Dynamics of Low Velocity, Rovibrationally Inelastic Li$_2$—Rare Gas Collisions

by

William Jasmine
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Abstract

This thesis presents a study of the dynamics of trajectory calculations at low velocity utilizing potentials for the Li$_2$-Ne and Li$_2$-Xe collisional systems. We have found that at these low velocities, significant rovibrational energy transfer still takes place. This is due to the fact that there exists a “capture radius” at these low velocities such that if the impact parameter of the incoming atom is within this capture radius, the mutual attraction between the rare gas atom and Li$_2$ molecule is strong enough to force the atom into the potential well of the collisional system. The energy that the atom gains as it falls down this steep potential well, in addition to the fact that there are actually a multitude of collisions that take place while the atom is in the well, allow for the possibility of significant energy transfer. In addition, we elucidate how changes in the initial vibrational and rotational quantum number affect the dynamics of this energy transfer. Finally, the fact that these low initial velocities correspond to ultra-cold temperatures suggest the possibility that these results can be tested experimentally in a device such as a magento-optical trap.
1 Introduction

The rate of inelastic molecular collisions typically declines at low velocity due to the fact that the low energy of the incoming atom is unlikely to induce significant energy transfer. By simulating these collisions with trajectory calculations, we can determine if an experiment is physically realizable. We have found that in certain cases, extremely low velocity collisions produce cross sections that could be measured in a device such as a magneto-optical trap (MOT). The work presented here shows that this is the case for low velocity collisions of the following systems:

\[
\text{Li}_2(^{1}\Sigma_u^+)(v_i,j_i) + \text{Xe} \rightarrow \text{Li}_2(^{1}\Sigma_u^+)(v_f,j_f) + \text{Xe}
\]

\[
\text{Li}_2(^{1}\Sigma_u^+)(v_i,j_i) + \text{Ne} \rightarrow \text{Li}_2(^{1}\Sigma_u^+)(v_f,j_f) + \text{Ne}
\]

where \(v\) and \(j\) are the vibrational and rotational quantum numbers of the \(\text{Li}_2\) molecule. In addition, through an in depth analysis of these collisions, we highlight a mechanism that is present in both systems. Specifically, low velocity collisions of these systems result in the incoming atom being “trapped” in the potential well of the system. Even further, the depth of this well (and thus the strength of the attractive force producing it) is dependent on \(\gamma\), the angle between the internuclear axis of the molecule and \(\mathbf{R}\), the vector from the center of mass of the molecule to the incoming atom. Finally, these results can be replicated through the use of a model potential that mimics only the basic components of the \textit{ab initio} [1] potential surfaces that were initially used, pointing to the fact that this mechanism may be more pervasive in the realm of molecular dynamics than originally suspected.
1.1 Quasiresonant Vibration Rotation Transfer

Quasiresonant vibration-rotation transfer (QVRT) is a type of energy transfer process that is of importance in the study of molecular dynamics due to the significant effects that it has on the outcome of a certain collisions. In particular, quasiresonant vibration-rotation transfer (QVRT) is a dominating process in atom-diatom collisions at high initial rotational levels [2]. On multiple occasions, an explanation of the work presented here will include mention of the effects of quasiresonance. As a result, a proficient understanding of quasiresonance is crucial.

1.1.1 Molecular Resonance

To understand the quasiresonant phenomena of a collisional system, one must first understand the purely resonant phenomena of that system. The criterion for molecular energy resonance is as follows:

\[
\frac{\Delta j}{\Delta v} = -\frac{\omega_v}{\omega_R}
\]  

(1)

where \(\omega_v\) is the angular frequency of the vibration and \(\omega_R\) is the angular frequency of the rotation. The equations for \(\omega_v\) and \(\omega_R\) are as follows:

\[
\omega_v = \frac{\partial E_v}{\partial v}
\]  

(2)

\[
\omega_R = \frac{\partial E_R}{\partial j}
\]  

(3)
where $E_v$ the vibrational energy of the molecule, and $E_R$ is the rotational energy of the molecule. More specifically, the classical expressions for both $\omega_v$ and $\omega_R$ are as follows [3],

$$\omega_v = \frac{\omega_e}{Q^3}$$  \hspace{1cm} (4)

$$\omega_R = 2\omega_v \lambda j$$  \hspace{1cm} (5)

where $\omega_e$ is the vibrational spectroscopic constant, and $\lambda$ is the ratio $B_e/\omega_e$ of the vibrational/rotational spectroscopic constants. In addition, the equations for $c$ and $Q$ seen in the above equations are as follows,

$$c = \sqrt{1 + 4\lambda^2 j^2}$$  \hspace{1cm} (6)

$$Q = 2\lambda v + c$$  \hspace{1cm} (7)

This gives the frequency ratio,

$$\frac{\omega_v}{\omega_R} = \frac{\sqrt{1 + 4\lambda^2 j^2}}{2\lambda j}$$  \hspace{1cm} (8)

Thus, the criterion for energy resonance is,

$$\frac{\Delta j}{\Delta v} = -\frac{\sqrt{1 + 4\lambda^2 j^2}}{2\lambda j}$$  \hspace{1cm} (9)

Notice how the dependence on $v$ has canceled out, meaning that the condition for resonance is wholly dependent on the value of $j$. For example, when $j_i=64$
there is almost a 4:1 ratio between the frequency of vibration to the frequency of rotation, and \( \Delta j/\Delta v \approx -4 \). Fig. 1 highlights this correlation between \( \Delta j \) and \( \Delta v \) in Li\(_2\)-Ne collisions at a relative velocity \( v_{rel} \) of 60,000 cm/sec. However, it is also important to note that because the Li\(_2\) molecule looks identical after a rotation of \( \pi \) radians, it is effectively a 2:1 resonance. Since the resonant values of \( j \) will be important in later sections, Tab. 1 lists the exact values of \( j \) for which \( \omega_v/\omega_R \) is an integer.

![Figure 1: Represents 50,000 Li\(_2\)-Ne trajectories with \( v_i=5, j_i=64 \) at \( v_{rel}=60,000 \) cm/sec. The strong correlation between \( \Delta j \) and \( \Delta v \) produces the thick, solid line in the center of this plot. The slope of this line is very close to -4, consistent with Eq. (9).](image)
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<th>$j$</th>
</tr>
</thead>
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<tr>
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<tr>
<td>8</td>
<td>32.2116</td>
</tr>
<tr>
<td>16</td>
<td>16.0168</td>
</tr>
</tbody>
</table>

Tab. 1: The values of $j$ for which $\omega_v/\omega_R$ is an integer value. The 16:1 resonance is included as it is mentioned frequently in later sections.

1.1.2 Defining Quasiresonance

It has been shown that Li$_2$-Ne collisions at high $j$ and low velocity are the result of a sequence of subcollisions that we refer to as “collisionettes” [4]. Additionally, each collisionette occurs when the end of Li molecule passes near the Ne atom. When $\omega_v/\omega_R$ is equal or close to an even integer value, there is an integer number of vibrations for each half rotation. This results in each collisionette occurring just before the molecule is about to reach its vibrational outer turning point, and just after the molecule was at its closest rotational approach, or vice versa. The result of the entire collision will then be significant, negatively correlated changes in $v$ and $j$ such that it is not unlikely for the molecule to change vibrational or rotational levels. Also, note that this negative correlation is consistent with Eq. (1). According to Eq. (9), this type of collision will occur when $\omega_v/\omega_R$ is close to an even integer value, such as when $j_i = 64$. But what if $j$ is not close to one of these “resonance values”? In that case, the sign of $\Delta j$ for different collisionettes need not be the same, seeing as the phase of the molecule will be different for
each collisionette. However, the magnitude of $\Delta j$ values that bring $j$ closer to a resonance value will be larger compared to the magnitude of $\Delta j$ values that push $j$ away from a resonance value [4]. Thus, the average value of $\Delta j$ for each collisionette $\Delta j_{avg}$ will almost always bring $j$ closer to a resonance value at the end of a collision. In other words, the result of almost every collision is a $j_f$ value that is closer to the nearest resonance value compared to $j_i$. This pull on $j$ also has the effect of pulling $\omega_R$ towards the closest value at which $\omega_v/\omega_R$ is an even integer. This “frequency locking” effect is the hallmark of quasiresonance: at high $j$, $\omega_v/\omega_R$ will tend towards the closest even integer value. As a result, for all values of $\omega_v/\omega_R$ such that $n - 1 < \omega_v/\omega_R < n + 1$, $\Delta j/\Delta v = -n$, for some even integer $n$. This is essentially a “quantization” of $\Delta j/\Delta v$, which can be more easily visualized in Fig. 2.

