Semiclassical Model for the Distribution of Final Polar Angles and m' States in Rotationally Inelastic Collisions

T. J. Price^a, A. C. Towne^{a,b}, D. Talbi^c, A. P. Hickman^{a,*}

^a*Department of Physics, 16 Memorial Drive East, Lehigh University, Bethlehem, PA 18017, USA*

^b*Department of Physics, 225 Nieuwland Science Hall, University of Notre Dame, South Bend, IN 46556*

^c*Laboratoire Univers et Particules de Montpellier, UMR 5299, Université Montpellier II, Place Eugène Bataillon, 34095 Montpellier, France*

Abstract

Using the venerable vector model, we develop an expression for the change in the polar angle of the angular momentum of a rotator caused by collisions in a cell-type experiment. For an initial $\mathbf{j}$ precessing with polar angle θ , and a given distribution of “tipping angles”, we derive the distribution of final polar angles θ' . Final m' levels are also determined. The results agree well with exact quantum calculations for thermal collisions of He or Ar with NaK. We also find that a simple Lorentzian function describes the distribution of θ' in a special case.

1. Introduction

This letter presents a semiclassical model for the change in the magnetic quantum number m in rotationally inelastic collisions in a cell-type experiment. The model provides an appealing physical picture of collisional reorientation of the angular momentum vector and, for the case investigated here, is very accurate.

*Corresponding author
Email address: aph2@lehigh.edu (A. P. Hickman)

Information about transitions from states jm to $j'm'$ is critical for a detailed understanding of the collisional transfer of orientation and alignment and of the alignment of molecules by laser pulses [1–19]. Our recent calculations [20] addressed this issue; we reported fully quantum mechanical calculations for collisions of NaK ($A^1\Sigma^+$) with He, including the Grawert coefficients [1] necessary to calculate transition cross sections $\sigma(jm \rightarrow j'm')$. The results reproduced the propensity observed by Wolfe *et al.* [14] for $|\Delta j|$ to be even and also included several calculations of the fraction of alignment preserved in collisions.

Many efforts to characterize the distribution of final m' states [4, 5, 17] have been based on the idea that the polar angle $\theta = \cos^{-1}(m/(j + \frac{1}{2}))$ is approximately conserved in collisions. Another body of work is based on the approximate conservation of m in a specific frame defined by the kinematic apse, which is a vector in the direction of linear momentum transfer in the collision. Khare *et al.* [21, 22] formulated this approximation and showed that it is exact for a classical, impulsive collision. In a recent analysis of crossed molecular beam experiments on $\text{NO}(X) + \text{Ar}$, Brouard *et al.* [18] found that this model was very accurate.

In the present work we present a semiclassical analysis that treats m and m' as continuous variables and that leads to an explicit, closed form expression for the distribution of final states m' . We determined the quantities needed to evaluate this expression quantum mechanically, but classical trajectory methods could also be used [13]. Our results confirm the propensity to conserve the polar angle θ and provide a foundation for further work.

This letter is organized as follows. Section 2 describes our calculations of the potential energy surfaces for HeNaK and ArNaK; section 3 summarizes the quantum mechanical scattering formulas. The model is derived in section 4, which considers polar angles of $\mathbf{j}$ and $\mathbf{j}'$, and in section 5, which extends the analysis to m and m' . Section 6 discusses our results, and section 7 contains concluding remarks.

2. Potential Surface Calculation

We determined the potential energy surfaces of the first excited states of HeNaK and ArNaK using standard techniques of electronic structure calculations, as implemented using the GAMESS code [23]. In the limit of large He– or Ar–NaK distances, this excited state correlates with He or Ar (1S_0) + NaK ($A^1\Sigma^+$). Our basis set was obtained using the EMSL basis set library [24, 25] for a 6-311+ G^{**} basis set [26–29]. We split the d functions on Ar, Na, and K using factors of 2, 4, and 3, respectively, and we split the p function on He using a factor of 2. We added three f functions to Na [30] and K [27] with exponents 0.6000, 0.1500, and 0.0375, and 3.33, 1.11 and 0.37, respectively, and one f function to Ar [31] with exponent 0.89. We also added one d function to He [30] with exponent 2.0. This resulted in a $5s2p1d/3s2p1d$ basis set for He, a $14s11p2d1f/7s6p2d1f$ basis set for Ar, and a 6-311+ $G^{**}(3d,3f)$ for Na and K. We performed an equation-of-motion coupled cluster calculation with singles and doubles (EOMCCSD) [32]. There were six frozen core orbitals in the HeNaK calculation: $1s$ for Na and $1s, 2s, 2p_{x,y,z}$ for K. There were 11 frozen core orbitals in the ArNaK calculation: $1s, 2s, 2p_{x,y,z}$ for Ar, $1s$ for Na, and $1s, 2s, 2p_{x,y,z}$ for K. The HeNaK potential was size consistent to within $10^{-10} E_h$ and the ArNaK potential was size consistent to within $10^{-9} E_h$. The potentials were corrected for the basis set superposition error [33].

We calculated the energies as a function of the Jacobi coordinates: r is the NaK bond length, and R and θ are the distance and angle from the NaK center of mass. The value of r was fixed at the experimental NaK bond length $r_e = 7.935 a_0$ measured by Ross *et al* [34]. For HeNaK we used 21 values of R between 3.5 and 25 a_0 , and for ArNaK, 21 values between 4.5 and 30 a_0 . For each R we typically calculated 13 angular points evenly spaced between 0° and 180° (every 15°). We used additional calculations with R set to a very large number (10000 a_0) and with several values of r_e near 7.935 a_0 , to determine the spectroscopic constants of NaK ($A^1\Sigma^+$). The results, which are the same for HeNaK and ArNaK, are tabulated in Table 1.

