INELASTIC COLLISIONS IN COLD DIPOLAR GASES

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ABSTRACT OF DISSERTATION

Catherine A. Newell

The Graduate School
University of Kentucky
2010
INELASTIC COLLISIONS
IN COLD DIPOLAR GASES

ABSTRACT OF DISSERTATION

A dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the College Arts and Sciences at The University of Kentucky

By

Catherine A. Newell
Lexington, Kentucky

Director: Dr. Michael Cavagnero, Professor of Physics
Lexington, Kentucky

2010

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ABSTRACT OF DISSERTATION

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Inelastic collisions between dipolar molecules, assumed to be trapped in a static electric field at cold (> $10^{-3}$K) temperatures, are investigated and compared with elastic collisions. For molecules with a Λ-doublet energy-level structure, a dipole moment arises because of the existence of two nearly degenerate states of opposite parity, and the collision of two such dipoles can be solved entirely analytically in the energy range of interest. Cross sections and rate constants are found to satisfy simple, universal formulas. In contrast, for molecules in a Σ electronic ground state, the static electric field induces a dipole moment in one of three rotational sublevels. Collisions between two rotor dipoles are calculated numerically; the results scale simply with molecule mass, rotational constant, dipole moment, and field strength.

It might be expected that any particles interacting only under the influence of the dipole-dipole interaction would show similar behavior; however, the most important and general result of this research is that at cold temperatures inelastic rate constants and cross sections for dipoles depend strongly upon the internal structure of the molecules. The most prominent difference between the Λ-doublet and rotor molecules is variation of the inelastic cross section with applied field strength. For Λ-doublet dipoles, cross sections decrease with increasing field strength. For rotor dipoles, cross sections increase proportionally with the square of field strength. Furthermore, the rate constants of the two types of molecules depend very differently on the angular orientations of the dipoles in the electric field.

KEYWORDS: Molecular Collisions, Inelastic Collisions, Cold Molecules, Dipolar Molecules, Electrostatically Trapped Molecules

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To my mother,

Barbara Catenazzo
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Chapter 1

Introduction

Bose-Einstein condensates and degenerate Fermi gases are exotic states of matter that occur when dilute gases are cooled near absolute zero. They were predicted in the 1920s, but for decades the technology to produce them did not exist. During the 1980s the ability to cool and trap atoms with lasers was developed, finally making it possible for experimentalists to attempt to turn these theoretical entities into reality. The first Bose-Einstein condensates (BECs) of dilute atomic gases were created in the laboratory in 1995 [1, 2], while the first degenerate Fermi gas was produced in 1999 [3]. The field of ultracold atomic physics expanded rapidly after that, with interest soon turning to the production and study of ultracold molecular gases.

Molecular interactions are much more complicated than those of atoms even at extremely low temperatures. Molecules have rotational and vibrational degrees of freedom that complicate their interactions. Another layer of complexity emerges when the molecules are polar for then their interactions become long-ranged and anisotropic. These factors make studies of few and many-body physics with molecules far more interesting—and difficult—than with atoms. Indeed, just producing molecules below 1 K is challenging.

Much fundamental research, interesting in and of itself, must yet be done to simply understand how ultracold molecules form and interact. Quantum degenerate gases of polar molecules, for example, should have very different characteristics compared to the atomic versions. A Bose-Einstein condensate of polar molecules is expected to be a quantum fluid sharing properties with both dilute atomic condensates and liquids, while a degenerate Fermi gas of dipoles might undergo Bardeen-Cooper-Schrieffer pairing to become a superfluid [8]. Polar molecules also offer interesting effects to study in ultracold plasmas and might even form entirely new phases of matter. Ultracold molecular gases are not merely a scientific curiosity, however; they also have
promise as useful tools in a number of different applications.

One of the anticipated practical applications for ultracold polar molecules is quantum computation. If the molecules can be trapped in optical lattices, their electric dipole moments, aligned parallel or anti-parallel to an external static electric field, might be used as the quantum bits, i.e. “qubits,” to be manipulated for calculations [13]. Compared to ultracold samples of neutral atoms, dipoles offer a distinct advantage. With ultracold polar molecules one still gets long coherence times for a collection of particles in a restricted number of quantum states, but unlike neutral atoms, the interactions of the dipoles can readily be tuned with fields to act over relatively long or short distances [8]. This is possible because the strength of the dipole moment that couples the qubits can be adjusted by an external electric field. In addition, the molecules have rotationally excited states, and transitions between these states can be controlled with microwave fields [8]. Further tuning can be achieved in some molecules because of fine or hyperfine structure or Λ-doublets [8]. Other versions of quantum computers using ultracold dipoles have been proposed including dilute gases with rovibronic superpositions serving as the qubits [14] and devices in which dipoles are trapped near mesoscopic circuit components [15, 16].

Cold chemistry is another field in which ensembles of polar molecules can play a unique role. Many experiments have achieved some measure of control over reactions involving single, isolated molecules—namely molecular dissociation and selective bond breaking, but controlling reactions between two or more molecules has thus far been unattainable [8]. Much of the difficulty is caused by random thermal motion, which makes collisions unpredictable and reduces or negates the effects of external fields. As thermal motion is reduced, it becomes possible to exert more control over reactions as the collision energy drops below the energy of externally applied electromagnetic fields. Thermal motion becomes insignificant below about 1 µK, and it is hoped that lasers and static fields can be used to manipulate reactants into specific reaction channels [8, 17].

Reducing temperatures into the ultracold regime means that molecular ensembles—even those with very large molecules—will display purely quantum mechanical be-
havior. The large de Broglie wavelengths at low temperatures change the dynamics of chemical reactions as quantum interference and tunneling become dominant [8]. Many-body interactions become more likely, and the geometry of the space in which the interacting particles is confined might affect how reactions progress [8]. Also, at higher temperatures the effects of internal degrees of freedom are often obscured by center-of-mass motion. In the ultracold regime, center of mass motion becomes insignificant, allowing study and control of more delicate quantum effects [8, 17].