1.1.3 Effects of Quasi-Resonance on Li$_2$-Ne Cross Sections

The previous section explained how QVRT induces correlated values of $\Delta v$ and $\Delta j$ for high $j$ collisions. For example, at $j_i = 64$, the relation of the vibrational energy transfer $\Delta v$ to the rotational energy transfer $\Delta j$ is:

$$\Delta j \approx -4\Delta v$$  \hspace{1cm} (10)

It is also the case that correlations like the one in Eq. (10) actually become enhanced as $v_{rel}$ decreases [5]. In other words, the spread around the line that is
Fig. 2: Image from Magill et. al., 1988 [4]. The figure represents the result of Li$_2$-Ne trajectories with $v_{rel}=31,800$ cm/sec, $v_i=9$ for a range of $j_i$. The figure shows the variation of (a) $\Delta j/\Delta v$ with the frequency ratio (b) $\omega_v/\omega_R$. Note how in (a) the values of $\Delta j/\Delta v$ are essentially quantized at even integer values, and do match up with the energy resonant line.

seen in Fig. (1) becomes significantly narrower at lower values of $v_{rel}$. This is shown happening in Fig. (3).

This, coupled with the fact that the number of collisionettes increases with decreasing velocity, makes it seem as though $\Delta j$ and $\Delta v$ will continue to rise as the velocity is lowered. It turns out that this is true, though only for a specific range of low collision velocities. Thus, in this range, certain large, vibrationally inelastic cross sections can be seen. However, it turns out that some of these inelastic cross sections do not continue to rise below a certain $v_{rel}$. This is for two reasons:
Fig. 3: Each plot represents approximately 5,000 Li₂-Ne trajectories at \( v_i=5, j_i=64 \). The solid line visible in each plot has a slope equal to -4. Note that as \( v_{rel} \) decreases, the correlation between \( \Delta j \) and \( \Delta v \) gets stronger.

(1) Despite inducing a tighter correlation between \( v \) and \( j \), a lower initial collision energy means that \( \Delta v \) and \( \Delta j \) will be smaller for each collisionionette. This is due to the fact that at low enough \( v_{rel} \), the effect of the tighter correlation between \( v \) and \( j \) becomes overshadowed by the lack of significant energy transfer. This is evidenced in Fig. 3, in which the length of the visible line shrinks as \( v_{rel} \) is lowered, indicating a decrease in the average energy transfer despite the tighter correlation. This decrease in energy transfer means that many trajectories do not reach the inelastic bins, causing a decrease in the cross section.
(2) Though a large number of collisionettes would seem to result in a larger overall energy transfer, there is a point at which the effects of subsequent collisionettes begin to undo the effects of previous ones [6]. This is because the subsequent changes in \( j \) begin to change \( \omega_R \), thus altering the frequency ratio between the vibration and rotation (Eq. (8)) so that \( \omega_v/\omega_R \) is no longer an even integer value. Because of the influence of QVRT, subsequent collisionettes will then change \( \omega_R \) in the opposite direction so that \( \omega_v/\omega_R \) begins to return to its initial even integer value. This means that the effect of earlier collisionettes will start to be undone.

In summary, for low velocity collisions of Li\(_2\) at high \( j \), there is a rise and fall of certain inelastic cross sections as \( v_{rel} \) is decreased. A clear example of this is the quasiresonant cross section (\( \Delta j = +4, \Delta v = -1 \)) for Li\(_2\) collisions with \( j_i = 64 \) and \( v_i = 5 \). This can be seen in Fig. 4.

### 1.2 Non-Zero Inelastic Cross Sections at Low Velocity

#### 1.2.1 Li\(_2\)-Xe Cross Sections

The previous section explained the rise and fall trend in certain cross sections with decreasing \( v_{rel} \) for Li\(_2\)-Ne collisions at high \( j \). The example given is the \( \Delta j = +4, \Delta v = -1 \) cross section when \( j_i = 64, v_i = 5 \). However, this cross section exhibits a very different behavior when using the results of Li\(_2\)-Xe calculations for the same values of \( v_i \) and \( j_i \). In particular, as \( v_{rel} \) decreases, \( \sigma \) continues to increase. There is no diminishing of the cross section below a certain \( v_{rel} \) as is seen in Fig. 4. This
Fig. 4: The $\Delta j = +4$, $\Delta v = -1$ cross section as a function of $v_{rel}$. Each point is calculated from the results of 100,000 Li$_2$-Ne trajectories with with $v_i=5$ and $j_i=64$. Note that as $v_{rel}$ decreases from 300,000 cm/sec there is a rise and then a fall in the cross section. Error bars are included in this figure, though they are too small to see clearly.

can be seen in Fig. 5, which shows the $\Delta j = +4$, $\Delta v = -1$ cross section for Xe-Li$_2$ collisions over a large span of $v_{rel}$.

These results were initially quite puzzling, especially at the extremely low velocities at which it seemed almost impossible that the relatively minuscule energy of the Xe atom could change the vibrational or rotational energy of the molecule, let alone by integer quantities of action. For example, at the lowest $v_{rel}$ for which trajectories were calculated, 30 cm/sec, the initial energy of the incoming Xe atom is approximately $5 \times 10^{-5}$ cm$^{-1}$. In comparison, according to Eqs. (4) and (5) the initial vibrational and rotational energies of the Li$_2$ molecule are 1402.5 cm$^{-1}$.
Fig. 5: The $\Delta j = +4, \Delta v = -1$ cross section as a function of $v_{rel}$ with $v_i=5$ and $j_i=64$. Each point is calculated from the results of 100,000 Li$_2$-Xe trajectories. Note that as $v_{rel}$ decreases from 200,000 cm/sec, the cross section continues to rise. Error bars are included in this figure, thought too small to see clearly.

and 2080.0 cm$^{-1}$, respectively. In addition, these low velocities also correspond to extremely low temperatures. Consider the following equation for the temperature $T$:

$$T = \frac{\langle v_{rel}\rangle^2 \pi \mu}{16 k_B}$$

where $\mu$ is the reduced mass and $k_B$ is the Boltzmann constant. If $\langle v_{rel}\rangle = 30$ cm/sec, and $\mu = \mu_{Li_2-Xe}=2.5 \times 10^{-23}$ g, then Eq. (13) yields a temperature of $T=3.2 \times 10^{-5}$ K. As it turns out, $3.2 \times 10^{-5}$ K is in the range of velocities seen in magneto optical traps [7].
1.2.2 Li₂-Ne Cross Sections

After the discovery that the Li₂-Xe $\Delta j = +4, \Delta v = -1$ cross section did not vanish as $v_{rel}$ decreased, we started checking other Ne-Li₂ cross sections at various $v_i$ and $j_i$ to see if the same kind of behavior could be observed. What we found is that while there seem to be no vibrationally inelastic cross sections that continue to rise at low velocity, there are a few rotationally inelastic cross sections that do. For example, Fig. 6 shows the $\Delta j = +2, \Delta v = 0$ cross section with $v_i=5, j_i=64$.