Table 1: Spectroscopic constants for NaK ($A^1\Sigma^+$).

	$r_e (a_0)$	$\omega_e (\text{cm}^{-1})$	$\omega_e x_e (\text{cm}^{-1})$
present calculation	7.953	84.01	0.2655
Ross <i>et al.</i> [34]	7.935	81.25	0.2747

The present HeNaK potential is slightly different from the one we reported in reference [20]. The previous calculation used the Multi-Reference Configuration Interaction (MRCI) method, and extending this method to ArNaK would have required an enormous amount of computer resources. We elected to perform new calculations for HeNaK and ArNaK that treated the two systems in a parallel fashion in order to facilitate comparison. The new potentials are shown in Figs. 1 and 2. Both are predominantly repulsive, with very shallow van der Waals wells at long range. For He + NaK the well in the coupled cluster calculation is about 3 cm^{-1} deep and occurs near $\theta = 90^\circ$ and $R = 11 a_0$. For comparison, our previous MRCI calculation (shown in [20]) had a well depth of about 11 cm^{-1} near $\theta = 105^\circ$. For Ar + NaK the well is about 18 cm^{-1} deep and also near $\theta = 90^\circ$ and $R = 11 a_0$.

3. Summary of Quantum Mechanical Formulas

Here we summarize the formulas used in our recent calculations for NaK ($A^1\Sigma^+$) + He [20], which were based on the Arthurs and Dalgarno [35] formalism for the scattering of a structureless atom by a rigid rotator. These calculations are based on a coupled angular momentum representation in the space-fixed frame. To compare with a cell-type experiment, one must average over the direction of the incident particle, which is taken to be random. Cross sections for m -dependent transitions may be written in terms of the Grawert

coefficients $B_\lambda(j, j')$ [1, 4]:

$$\sigma(jm \rightarrow j'm') = \frac{\pi}{k_j^2} \sum_{\lambda=|j-j'|}^{j+j'} (2\lambda+1) \left(\begin{array}{ccc} j & j' & \lambda \\ -m & m' & m-m' \end{array} \right)^2 B_\lambda(j, j'), \quad (1)$$

where k_j is the wave number of the incident particle; $(\cdots)$ is a $3j$ symbol, and the $B_\lambda(j, j')$ depend on the T matrix elements according to

$$B_\lambda(j, j') = \sum_{l, l'} \left| \sum_J (2J+1)(-1)^J \left\{ \begin{array}{ccc} j & j' & \lambda \\ l' & l & J \end{array} \right\} T_{jl, j'l'}^J \right|^2, \quad (2)$$

where $\{\cdots\}$ is a $6j$ symbol.

The coupled channel calculations that determined the T matrix elements for He + NaK included all channels constructed from rotational levels $j = 0-50$, and total angular momenta $J = 0-127$. The numerical integration was carried out to $R = 25 a_0$. For Ar + NaK, the corresponding parameters were $j = 0-50$, $J = 0-447$, and $R = 30 a_0$.

In many cases it is advantageous to define cross sections for the transfer of the moments (population, orientation, alignment, etc.) of the m state distribution [3-5]. Alexander and Davis [4] defined the tensor cross sections

$$\sigma_K(j \rightarrow j') = \frac{\pi}{k_j^2} \sqrt{[j']/[j]} d_K(j, j'), \quad (3)$$

where $[n] = 2n+1$, and the coefficients $d_K(j, j')$ are given by

$$d_K(j, j') = \sum_{\lambda=|j-j'|}^{j+j'} (-1)^{j+j'+\lambda+K} (2\lambda+1) \left\{ \begin{array}{ccc} \lambda & j & j' \\ K & j' & j \end{array} \right\} B_\lambda(j, j'), \quad (4)$$

where $\{\cdots\}$ is a $6j$ symbol. For $K = 0$, Eq. (3) refers to the isotropic cross section $\sigma(j \rightarrow j')$.

Using the orthogonality relations of $6j$ coefficients to invert Eq. (4) and then invoking the semiclassical approximations of Derouard [5], one finds that the semiclassical counterpart of the Gravert coefficient $B_\lambda(j, j')$ is the distribution of the angle α , the “tipping angle” between the initial and final angular momenta of the target rotator,

$$B(j, j'; \cos \alpha) = \frac{1}{\sqrt{[j][j']}} \sum_{K=0}^{2j<} (2K+1) d_K(j, j') P_K(\cos \alpha), \quad (5)$$

where $j_{<} = \min(j, j')$. The tipping angle α is related semiclassically to the angular momentum λ transferred by the collision [5]:

$$\lambda(\lambda + 1) \approx (j + \frac{1}{2})^2 + (j' + \frac{1}{2})^2 - (j + \frac{1}{2})(j' + \frac{1}{2}) \cos \alpha. \quad (6)$$

4. Expression for the Distribution $\mathcal{P}_{jj'}(\theta, \theta')$

Our analysis is based on the well-known vector model. As shown in Fig. 3, the initial and final angular momenta $\mathbf{j}$ and $\mathbf{j}'$ precess around the z axis with cone angles θ and θ' , respectively. We wish to calculate the probability $\mathcal{P}_{jj'}(\theta, \theta') \sin \theta' d\theta'$ that an average collision changes the cone angle of the precessing angular momentum from its initial value θ to a final value in the range between θ' and $\theta' + \sin \theta' d\theta'$. ($\sin \theta' d\theta'$ is the surface area element for a given θ' on the unit sphere.)