Ultracold molecules could also lead to further development in the areas of precision measurement and spectroscopy. Ultracold atoms have already sparked a revolution in this field. Their low temperatures result in a reduced number of populated states in an ensemble and long coherence times. Ultracold molecules share these characteristics with atoms but the complex structure of molecules offer additional advantages. The many combinations of electronic, vibrational, and rotational energy levels offer a series of precise frequency benchmarks from the microwave through the visible spectrum. This allows even more precise measurements [8].

In particular, ultracold polar molecules are expected to provide a unique platform to check for violations of certain symmetries and test predictions of fundamental physical theories. Tiny deviations from expected values that might be unnoticeable in a neutral atom can be exaggerated due to the internal structure and interactions within molecules [8]. Ultracold molecules could be used, for example, to answer the question of whether or not the electron has an intrinsic dipole moment. The large internal fields of polar molecules normally create interaction energies $10^3$ times larger than those of atoms; as a consequence, if electrons do have a dipole moment, there will be a measurable difference in their energy levels compared to what would be expected if they do not [18, 19]. A related problem is violation of parity and time-reversal invariance. In this case polar molecules are useful because the rovibrational spectra of diatomic molecules are quite sensitive to the effects these symmetry violations have on the nucleus [8, 20, 21, 22]. Also, certain astronomical measurements [23, 24] have indicated that fundamental constants, such as the fine-structure constant and the ratio of proton to electron mass, may have changed significantly during the life of the
universe. One way to test this in the laboratory involves simultaneous measurements of both electronic and vibrational transitions [8, 25].

Before any practical applications can come to fruition experimentalists must master techniques to produce, store, and manipulate ultracold polar molecules. Unfortunately, that is still a long way off. Homonuclear molecular condensates were first produced in 2003 [4, 5], and since then many groups have successfully produced trapped heteronuclear gases using a number of different methods. While near-degeneracy has been achieved recently with polar gases [6, 7], true degenerate states have not been created yet. Part of the problem is that the fundamental mechanics of molecular gases at these temperatures are still not well understood. Experiments exploring the dynamics and interactions of the gases are still being performed at higher temperatures than are ultimately desired. The lack of good theoretical models for polar gases at low temperatures is a hindrance to experimental endeavors at controlling and manipulating them and will delay the anticipated practical applications of this research field.

It is useful to define two temperature regimes for molecular ensembles: cold and ultracold. These regimes result from the existence of a natural energy scale, $E_D$, defined in Chapter 2, associated with the dipole-dipole interaction. (This is analogous to the Rydberg energy scale in systems interacting via the Coulomb potential.) If the thermal energy $kT$ is less than $E_D$, an ensemble is considered ultracold, and it will have different properties depending on whether its constituent particles are fermions or bosons. For thermal energies greater than $E_D$ the ensembles are considered merely “cold.” While the behavior of a cold gas can still exhibit quantum effects, the molecules can be treated as distinguishable particles, and the quantum statistics of bosons and fermions can be avoided. The temperature for which a system changes from cold to ultracold will be different depending upon the mass of the molecules. The vast majority of experiments using trapped ensembles of polar molecules are still in the cold rather than the ultracold regime.

The high expectations for ultracold polar molecules in experiments and applications have created a demand for theoretical support. Theoreticians have met the
challenge by producing volumes of detailed work. Unfortunately, much of the emphasis has been either very specific to particular molecular species under very specific conditions or has focused on the ultracold regime. A lot of experimental work is still being done in the cold regime, and much about molecular behavior and interactions in that arena must yet be explained before experimental energies can be pushed lower. One of the important questions that must be answered prior to cooling and trapping cold polar molecules on a large scale is the relative importance of elastic and inelastic collisions.

The simplest means of trapping a particle with an electric dipole moment is in an electrostatic trap. In this type of device the particles are confined by means of a non-uniform, static electric field $\vec{E}$. Since electric fields satisfy Laplace’s equation, static field maxima can only occur on the boundaries of an area [11, 12]. That means electrostatic traps can only be designed to contain particles in an electric field minimum, and only particles in an internal state that will move toward an area of relatively weak electric field—so-called “low-field seekers”—can be trapped. Inevitably, particles in a trapped gas will collide; these collisions can be either elastic or inelastic. Elastic collisions involve no change in the internal state of the colliding molecules and are generally desirable. Not only do they serve to keep particles in the state that can be retained in the trap, but they also facilitate evaporative cooling. Inelastic collisions occur when one or more of the colliding molecules undergo a change in internal state. They are generally undesirable because particles that become “high-field seekers” during the collision will be ejected from the trap. If particles are lost from the trap at too high a rate the trapped gas will be unstable. On the other hand, some experiments consist of trapped ensembles interacting with a velocity tuned molecular beam. In that type of experiment, inelastic collisions will be an important tool for analyzing the interaction between the beam and the trapped gas [26]. In any type of experiment utilizing an electrostatic trap, it is necessary to have some idea of the relative importance of elastic and inelastic collision processes.

The work described in this dissertation is intended to provide a basic foundation for the theory of inelastic collisions of cold dipolar molecules in an electric field.
We limit our investigation to two-body collisions. Since the gases used in cold and ultracold experiments are relatively diffuse, it can be assumed that negligibly few collisions will involve more than two molecules. The two colliding molecules with electric dipole moments \( \vec{\mu}_1 \) and \( \vec{\mu}_2 \) will be aligned in a particular low-field seeking state prior to the collision. Quantum-mechanical dipoles can align parallel or antiparallel to an applied electric field \( \vec{E} \). The low-field seeking states are those that are aligned antiparallel to the field \([41]\). The dipoles will approach each other on a classical trajectory with impact parameter \( \vec{\rho} \) that is arbitrary with respect to the electric field direction. It is assumed that the colliding molecules remain separated by a large enough distance that the dipole-dipole potential is the only interaction involved in the collision and short-range quantum physics may be ignored. The situation is illustrated in Figure 1.1. After an elastic collision, both dipoles will still be in the same low-field seeking state that they started in. If an inelastic collision occurs, one or both of the dipoles will “flip” into a high-field seeking state.

