ENERGY TRANSFER PROCESSES OF AlIGNED EXCITED STATES OF Ca ATOMS

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Effects of orbital alignment on the near resonant energy transfer process from Ca(4s5p $^1\!P_1$) to Ca(4s5p $^3\!P_3$) induced by collisions with rare gases are studied in a crossed molecular beam. A linearly polarized, pulsed ultraviolet laser is used to introduce the initial orbital alignment, and the relative energy transfer cross sections as a function of alignment are monitored by time-gated fluorescence detection. Different results are observed with several rare gases; a rather large, -50% enhancement in the rate is observed for the perpendicular vs. parallel approach with He and Ne. A smaller, but opposite effect is observed for Xe, and no effect of alignment occurs with Kr.

1. INTRODUCTION

Studies of the effects of alignment on inelastic collision phenomena are just beginning. In spite of the fact that there are very few direct measurements of the influence of atomic or molecular alignment on energy transfer probabilities, a number of recent experiments show promising new details concerning the effects of alignment and orientation on both reactivity and energy transfer [1-10]. Such experiments have the capability to elucidate important geometry-dependent aspects of potential energy surfaces and the curve crossing mechanisms that occur during collisions.

In the experiments to be described here, a simple energy transfer system is considered between near resonant states of electronically excited calcium atoms induced by collisions with rare gas atoms. The particular process of interest is the near resonant spin-change:

$$\text{Ca}(4s5p \, ^1\!P_1) + M \rightarrow \text{Ca}(4s5p \, ^3\!P_3) + M + \Delta E = 177 \text{ cm}^{-1} \quad .$$

Since the wave functions of the two electronically excited states in this case are mixed, the spin change is not rigorously forbidden. A facile transfer occurs even with weak perturbers such as rare gas atoms and has the appearance more like a fine structure-changing process.

This energy transfer system provides an almost ideal case for both experimental and theoretical studies of the effects of orbital alignment on a near
resonant energy transfer process that involves a curve-crossing mechanism. Several experimental advantages can be noted. Because of the absence of nuclear spin hyperfine interactions, the Ca \( ^{1}P_{1} \) state can be completely aligned via direct excitation from a linearly polarized, pulsed ultraviolet laser at 272 nm. These are the first experiments on alignment effects which employ pulsed laser excitation; the high signal-to-noise is encouraging for the future success of other studies requiring pulsed lasers to achieve wavelengths not available with cw lasers. The short 60 ns lifetime of the \( ^{1}P_{1} \) state minimizes the loss of the initial alignment by interaction with the Earth's magnetic field to about 5-10%. Fluorescence transitions from both the \( ^{1}P_{1} \) and \( ^{3}P_{J} \) states are readily monitored simultaneously in the visible region of the spectrum with time-resolved detection to obtain the relative transition probabilities as a function of orbital alignment.

In consideration of the theoretical aspects of this problem, the Ca\(^{+} \) + rare gas systems are relatively easy ones to obtain potential energy surfaces. It should be possible in the two-atom system to incorporate all the important aspects of angular momentum coupling from initial to final states and to calculate the dynamics of the energy transfer process.

2. EXPERIMENTAL

The experimental apparatus (Fig. 1) consists of crossed beams between Ca atoms and the rare gas, a pulsed, frequency-doubled, Nd:YAG-pumped dye laser, a polarization rotator (Pockels cell or Fresnel rhomb), photomultiplier tubes, and time-gated photon counting equipment [1]. The Ca beam is an effusive beam from an oven at 950 K. The beam is skimmed by an orifice placed 0.75 cm away from the Ca nozzle to produce a ~0.3 mm diam. beam at a distance of 1.5 cm from the nozzle. The rare gas beam is a continuous, supersonic expansion from a 100 \( \mu m \) orifice which is placed 7 mm below the Ca beam. The rare gas beam is

![Schematic of the crossed beam apparatus](attachment:image.png)

**FIGURE 1**
Schematic of the crossed beam apparatus for studies of energy transfer with aligned Ca\(^+\).

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established with a backing pressure of 1 atm behind the orifice. The fluxes
of both atom beams and the required relative velocity vectors are calculated
from the properties of the expansions and have been discussed in detail before
(1). Under typical conditions, only one excited atom in 10^4 suffers a colli-
sion that results in transfer of the 1P₁ state to the 3P₂ states.