We consider a geometrical analysis based on the semiclassical notion that collisions lead to a distribution of tipping angles α between $\mathbf{j}$ and $\mathbf{j}'$. The relation between given values of θ and θ' and the tipping angle α depends on the azimuthal angle between $\mathbf{j}$ and $\mathbf{j}'$. One can write

$$\cos \alpha = \cos \theta \cos \theta' + \sin \theta \sin \theta' \cos(\phi - \phi'). \quad (7)$$

(This formula can be derived by noting that $\cos \alpha$ is the dot product of unit vectors in the directions of $\mathbf{j}$ and $\mathbf{j}'$.)

The premise of our model is that $\mathcal{P}_{jj'}(\theta, \theta')$ is just the average value of $B(j, j'; \cos \alpha)$ as $\mathbf{j}$ and $\mathbf{j}'$ sweep around their circular paths in the diagram. Since the values of $\phi - \phi'$ between 0 and π cover the whole range of possible values of α , we can set $\phi' = 0$ and just average over ϕ :

$$\mathcal{P}_{jj'}(\theta, \theta') = \frac{1}{\pi} \int_0^\pi B(j, j'; \cos \alpha) d\phi. \quad (8)$$

Following Vilenkin [36], we can evaluate this integral by changing the integration variable from ϕ to α . Using Eq. (7), we obtain

$$d\phi = \frac{\sin \alpha d\alpha}{\sqrt{(\cos \alpha - \cos(\theta + \theta'))(\cos(\theta - \theta') - \cos \alpha)}}, \quad (9)$$

which leads to

$$\mathcal{P}_{jj'}(\theta, \theta') = \frac{1}{\pi} \int_{\alpha_{\min}}^{\alpha_{\max}} \frac{B(j, j'; \cos \alpha) \sin \alpha d\alpha}{\sqrt{(\cos \alpha - \cos(\theta + \theta')) (\cos(\theta - \theta') - \cos \alpha)}}, \quad (10)$$

where the condition that $0 \leq \alpha \leq \pi$ yields

$$\alpha_{\min} = |\theta - \theta'|, \quad \alpha_{\max} = \begin{cases} \theta + \theta' & \text{if } \theta + \theta' \leq \pi \\ 2\pi - (\theta + \theta') & \text{if } \theta + \theta' > \pi. \end{cases} \quad (11)$$

The range of integration includes the values of α for which the radicand in the denominator of Eq. (10) is nonnegative. A further change of variable to $x = \cos \alpha$ leads to

$$\mathcal{P}_{jj'}(\theta, \theta') = \frac{1}{\pi} \int_{\cos(\theta'+\theta)}^{\cos(\theta'-\theta)} \frac{B(j, j'; x) dx}{\sqrt{(x - \cos(\theta + \theta')) (\cos(\theta - \theta') - x)}}. \quad (12)$$

We can evaluate Eq. (12) using the following special case of a result due to Vilenkin [36]:

$$\frac{1}{\pi} \int_{\cos(\theta'+\theta)}^{\cos(\theta'-\theta)} \frac{P_K(x) dx}{\sqrt{(x - \cos(\theta' + \theta)) (\cos(\theta' - \theta) - x)}} = P_K(\cos \theta) P_K(\cos \theta'). \quad (13)$$

In this equation, $P_K(x)$ is a Legendre polynomial. Since the tipping function $B(j, j'; x)$ is a sum over Legendre polynomials, we can substitute Eq. (5) into Eq. (12) and evaluate each term separately, leading to

$$\mathcal{P}_{jj'}(\theta, \theta') = \frac{1}{\sqrt{[j][j']}} \sum_{K=0}^{2j_{<}} (2K+1) d_K(j, j') P_K(\cos \theta) P_K(\cos \theta'). \quad (14)$$

This expression has the correct behavior for the limiting case $\theta = 0$. Then the tipping angle $\alpha = \theta'$; all the $P_K(\cos 0)$ are equal to one, and Eq (14) reduces to Eq. (5). We can also show that the total cross section for changing j to j' is a constant times the integrated probability for changing θ to any θ' , independent of θ . Integrating Eq (14) over θ' and using Eq. (3) for $K = 0$ leads to

$$\sigma(j \rightarrow j') = \frac{\pi}{k_j^2} (j' + \frac{1}{2}) \int_0^\pi \mathcal{P}_{jj'}(\theta, \theta') \sin \theta' d\theta' \quad (15)$$

Eq. (15) is consistent with the quantum result for collisions in a cell-type experiment: when one averages over the direction of the initial particle, the sum over m' of the cross sections for the $jm \rightarrow j'm'$ transitions is independent of the initial m .