In the following chapter the theory of elastic collisions between cold dipoles is introduced for purposes of comparison. In Chapters 3 and 4, models for two different types of dipoles, i.e. molecules with a \( \Lambda \)-doublet and molecules that can be described as rigid rotors, are presented and analyzed to compare the relative probabilities for inelastic and elastic collisions. Chapter 5 describes the numerical work required to complete the analysis for the rotor dipoles.
Figure 1.1: Two dipoles with electric dipole moments $\mu_1$ and $\mu_2$ colliding in a static electric field. Prior to the collision both dipoles are aligned antiparallel to the electric field $\vec{E}$ in a low-field seeking state. $\rho$ is the classical impact parameter.
Elastic Collisions of Cold Polar Molecules

The dynamics of a trapped gas depends upon both elastic and inelastic collisions. Elastic collisions promote evaporative cooling while inelastic collisions contribute to trap loss. As it will be helpful to compare the relative contributions of elastic and inelastic rate constants, we will briefly discuss the theory of elastic collisions in the cold temperature regime before discussing inelastic collisions. This chapter summarizes the first complete description of elastic collisions of polar molecules at cold temperatures given by Bohn, Cavagnero, and Ticknor in [27].

2.1 The Elastic Collision Problem

Assume that the collision is between two dipoles aligned in a static electric field $\vec{E}$. The dipole-dipole interaction is

$$V(\vec{R}) = \frac{\mu_1\mu_2}{R^3} \left[ 1 - 3(\hat{R} \cdot \hat{E})^2 \right]$$

(2.1)

where $\vec{R}$ is the relative displacement of the two molecules, $\mu_1$ and $\mu_2$ are their dipole moments, $\hat{R} = \vec{R}/|\vec{R}|$, and $\hat{E} = \vec{E}/|\vec{E}|$. This potential diverges at small $R$. In the following calculations it is assumed that the vast majority of collisions will occur at distances where the dipole-dipole potential dominates and the short-range physics may be neglected.

The Schrödinger equation for the relative motion of the molecules is written

$$\left[ -\frac{\hbar^2}{2M} \nabla^2_{\vec{R}} + \frac{\mu_1\mu_2}{R^3} \left[ 1 - 3(\hat{R} \cdot \hat{E})^2 \right] \right] \psi = E\psi$$

(2.2)

where $M$ is the reduced mass. This equation can be rescaled in terms of a “dipole length” $D$ and the “dipole energy” $E_D$ discussed in the Introduction. The scale of the dipole-dipole interaction defines the dipole energy

$$E_D = \frac{\mu_1\mu_2}{D^3}$$

(2.3)
while $D$ is the distance at which the centrifugal energy $\frac{\hbar^2}{MD^2}$ is equal to $E_D$

$$D = \frac{M\mu_1\mu_2}{\hbar^2}$$

(2.4)

If the substitution $\vec{R} = D\vec{r}$ and $E = \epsilon E_D$ is made, the Schrödinger equation becomes

$$\left[-\frac{1}{2}\nabla^2_{\vec{r}} + \frac{1}{r^3} \left[1 - 3(\hat{r} \cdot \hat{E})^2\right]\right] \psi = \epsilon \psi$$

(2.5)

In this form, the Schrödinger equation is dimensionless and independent of $M$, $\mu_1$, $\mu_2$, and $\mathcal{E}$, and its solution will display universal behavior valid throughout the cold temperature regime. The equation may be solved numerically as discussed in [27], but a high-energy approximation explicitly shows the universal scaling of the cross section while allowing the complex interactions at close approach ($\vec{r} \to 0$) to be neglected.

A complete solution of (2.5) was presented in [27], with boundary conditions applied at small $r$ to account for the unphysical divergence of the potential energy term at $r = 0$. Variations of the boundary conditions were used to simulate the effects of short-ranged interactions on the collision cross sections. A typical result is displayed in Figure 2.1, which provides a clear indication of the separation of the cold and ultracold regimes defined in the Introduction.

For the lowest collision energies, elastic cross sections become insensitive to the energy but are strongly dependent on both the short-range physics and on the indistinguishability of the colliding molecules. This defines the ultracold regime.

At high energies, in contrast, the elastic cross section is inversely proportional to the collision speed (the red curve labeled “Eikonal” in Figure 2.1) and is independent of both short-ranged interactions and the indistinguishability of the molecules. This high-energy regime is referred to as “cold” in this dissertation because it corresponds to sub-Kelvin temperatures for many molecules of interest.

At still higher energies (not shown in the figure), elastic cross sections will become comparable to the geometric size of the molecules, and dipole-dipole interactions are less significant.
Figure 2.1: The total scattering cross section $\sigma/D^2$ averaged over all incident directions for two dipoles aligned in a static electric field. The black line is the complete numerical solution using the close-coupling formalism. The low energy limit is given by the Born approximation (blue line) and the high-energy limit by the eikonal approximation. This diagram is based on Figure 1 from Ref. [27].
2.2 The Eikonal Approximation

The eikonal approximation was originally developed as part of the short-wavelength approximation for light propagation [29, 30]. In the 1950s it was adopted to solve particle scattering problems in the high-energy limit, primarily in nuclear physics [28, 31, 32]. In this approximation it is assumed that the potential varies slowly compared to the wavelength, which leads to the approximate wavefunction

\[ \psi(\vec{r}) = e^{i\vec{k} \cdot \vec{r}} e^{i\chi(\vec{\rho})} \]  

(2.6)

where

\[ \chi(\vec{\rho}) = -\frac{1}{k} \int_{-\infty}^{\infty} dz V(\vec{\rho}, z) \]  

(2.7)

is the eikonal phase. In the cylindrical coordinates used in the above equations, the \( z \)-axis is aligned with the average collision momentum, \( \vec{k}_{av} = (\vec{k}_i + \vec{k}_f)/2 \). We can consider that \( \rho \) corresponds to the classical impact parameter, and \( \phi \) is the azimuthal angle.