Fig. 6: The $\Delta j = +2, \Delta v = 0$ cross section as a function of $v_{rel}$ with $v_i=5$ and $j_i=64$. Each point is calculated from the results of 100,000 Li₂-Ne trajectories. Note the clear difference in the trend of the cross section seen here compared to the trend seen in Fig. 4.

Even at 10 cm/sec, the cross section continued to rise. This was extremely ex-
citing, as it meant that the mechanism behind these rising cross sections was not specific to just Li₂-Xe collisions.

It was the discovery of results seen in Figs. 5 and 6 that acted as the primary motive for us to explore the dynamics of all low velocity Li₂-Xe(Ne) collisions, forcing us to expand our trajectory calculations over a larger range of $v$ and $j$.

In the following sections, we present the progression of our understanding of the dynamics through use of our varying methods of analysis.
2 Methods

All of the trajectory calculations presented in this thesis are the result of the utilization of a classical trajectory method that models a vibrating rotor. Specifically, our trajectory method implements the use of action-angle variables to numerically integrate Hamilton’s classical equations of motion for the 3-body problem. A visualization of the relationship between the Cartesian and action angle variables is seen in Fig. 7.

Fig. 7: Image from Smith (1986) [3]: Represents the action angle and cartesian coordinates used to describe the dynamical motion of the atom-diatom collision system. The coordinate system is chosen so that the total angular momentum $\mathcal{J} = J + L$ lies along the $\hat{z}$ axis.
In addition, some of the transformations between the variables are listed below:

\[
\cos \gamma = \hat{R} \cdot \hat{r} = -[\cos \psi_J \cos psi_L + C \sin \psi_J \sin \psi_L] \tag{12}
\]

\[
C = \hat{J} \cdot \hat{L} = \frac{\mathcal{J}^2 - J^2 - L^2}{2JL} \tag{13}
\]

\[
J_z = \frac{J}{\mathcal{J}} (J + C L) \tag{14}
\]

\[
\phi_J = \psi_J + \frac{\pi}{2} \tag{15}
\]

\[
L_z = \mathcal{J} - J_z \tag{16}
\]

\[
\phi_L = \psi_J - \frac{\pi}{2} \tag{17}
\]

The generalized atom-vibrator Hamiltonian utilized by the trajectory method is as follows,

\[
H = \frac{p_r^2}{2\mu_m} + \frac{L^2}{2\mu R^2} + \frac{J^2}{2\mu_m^2} + \frac{p_r^2}{2\mu_m} + U(R) + V(R, r, \cos \gamma) \tag{18}
\]

where \( r \) is the internuclear separation, \( p_r \) is the momentum along the internuclear axis, \( \mu_m \) is the reduced mass of the diatom, and \( U(R) \) is the interatomic potential. Eq. (7) also gives the following two equations of motion for the cartesian coordinates \((p_r, r)\), which are given by,

\[
\frac{dp_r}{dt} = -\frac{\partial H}{\partial r} = \frac{J^2}{2\mu_m r^3} - \frac{dU}{dr} - \frac{\partial V}{\partial R} \tag{19}
\]

\[
\frac{dr}{dt} = \frac{\partial H}{\partial p_r} = \frac{1}{\mu_m} p_r \tag{20}
\]
Eqs. (19) and (20) along with Hamilton’s equations derived from Eqs. (12)-(17) completely describe the evolution of the atom-vibrator system in motion [3].

Our choice for the interatomic potential $U(R)$ is a modified harmonic oscillator potential given by,

$$U(r) = \frac{1}{2} \mu \omega^2 r_0^2 \left( \frac{r - r_0}{r} \right)^2$$  \hspace{1cm} (21)

Additionally, the adapted harmonic potential shown in Eq. (21) has been shown to produce better results than that of a Morse potential, for which errors in $r(t)$ grow continuously over time [8]. The actual integration of the equations of motion is carried out by our trajectory program, the mathematics of which is outlined in Smith (1986) [3]. The implementation of action-angle variables to calculate classical trajectories has a few benefits: the calculations are faster than classical calculations carried out in cartesian coordinates [3], and the numerical integration at each time step allows us to track the time evolution of dynamical variables such as $v$ and $j$.

The continuous, classical final actions of the rotational and vibrational levels that are a result of the classical calculation are then quantized via the standard histogram binning method [9]. In short, this involves binning the final rotational and vibrational levels via the following rules,

$$\dot{j}_f = j_i + 2 \left[ \frac{1}{2} (\dot{j}_i - j_i + 1) \right] \hspace{1cm} (22)$$

$$v_f = v_i + \left[ \frac{1}{2} + (v_f^o - v_i) \right] \hspace{1cm} (23)$$
where \([\cdot]\) = the greatest integer function and \(j_f^c\) and \(v_f^c\) are the classical final actions of the rotation and vibration, respectively. Once every trajectory has been placed into its appropriate bin (corresponding to an integer value of \(v_f\), and an even integer value of \(j_f\)), the collisional cross section \(\sigma\) for that bin can be calculated as follows:

\[
\sigma = \frac{s}{n} \pi b_{\text{max}}^2
\]

(24)

In Eq. (24), \(s\) is the number of trajectories in the bin of interest, \(n\) is the total number of trajectories, and \(b_{\text{max}}\) is the maximum value of the impact parameter, an initial input required by our trajectory program. While there do exist more complex binning methods that weight trajectories in a way that is potentially more realistic, standard binning turns out produce the best results for the regimes studied here [10]. In particular, many of the trajectories calculated for results and analysis presented here have a very tight correlation between \(\Delta v\) and \(\Delta j\). As a result, any method to weight the contribution to the cross section for these trajectories causes a significant increase or decrease in the cross section, depending on the value of \(\Delta v\) and \(\Delta j\). This is shown in Fig. 8, which shows a tightly correlated \(\Delta v\) and \(\Delta j\) distribution, along with the bins that the trajectories are grouped into.
Fig. 8: Represents 3,000 trajectories utilizing the Li$_2$-Ne \textit{ab initio} potential with $v_i=5$, $j_i=64$, and $v_{rel}=60,000$ cm/sec. The grid represents the various bins the trajectories can reach. Observe that in the $\Delta v=1$, $\Delta j=2$ bin (labeled a.), and the $\Delta v=0$, $\Delta j=2$ bin (labeled b.), most of the trajectories only reach the corners of the bin due to the fact that there is a high correlation between $\Delta v$ and $\Delta j$. As a result, any method to weight the contribution to the cross section by how close these trajectories are to the center of the bin will result in a cross section that is too small.
3 Trapping Behavior

Sections 1.3.1 and 1.3.2 highlighted the fact that there are certain inelastic cross sections that continue to rise as $v_{rel}$ is lowered. In order for this to happen, there needs to be a significant amount of energy transfer taking place at these low collision velocities, yet at low collision speeds, collisions should be adiabatically damped. The first insight that we had into this surprising behavior was the discovery that if $v_{rel}$ is small enough, there exists a well defined impact parameter below which all the inelastic collisions take place. The elucidation and understanding of this “capture radius,” which we refer to as $b^*$, was the first step forward in understanding the dynamics of these low velocity collisions.

3.1 Defining $b^*$

The effect of $b^*$ can be summarized as follows: if the impact parameter $b$ of an incoming atom is below $b^*$, a collision consisting of one or more of collisionettes will be guaranteed to take place, and inelastic energy transfer can result. On the contrary, if the incoming atom has an impact parameter that is larger than $b^*$, then the collision will be completely elastic. This trapping behavior can be visualized in Fig. 9.

The trapping behavior seen in Fig. 9 results in a uniform nature to the distribution of $\Delta v$ for $b < b^*$. However, while it is the case that non-zero values of $\Delta v$ only occur when $b < b^*$, it is important to note that a $b < b^*$ does not guarantee that the outcome of the collision will be inelastic. This is due to the fact that
the combined effect of multiple collisionettes may result in a \( \Delta v \) and \( \Delta j \) close to 0. Rather, a \( b < b^* \) simply allows for the possibility of an inelastic collision by guaranteeing at least one collisionette takes place.