Typical results for $\mathcal{P}_{jj'}(\theta, \theta')$ when j and j' are large are shown in Fig. 4. For angles θ not too close to 0 or π , the curves for each θ shown are very similar in shape and have a peak at $\theta' = \theta$. The angular distribution in Eq. (14) also satisfies

$$\mathcal{P}_{jj'}(\theta, \theta') = \mathcal{P}_{jj'}(\pi - \theta, \pi - \theta'), \quad (16)$$

which accounts for the obvious symmetry of the distributions for $\theta = 45^\circ$ and $\theta = 135^\circ$ in Fig. 4. For the same reason, the curves for $\theta = 90^\circ$ are symmetric about $\theta' = 90^\circ$. When $\theta = 0$, $\mathcal{P}_{jj'}(0, \theta') = B(j, j', \cos \theta')$, as discussed in the text.

When j and j' are small, the angular distributions are much broader, as shown in Fig. 5. Even in this case, the largest peak is still clearly near $\theta' = \theta$, although there are also secondary oscillations. Since the distributions overlap for different θ , we show distributions only for $\theta \leq 90^\circ$.

5. Extension to Transitions from m to m'

The final polar angle θ' is simply related to the final azimuthal quantum number m' by

$$\cos \theta' = \frac{m'}{\sqrt{j'(j'+1)}} \approx \frac{m'}{j' + \frac{1}{2}}. \quad (17)$$

Taking differentials of both sides of Eq. (17), we have

$$d(\cos \theta') = \frac{dm'}{j' + \frac{1}{2}} \quad \Rightarrow \quad -\sin \theta' d\theta' = \frac{dm'}{j' + \frac{1}{2}}. \quad (18)$$

Using this result and explicitly writing θ and θ' as functions of the continuous variables m and m' , respectively, we can transform Eq. (15) from an integral over θ' to one over m' . We obtain

$$\sigma(j \rightarrow j') = \frac{\pi}{k_j^2} (j' + \frac{1}{2}) \int_{-(j'+1/2)}^{j'+1/2} \mathcal{P}_{jj'}(\theta(m), \theta'(m')) \frac{dm'}{j' + \frac{1}{2}} \quad (19)$$

After cancelling the factors of $(j' + \frac{1}{2})$, we can identify the right hand side of Eq. (19) as the integral over m' of a semiclassical cross section $\sigma_{\text{sc}}(jm \rightarrow j'm')$. Using Eqs. (14) and (17), we obtain the following explicit expression:

$$\sigma_{\text{sc}}(jm \rightarrow j'm') = \frac{\pi}{k_j^2 \sqrt{[j'][j]}} \sum_{K=0}^{2j_{<}} (2K+1) d_K(j, j') P_K\left(\frac{m}{j + \frac{1}{2}}\right) P_K\left(\frac{m'}{j' + \frac{1}{2}}\right). \quad (20)$$

In principle one could include a factor dm' on both sides of this equation. This factor will usually be one, corresponding to a final azimuthal quantum number in the range $m' - \frac{1}{2}$ to $m' + \frac{1}{2}$, so we have omitted it.

We now consider the relation between Eq. (20) and the exact quantum mechanical expression, Eq. (1). Following previous work [5, 20], one can change the sum over λ to an integral over α :

$$\sum_{\lambda} (2\lambda + 1) \rightarrow \frac{[j][j']}{2} \int \sin \alpha d\alpha. \quad (21)$$

The work of Brussaard and Tolhoek [37] showed that a classical approximation to the square of the $3j$ coefficient in Eq. (1) can be written

$$\left(\begin{array}{ccc} j & j' & \lambda \\ -m & m' & m - m' \end{array} \right)^2 = \frac{2}{\pi [j][j']} \frac{1}{\sqrt{(\cos \alpha - \cos \alpha_{\text{max}}) (\cos \alpha_{\text{min}} - \cos \alpha)}}, \quad (22)$$

where the quantum values m , m' , and λ are related to α , α_{min} and α_{max} by Eqs. (6), (11), and (17). In the “classical region” where the radicand on the right hand side of Eq. (22) is positive, the square of the $3j$ coefficient is oscillatory, and this classical approximation goes through the average value of the oscillations. Figure 6 illustrates this behavior. (Others [38, 39] have also considered approximations to the Clebsch-Gordan coefficients that lead to similar results.)

Using Eq. (22), one can replace the sum over the squares of the $3j$ coefficients times the $B_{\lambda}(j, j')$ in the quantum expression Eq. (1) by an integral over α and obtain an expression similar to the right hand side of Eq. (10). Following the same analysis as in Section 4 then leads to the semiclassical formula Eq. (20).

Figure 7 compares the distribution of final m' levels for collisions of Ar with NaK ($A^1\Sigma^+$) calculated quantum mechanically [20] and with Eq. (20). Results for several initial levels m when $j = 29$ and $j' = 33$ are shown; the agreement is quite good. Since the final distribution of polar angles θ' tends to have a peak value at $\theta' = \theta$, one expects that the maximum value of the m' distribution will be near the value of m' for which $\theta' = \theta$. The quantum results confirm this behavior, which is easily understood by considering Eq. (17). If we consider transitions $j m \rightarrow j' m'$ and denote the most probable value of m' by m'_{peak} , we have

$$m'_{\text{peak}} = \left(\frac{j' + \frac{1}{2}}{j + \frac{1}{2}} \right) m \quad (23)$$

Figure 8 shows a similar comparison for smaller values of j and j' ; the semiclassical result still agrees very well with the quantum calculation. For $m = 4$ there is the expected peak near $m' = 7$, but there is also a strong secondary peak near $m' = -7$.

