Semiclassical Analysis of Quantum Mechanical Calculations of Rotational Inelastic Collisions of He and Ar with NaK

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1 Abstract

2 Introduction

NaK, like any molecule, can vibrate and rotate and can be described by its rotational and vibrational states. Upon collision with a perturbing atom, such as helium or argon, these states can change. This project was primarily concerned with collisions where the vibrational state is conserved, but the rotational state is not, as equation 1 specifies.

$$\begin{aligned} He + NaK(v,m,j) &\rightarrow He + NaK(v,m',j') \\ Ar + NaK(v,m,j) &\rightarrow Ar + NaK(v,m',j') \end{aligned} \tag{1}$$

Specifically, the purpose of this investigation was to explore the physical interpretations of how the quantum numbers that describe angular momentum change during collision.

In addition to its rotational and vibrational states, NaK can also be described by its electronic state, of which the set of potential curves are an expression. A set of NaK's potential curves can be seen in figure 1. The potential curves represent energy as a function of internuclear separation between sodium and potassium. Both experimental and theoretical investigations choose one potential curve to study, specifying the electronic energy level at which the collisions in question take place.

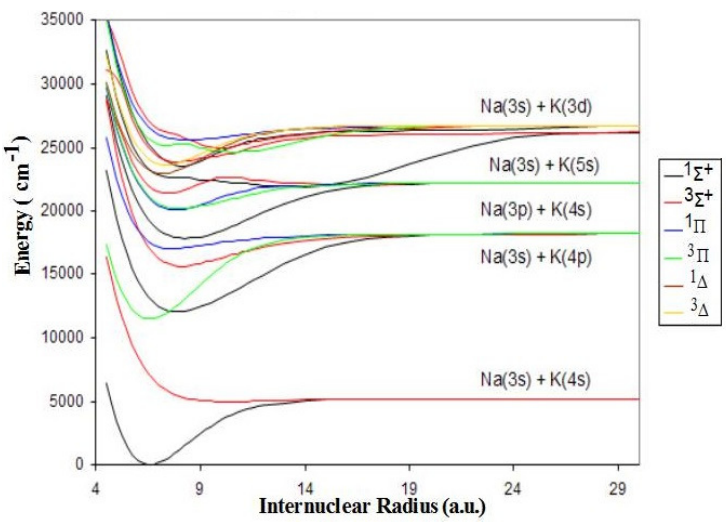

Figure 1: Potential curves for NaK

At Lehigh University, the experimental and theoretical investigations have worked together to form a more complete picture of the collisions in question. Professor Huennekens leads the experimental group, and Professor Hickman leads the theory group.

3 Background

3.1 Experimental Measurements

Professor Huennekens' experimental group has measured the rate constants (k) of transitions, which are related to the cross sections. The rate constants are proportional to the expectation value of the product of the cross section and velocity, which can be approximated as the cross sections times the average velocity:

$$\begin{aligned} k &= \langle \sigma v \rangle \\ k &\approx \sigma \overline{v} \end{aligned} \tag{2}$$

The cross section is a metric of the likelihood that a particular transition will occur from one j state to another. The rate constants average over all values of the quantum number m.

The experimental group has also measured the fraction of orientation that is preserved throughout the collisions. Collisions tend to be randomizing processes, so studying the extent to which orientation is preserved gives a metric of the extent to which a particular type of collision is actually a randomizing process. In a cell environment, such as the system that the experimental group studies, the angular momenta initially point in all directions and the average value of m is zero. In order to measure the change in orientation, the initial orientation must be nonzero. The orientation is proportional to the expectation value of m for a particular j state:

$$O^j = \frac{\langle m \rangle}{\sqrt{j(j+1)}} \tag{3}$$

Physically, it is the extent to which all angular momenta point in the same direction.

3.2 Vector Model

The orientation is related to the geometric relationship between m and j in the vector model, as seen in figure 2.