The pulsed dye laser is frequency doubled and tuned to the transition to
excite the second 1P₁ state at 272 nm (Fig. 2). The polarization is rotated
manually with a Fresnel-rhomb retarder or electrically with a voltage on a UV
transparent Pockels cell. The resultant polarization is checked for the de-
gree of linearity with polarization analyzer sheets and is ≤90%. The Ca 1P₁
state is excited with a 5 ns pulse, and fluorescent emissions from both the
initially-excited 1P₁ state at 672 nm and from the resulting collisional
energy transfer state (3P₂) at 616 nm are collected with two fiber bundles
and collimated onto separate photomultipliers. A typical gate time for the
fluorescence detection is an open time of 200 ns beginning 100 ns after the
laser pulse. High quality baffle arms reduce the scattered laser light
reaching the photomultipliers to less than one count per laser pulse (laser
power ~600 μJ per pulse).

The signal from the 1P₁ state is large and is used to normalize for the
amount of the initial excitation. The 3P₂ signal is 10^4 times weaker and is

FIGURE 2
Energy level diagram of the relevant states for the collision-induced transfer
between Ca(4s5p 1P₁) and Ca(4s5p 3P₂).
detected with time-gated photon counting equipment. Two filters which have a high rejection at 672 nm are required to prevent the much stronger $^3P_j$ emission signal from reaching the photomultiplier. The counts from the $^3P_j$ emission are integrated for 5000-8000 laser pulses at each angle of polarization. Both signals are monitored as a function of the angle of rotation of the polarization to obtain the relative cross sections as a function of orbital alignment. In addition, full time resolved signals are acquired with a fast transient digitizer/signal averager in order to verify the lifetimes of the emitting states (11).

3. RESULTS AND DISCUSSION

Figure 3 shows the relative probability for energy transfer from the $^1P_j$ state to the $^3P_j$ states as a function of the angle of polarization in the center-of-mass frame for four different collision partners, He, Ne, Kr and Xe. With Ar no fluorescence intensity from $^3P_j$ could be detected because of the small cross section. It can be seen that for He and Ne the effect is large and the maximum comes at approximately a 90° angle with respect to the maximum effect for Xe. By the transformation from the laboratory to the center-of-mass frame, it is found that the maximum energy transfer cross section for He occurs when the Ca $^8$ p-orbital is aligned essentially perpendicular to the relative velocity of approach (1). This establishes for the Ca $^8$ + He and Ne systems that the molecular $\pi$-state is the preferred geometry to bring about

![Figure 3](image)

**Figure 3**

Data for the energy transfer probability from $^1P_j$ to $^3P_j$ with He, Ne, Kr, and Xe as a function of p-orbital alignment angle.
the curve crossing from the $^3P_1$ to the $^3P_3$ states. Although the effect is smaller for $\text{Kr}$, there is a clear preference for the molecular $\Sigma$-state. For $\text{Kr}$, no preferential alignment effect is observed.

The results for each of the different rare gases are summarized in Table I, along with the total cross section obtained in static cell experiments for the transfer from $^3P_1$ to $^3P_3$ (11).

Table I. Results of alignment experiments for energy transfer between $\text{Ca}(4s4p \ ^3P_1)$ and $\text{Ca}(4s4p \ ^3P_3)$ induced by collisions with rare gases.

<table>
<thead>
<tr>
<th>Rare Gas</th>
<th>Total ($A^2$)</th>
<th>$I_{\text{max}}/I_{\text{min}}$</th>
<th>Angle of $I_{\text{max}}$</th>
<th>State</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>25</td>
<td>$1.4 \pm 0.2$</td>
<td>$100 \pm 10^\circ$</td>
<td>$\Pi$</td>
</tr>
<tr>
<td>Ne</td>
<td>5</td>
<td>$1.7 \pm 0.2$</td>
<td>$90 \pm 10^\circ$</td>
<td>$\Xi$</td>
</tr>
<tr>
<td>Ar</td>
<td>3</td>
<td>no signal</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Kr</td>
<td>13</td>
<td>$1.0 \pm 0.1$</td>
<td>constant</td>
<td>--</td>
</tr>
<tr>
<td>Xe</td>
<td>31</td>
<td>$1.25 \pm 0.2$</td>
<td>$-5 \pm 10^\circ$</td>
<td>$\Xi$</td>
</tr>
</tbody>
</table>

The qualitative trend in the total cross sections has been considered previously (11). It is explained by a competition between the effect of velocity on the Landau-Zener curve-crossing probability and the effect of the rare gas polarizability on the potential energy surfaces. The heavier rare gas atoms have significantly greater attraction and typically are expected to involve curve crossings at longer range and with greater interaction strength. The lighter rare gases, especially $\text{He}$, are weaker perturbers, but the curve crossing probability can be enhanced by rapid passage through the crossing region.