6. Lorentzian Approximation to Polar Angle Distribution

A characteristic feature of the results calculated using Eq. (14) is that the final angular distributions $\mathcal{P}_{jj'}(\theta, \theta') \sin \theta'$ tend to have their maximum values at $\theta' = \theta$, as long as θ is not too close to 0 or π . Also, in this range of θ , the final distributions all tend to have the same shape. In other words, the final distributions tend to depend only on $\theta' - \theta$. In the Appendix, we present an analysis that shows why one might expect this behavior.

The analysis shows that if j and j' are large and the moments $d_K(j, j')$ fall off exponentially according to $d_K \approx A \exp(-\beta K)$, then Eq. (14) can be reduced (after many approximations) to a Lorentzian distribution of the form

$$\mathcal{P}_{jj'}(\theta, \theta') \sin \theta' \approx \frac{\pi}{4\sqrt{[j][j']}} \frac{A\beta}{(\theta' - \theta)^2 + \beta^2}. \quad (24)$$

In those cases where the behavior of the d_K is approximately exponential, Eq. (24) works reasonably well. We also identified some cases where d_K could

be well fit by a sum of two exponentials:

$$d_K(j, j') \approx \sum_{i=1}^2 A_i \exp(-\beta_i). \quad (25)$$

One then obtains the corresponding angular distribution $\mathcal{P}_{jj'}(\theta, \theta') \sin \theta'$ by generalizing Eq. (24) to the sum of two Lorentzians.

We found that the $d_K(j, j')$ for even Δj transitions of NaK ($A^1\Sigma^+$) induced by He could often be well fit by a single exponential. The $d_K(j, j')$ for some transitions in Ar + NaK ($A^1\Sigma^+$) collisions were well fit by the sum of two exponentials. Figure 9 shows the exact quantum $d_K(29, 33)$ for He + NaK ($A^1\Sigma^+$) and $d_K(28, 33)$ for Ar + NaK ($A^1\Sigma^+$). The corresponding angular distributions $\mathcal{P}_{jj'}(\theta, \theta') \sin \theta'$ are shown in Fig. 10. Figure 10(a) compares the exact value of $\mathcal{P}_{jj'}(\theta, \theta')$ [Eq. (14)] with the approximation given in Eq. (24). The calculations shown are for $\theta = 90^\circ$, but the results for other values of θ between 30° and 150° are very similar. The value of the Lorentzian approximation is about 20% high at the peak, and the FWHM is about 10% low. Figure 10(b) shows the results for the two-exponential case. The approximate two-Lorentzian angular distribution is reasonably close to the exact semiclassical formula. Figure 10(b) also shows (with dotted lines) the separate Lorentzian terms. The narrow Lorentzian is most important at small values of $\theta - \theta'$ and arises from the slow exponential that dominates the large- K behavior of $d_K(j, j')$ shown in Fig. 9. Conversely, the much broader Lorentzian that dominates the angular distribution for large $\theta - \theta'$ comes from the rapid decay of $d_K(j, j')$ at small K .

The Lorentzian approximation may provide valuable qualitative understanding of the shape of the polar angle distribution, but a one- or two-exponential fit will not always accurately represent the behavior of the d_K . For quantitative results the exact semiclassical formula Eq. (14) is more accurate.

7. Concluding Remarks

We have derived a closed-form expression for the change in the polar angle θ of the angular momentum of a rotator caused by collisions in a cell-type

experiment. Numerical calculations demonstrate that the distribution of final polar angles θ' tends to have its maximum value at or near the initial polar angle.

A striking feature of the calculations is that the distribution of final angles θ' depends primarily on $\theta - \theta'$ and only weakly on θ . We developed a simple Lorentzian model for the θ' distribution that exhibits the strong dependence on $\theta - \theta'$. The model also clearly identifies the connection between the width of the distribution of final polar angles θ' for a particular transition and the rate of fall-off of the corresponding moments $d_K(j, j')$. The connection between θ' and m' [Eq. (17)] provides a way to estimate the magnitude of Δm .

The distribution of final polar angles θ' , for a given initial θ , can be easily converted to a distribution of final m' levels, for a given initial m . The semiclassical expression thereby obtained for the cross section, $\sigma_{\text{sc}}(jm \rightarrow j'm')$, was shown to be in very good agreement with quantum coupled channel calculations for collisions of He and Ar with NaK ($A^1\Sigma^+$). The expression for $\sigma_{\text{sc}}(jm \rightarrow j'm')$ depends on the moments $d_K(j, j')$, which we calculated quantum mechanically. However, the $d_K(j, j')$ can also be determined by classical trajectory methods [13]. Applying such methods may facilitate the quantum treatment of much larger systems.

Acknowledgments

A.P.H. and T.J.P. acknowledge support by NSF under grant PHY-1403060. Computational facilities at the Texas Advanced Computing Center (TACC) used for this research were supported by NSF through XSEDE resources provided by the XSEDE Science Gateways Program. A.C.T. was supported by NSF REU Site Grant PHY-1359195 to the Lehigh University Physics Department. D.T. acknowledges support from the French national PCMI program.