Fig. 10 highlights the effect of \( b^* \) in a different way by showing the comparison of the paths of two trajectories, one with \( b < b^* \), and one with \( b > b^* \).

As Fig. 10 indicates, the collisions at these low velocities can be quite complex, as some are the result of an alarmingly large number of collisionettes. Fig. 11 shows the effect of these collisionettes over time for the inelastic trajectory shown in Fig. 10.
Fig. 10: A comparison of the paths of two different Li₂-Xe trajectories with \( v_i = 5, \) \( j_i = 64, \) \( v_{rel} = 5000 \) cm/sec. The open circle at the origin represents the location of the center of mass of the Li₂ molecule. Initially, both trajectories are traveling from left to right. However, only the one with an impact parameter below \( b^* \) goes on to produce an inelastic collision. It is worth noting that while this figure is 2-dimensional, the collision actually takes place in a 3-dimensional space. For this reason, it appears as if there are points in the figure where the atom might be inside the space occupied by the molecule, which is not actually the case.

3.2 Dependence of \( b^* \) on \( v_{rel} \)

After further analysis of this trapping behavior, we observed that the value of \( b^* \) increased with decreasing velocity. This seemed consistent with rising trend in the cross section, since it meant that a lower value of \( v_{rel} \) allows for a larger
Fig. 11: This figure represents the inelastic trajectory in Fig. 10 with \( b < b^* \). Here we can see how the dynamical variables \( v \) and \( j \), along with the strength of the potential \( V \) change over the course of the trajectory, and its many collisionettes. Note the long time over which these collisions take place. While this is in part due to the many collisionettes, for most of the collision the slow moving atom and molecule are being drawn together by their mutual attraction. This is omitted from the figure, due to the fact that there are only minuscule variations in \( v \) and \( j \) over that course of time.

percentage of the trajectories to be within \( b^* \) and possibly induce an inelastic collision. The velocity dependence of \( b^* \) can be seen in Fig. 12. The values of \( b^* \) seen in Fig. 12 were calculated by simply determining the largest \( b \) for which an inelastic collision took place in a batch of trajectory calculations. Physically, \( b^* \) represents the minimum impact parameter for which the relative energy of the atom is at the height of the centrifugal energy barrier. It is this observation that enables us to create a model that can predict \( b^* \). Consider an effective potential
Fig. 12: Values of $b^*$ for Li-Xe collisions with $v_i=5$ and $j_i=64$. $b^*$ for a range of velocities. Here, each value of $b^*$ represents the largest impact parameter for which there is an inelastic collision.

for a purely attractive Van Der Waals potential:

$$V_{\text{eff}} = \frac{-C_6}{r^6} + \frac{L^2}{2\mu r^2}$$  \hspace{1cm} (25)$$

The first term represents a long-range attraction, while the second term represents the centrifugal potential, which depends on the angular momentum $L$. The constant $C_6$ is associated with the attractive part of the potential; it determines the strength of the attraction at long range. Fig. 13 shows an example of the effective potential, and how it relates to $b^*$.  

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Effective Potential: $V_{\text{eff}} = V_{\text{cent}} - V(R)$
Centrifugal term: $V_{\text{cent}} = \frac{L^2}{2\mu R^2}$
Attractive term: $V(R) = \frac{C_6}{R^6}$

Fig. 13: Sample attractive and centrifugal potentials, and their combined effective potential. Note that $b^*$ represents the maximum impact parameter for which the barrier does not exceed $E$. The height of the centrifugal barrier and cannot be surmounted unless $R < b^*$.

By taking the derivative of Eq. (25) and setting it to zero we can solve for $b^*$, as it is the value of $R$ for which $V_{\text{eff}}$ is equal to the height of the centrifugal barrier. Carrying out this process yields the result:

$$b^* = \left(\frac{6C_6\mu}{L^2}\right)^{\frac{1}{4}}$$

(26)

Since $E = \frac{1}{2}\mu v_{\text{rel}}^2$, and $L = \mu bv_{\text{rel}}$, substituting Eq. (26) back into Eq. (25) will return an equation that models the dependence of $b^*$ on $v_{\text{rel}}$. After some algebraic
manipulation, we find:

\[ b^*(v_{rel}) = \sqrt{6} \left( \frac{C_6}{\mu} \right)^{\frac{1}{6}} \left( \frac{1}{4v_{rel}} \right)^{\frac{1}{3}} \]  \hspace{1cm} (27)

Eq. (27) is a satisfying result, as it indicates that \( b^* \) only changes when \( v_{rel} \) (or \( E \)) changes, and does not depend on other dynamical variables such as \( v \) and \( j \). We tested this computationally, and confirmed that this is indeed the case: \( b^* \) stays the same for all values of \( v \) and \( j \). In addition, we have confidence in this result as it agrees with the result of a similar derivation carried out by Smith [11].

### 3.3 \( C_6 \) and the Strength of Attraction

Despite the fact that Eq. (27) models the dependence of \( b^* \) on \( v_{rel} \), it cannot completely model the behavior unless the correct value of \( C_6 \) is known. As mentioned in section 3.2, \( C_6 \) is a constant that determines the depth of the potential well, and thus the strength of the potential’s attraction. In the case of Li\(_2\)-Xe collisions, a large value of \( C_6 \) causes the atom to experience a strong attractive force that pulls it towards the Li\(_2\) molecule. This physical representation \( C_6 \) makes clearer a slightly different way to think about \( b^* \), as \( b^* \) would be the minimum possible impact parameter for which the strength of the attraction (the magnitude of \( C_6 \)) is enough to drag the incoming atom into the molecule, consistent with Fig. 10.
3.3.1 $C_6$ for Li$_2$-Xe Collisions

To determine the value of $C_6$ for the potential governing the Li$_2$-Xe collisions, we analyzed the \textit{ab initio} potential surface we use to calculate the Li$_2$-Xe trajectories. Fig. 14 shows a contour plot of the potential well of the Li$_2$-Xe potential, which makes clear the presence of a strong attractive component. Fig. 14 also elucidates the fact that $C_6$ is different for different values of $\gamma$, seeing as the depth of the well is different for different points outside of the Li$_2$ molecule. This is more clearly shown in Fig. 15 which plots multiple 2-D “slices” of the potential, with each corresponding to a particular value of $\gamma$. The dependence of $C_6$ on $\gamma$ means that

![Fig. 14](image)
there exists a range of possible $C_6$ values for every Li$_2$-Xe trajectory. According to Eq. (27), this means that there is also a range of possible $b^*$ values for each Li$_2$-Xe trajectory. This effect is made clear in Fig. 16 which shows only the trajectories from Fig. 9 that have values of $b$ close to $b^*$. To actually determine the value of $C_6$ at a particular $\gamma$, we fitted the function $-C_6R^6$ to the long range part of the potential, where the strength of the attraction dominates the contributions made by other terms. The results of these calculations can be seen in Fig. 17. To find an average value of $b^*$, we fit the points in Fig. 17 from 0 to $\frac{\pi}{2}$ to a cubic polynomial.