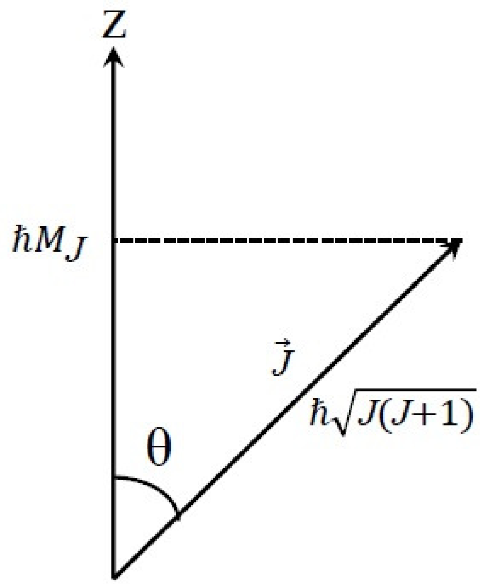

Figure 2: Vector model of angular momentum

The vector model is a way of understanding angular momentum, where j is the angular momentum vector. The quantum number m is the projection of j onto the z axis. j can precess around the z axis at a constant θ without changing its magnitude or the magnitude of m, as stated by equation 4:

$$\cos\theta = \frac{m}{\sqrt{j(j+1)}} \tag{4}$$

The expectation value of the $\cos\theta$ is the orientation, as equation 3 stated.

3.3 Experimental Procedure

In order to choose a nonzero orientation for the initial state of the system, the experimental group excites the system from the ground state to a higher potential, the A state. These states are selected potential curves from figure 1, shown in more detail in figure 3. A pump laser that is left circularly polarized populates the A state's vibrational and rotational states. After the collisions, the probe laser is swept across a range of frequencies to measure the orientation.

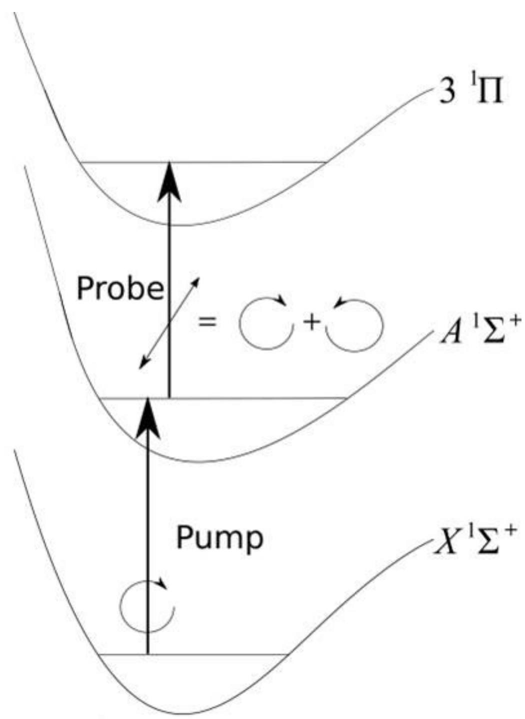

Figure 3: States used in experiment. $X^1\Sigma^+$ is the ground state, $A^1\Sigma^+$ is the chosen excited state, and $3^1\Pi$ is the state to which the system is excited by the probe laser

Polarized light always has selection rules for which states it populates, and the circularly polarized pump laser's selection rule for $\Delta m = +1$ leads to a preferential population of large m. This can be seen in figure 4.

