U_o) \]

where \( E_m \) and \( E_2 \) are the energies where the cross section maximum and half maximum occurs. Equating the values for \( E_c \) provides a value for \( n \).

\[ n = \frac{1.01940}{\ln(E_m-U_o) - \ln(E_2-U_o)} \]  
Eq. (15)

Typical values of the exponent \( n \) which fit the cross sections of Figure(5) are about 0.7. The above equations fit the half maximum cross section at the lowest energy, since this is the most important wing of the function for the integration of Eq.(12) when \( kT \) is less than \( E_m \), which is normally the case for gas temperatures of interest. However, the same value of the exponent \( n \) also approximates the higher energy half maximum reasonably well for the cross sections shown.
EXCITATION RATE COEFFICIENTS

For thermal energies $kT$ that are small compared with $E_\ast$ a sufficiently good approximation of the cross section for the rate coefficient integral is

$$ S(x) = 4 \ S_m \ g = 4 \ S_m \ e^{-(x'/x)^p}, \quad x' = E_c/kT \quad \text{Eq. (16)} $$

and the rate coefficient is

$$ k = 4 \overline{u} \ S_m \ e^{-x_o} \int_0^\infty (x_o+x) \ e^{-[x'/(x)^q]} dx \quad \text{Eq. (17)} $$

Expand the exponent about its minimum and approximate the integral by the method of steepest descent.

$$ x'/(x)^q = b + c^2(x-x_m)^2 + \cdots $$

$$ x_m = n \frac{1}{n+1} \ , \quad b = \frac{n+1}{n} x_m \ , \quad c^2 = \frac{n+1}{2x_m} \quad \text{Eq. (18)} $$

The result is

$$ k = 4\overline{u} \ S_m (x_o+x_m) e^{-(x_o+b)} \int_0^\infty e^{-c^2(x-x_m)^2} d(x-x_m) \quad \text{Eq. (19)} $$

$$ = \frac{4(\pi)^{1/2}}{c} \overline{u} \ S_m (x_o+x_m) e^{-(x_o+b)} $$

RELAXATION RATE FOR ELECTRONIC EXCITATION

For the case where the gas atoms are initially in the ground electronic state but at high kinetic temperature, the rate of change in electronic energy is the sum over all possible transitions from the ground state and the reciprocal product of gas density and relaxation time is this rate of change divided by the equilibrium electronic energy

$$ \frac{1}{n^*} = \frac{\sum_{i} \epsilon_{i} \ k_{oi}}{1/ \ Q \ \sum_{i} \epsilon_{i} \ n_{i}/ n} \quad \text{Eq. (20)} $$
where $n_i$ is the density of atoms in state $i$ with the electronic energy $\epsilon_i$, $k_{oi}$ is the rate coefficient for excitation of ground state atoms to state $i$, $n$ is the total atom density, and $Q$ is the partition function. For an optically thick gas in which the photon absorption equals the photon decay, the distribution function is the usual Boltzmann distribution, except that an approximation is used to allow for depletion of the upper levels about $kT$ below the ionization limit.

$$Q = \sum_i \frac{n_i}{n} = \sum_i g_i e^{-\epsilon_i/kT} \left[ 1 - e^{-(I - \epsilon_i)/kT} \right] \quad \text{Eq. (21)}$$

The density relaxation time products $(nT)$ calculated in the above manner are shown in Figure(6) in units of both molecule-sec/cc and mol-sec/cc. Figure(7) compares the $(nT)$ products for the heavy particle collision relaxation with values for vibrational relaxation by heavy particle collision and for the free electron collision relaxation of both vibrational and bound electron energy. The times predicted here for electronic relaxation by heavy particle collision are larger than for vibrational relaxation at the same temperature. However, the two processes have similar relaxation times over the temperature range that is relevant for their reaction. $(nT)$ spans from about $10^{-8}$ to $10^{-13}$ molecule-sec/cc over the range of $kT$ from 0.3 to 1.0 ev, while the estimates made for electronic energy relaxation span from $10^{-8}$ to $10^{-12}$ for the range of $kT$ from 1 to 5 ev. In both cases $\ln(nT)$ is nearly linear with $(kT)^{-1/3}$ and the predicted $\text{N atom collision relaxation of N atom electronic energy is approximately}$

$$nT = 4.5 \times 10^{-19} e^{23.7/(kT)^{1/3}} \quad \text{mol-sec/cc}$$

$$= 2.7 \times 10^5 e^{23.7/(kT)^{1/3}} \quad \text{molecule-sec/cc} \quad \text{Eq. (22)}$$

Electron collision relaxation processes, on the other hand, tend to be relatively independent of temperature. Electron impact excitation of $\text{N}_2$ vibrations is based on some good experimental data by Schultz. However relaxation of $\text{N}$ atom electronic states by electron bombardment is based on rate coefficients that are also quite speculative, and the functional trend shown may not be realistic. However, if the order of magnitude is at all correct, $10^{-18}$ mol-sec/cc for $nT$, the assumption that free electron and bound electron energies are instantly equilibrated in the flow is good for many cases of interest.

An interesting feature of the free electron collision relaxation times is that they are essentially independent of the electronic temperature. This is the same result that one obtains for heavy particle collision excitation of vibrational energy, even though unlike the case for vibrational states, electronic energy
levels are randomly spaced and degeneracies vary widely. If this same independence on electronic temperature should apply to the heavy particle collisions, then the estimates made here for relaxation times of atoms in the ground state would also apply at finite electronic temperatures. However, this might not hold true since another mechanism may be involved in the excitation and deexcitation of the upper Rydberg like states.

CONCLUDING REMARKS

The assumptions used to obtain heavy particle collision excitation rates of bound electron energy are so severe that the results can be little better than an indication of the functional trends that may occur, with quantitative uncertainty probably more than an order of magnitude. These rates are, however, the first estimates that seem to have been made for a reaction process that could be important in very high temperature gasdynamic flow about space vehicles. Although it may be possible to obtain more rigorous cross sections than the present estimates, this will require much effort and the results are not really totally reliable anyway, unless some experimental data can be obtained to validate the calculations. And even when experiments are available that define the cross sections around the maximum quite well, the most important region for present purposes is within 25ev of threshold, where measurements are generally too difficult. Cross sections near threshold will probably remain unreliable so measurements of rate coefficients, if possible, would provide the best validation of theory.

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FIGURES

1. EXPERIMENTAL CROSS SECTIONS FOR H EXCITATION BY Ar COLLISION

2. ARGON + HYDROGEN COLLISION POTENTIALS

3. LANDAU-ZENER CROSS SECTIONS FOR H EXCITATION BY Ar COLLISION

4. N + N COLLISION POTENTIALS

5. CROSS SECTIONS FOR N ATOM EXCITATION IN N + N COLLISIONS

6. DENSITY-RELAXATION TIME PRODUCTS FOR N ATOM EXCITATION IN N + N COLLISIONS

7. COMPARISON OF DENSITY-RELAXATION TIME PRODUCTS FOR VARIOUS ATOM AND ELECTRON COLLISION PROCESSES.
1. EXPERIMENTAL CROSS SECTIONS FOR H EXCITATION BY Ar COLLISION
2. ARGON + HYDROGEN COLLISION POTENTIALS
3. LANDAU-ZENER CROSS SECTIONS FOR H EXCITATION BY Ar COLLISION
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5. CROSS SECTIONS FOR N ATOM EXCITATION IN N + N COLLISIONS
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COMPARISON OF DENSITY-RELAXATION TIME PRODUCTS FOR VARIOUS ATOM AND ELECTRON COLLISION PROCESSES.