The approximate wavefunction can be used to solve for the eikonal scattering amplitude

\[ f^{Ei}(\vec{k}_f, \vec{k}_i) = \frac{k}{2\pi i} \int \rho \ d\rho \ d\phi \ e^{i\vec{q} \cdot \vec{\rho}} [e^{i\chi(\vec{\rho})} - 1] \]  

(2.8)

where \( \vec{q} = \vec{k}_i - \vec{k}_f \) is the momentum transfer, and \( k = |\vec{k}_i| = |\vec{k}_f| = \sqrt{2e} \) is the dimensionless wave number \( 2\pi D/\lambda \). The integration here is performed in cylindrical coordinates in a plane containing \( \vec{q} \) but orthogonal to \( k_{av} \).

We can simplify the expression by defining an \( x \)-axis along \( \vec{q} \) and letting the \( y \)-axis lie in the direction \( \vec{k}_{av} \times \vec{q} \). So defined, the \( y \)-axis is orthogonal to the collision plane. The impact parameter can then be written as \( \vec{\rho} = \rho \cos(\phi) \hat{x} + \rho \sin(\phi) \hat{y} \) and \( \vec{r} = \vec{\rho} + z\vec{k}_{av} \). The eikonal amplitude becomes

\[ f^{Ei}(\vec{k}_f, \vec{k}_i) = \frac{k}{2\pi i} \int \rho \ d\rho \ d\phi \ e^{i\rho \cos(\phi)} [e^{i\chi(\vec{\rho})} - 1] \]  

(2.9)

Once the interaction potential is expressed in cylindrical coordinates

\[ V(\vec{r}) = \frac{1}{(\rho^2 + z^2)^{3/2}} \left[ 1 - 3\left(\frac{\vec{\rho} \cdot \hat{z} + z \vec{k}_{av} \cdot \hat{E}}{\rho^2 + z^2} \right)^2 \right] \]  

(2.10)
it is not difficult to evaluate the eikonal phase. Setting \( \sigma = z/\rho \) gives

\[
\chi = -\frac{1}{k\rho^2} \left[ \int_{-\infty}^{\infty} \frac{d\sigma}{(1 + \sigma^2)^{3/2}} - 3(\hat{\rho} \cdot \hat{\mathcal{E}})^2 \int_{-\infty}^{\infty} \frac{d\sigma}{(1 + \sigma^2)^{5/2}} \right]
- 3(\hat{k}_{avg} \cdot \hat{\mathcal{E}})^2 \int_{-\infty}^{\infty} \frac{\sigma^2 d\sigma}{(1 + \sigma^2)^{5/2}} \right]
\]

(2.11)

The integrals evaluate to 2, 4/3, and 2/3 respectively, which gives

\[
\chi = -\frac{1}{k\rho^2} \left[ 1 - (\hat{k}_{avg} \cdot \hat{\mathcal{E}})^2 - 2(\hat{\rho} \cdot \hat{\mathcal{E}})^2 \right]
\]

(2.12)

Expressing the electric field direction in terms of the coordinate axes above (\( \hat{x} = \hat{q} \), \( \hat{y} = \hat{k}_{avg} \times \hat{q} \), \( \hat{k}_{avg} \))

\[
\hat{\mathcal{E}} = \sin \alpha \cos \beta \hat{x} + \sin \alpha \sin \beta \hat{y} + \cos \alpha \hat{k}_{avg}
\]

(2.13)

the phase becomes

\[
\chi(\rho, \phi) = \frac{2}{k\rho^2} \sin^2 \alpha \cos(2\phi - 2\beta)
\]

(2.14)

The eikonal amplitude is then

\[
f^{Ei}(\hat{k}_f, \hat{k}_i) = \frac{k}{2\pi i} \int \rho \, d\rho \, d\phi \, e^{iq\rho \cos(\phi)} \left[ \exp \left\{ \frac{i}{k\rho^2} \sin^2 \alpha \cos(2\phi - 2\beta) \right\} - 1 \right]
\]

(2.15)

Unfortunately, the integrals become difficult at this point. The solution of this equation for general \( \hat{k}_f \) would have to be solved using numerical methods. Because the eikonal approximation is unitary [31], however, the total cross section can still be determined using

\[
\frac{\sigma_{tot}(\hat{k}_i)}{D^2} = \frac{4\pi}{k} \Im(f(\hat{k}_i, \hat{k}_i))
\]

(2.16)

This equation is the optical theorem [34], which relates total cross section to the imaginary part of the forward scattering amplitude. When \( \hat{k}_f = \hat{k}_i \), \( q \) is equal to zero, and the first exponential in (2.15) is equal to one. In addition we can make the substitution \( \ell = k\rho \) to express the resulting integral in terms of the orbital angular momentum, \( \ell \). This will prove useful for later analysis. We get

\[
f^{Ei}(\hat{k}_i, \hat{k}_i) = \frac{1}{2\pi i k} \int \ell \, d\ell \, d\phi \left[ \exp \left\{ \frac{2k}{\ell^2} \sin^2 \alpha \cos(2\phi - 2\beta) \right\} - 1 \right]
\]

(2.17)
This expression appears to be problematic because when \( q = 0 \), \( \hat{x} \) and \( \hat{y} \) are undefined. That means that \( \beta = \arctan(\hat{y} \cdot \hat{E} / \hat{x} \cdot \hat{E}) \) is also undefined (although \( \alpha = \arccos(\hat{k} \cdot \hat{E}) \) is defined.) Upon examination, one sees that the azimuthal integral is independent of \( \beta \), and the remaining exponential integrates to a Bessel function:

\[
f_{Ei}(\hat{k}_i, \hat{k}_i) = \frac{1}{ik} \int \ell \, d\ell \left[ J_0\left(\frac{2k}{\ell^2} \sin^2 \alpha\right) - 1 \right]
\]