The probe laser is linearly polarized; linear polarization can be expressed as a superposition of left and right circularly polarized light. Because of the

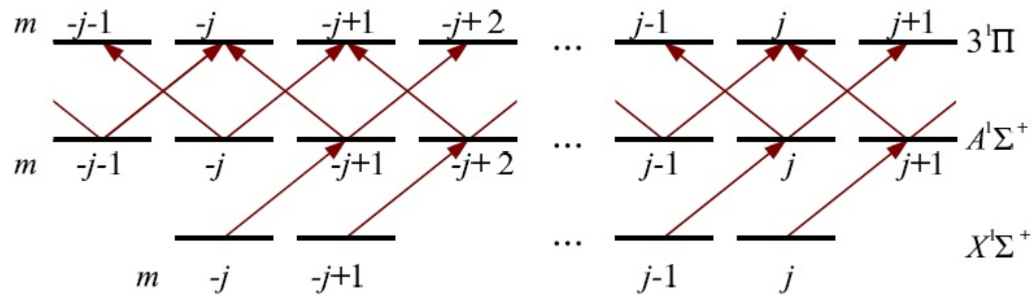

Figure 4: Bottom row: m states available in the ground state Middle row: m states available in the $A^1\Sigma^+$ state Top row: m states available in the $3^1\Pi$ state Arrows show possible transitions

initial nonzero orientation of the system, the different circular polarizations interact with the system differentially. Essentially, the left circular polarization will see a different system than the right circular polarization because of the states occupied and available states for transition. After interacting with the sample, the superposition of light that was not absorbed is passed through a linear polarizer perpendicular to the intial polarization. If the laser is unchanged, no signal will pass through the polarizer. However, because the left and right circular polarizations are absorbed differently, the superposition after interacting with the system is no longer perfectly linear but rather elliptically polarized. Therefore, whatever signal is detected after the polarizer is a metric of the final orientation.

3.4 Previous Results

Experiment and theory tend to agree in their determinations of the rate constants. For helium, past work has shown that there is a propensity for the change in j to be an even number. See figure 5.

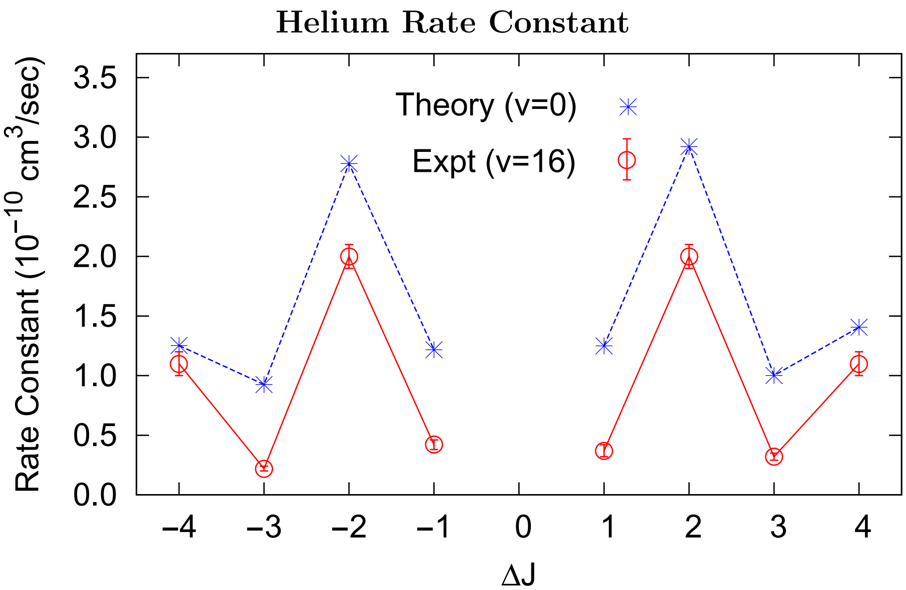

Figure 5: Rate constants for helium vs. Δj (Malenda et al)

It was originally thought that this propensity was related to the strict selection rule for homonuclear diatomic molecules where no odd Δj transitions are allowed. Sodium and potassium are in the same column of the periodic table, so it was thought that perhaps NaK was approximately homonuclear, which would explain the propensity. However, it has been demonstrated that the propensity for an even Δj depends on the collision partner, where as behavior of an approximately homonuclear molecule should depend solely on the molecule. Some initial experimental results for certain states in a collision with potassium show no propensity for even Δj at all. Unfortunately, theory has large computational requirements, and it is too computationally expensive to model NaK+K to confirm.