Fig. 15: Represents the potential as a function of $R$ for various values of $\gamma$. As $\gamma$ approaches 0 (or as $\cos \gamma$ approaches 1), the depth of the well shrinks. These results are consistent with Fig. 14.
Fig. 16: Represents the same data shown in Fig. 9 over a smaller $b$-range. The inelastic “line” of trajectories extends into the inelastic “cloud” due to the fact that there is actually a range of $b^*$ values at each relative velocity. Note that $b^*_{\text{max}} \approx 18.9\,\text{Å}$ corresponds to a $C_6$ value of $7.86 \times 10^6\,\text{cm}^{-1}\,\text{Å}^6$, while $b^*_{\text{min}} \approx 17.7\,\text{Å}$ corresponds to a $C_6$ value of $4.75 \times 10^6\,\text{cm}^{-1}\,\text{Å}^6$, consistent with Fig. 10. Note that the relatively large difference in the values of $C_6$ corresponds to only a 1.2 Å difference between $b^*_{\text{max}}$ and $b^*_{\text{min}}$.

of the form $f(\gamma) = a\gamma^3 + b\gamma^2 + c\gamma + d$, integrated $f(\gamma)$ over the range $0$ to $\frac{\pi}{2}$, and then divided by $\frac{\pi}{2}$. The result of this calculations yielded the result: $C_{6_{\text{avg}}} = 5.77 \times 10^6\,\text{cm}^{-1}\,\text{Å}^6$. However, it is important to note that while the $\gamma$ dependence of $C_6$ is interesting, the effect it has on the range of possible $b^*$ values is much less significant due to the fact that $b^* \propto C_6^{\frac{1}{2}}$.

After the determination of $C_6$, we were able to determine how well the model matched up with our calculated results. Fig. 18 shows the data from Fig. 12.
Fig. 17: These values represent the values of $C_6$ that produce the best fit of the equation $-\frac{C_6}{R^6}$ to the long-range part of the Li$_2$-Xe *ab initio* potential, for a range of $\gamma$. All values are within the error range of $+/- \ 1 \times 10^{-3}$

replotted along with the theoretical predictions from Eq. (27).

While Fig. 18 shows that the $b^*$ values at higher $v_{rel}$ do not match up perfectly, we attribute this to the fact that trapping behavior, and thus the existence of a $b^*$, starts to dissipate at velocities that exceed 10,000 cm/sec for collisions of Li$_2$-Xe. This can be seen happening in Fig. 19, which shows $\Delta v$ as a function of $b$ at a larger value of $v_{rel}$. However, for all other values of $b^*$, there is strong agreement between the theory and calculations, giving us confidence that our model accurately predicts $b^*$.
Fig. 18: The data from Fig. 12 replotted on a log-log scale to highlight the power law behavior of Eq. (27). The value of $C_6$ used here for the theoretical predictions is the highest value of $C_6$ for Li$_2$-Xe trajectories, which is equal to $7.89 \times 10^6 \text{ cm}^{-1} \text{ Å}^6$, and corresponds to the potential when $\gamma=\frac{\pi}{2}$. The reason this value was used instead of the average value is because the computationally calculated values of $b^*$ are the highest values of $b$ for which there is an inelastic collision. Since there is a positive correlation between $C_6$ and $b^*$, this corresponds to the largest value of $C_6$.
Fig. 19: Change in vibrational action as a function of impact parameter for approximately 3,000 Li2-Xe trajectories with $v_i=5$, $j_i=64$, and $v_{rel}=60,000$ cm/sec. Observe that at these higher velocities, a clear $b^*$ value cannot be seen, as there is a “smoothing out” of the distribution of $\Delta v$ as $b$ increases.

3.3.2 $C_6$ For Li2-Ne Collisions

Initially, we thought that Li2-Ne collisions would not indicate the presence of a $b^*$ due to the fact that the long range attraction present in the Li2-Ne ab initio potential surface is much weaker compared to that of the Li2-Xe potential. Despite this, it turns out that Li2-Ne trajectories calculations are also influenced by the existence of a $b^*$, in a manner very similar to what is seen in section 3.3.1. The only difference is that the values of $b^*$ for the Li2-Ne trajectories are diminished due to the weaker attractive potential. Fig. 20 shows a contour plot of the potential well
for the Li$_2$-Ne \textit{ab initio} potential surface, which highlights the fact that it does not possess the deep wells that dominate the Li$_2$-Xe \textit{ab initio} potential surface.

![Equipotentials of the Li$_2$-Ne \textit{ab initio} potential with $r$ fixed at the equilibrium nuclear distance $r_e=3.108$ Å. The contours span the range from $V = V_{\text{min}}$ to $V = 0$ using 15 cm$^{-1}$ contour intervals. Note that while there is still a well at the side of the molecule, it is neither as deep or steep as the well present in the Li$_2$-Xe potential. Here, the well only has a depth of approximately 52 cm$^{-1}$.]

Because the attractive part of the potential is weaker in the case of Li$_2$-Ne collisions, it must be the case that $C_6$ is of smaller magnitude. To determine the average value of $C_6$ for Li$_2$-Ne potential, we utilized the same method that was outlined in section 3.3.1 to determine the average value of $C_6$ for the Li$_2$-Xe potential. The result of that process yielded the result, \( C_{6\text{avg}} = 4.91 \times 10^5 \) cm$^{-1}$ Å$^6$. This value is about an order of magnitude lower than than the average value.
of $C_6$ for Li$_2$-Xe collisions, resulting in smaller values of $b^*$ at each $v_{rel}$. However, because $b^*$ depends so weakly on the value of $C_6$, the order of magnitude difference in $C_6$ results in $b^*$ values that differ by just a few angstroms. Despite the different values of $C_6$, the results of the Li$_2$-Ne calculations showed that our results still agreed with our theory, as can be seen in Fig. 21.

![Graph showing the relationship between $b^*$ and $v_{rel}$](image)

Fig. 21: The value of $C_6$ used here for the theoretical predictions is highest value of $C_6$ for Li$_2$-Ne trajectories, which is equal to $6.25 \times 10^6$ cm$^{-1}$ Å$^6$, and corresponds to the potential when $\gamma=\frac{\pi}{2}$. The reason this value of $C_6$ was used instead of the average value is explained in caption of Fig. 18.
4 Langevin Cross Sections

The previous section highlighted that at low enough $v_{\text{rel}}$, there exists a capture radius such that if the impact parameter of an incoming atom is within this radius, it and the Li$_2$ molecule will be drawn together. Since the collisions with $b < b^*$ result in a hard impact, and none with $b > b^*$ do, we can define a capture cross section, also known as the Langevin cross section \cite{12} by $\sigma_L = \pi b^*^2$. We see that,

\begin{equation}
\sigma_L = \pi b^*^2
\end{equation}

\begin{equation}
= \pi \left( \sqrt{6} \left( \frac{C_6}{\mu} \right)^{\frac{1}{3}} \left( \frac{1}{4v_{\text{rel}}} \right)^{\frac{1}{3}} \right)
\end{equation}

\begin{equation}
\sigma_L(v_{\text{rel}}) = \frac{6\pi}{4^{\frac{2}{3}}} \left( \frac{C_6}{\mu v_{\text{rel}}^2} \right)^{\frac{1}{3}}
\end{equation}

The results of the above substitution indicates that the Langevin cross section $\sigma_L \propto v_{\text{rel}}^{-\frac{2}{3}}$, consistent with the rising trend in the cross section as $v_{\text{rel}}$ decreases.