(2.18)

\( f_{Ei} \) is entirely imaginary, so from the optical theorem

\[
\frac{\sigma_{tot}(\hat{k}_i)}{D^2} = \frac{4\pi}{k^2} \int_0^\infty \ell \, d\ell \left[ 1 - J_0\left(\frac{2k}{\ell^2} \sin^2 \alpha\right) \right]
\]

(2.19)

To solve this, let

\[
s = \frac{2vm^2\mu^2}{\ell^2} \sin^2 \alpha, \quad \ell \, d\ell = -vm^2\mu^2 \sin^2 \alpha \frac{ds}{s^2}
\]

(2.20)

so the cross section can be expressed as a dimensionless integral

\[
\sigma_{Ei} = \frac{4\pi\mu^2 \sin^2 \alpha}{v} \int_0^\infty \frac{ds}{s^2} [1 - J_0(s)]
\]

(2.21)

The integral is equal to unity, so

\[
\sigma_{Ei} = \frac{4\pi\mu^2 \sin^2 \alpha}{v} = \frac{4\pi\mu^2}{v} \left[ 1 - (\hat{k}_i \cdot \hat{E})^2 \right]
\]

(2.22)

which gives a rate constant \( (K = v\sigma) \) of

\[
K_{Ei} = 4\pi\mu^2 \sin^2 \alpha = 4\pi\mu^2 \left[ 1 - (\hat{k}_i \cdot \hat{E})^2 \right]
\]

(2.23)

In a trapped gas collisions will be random; one must average over incident directions to get a measurable cross section. This gives the final result

\[
\frac{\sigma_{Ei}}{D^2} = \frac{8\pi}{3k} = \frac{4\lambda}{3D}
\]

(2.24)

where \( \lambda \) is the wavelength.

The first thing to note about these results is the fact that the cross section is identically zero when the electric field and the incident direction are aligned. This would not have a noticeable affect on the behavior of an isolated trapped gas because the incident direction is random; however, in an experiment that involved a beam of
dipole molecules passing through a trapped gas, it is possible to orient the incident
direction with respect to the field. In the latter case, a strong dependence on the
relative orientation of the beam and the field could be expected.

The next interesting aspect is the $1/k$ scaling. This scaling of cross sections with
energy has been suggested before for inelastic collisions in the high-energy limit: Gal-
lagher derived it for Rydberg-Rydberg collisions using the uncertainty principle [33],
DeMille for dipole-dipole collisions in a microwave trap also using the eikonal approx-
imation [35], and Kajita using a renormalized perturbation theory method [36, 37].
Moreover, this result agrees with numerical close-coupling calculations for the tem-
perature range of interest as shown in Figure 2.1. This cross section typifies the
universal behavior of dipole-dipole scattering in the cold regime. The elastic scatter-
ing behavior is dependent only upon the collision energy and the dipole length—not
upon any species-specific characteristics such as dipole moment or mass.
Chapter 3

Inelastic Collisions of Cold Two-state Dipoles

The first and simplest model for a dipole describes a molecule with a simplified Λ-doublet. Such molecules have two nearly degenerate states of opposite parity that become coupled in the presence of an electric field. Λ-doubling is higher order splitting superimposed on the rotational structure of a molecule. The energy difference between the states in a Λ-doublet is on the order of $10^{-3}$ Kelvin, which is an order of magnitude smaller than the energy difference between rotational levels. To exclude transitions between rotational levels, gases must be cooled to lower temperatures when utilizing the Λ-doublet energy levels. On the other hand, Λ-doublet molecules are of particular interest in the study of ultracold gases because very small applied fields can be used to control and “tune” their dipole moments [47, 8, 38, 39].

In this chapter we calculate inelastic cross sections and rate constants for these types of molecules at cold temperatures and compare the results with the elastic cross section from Chapter 2. The content of this chapter was developed for inclusion in this dissertation although it was published in advance in [40].

3.1 The States of a Single Dipole

Consider a molecule whose electronic angular momentum has a nonzero component along the molecular symmetry axis, such as a Π or ∆ state. The projection of the electronic angular momentum along the molecular axis depends upon the direction of the molecule’s rotation with respect to the axis and can be either positive or negative. The states corresponding to these two projections are degenerate until the rotation of the molecule is taken into account. The degeneracy is broken by rotations of the molecular axis either into or perpendicular to the electronic charge distribution, producing an energy splitting between the two states. This is called a Λ-doublet [55].
Because the energy difference between the opposite parity states of a \( \Lambda \)-doublet is always much smaller than the differences between rotational levels of the molecule, a smaller field is required to couple these two states than to couple different rotational levels.\[41\]

Assume that the molecule has only two characteristics—a pair of opposite parity states in a field-free region that are separated by an energy gap \( \delta \) and a field-independent (or “intrinsic”) dipole moment \( d \) that couples the two states when \( \mathcal{E} \neq 0 \). For simplicity, consider the lowest state \( |e\rangle \) to have even parity and energy \(-\delta/2\) and the excited state \( |o\rangle \) to have odd parity and energy \(+\delta/2\). Within this representation of parity eigenstates, the molecular Hamiltonian \( H_0 - \mathbf{d} \cdot \mathbf{E} \) in the presence of a polarizing field \( \mathbf{E} = \mathcal{E} \hat{\mathbf{E}} \) is

\[
H = \begin{pmatrix}
-\delta/2 & -d\mathcal{E} \\
-d\mathcal{E} & +\delta/2
\end{pmatrix} = -\Delta \begin{pmatrix}
\cos \gamma & \sin \gamma \\
\sin \gamma & -\cos \gamma
\end{pmatrix}
\]

where we have introduced a pair of parameters

\[
\Delta = +\sqrt{\frac{(\delta/2)^2}{\delta^2}}
\]

and

\[
\gamma = \tan^{-1}\left(\frac{2d\mathcal{E}}{\delta}\right)
\]

tan \( \gamma \) will be referred to as the “aspect ratio” because it is the ratio of the energy difference between the two states in the presence of an electric field and the energy difference between the states in zero field. (See Figure 3.1.)