Appendix

We have found a very simple analytic expression for the angular distribution in Eq. (14) by making additional approximations. We invoke equation 8.10.7 from reference [40] for the Legendre polynomials,

$$P_K(\cos \theta) = \frac{\Gamma(K+1)}{\Gamma(K+\frac{3}{2})} \left(\frac{\pi}{2 \sin \theta} \right)^{1/2} \cos \left((K + \frac{1}{2})\theta + \pi/4 \right) + O(K^{-1}). \quad (26)$$

From asymptotic formula 6.1.39 in [40], we have

$$\frac{\Gamma(K+1)}{\Gamma(K+\frac{3}{2})} \approx \frac{1}{\sqrt{K+1}}. \quad (27)$$

If we substitute Eq. (26) into Eq. (14) we obtain the product of two cosines, which can be transformed using the identity

$$2 \cos a \cos b = \cos(a-b) + \cos(a+b). \quad (28)$$

In the present case, we keep only the first term, which involves the factor $\cos(K(\theta' - \theta))$ that varies slowly in the sum over K . We drop the more rapidly varying term that depends on $\cos(K(\theta' + \theta))$. With these approximations, we can rewrite Eq. (14) as

$$\mathcal{P}_{jj'}(\theta, \theta') \sin \theta' \approx \frac{\pi}{4\sqrt{[j][j']}} \left(\frac{\sin \theta'}{\sin \theta} \right)^{1/2} \sum_{K=0}^{2K_{<}} \frac{2K+1}{2(K+1)} d_K(j, j') \cos \left((K + \frac{1}{2})(\theta' - \theta) \right) \quad (29)$$

We further assume that $(2K+1)/(2K+2) \approx 1$. Also, since we expect the θ' distribution to peak near $\theta' = \theta$, we will assume that $(\sin \theta' / \sin \theta)^{1/2} \approx 1$. Finally we drop the “ $\frac{1}{2}$ ” in the argument of the cosine. Now we have

$$\mathcal{P}_{jj'}(\theta, \theta') \sin \theta' \approx \frac{\pi}{4\sqrt{[j][j']}} \sum_{K=0}^{2K_{<}} d_K(j, j') \cos \left(K(\theta' - \theta) \right) \quad (30)$$

We replace this sum with an integral that can be evaluated analytically. If we assume that

$$d_K(j, j') = A e^{-\beta K}, \quad (31)$$

and assume the upper limit of the integral is very large, then we have

$$\mathcal{P}_{jj'}(\theta, \theta') \sin \theta' \approx \frac{\pi}{4\sqrt{[j][j']}} \int_0^\infty A e^{-\beta K} \cos(K(\theta' - \theta)) dK. \quad (32)$$

The final result is

$$\mathcal{P}_{jj'}(\theta, \theta') \sin \theta' \approx \frac{\pi}{4\sqrt{[j][j']}} \frac{A\beta}{(\theta' - \theta)^2 + \beta^2}. \quad (33)$$

This angular distribution is a Lorentzian centered at $\theta' = \theta$, with a FWHM of 2β .

References

- [1] G. Grawert, Zur Theorie der Stöße angeregte Alkaliatome mit Edelgasatomen [On the theory of the scattering of excited alkali atoms by inert gas atoms], Z. Phys. 225 (1969) 283–292.
- [2] M. D. Rowe, A. J. McCaffery, Transfer of state multipoles in excited $a^1\sigma_u^+ {}^7\text{Li}_2$ following rotationally inelastic collisions with He: Experiment and Theory, Chem. Phys 43 (1979) 35–54.
- [3] C. H. Green, R. N. Zare, Photofragment alignment and orientation, Ann. Rev. Phys. Chem. 33 (1982) 119–150.
- [4] M. H. Alexander, S. L. Davis, m dependence in rotationally inelastic scattering in cell experiments: Implications of an irreducible tensor expansion for molecules in $^1\sigma$ electronic states, J. Chem. Phys. 78 (1983) 6754–6762.
- [5] J. Derouard, Reorientation, polarization and scaling laws in rotational transfer experiments, Chem. Phys. 84 (1984) 181–192.
- [6] J. I. Cline, K. T. Lorenz, E. A. Wade, J. W. Barr, D. W. Chandler, Ion imaging measurement of collision-induced rotational alignment in Ar-NO scattering, J. Chem. Phys 115 (2001) 6277–6280.
- [7] M. L. Costen, H. J. Crichton, K. G. McKendrick, Measurement of orientation and alignment moment relaxation by polarization spectroscopy: Theory and experiment, J. Chem. Phys 120 (2004) 7910–7926.

- [8] M. L. Costen, H. J. Crichton, K. G. McKendrick, Orientation and alignment moments in two-color polarization spectroscopy, J. Chem. Phys 122 (2005) 164309 (12 pages).
- [9] G. Paterson, S. Marinakis, M. L. Costen, K. G. McKendrick, J. Kłos, R. Toboła, Orientation and alignment depolarization in OH ($x^2\pi$) + ar/he collisions, J. Chem. Phys 129 (2008) 074304 (18 pages).
- [10] M. Brouard, A. Bryant, Y.-P. Chang, R. Cireasa, C. J. Eyles, A. M. Green, S. Marinakis, F. J. Aoiz, J. Kłos, Collisional depolarization of OH(A) with ar: Experiment and theory, J. Chem. Phys 130 (2009) 044306 (12 pages).
- [11] P. J. Dagdigian, M. H. Alexander, Tensor cross sections and the collisional evolution of state multipoles: Oh($x^2\pi$)-ar, J. Chem. Phys. 130 (2009) 094303 (11 pages), erratum **131**, 229902 (2009).
- [12] P. J. Dagdigian, M. H. Alexander, Tensor cross sections and the collisional depolarization of oh($x^2\pi$) in collisions with helium, J. Chem. Phys. 130 (2009) 164315 (9 pages).
- [13] F. J. Aoiz, M. Brouard, C. J. Eyles, J. Kłos, M. P. de Miranda, The collisional depolarization of $^{2S+1}\sigma$ radicals by closed shell atoms: Theory and application to oh($x^2\pi$)+ ar, J. Chem. Phys. 130 (2009) 044305 (15 pages).
- [14] C. M. Wolfe, S. Ashman, J. Bai, B. Beser, E. H. Ahmed, A. M. Lyyra, J. Huennekens, Collisional transfer of population and orientation in NaK, J. Chem. Phys. 134 (2011) 174301 (17 pages).
- [15] M. Brouard, H. Chadwick, C. J. Eyles, F. J. Aoiz, J. Kłos, The k - j - j' vector correlation in inelastic and reactive scattering, J. Chem. Phys. 135 (2011) 084305 (13 pages).
- [16] M. Brouard, H. Chadwick, Y.-P. Chang, C. J. Eyles, F. J. Aoiz, J. Kłos, Collisional angular momentum depolarization of OH(a) and NO(a) by Ar: A comparison of mechanisms, J. Chem. Phys. 135 (2011) 084306 (17 pages).