4.1 Langevin Behavior in Individual and Total Inelastic Cross Sections

To check the consistency of Eq. (30) with our numerical results, we fitted the cross sections seen in Figs. 5 and 6 to a function proportional to $v_{\text{rel}}^{-\frac{2}{3}}$. This is shown in Fig. 22, in which the data agrees well with the fitted function. In fact, the Langevin ($v_{\text{rel}}^{-\frac{2}{3}}$) dependence seen in Fig. 22 holds true for every inelastic cross section that was observed to continue rising as $v_{\text{rel}}$ decreases. This is evidenced by the fact that the total inelastic cross section, or the sum of the cross sections
Fig. 22: The cross sections plotted here are the same as the ones in Figs. 5 and 6, along with their corresponding fits to the equation \( a * v_{rel}^{2/3} \). It is clear that Eq. (30) correctly models the dependence of the cross section on \( v_{rel} \) as indicated by the strong agreement: the fit of the parameter \( a \) is within a +/- .4 % margin of error. In addition, the fit only included the cross sections at velocities for which there is a well defined \( b^* \). For the \( \text{Li}_2\text{-Ne} \) collisions, trapping behavior ceases to dominate for velocities above 3000 cm/sec, and is the source of the disagreement between the fit and the data seen for some of the higher velocity cross sections.

for every pair of \( \Delta v \) and \( \Delta j \), also has a Langevin dependence, which is shown in Fig. 23. Note that in Fig. 23, the total inelastic cross section falls short of the theoretical Langevin cross section calculated from Eq. (30). This is due to the fact that the Langevin cross section represents the total cross section for every trajectory with an impact parameter below \( b^* \). As previously stated, \( b < b^* \) does not guarantee that the end result of a collision be inelastic, as the cumulative
Fig. 23: The total inelastic cross section was calculated by summing all of the rotationally inelastic collisions, vibrationally inelastic collisions, and both vibrationally and rotationally inelastic collisions with $v_i=5$ and $j_i=64$. The functions representing Langevin cross section were obtained by using Eq. (30), and the maximum value of $C_6$ for both Li$_2$-Xe and Li$_2$-Ne collisions.

result of every collisionette may result in little to no change in the vibrational and rotational energy. Thus, the Langevin cross section includes total inelastic cross section as well as the total elastic cross section for elastic trajectories with $b < b^*$. 
4.2 $v_i$ and $j_i$ Dependence of the Total Inelastic Cross Section

Up until now, this section has only concentrated on the Langevin dependence of the cross section from $\text{Li}_2$-Ne and $\text{Li}_2$-Xe collisions with $v_i=5$, and $j_i=64$. However, because of the fact that $b^*$ does not depend on $v_i$ or $j_i$, the total inelastic cross section resulting from collisions with any $v_i$, $j_i$ exhibit the same Langevin dependence. For the same reason, the theoretical Langevin cross section is the same for any $v_i$, $j_i$ at a $v_{\text{rel}}$. Thus, for any $v_i$, and $j_i$ at a particular $v_{\text{rel}}$, the ratio of the total inelastic cross section to the Langevin cross section $\sigma_{\text{tot}}/\sigma_L$ represents the fraction of trapped trajectories that are inelastic. In other words, it represents the probability that the collision guaranteed to occur by having a $b < b^*$ results in non-zero values of $\Delta v$ and $\Delta j$. Fig. 24 shows $\sigma_{\text{tot}}/\sigma_L$ as a function of $j_i$ for $\text{Li}_2$-Xe trajectories at six different values of $v_i$.

The results seen in Fig. 24 were quite unexpected, since the fraction of the inelastic cross section had a $j$ dependence that weakens with increasing $v$. In particular, the variation in the size of the total inelastic cross section varies greatly when $v_i=0$, in which there are multiple minima and maxima. At first, we thought that these peaks corresponded to the values of $j$ for which $\omega_v/\omega_r$ is equal to an even integer value, assuming that the structure was a product of the quasiresonant frequency locking effect. Similarly, we expected the troughs to be a product of the anti-resonances, when $\omega_v/\omega_r$ is equal to an odd integer value, meaning there is an odd number of full vibrations for every full rotation. While almost all of the $j_i$ values
that correspond to a peak of trough are close to an even integer resonance value, they are not close enough to give us confidence that it is the only mechanism behind the figure's structure. In addition, while the peak at $j_i=16$ seems to match up very well with the 16:1 resonance, this low value of $j$ means that the integer values of $\omega_n/\omega_R$ are spaced extremely close to each other. For example, the 17:1 resonance corresponds to a $j \approx 15.0$, and the 15:1 resonance corresponds to a $j \approx 17.1$. For this reason, it must the case that the 16:1 resonance cannot have a very
strong effect, and that the peak must be a result of some other mechanism. This can be seen in Fig. 25, which shows only the $v_i=0$ data along with lines to indicate the even integer frequency values. Fig. 25 makes it clear that there was still more

![Graph](image_url)

**Fig. 25:** The $v_i=0$ data from Fig. 24, where the $v_i$ and $j_i$ dependence is most clearly visible. The lines represent the values of $j_i$ at which $\omega_{v_i}/\omega_r$ is equal to an integer value, and these values are labeled to the right of each line. Note that the resonance values of $j$ do not match up perfectly with the peaks and troughs seen in the data.

to be learned about the dynamics of these low velocity collisions. However, due to the complex nature of the *ab initio* potential surfaces, we chose to make a much simpler model potential in the hope that it would allow us to more easily identify any mechanism that resulted in a $v_i$ and $j_i$ dependence of $\sigma_{\text{tot}}/\sigma_L$. 

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5 Model Potential

To better understand the mechanism behind the $v$ and $j$ dependence of $\sigma_{\text{tot}}/\sigma_L$, we created a model potential that included only the basic components of the more complex \textit{ab initio} potential surfaces used to calculate the trajectories. By doing this, we hoped to more easily single out the dominant process in the dynamics. Our first attempt was not successful, but it did alert us to a feature of the potential necessary to produce agreement with the results from the \textit{ab initio} potential.

5.1 Repulsive Potential with an Attractive Component

5.1.1 Creating the Potential

We started out by creating the most basic potential for which we thought that both Langevin behavior and the $v_i, j_i$ behavior described in chapter 4 could be seen: an exponentially repulsive potential with an attractive component. To induce the repulsion, we utilized the Born-Mayer potential energy function \cite{13}, which is the sum of two exponentially repulsive potentials, representative of the two Li atoms in the molecule. For this reason, the strength of this repulsion depends on the distance between the incoming atom and each of the two atoms in the Li dimer. By convention, the incoming atom is referred to as $C$, while the two atoms in the molecule are referred to as $A$ and $B$. If $A$ and $B$ are placed so that their centers
of mass are at a distance \( r \) apart from one another, then,

\[
R_{AC}(R, r, \gamma) = \sqrt{\frac{r^2}{4} + R^2 + rR \cos \gamma}, \quad \text{and} \quad (31)
\]

\[
R_{BC}(R, r, \gamma) = \sqrt{\frac{r^2}{4} + R^2 - rR \cos \gamma}, \quad (32)
\]

where \( R_{AC} \) and \( R_{BC} \) are the distances between \( A \) and \( C \), and \( B\) and \( C \), respectively. Equations (31) and (32) can then be utilized to determine the strength of repulsion \( e \) between \( C \) and the two atoms of the molecule:

\[
e_{AC}(R, r, \gamma) = \exp(-\alpha R_{AC}(R, r, \gamma)) \quad (33)
\]

\[
e_{BC}(R, r, \gamma) = \exp(-\alpha R_{BC}(R, r, \gamma)) \quad (34)
\]

The sum of Eqs. (33) and (34) is the Born-Mayer potential, which accurately models the repulsive nature of a collision for small values of \( R \) (when the atom is close to the molecule). To account for the vibration of \( A \) and \( B \), we utilize the modified harmonic oscillator potential, which is identical to Eq. (9) but shown again here for convenience:

\[
U(R) = \frac{1}{2} \mu m \omega^2 r_0^2 \left( \frac{r - r_0}{r} \right)^2 \quad (35)
\]

However, the sum of the Born-Mayer potential with Eq. (35) completely ignores any long-range attraction, which is the catalyst behind the behavior seen in pre-
vious sections. To model the attraction, we used the simple potential,

$$V(R) = \frac{-C_6}{R^6} \quad (36)$$

The synthesis of Eq. (36) together with the Born-Mayer repulsion and modified harmonic oscillator potential was the simplest potential we could imagine that might mimic the effects of the \emph{ab initio} potential. However, before the potential could be utilized, we had to come up with a switching function $S(R)$ that “turns off” the attractive potential at low values of $R$, where the overpowering effect of the $R^{-6}$ term in Eq. (36) threatens to produce a divergence in the potential towards $-\infty$. After experimenting with a few options for $S(R)$, a simple exponential function that turned out to be the most effective at preventing this divergence while also keeping a realistic form to the potential:

$$S(R) = \exp \left( -\frac{a}{R} \right) \quad (37)$$

Note that the parameter $a$ determines the steepness of the potential, or how quickly the attractive part of the potential turns off. Thus, the final form of the potential is as follows:

$$V(R, r, \gamma) = A(e_{AC}(R, r, \gamma) + e_{BC}(R, r, \gamma)) + U(R) - \left( S(R) \cdot \frac{C_6}{R^6} \right) \quad (38)$$

where $A$ is a constant.
5.1.2 Results

To actually utilize the potential described in Eq. (38), we substituted in the value of $C_6$ calculated from the \textit{ab initio} Li$_2$-Xe potential and used the resultant potential in our quasi classical trajectory program to run new calculations. It turns out that the model potential also exhibited a Langevin dependence in the cross sections that continued to rise at low velocity, as can be seen in Fig. 26. While the results from Fig. 26 are promising, it would have been strange not to observe Langevin behavior seeing as the potential consisted of a long range attraction.