In the parity basis, the intrinsic dipole operator coupling opposite parity states is

\[
\mathbf{d} = \mathbf{d}\mathcal{E} = \begin{pmatrix}
0 & d \\
d & 0
\end{pmatrix} \hat{\mathbf{E}}
\]

An alternate basis—the energy basis—results from the diagonalization of the Hamiltonian. Operators and vectors in this basis will be indicated with a single prime. The diagonalization yields a pair of states of energy

\[
H' = \begin{pmatrix}
-\Delta & 0 \\
0 & +\Delta
\end{pmatrix}
\]
according to the prescription

\[
\left( | - \Delta \rangle \ | + \Delta \rangle \right) = \left( |e\rangle \ |o\rangle \right) \left( \begin{array}{cc}
\cos(\gamma/2) & -\sin(\gamma/2) \\
\sin(\gamma/2) & \cos(\gamma/2)
\end{array} \right)
\] (3.6)

These states have field-dependent (or “induced”) dipole moments of

\[
\mu' = -\frac{dH'}{dE} = \left( \begin{array}{cc}
\mu & 0 \\
0 & -\mu
\end{array} \right)
\] (3.7)

where \( \mu = d^2\mathcal{E}/\Delta \) (which tends to \( d \) at high field strengths as shown by equation (3.2)). The moment of the lower energy state is aligned with the field axis so that in an inhomogeneous field the molecule would accelerate in the direction of increasing field strength; we call this state a “high-field seeker”. Conversely, the moment of the high-energy state is aligned antiparallel to the field and the molecule is a “low-field seeker”.

For completeness, we also cite the dipole operator (3.4) in the energy basis:

\[
d' = d \left( \begin{array}{cc}
\sin \gamma & \cos \gamma \\
\cos \gamma & -\sin \gamma
\end{array} \right) = \mu \left( \begin{array}{cc}
1 & \delta/2d\mathcal{E} \\
\delta/2d\mathcal{E} & -1
\end{array} \right)
\] (3.8)

We emphasize that \( d'/\mu \) is dependent on both the field and the gap in this model, a characteristic not shared by the more complex model presented in the next chapter.

Throughout this dissertation, we will refer to field-dependent dipole moments as “induced” moments because they vanish in the absence of an external field. Some references use the term “effective” for the field-dependent dipole moment. We prefer the term “induced” because it more clearly implies that \( \mu \) vanishes as \( \mathcal{E} \to 0 \). In contrast, field-independent moments will be called “intrinsic.” Many references use the term “permanent” rather than “intrinsic.” Both induced and intrinsic moments are, in principle, observable.

Finally, it will prove useful to introduce a third representation—the eigendipole basis [42]—in which the field-dipole interaction alone is diagonal (as if the splitting of the alternate parity states were zero). Operators and vectors in this basis will be indicated with a double prime. In the eigendipole basis

\[
\left( | + d \rangle \ | - d \rangle \right) = \frac{1}{\sqrt{2}} \left( |e\rangle \ |o\rangle \right) \left( \begin{array}{cc}
1 & -1 \\
1 & 1
\end{array} \right)
\]

\[
= \left( | - \Delta \rangle \ | + \Delta \rangle \right) \left( \begin{array}{cc}
\cos[\frac{1}{2}(\gamma - \pi/2)] & \sin[\frac{1}{2}(\gamma - \pi/2)] \\
-\sin[\frac{1}{2}(\gamma - \pi/2)] & \cos[\frac{1}{2}(\gamma - \pi/2)]
\end{array} \right)
\] (3.9)
Here the dipole operator is diagonal

\[ \mathbf{d}'' = \begin{pmatrix} d & 0 \\ 0 & -d \end{pmatrix} \]  

while the energy is not

\[ \mathbf{H}'' = \begin{pmatrix} -d\varepsilon & \delta/2 \\ \delta/2 & d\varepsilon \end{pmatrix} \]  

(3.10)

(3.11)

The three different representations are displayed in Figure 3.1 along with their diagonal energies. The different descriptions produce distinct dynamical equations leading to useful approximations for collision processes.

### 3.2 The States of Two Dipoles

Now that we have defined the states for single dipoles in an electric field, we can combine them to form two-molecule states in the three representations. The convention introduced in the previous section—namely, using unprimed operators for the parity basis, primed operators for the energy basis, and double-primed operators for the eigendipole basis—will be retained in this section.

No matter which basis we choose, we should recognize that the long-range dipole-dipole interaction

\[ V(\vec{R}) = \frac{1}{R^3} \left( \vec{d}_1 \cdot \vec{d}_2 - 3(\vec{d}_1 \cdot \vec{R})(\vec{d}_2 \cdot \vec{R}) \right) \]  

(3.12)

with \( \vec{R} \) the relative displacement of the center of mass of the two dipoles, is invariant under exchange of the locations of the two dipoles. Accordingly, of the four possible states of a pair of two-state dipoles, we can choose three that are even and one that is odd under dipole interchange. Because both the Hamiltonian and the dipole-dipole potential conserve parity, the odd state is not coupled to the others and does not contribute to inelastic processes; we will ignore it here.