- [17] J.-M. Hartmann, C. Boulet, Quantum and classical approaches for rotational relaxation and nonresonant laser alignment of linear molecules: A comparison for CO_2 gas in the nonadiabatic regime, *J. Chem. Phys.* 136 (2012) 184302 (17 pages).
- [18] M. Brouard, H. Chadwick, C. J. Eyles, B. Hornung, B. Nichols, F. J. Aoiz, P. G. Jambrina, S. Stolte, M. P. de Miranda, Rotational alignment effects in $\text{NO}(X) + \text{Ar}$ inelastic collisions: A theoretical study, *J. Chem. Phys.* 138 (2013) 104309 (15 pages).
- [19] M. Brouard, H. Chadwick, C. J. Eyles, B. Hornung, B. Nichols, F. J. Aoiz, P. G. Jambrina, S. Stolte, Rotational alignment effects in $\text{NO}(X) + \text{Ar}$ inelastic collisions: An experimental study, *J. Chem. Phys.* 138 (2013) 104309 (13 pages).
- [20] R. F. Malenda, T. J. Price, J. Stevens, S. L. Uppalapati, A. Fragale, P. M. Weiser, A. Kuczala, D. Talbi, A. P. Hickman, Theoretical calculations of rotationally inelastic collisions of He with $\text{NaK}(a^1\sigma^+)$: Transfer of population, orientation, and alignment, *J. Chem. Phys.* 142 (2015) 224301 (12 pages).
- [21] V. Khare, D. J. Kouri, D. K. Hoffman, On j_z -preserving propensities in molecular collisions: I. Quantal coupled states and classical impulsive approximations, *J. Chem. Phys.* 74 (1981) 2275–2286.
- [22] V. Khare, D. J. Kouri, D. K. Hoffman, On j_z -preserving propensities in molecular collisions: II. Close-coupling study of state-to-state differential cross sections, *J. Chem. Phys.* 76 (1982) 4493–4501.
- [23] M. W. Schmidt, K. K. Baldridge, J. A. Boatz, S. T. Elbert, M. S. Gordon, J. H. Jensen, S. Koseki, N. Matsunaga, K. A. Nguyen, S. Su, T. L. Windus, M. Dupuis, J. A. Montgomery, Jr., General atomic and molecular electronic structure system, *J. Comp. Chem.* 14 (1993) 1347–1363.

- [24] D. Feller, The role of databases in support of computational chemistry calculations, *J. Comp. Chem.* 17 (1996) 1571–1586.
- [25] K. L. Schuchardt, B. T. Didier, T. Elsethagen, L. Sun, V. Gurumoorthi, J. Chase, J. Li, T. L. Windus, Basis set exchange: A community database for computational sciences, *J. Chem. Inf. Model.* 47 (2007) 1045–1052.
- [26] A. D. McLean, G. S. Chandler, Contracted Gaussian basis sets for molecular calculations. I. Second row atoms, $Z = 11$ –18, *J. Chem. Phys.* 72 (1980) 5639–5648.
- [27] J. P. Blaudeau, M. P. McGrath, L. A. Curtiss, L. Radom, Extension of Gaussian-2 (G2) theory to molecules containing third-row atoms K and Ca, *J. Chem. Phys.* 107 (1997) 5016–5021.
- [28] R. Krishnan, J. S. Binkley, R. Seeger, J. A. Pople, Self-consistent molecular orbital methods. xx. a basis set for correlated wave functions, *J. Chem. Phys.* 72 (1980) 650–654.
- [29] P. M. W. Gill, B. G. Johnson, J. A. Pople, The performance of the becke-lee-
yang-parr (b-lyp) density functional theory with various basis sets, *Chem. Phys. Lett.* 197 (1992) 499–505.
- [30] M. J. Frisch, J. A. Pople, J. S. Brinkley, Self-consistent molecular orbital methods 25. supplementary functions for gaussian basis sets, *J. Chem. Phys.* 80 (1984) 3265–3269.
- [31] D. E. Woon, T. H. Dunning, Jr., Gaussian basis sets for use in correlated molecular calculations. iii. the atoms aluminum through argon, *J. Chem. Phys.* 98 (1993) 1358–1371.
- [32] K. Kowalski and P. Piecuch, New coupled-cluster methods with singles, doubles, and noniterative triples for high accuracy calculations of excited electronic states, *J. Chem. Phys.* 120 (2004) 1715–1738.