Fig. 26: Each point represents 100,000 trajectories of Li$_2$-Xe utilizing the model potential in Eq. (38) with $v_i=5$, $j_i=64$. The same $v_{rel}^{-\frac{2}{3}}$ dependence in the cross section can be seen, as the cross sections are fit the the function $a v_{rel}^{-\frac{2}{3}}$ in which the percent error for the best fit value of the parameter $a$ is approximately +/- 2.0%.
that enabled us to see distinct values of $b^*$. However, this model potential did not show any indication of the same $v_i$ or $j_i$ dependence of $\sigma_{\text{tot}}/\sigma_L$ seen in the previous chapter. This is made clear in Fig. 27, where $\sigma_{\text{tot}}/\sigma_L$ is plotted as a function of $j_i$ for the same range of $j_i$ seen in Fig. 25.

![Graph showing $\sigma_{\text{tot}}/\sigma_L$ vs. $j_i$ for $v_i = 0$.]

Fig. 27: Each point represents 150,000 trajectories of Li$_2$-Xe utilizing the model potential in Eq. (38) with $v_{\text{rel}} = 5,000$ cm/sec. To calculate $\sigma_{\text{tot}}/\sigma_L$, the total inelastic cross section is divided by the Langevin cross section at 5,000 cm/sec, which is calculated by from Eq. (30).

### 5.2 Model Potential with an Anisotropic Well

#### 5.2.1 Creating the Potential

Clearly, another component needed to be added to Eq. (38) if the model potential was going to mimic the behavior of $\sigma_{\text{tot}}/\sigma_L$ with $v_i = 0$ using the $ab\ initio$ potential. Going one step up in complexity, we added an anisotropic component to the well
so that the strength of the attraction now had a dependence on $\gamma$. To do this, we multiplied the attractive term in Eq. (38) by a slightly modified form of the second Legendre polynomial:

$$P(\gamma) = 3\sin^2\gamma$$

(39)

The result gives the following new form of the potential:

$$V(R, r, \gamma) = A(\epsilon_{rBC}(R, r, \gamma) + \epsilon_{rAC}(R, r, \gamma)) + U(R) - \left(S(R) \cdot P(\gamma) \cdot \frac{C_6}{R^6}\right)$$

(40)

The addition of the second Legendre polynomial means that the updated potential is directionally dependent, which is a more realistic approximation.

5.2.2 Results

As before, the potential produced cross sections that have a Langevin dependence, which can be seen in Fig. 28. However, much more exciting was the fact that $\sigma_{\text{tot}}/\sigma_L$ had a dependence on $j_i$ that was extremely similar to what was observed when using the ab initio Li$_2$-Xe potential surface. This can be seen in Fig. 29. While the magnitude of the peaks seen in Fig. 29 are not the same as the ones seen in Fig. 25 (plot from previous section), the placement of them certainly is. Given that we now identified this behavior in a model potential that is much simpler than the Li$_2$-Xe potential, we could now run analysis to attempt to identify a mechanism.
Fig. 28: Each point represents 100,000 trajectories of Li$_2$-Xe utilizing the model potential in Eq. (40) with $v_i=5$, $j_i=64$. The same $v_{rel}^{-2/3}$ dependence in the cross section can be seen, as the cross sections are fit the the function $a v_{rel}^{-2/3}$ in which the percent error for the best fit value of the parameter $a$ is approximately $\pm 1.7\%$. 
Fig. 29: Each point represents 150,000 trajectories of Li$_2$-Xe utilizing the model potential in Eq. (40) with $v_{rel}=5,000$ cm/sec. To calculate $\sigma_{tot}/\sigma_L$, the total inelastic cross section is divided by the Langevin cross section at 5,000 cm/sec, which is calculated by Eq. (30). The lines represent the $j$ values for which $\omega_v/\omega_R$ is an integer.
6 Analysis

The model potential in the previous section turned out to be extremely useful, as it highlighted the fact that the \( v_i \) and \( j_i \) dependence of \( \sigma_{\text{tot}}/\sigma_L \) was related to the angle \( \gamma \). It was not until the attractive component of the potential was given that the model potential produced results similar to that of the Li\(_2\)-Xe \textit{ab initio} potential. After elucidating this fact, we reverted back to using the Li\(_2\)-Xe \textit{ab initio} potential to study how \( \gamma \) affected the outcome of a collision. In particular, we found that the value of \( \gamma \) at the moment when the first collisionette takes place, \( \gamma_1 \), seems to have an effect on the trapping time of a collision. We define the trapping time of a collision as the difference in time between when the atom has its first collisionette and its last. Fig. 30 plots the trapping time \( t^* \) as a function of \( |\cos \gamma_1| \) for collisions with \( v_i=0 \), and \( j_i=16 \), the first peak in the \( \sigma_{\text{tot}}/\sigma_L \) distribution shown in Fig. 29. To contrast, Fig. 31 shows \( |\cos \gamma_1| \) as a function of \( t^* \) with \( j_i=48 \), where there exists a minimum in Fig. 29. Figs. 30 and 31 show a clear difference from each other: when \( j_i=16 \), a large number of the trajectories have \( \cos \gamma_1 \approx +/-0.45 \), while when \( j_i=48 \), a large portion of the trajectories have \( \cos \gamma_1 \approx +/- 1.0 \).

This difference also affects the trapping time distributions of the two different sets of calculations. This is shown in Fig. 32 which plots the trapping times distributions for the trajectories with \( j_i=16 \) and \( j_i=48 \). More specifically, Fig. 32 highlights the fact that the trapping time distribution for collisions with \( j_i=16 \) has a local minimum at around 175 ps, and that this minimum that is not absent
Fig. 30: Trapping times $t^*$ of approximately 3,000 Li$_2$-Xe trajectories with $v_i=0$, $j_i=16$ and $v_{rel}=5,000$ cm/sec. The trajectories bunch around the value $|\cos \gamma_1| \approx +/-.0.45$. Note that there are a small number of trajectories such that $t^* > 500$ ps, but these points were omitted from the figure as they are not the focus of attention.

Fig. 31: Trapping times $t^*$ of approximately 3,000 Li$_2$-Xe trajectories $v_i=0$, $j_i=48$ and $v_{rel}=5,000$ cm/sec. Notice how many of the trajectories bunch around the value $|\cos \gamma_1| \approx 1$. 

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Fig. 32: In total 100,000 trapping times were calculated from Li$_2$-Xe trajectories with $v_i=0$, $v_{rel}=5,000$ cm/sec at both values of $j_i$. $N$ represents the number of trajectories in a bin with bin intervals of 100 ps. The distribution is plotted on a log-lin scale.

in the trapping time distribution for collisions with $j_i=48$. This is consistent with the results in Figs. 28 and 29, in which the collisions that bunch around the value $|\cos \gamma_1| \approx 1$ appear to have slightly longer trapping times than collisions with $|\cos \gamma_1|$ closer to 0. Because many of the the collisions with $j_i=16$ have $|\cos \gamma_1| \approx .5$, we get the dip in the trapping time distribution seen in Fig. 32.