We will form the three remaining states from direct products of independent-dipole states, and order them in terms of increasing energy: For the parity basis, we have

\[ |1\rangle = |e, e\rangle \]
Figure 3.1: The two-state molecule, in which even $|e\rangle$ and odd $|o\rangle$ parity states are coupled by an applied electric field $\mathcal{E}$. Two alternative base pairs, the energy eigenstates $|\pm \Delta\rangle$ (blue) and the eigendipole states $|\pm d\rangle$ (dashed) are also displayed.
\[ |2\rangle = \frac{1}{\sqrt{2}} (|e, o\rangle + |o, e\rangle) \]
\[ |3\rangle = |o, o\rangle \] (3.13)

where, for example, \(|e, o\rangle = |e\rangle |o\rangle\). Likewise, in the energy basis, we have
\[ |1\rangle' = | -\Delta, -\Delta\rangle \]
\[ |2\rangle' = \frac{1}{\sqrt{2}} (| -\Delta, +\Delta\rangle + | +\Delta, -\Delta\rangle) \]
\[ |3\rangle' = | +\Delta, +\Delta\rangle \] (3.14)

and in the eigendipole basis
\[ |1\rangle'' = | +d, +d\rangle \]
\[ |2\rangle'' = \frac{1}{\sqrt{2}} (| +d, -d\rangle + | -d, +d\rangle) \]
\[ |3\rangle'' = | -d, -d\rangle \] (3.15)

The Hamiltonian for the system of two dipoles consists of a kinetic energy of relative motion, \(T_{\vec{R}}\), the internal energies of the field-fixed dipoles, and the dipole-dipole interaction (3.12):
\[ H = T_{\vec{R}} + H^{(0)} + V(\vec{R}) \] (3.16)

where the internal energy of the dipoles is
\[ H^{(0)} = (H_1^{(0)} - \vec{d}_1 \cdot \vec{E}) + (H_2^{(0)} - \vec{d}_2 \cdot \vec{E}) \] (3.17)

and
\[ T_{\vec{R}} = -\frac{\hbar^2}{2M} \nabla_{\vec{R}}^2 \] (3.18)

\(M\) is the reduced mass of the pair. Interactions associated with close approach of the molecules are explicitly disregarded since we seek only to evaluate the contribution to scattering processes from high partial waves at cold temperatures.

It is an elementary exercise to construct these operators in the three different representations (3.13), (3.14), and (3.15). In the parity basis, we have
\[ H^{(0)} = \begin{pmatrix} -\delta & -\sqrt{2}dE & 0 \\ -\sqrt{2}dE & 0 & -\sqrt{2}dE \\ 0 & -\sqrt{2}dE & \delta \end{pmatrix} \] (3.19)
and

\[ V(\vec{R}) = \frac{d^2}{R^3} \left( 1 - 3(\vec{R} \cdot \hat{E})^2 \right) \begin{pmatrix} 0 & 0 & 1 \\ 0 & 1 & 0 \\ 1 & 0 & 0 \end{pmatrix} \]  

(3.20)

In the energy basis

\[ H^{(0)\prime} = \begin{pmatrix} -2\Delta & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & +2\Delta \end{pmatrix} \]  

(3.21)

and

\[ V(\vec{R})^{\prime} = \frac{d^2 \sin^2 \gamma}{R^3} \left( 1 - 3(\vec{R} \cdot \hat{E})^2 \right) \times \]

\[ \begin{pmatrix} 1 & \sqrt{2} \cot \gamma & \cot^2 \gamma \\ \sqrt{2} \cot \gamma & \cot^2 \gamma - 1 & -\sqrt{2} \cot \gamma \\ \cot^2 \gamma & -\sqrt{2} \cot \gamma & 1 \end{pmatrix} \]  

(3.22)

And in the eigendipole basis

\[ H^{(0)\prime\prime} = \begin{pmatrix} -2d\mathcal{E} & \delta/\sqrt{2} & 0 \\ \delta/\sqrt{2} & 0 & \delta/\sqrt{2} \\ 0 & \delta/\sqrt{2} & 2d\mathcal{E} \end{pmatrix} \]  

(3.23)

and

\[ V(\vec{R})^{\prime\prime} = \frac{d^2}{R^3} \left( 1 - 3(\vec{R} \cdot \hat{E})^2 \right) \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \]  

(3.24)

In the limit of small zero-field splittings, \( \delta \to 0 \), the channels uncouple and are explicitly diagonal in both the energy and the eigendipole bases (which become identical). A curious feature of the eigendipole representation is that the extreme states \( |1\rangle^{\prime\prime} \) and \( |3\rangle^{\prime\prime} \) are not directly coupled, but interact only through the intermediate state \( |2\rangle^{\prime\prime} \).

In a field free region state \( |2\rangle \) (expressed in the representation (3.13) of parity eigenstates) decouples from \( |1\rangle \) and \( |3\rangle \) as a consequence of parity conservation. As the latter two states remain coupled by \( V(\vec{R}) \), inelastic collisions should be expected even in the absence of an aligning field, and will require the “flipping” of both dipoles (with energy defect \( 2\delta \)). Accordingly, using this simple molecular model, we should expect that for very low fields “double-flip” processes will dominate “single-flip” processes despite the lower energy defect (i.e. \( \delta \)) of the latter.

21
Since we will assume that the highest energy state, in which both molecules are weak-field seekers, is the initial state of the system, we will shift all energies by $E_3 = +2\Delta$, and remove it from the equations of motion.

### 3.3 The Schrödinger Equation in Dimensionless Form

Let us now examine the Schrödinger equation associated with the Hamiltonian (3.16), expressed here in the energy basis:

$$
\left[ -\frac{\hbar^2}{2M} \nabla_R^2 - (E' + 2\Delta A') \right] \Psi(R)' = -\frac{\mu^2}{R^3} \left( 1 - 3(R \cdot \hat{E})^2 \right) B' \Psi(R)' \tag{3.25}
$$

where $E' = E - 2\Delta$, $\Psi$ is a 3-component column vector,

$$
A' = \begin{pmatrix} 2 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 0 \end{pmatrix} \tag{3.26}
$$

and

$$
B' = \begin{pmatrix} 1 & \sqrt{2} \cot \gamma & \cot^2 \gamma \\ \sqrt{2} \cot \gamma & \cot^2 \gamma - 1 & -\sqrt{2} \cot \gamma \\ \cot^2 \gamma & -\sqrt{2} \cot \gamma & 1 \end{pmatrix} \tag{3.27}
$$

As in the case of elastic scattering discussed earlier, we can introduce dipole units by rescaling both the displacement $\bar{R} = D\bar{r}$ and the energy $E' = \epsilon E_D$, where $D = M\mu^2/\hbar^2$ and $E_D = \hbar^6/M^3\mu^4$, to render (3.25) in the dimensionless form

$$
\left[ -\frac{1}{2} \nabla_{\bar{r}}^2 - \left( \epsilon 1 + 2\frac{\Delta}{E_D} A' \right) \right] \Psi(\bar{r})' = -\frac{1}{\bar{r}^3} \left( 1 - 3(\bar{r} \cdot \hat{\bar{E}})^2 \right) B' \Psi(\bar{r})' \tag{3.28}
$$

Measured in dipole units, and neglecting any contributions from close approach of the molecules, collision dynamics are independent of $M$ and depend only on the scale of Figure 3.1 (i.e. $\Delta/E_D$) and on the aspect ratio $\delta/2d\bar{E}$ (i.e. $\cot \gamma$).