The effects of alignment can be explained by consideration of a schematic set of potential energy curves for the quasimolecular states. Figure 4 shows two extremes, Ca* + $\text{He}$ and Ca* + $\text{Xe}$. The shallow potential well for interaction of the Ca $p$-orbital with He in the $\pi$ molecular state leads to a substantial enhancement of the transfer cross section for the perpendicular alignment compared to the more repulsive $\Sigma$ molecular state (parallel alignment). The laser preselects the collision system on either the $\pi$ molecular state or the $\Sigma$ molecular state via the initial polarization. Provided that the initial alignment is at least partially retained in the transition from the laboratory-fixed frame to the molecular-fixed frame (termed the locking radius), then the colliding system will follow through with some preferential character of one potential surface over the other. Hale et al. (11) have given a more rigorous discussion of these considerations of the locking radius and the maximum alignment effect that can be observed when averaged over all impact parameters.

The greater the retention of the initial alignment, the greater can be the effect due to the orbital alignment in the energy transfer. As shown in Fig. 4, the energy splitting between the $\pi$ and $\Sigma$ molecular states as a function of internuclear separation can become large well before the curve crossing region. The orbital then locks into the molecular frame early in the collision and can retain the memory of the initial alignment throughout the curve crossing region. A significant point to explain the observed behavior is that for He and Ne the curve crossing for the more repulsive $\Sigma$ state occurs only at higher energies. Thus, the $\Sigma$ state because of its greater attraction leads to an efficient crossing between the $^3P_1$ and $^3P_3$ states at a longer distance than does the more repulsive $\Pi$-state.

In contrast, the stronger attraction between Ca* and Xe or Kr could cause the effect of the orbital alignment on the energy transfer to be both smaller and of opposite character to the results for He and Ne. One possible pictorial
view is offered in Fig. 4. The higher polarizability of Xe and Kr increases the well depths as well as the slope of the repulsive part of the potential curves, especially for the Ca \((^3P_J) + \text{rare gas complex. Thus a curve crossing between the two} \Sigma \text{ states may be accessible for energies used in this experiment, leading to a contribution to the} \ 3P_J \text{ fluorescence via the} \ 3 \Sigma \text{ state.}

An alternative possibility for the change from \(\pi\) to \(\Sigma\) on going from He to Xe has to do with the validity of the long-range locking model. For Xe and Kr, the curve crossing of the \(\pi\) state occurs at larger internuclear distances than with He and Ne. Therefore the ratio of the locking radius to the curve crossing radius may decrease. Thus the original alignment of the \(1 \Pi\) orbital defined by the laser can already be changed from \(\pi\) to \(\Sigma\) at the internuclear separation where the orbital is locked, i.e., the long-range \(\pi\) and \(\Sigma\) states are no longer good quantization frames in the collision system.

In order to test the hypothesis that the efficient transfer for He and Ne is from the \(\pi\) state out of \(4P_J\) to the \(\Sigma\) state in \(3P_J\), experiments are in progress to run the reaction in reverse. A clear prediction is that the transfer in the reverse process should be more efficient for initial excitation of the \(\Sigma\) state.

**FIGURE 4**

Hypothetical schematic of potential energy curves for Ca*–He and Ca*–Xe showing possible curve crossings.
4. CONCLUSION

Collisional energy transfer events between electronically excited states can show significant effects due to orbital alignment in the collision. These experiments are the first alignment-dependent studies carried out with pulsed laser excitation. The results can be interpreted in terms of simple curve crossing pictures and await more detailed dynamical calculations, which should be possible with accurate potential energy surfaces.

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REFERENCES

ALKALINE

By M. J. Coggiola

Tune: My Darling Clementine

In a magnet, in a light trap, pumping on the hyperfine,
Dwelt a laser, standing-waver, and some atoms Alkaline.

Gettin colder, gettin colder, gettin colder Alkaline,
Till you can't skip less you spin flip, you're sub-Doppler, Alkaline.

H-hep up, and h-new down then, so you're rambling will decline,
With no mode hop, you can all stop, and the record will be mine.

Gettin colder, gettin colder, gettin colder Alkaline,
Till you can't skip less you spin flip, you're sub-Doppler, Alkaline.

There's a substrate got the wrong fate, with a moment can't align
Thermal spreading I was dreading, so I lost my Alkaline.

Gettin colder, gettin colder, gettin colder Alkaline,
Till you can't skip less you spin flip, you're sub-Doppler, Alkaline.