However, it turns out that the clear difference seen between Figs. 30 and 31 is not nearly as prominent when plotting $\gamma_1$ as a function of $t^*$ at other values of $j$ for which $\sigma_{tot}/\sigma_L$ is a minima or maxima. For example, Figs. 33 and 34, plot $\gamma_1$ as a
function of $t^*$ with $j_i=70$, and $j_i=84$, the next two values of $j$ for which $\sigma_{\text{tot}}/\sigma_L$ is a maximum and a minimum, respectively.

**Fig. 33:** Represents approximately 3,000 Li$_2$-Xe trajectories $v_i=0, j_i=70$. Notice how the distribution differs from Fig. 30, despite the fact that $j_i=16$ and $j_i=72$ both correspond to maximum values of $\sigma_{\text{tot}}/\sigma_L$.

**Fig. 34:** Represents approximately 3,000 Li$_2$-Xe trajectories $v_i=0, j_i=84$.

Note that despite the fact that $j_i=70$ corresponds to a maximum value of $\sigma_{\text{tot}}/\sigma_L$. 
and $j_i=84$ corresponds to a minimum value of $\sigma_{\text{tot}}/\sigma_L$, Figs. 33 and 34 both look quite similar to Fig. 31 in which $j_i=48$ and $\sigma_{\text{tot}}/\sigma_L$ is at a minimum. In addition, the trapping time distributions for trajectories with $j_i=70$, and for trajectories $j_i=84$ do not exhibit the significant difference seen when comparing the $j_i=16$ and $j_i=48$ trap time distributions. The comparison of these two distributions is seen in Fig. 35.

![Graph showing trapping times](image)

**Fig. 35:** In total 100,000 trapping times were calculated from Li$_2$-Xe collisions with $v_i=0$, $v_{\text{rel}}=5,000$ cm/sec, and $j_i=70$ or 84. $N$ represents the number of trajectories in a bin with bin intervals of 100 ps. The distribution is plotted on a log-lin scale.

Thus, we believe that the effect that $\gamma_1$ has on $t^*$ cannot be the only mechanism that influences the behavior of a collision at low velocity with $v_i=0$. However, by plotting the cross section distributions of the same trajectories from Fig. 35, we gain further insight into another component of the dynamics. These cross section distributions are shown in is Figs. 36 and 37, which plot the $\Delta v=+1$ and $\Delta v=0$
cross section distributions for collisions with \( j_i=70 \), and \( j_i=84 \), respectively. Note that the cross sections seen in Fig. 36 are almost twice as large as the ones seen in Fig. 37. This is almost certainly due in part to the effects of quasiresonance. For example, in Fig. 36, the \( \Delta v=+1 \) cross section distribution is very narrow, and centered around the quasiresonant \( j=66 \) peak, for which \( \omega_v/\omega_r \) is an even integer ratio. This is hallmark quasiresonant behavior [2], and is further characterized by the observed, substantially large cross sections.

The result of these various methods of analysis give a basic understanding of the dynamics of these low velocity collisions.

Fig. 36: Each point represents the result of 200,000 Li\(_2\)-Xe trajectories with \( v_i=0 \), \( j_i=70 \), and \( v_{rel}=5,000 \) cm/sec. Error bars are included, but in most cases are too small to see.
Fig. 37: Each point represents the result of 200,000 Li$_2$-Xe trajectories with $v_i=0$, $j_i=84$, and $v_{rel}=5,000$ cm/sec. Error bars are included, but in most cases are too small to see.
7 Conclusion and Discussion

7.1 Summary of Results

The work presented in this thesis indicates that Li$_2$-Xe and Li$_2$-Ne collisions at low velocity are dominated by trapping behavior. This primary mechanism behind this trapping behavior is the quantity $b^*$, which represents the largest impact parameter for which the centrifugal barrier of a potential can be surpassed. For every trajectory with $b < b^*$, the mutual attraction between the atom and molecule will result in a collision consisting of at least one collisionette, allowing for the possibility that the end result of the collision be inelastic, though this is not always the case. In other words, the primary effect of the trapping behavior induced by $b^*$ is to make uniform the $\Delta v$ and $\Delta j$ distribution of a set of calculated trajectories.

One of the primary outcomes of this trapping behavior is that it enables certain inelastic cross to continue to rise even at extremely low values of $v_{rel}$. The rising trend in these cross sections can be modeled successfully by a Langevin capture model, in which $\sigma \propto v_{rel}^{-\frac{3}{2}}$. For trajectories that are calculated by the Li$_2$-Xe \textit{ab initio} potential, some of these rising cross sections are both vibrationally and rotationally inelastic. While there are inelastic cross sections that continue to rise for trajectories calculated by the Li$_2$-Ne \textit{ab initio} potential, these cross sections are only rotationally inelastic. In addition, for trajectories calculated for either of the \textit{ab initio} potentials, the total inelastic cross section calculated at a particular $v_i$ and $j_i$ also have a Langevin dependence on $v_{rel}$.

Finally, for trajectories calculated by the Li$_2$-Xe potential, the value of $\sigma_{tot}/\sigma_L$
has a clear dependence on \( j_i \) that is only clear for small values of \( v_i \). While the exact mechanism behind this dependence has yet to have been identified, a model potential that consisted of only the basic components of the \textit{ab initio} potential was able to reproduce these results. Through use of the model potential, we identified that the \( v_i \) and \( j_i \) dependence of \( \sigma_{\text{tot}}/\sigma_L \) is only visible when the long-range attractive component of the potential has a \( \gamma \) dependence. Chapter 6 explained how this angular dependence, in particular the value of \( \gamma \) at the time in which the first collisionette takes place, may be able to explain the maximum value of \( \sigma_{\text{tot}}/\sigma_L \) at \( j_i=16 \). Though an analysis of the cross section distributions at the higher values of \( j \) for which there exist maxima and minima in \( \sigma_{\text{tot}}/\sigma_L \), we see quasiresonant effects begin to materialize.

### 7.2 Discussion and Next Steps

We hope that the result of the analysis carried out in Chapter 6 may make clear to us the next steps required to understand mechanism that is the cause of the \( v \) and \( j \) dependence of \( \sigma_{\text{tot}}/\sigma_L \). In particular, the peak in \( \sigma_{\text{tot}}/\sigma_L \) at \( j_i=16 \) is different from the rest in that is the only one that seems to be influenced by \( \gamma_1 \). Strangely, many of the collisions with \( v_i=0 \) and \( j_i=16 \) have a \( \cos \gamma_1 \approx \pm 0.45 \), as seen in Fig. 30. At this value of \( \gamma \) the atom is directly in the path of the molecule’s rotation, and we suspect that as a result the slow moving atom is “smacked” away by the comparatively rapidly rotating molecule. A collision of this type would be short, and inelastic, and contribute to the total inelastic cross section. The result of
many collisions of this type would be a large total inelastic cross section which lends itself to a large value of $\sigma_{\text{tot}}/\sigma_L$. Thus, it will be beneficial to test this computationally.

We have less insight as to a method by which to highlight the reason behind the maxima and minima at higher values of $j$, but suspect that quasiresonance does play a dominant role, given the results of Figs. 34 and 35. Despite the fact that the peaks and troughs do not match up exactly with the integer values of $\omega_c/\omega_R$, it might be the case that the quasiresonance is somehow influenced by a yet undermined effect.

Once we do identify and understand these mechanisms, we can consider the prospect of carrying out these calculations experimentally, seeing at the temperatures which these collisions take place correspond to the temperatures seen inside a MOT.
References


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