- [33] S. F. Boys, F. Bernardi, The calculation of small molecular interactions by the differences of separate total energies. some procedures with reduced errors, *Molec. Phys.* 19 (1970) 553–566.
- [34] A. Ross, R. Clements, R. Barrow, The $a(2)^1\sigma^+$ state of NaK , *J. Mol. Spectrosc.* 127 (1988) 546–548.
- [35] A. M. Arthurs, A. Dalgarno, Theory of scattering by a rigid rotator, *Proc. Roy. Soc. (London) Series A, Mathematical and Physical Sciences* 256 (1960) 540–551.
- [36] N. J. Vilenkin, *Special Functions and the Theory of Group Representations*, American Mathematical Society, Providence, RI, 1968, p. 134.
- [37] P. J. Brussaard, H. A. Tolhoek, Classical limits of Clebsch-Gordan coefficients, Racah coefficients and d -functions, *Physica (Amsterdam)* 23 (1957) 955–971.
- [38] W. H. Miller, Classical-limit quantum mechanics and the theory of molecular collisions, in: I. Prigogine, S. A. Rice (Eds.), *Advances in Chemical Physics*, Vol. 25, John Wiley & Sons, Inc., New York, 1974, pp. 69–177.
- [39] K. Schulten, R. G. Gordon, Semiclassical approximations to $3j$ - and $6j$ -coefficients for quantum mechanical coupling of angular momenta, *J. Math. Phys.* 16 (1975) 1971–1988.
- [40] M. Abramowitz, I. A. Stegun (Eds.), *Handbook of Mathematical Functions*, U. S. Government Printing Office, Washington, D.C., 1972.

FIGURES

Figure 1: Coupled cluster calculation of the He + NaK potential. The NaK bond length is fixed at its equilibrium value.

Figure 2: Coupled cluster calculation of the Ar + NaK potential. The NaK bond length is fixed at its equilibrium value.

Figure 3: Definitions of the angles θ , θ' , and α related to the initial and final angular momenta $\mathbf{j}$ and $\mathbf{j}'$. The azimuthal angles of $\mathbf{j}$ and $\mathbf{j}'$ are ϕ and ϕ' , respectively.

Figure 4: The distribution $\mathcal{P}_{jj'}(\theta, \theta') \sin \theta'$ of final polar angles is shown for several initial polar angles θ for the $j = 28$ to $j' = 32$ transition of $\text{NaK}(A^1\Sigma^+)$ induced by He collisions at $E = 0.002$ au (440 cm^{-1}). The distribution of final polar angles is clearly peaked near the initial polar angle. The curves shown with dashed lines are related to those shown with solid lines by Eq. (16).

Figure 5: The distribution $\mathcal{P}_{jj'}(\theta, \theta') \sin \theta'$ of final polar angles is shown for several initial polar angles θ for the $j = 5$ to $j' = 6$ transition of NaK ($A^1\Sigma^+$) induced by He collisions at $E = 0.002$ au (440 cm^{-1}). The distribution of final polar angles still has its largest value at the initial polar angle, but the distributions are much broader than those in Fig. 4.

Figure 6: Comparison of the square of classical and quantum mechanical $3j$ coefficients for the case $j = 36$, $m = 0$, $j' = 35$, $m = 30$. The dependence of these coefficients on $\cos \alpha$ is discussed in the text following Eq. (22).

Figure 7: Distribution of final m' levels for transitions from $j = 29$ to $j' = 33$ of NaK ($A^1\Sigma^+$) induced by collisions with Ar at energy 0.002 au (440 cm^{-1}), for selected values of m . The solid curves are the semiclassical approximation, Eq. (20), with m' treated as a continuous variable; the points are exact quantum mechanical calculations. The peaks of each distribution are displaced from the point $m' = m$ (unless $m = 0$).

Figure 8: Distribution of final m' levels for transitions from $j = 4$ to $j' = 7$ of NaK ($A^1\Sigma^+$) induced by collisions with He at energy 0.002 au (440 cm^{-1}), for the initial values $m = 0, 2$, and 4. The solid curves are the semiclassical approximation, Eq. (20), with m' treated as a continuous variable; the points are exact quantum mechanical calculations. The peaks of each distribution are displaced from the point $m' = m$ (unless $m = 0$).

Figure 9: Exponential fits to the moments $d_K(j, j')$ for two different transitions: (a) $j = 29$ to $j' = 33$ for collisions of He with NaK ($A^1\Sigma^+$) at energy 0.002 au (440 cm^{-1}), and (b) $j = 28$ to $j' = 33$ for collisions of Ar with NaK ($A^1\Sigma^+$) at the same total energy.

Figure 10: Comparison of the Lorentzian approximation (dashed lines) with the exact semiclassical results (solid lines) for the two situations for which the moments $d_K(j, j')$ were shown in Fig. 9. (a) $j = 29$ to $j' = 33$ for collisions of He with NaK ($A^1\Sigma^+$). The distribution is well described by a single Lorentzian. (b) $j = 28$ to $j' = 33$ for collisions of Ar with NaK ($A^1\Sigma^+$). The distribution closely resembles the sum of two Lorentzians (shown separately by dotted lines), consistent with the two-exponential fit necessary to model the moments d_K .