Some mechanism other than approximate homonuclear behavior is affecting the Δj propensity, so theory and experiment are still investigating and getting good agreement.

4 This Project

4.1 Goals: Physical Interpretations

The large calculations for the theoretical analysis are used to calculate B_λ values. These values are the discrete probabilities for transferring a specific amount of angular momentum to the NaK molecule in the transition. These calculations were done prior to the beginning of the summer.

The goal of this summer's project was to gain a deeper physical understanding of this angular momentum transition. Using the vector model facilitated understanding the relationship between j, j', λ, and α. The vector model definition of λ is a metric of the discrete value of angular momentum transferred in the collision, or the distance between the tip of the j vector and the tip of the j' vector. There are a finite number of discrete λ values for a given $j \to j'$ transition. α is the angle between j and j' and is likewise discrete.

4.2 Quantum Mechanical Model

The extensive calculations which the theoretical investigation requires calculate the quantum mechanical (QM) B_λ values, which are used to calculate the cross section of interaction, given by equation 5. B_λ's are discrete probabilities for a particular transfer of angular momentum; this transfer is related to the parameter λ.

$$\sigma(j \to j') = \frac{\pi}{(2j+1)k_j^2} \sum_{\lambda=|j-j'|}^{j+j'} (2\lambda+1) B_\lambda(j,j') \tag{5}$$

λ can best be described by going back to the vector model and extending it to include two different j vectors rather than one such that j is the initial angular momentum vector and j' is the final angular momentum vector. See figure 6.

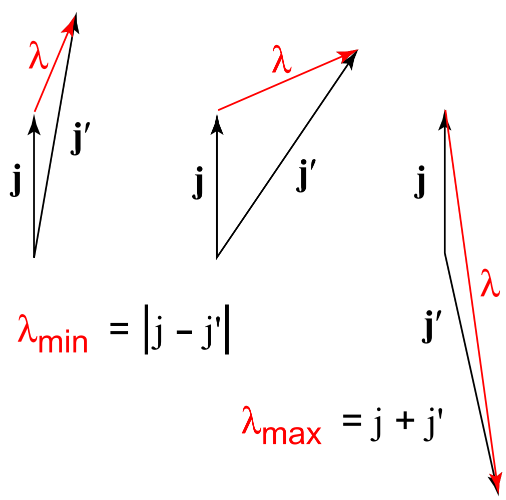

Figure 6: λ's relation to j, j', and α.

λ is the distance between the tip of the j and j' vectors. As j and j' can precess about the z axis as well as have an altitude of any allowed θ, λ can range in magnitude from the difference in the two j vectors to their sum. Physically, λ represents how much angular momentum was transferred in the collision.

The angle α is the angle between j and j'. This parameter is called the tipping angle; it is a measure of how much the collision "tipped" j' from j.

4.3 Semiclassical Model

In order to find a more intuitive physical interpretation, a semiclassical (SC) model was used. Using the law of cosines and the relationship shown in figure 6, the tipping angle can be related to the discrete amount of angular momentum, as in equation 6. By allowing α to be a continuous variable and making the appropriate substitutions, the discrete sum over λ becomes a continuous integral over α, as in equation 7.

$$\lambda(\lambda+1) = j(j+1) + j'(j'+1) - 2\sqrt{j(j+1)j'(j'+1)}\cos\alpha \tag{6}$$

$$\sigma(j \to j') = \frac{\pi(j'+1/2)}{k_j^2}\int_0^\pi B(j, j', \cos\alpha)\sin\alpha d\alpha \tag{7}$$

$B(j, j', \cos\alpha)$, or B_α, is related to B_λ; rather than a discrete probability, it is the distribution of tipping angles.

SC analysis
law of cosines, relate lambda and alpha * tipping angle
instead of summing over lambda, integrate over alpha
alpha is the tipping angle (remember the vector model)
B is the distribution of tipping angles