### 3.4 Application of the High-energy Approximation

The solution of equation 3.28 is complicated due to the anisotropy of the dipole-dipole potential. The interaction couples all like-parity partial waves so that in a partial wave analysis with polar axis along $\hat{E}$, (3.28) consists of approximately $3L_{max}/2$ coupled second-order differential equations, where $L_{max}$ is the maximum angular momentum
quantum number required for convergence of the cross sections. Furthermore, this set of equations must be solved for approximately $L_{\text{max}}$ alternative conserved magnetic quantum numbers $m = \hat{\mathbf{E}} \cdot \hat{\mathbf{L}}$, although this number decreases for particular collision geometries. Finally, the entire procedure must be repeated for alternative collision geometries (i.e. $k_{\text{inc}} \cdot \hat{\mathbf{E}}$) and for each energy of interest.

For purposes of calculation, we define the minimal requirement for use of a high-energy approximation to be that the de Broglie wavelength be less than the intrinsic length scale $D$ of the dipole-dipole interaction. That means that collisions will be in the cold temperature regime when

$$E' > 2\pi^2 E_D \quad (3.29)$$

Note that this is precisely the energy range in which the eikonal (or high-energy) approximation closely reproduced the elastic scattering cross sections in Figure 2.1. This requirement is therefore equivalent to the definition of “cold” given in the introduction. To estimate $L_{\text{max}}$, we note that partial wave contributions to elastic scattering peak at $L \sim \sqrt{k}$ in units of $\hbar$ [27, 44, 45], with the onset of the cold temperature regime at $k \sim 2\pi$. This suggests a minimal requirement of $L_{\text{max}} \sim 6$ at the onset of the cold temperature regime, and increasing by a factor of 3 for every 10-fold increase in the collision energy or temperature. Progress has been made in performing such calculations (often with more realistic molecular models) though most emphasis has been on energies far colder than suggested by (3.29), and including only a few partial waves [46, 47, 48, 49].

In contrast, our approach will be to identify the limiting behavior of inelastic cross sections and rate constants at energies considerably higher than temperatures that can be considered cold. The second term on the left side of (3.28) can be rewritten in terms of dimensionless wave numbers

$$\epsilon \mathbf{1} + \frac{\Delta}{E_D} \mathbf{A}' = \begin{pmatrix} k_1^2 & 0 & 0 \\ 0 & k_2^2 & 0 \\ 0 & 0 & k_3^2 \end{pmatrix} \quad (3.30)$$

where $k_1$, $k_2$, and $k_3$ are the de Broglie wave numbers for each of the three energy
basis states (respectively) far from the scattering region. Explicitly,

\[ k_1 = \sqrt{2 \left( \epsilon + 4 \frac{\Delta}{E_D} \right)} \]
\[ k_2 = \sqrt{2 \left( \epsilon + 2 \frac{\Delta}{E_D} \right)} \]
\[ k_3 = \sqrt{2\epsilon} \] (3.31)

As collision energy increases beyond the minimal requirement (3.29), the differences in these three wave numbers becomes small:

\[ k_1 = k + \frac{4\Delta}{kE_D} + \cdots \]
\[ k_2 = k + \frac{2\Delta}{kE_D} + \cdots \]
\[ k_3 = \sqrt{2\epsilon} = k \] (3.32)

a requirement satisfied providing \( E' \gg \Delta \).

We can thus extract from the wavefunction its dominant phase

\[ \Psi(\vec{r}) = e^{i\vec{k} \cdot \vec{r}} \psi(\vec{r}) \] (3.33)

where the magnitude of \( \vec{k} \) is simply \( \sqrt{2\epsilon} \), and its direction, \( \hat{k} \), can be chosen at our discretion. Schrödinger’s equation (3.28) is then

\[ \left[ -\frac{1}{2} \nabla^2_{\vec{r}} - i\vec{k} \cdot \nabla_{\vec{r}} \right] \psi(\vec{r})' = \left[ +2\frac{\Delta}{E_D} A' - \frac{1}{r^3} \left( 1 - 3(\hat{r} \cdot \hat{E})^2 \right) B' \right] \psi(\vec{r})' \] (3.34)

With the dominant phase extracted, the remaining amplitude \( \psi(\vec{r}) \) should vary slowly on the scale of the wavelength \( 2\pi/k \), in which case its second derivative is negligible:

\[ i\vec{k} \cdot \nabla_{\vec{r}} \psi(\vec{r})' = \left[ -2\frac{\Delta}{E_D} A' + \frac{1}{r^3} \left( 1 - 3(\hat{r} \cdot \hat{E})^2 \right) B' \right] \psi(\vec{r})' \] (3.35)

Choosing cylindrical coordinates aligned with the \( \hat{k} \) axis, \( \vec{r} = \vec{\rho} + z\hat{k} \), and expressing the dipole-dipole potential in more symmetric form gives

\[ ik \frac{\partial}{\partial z} \psi(\vec{\rho}, z)' = \left[ -2\frac{\Delta}{E_D} A' + \frac{T\rho^2 - 3Cz\rho + Lz^2}{(\rho^2 + z^2)^{5/2}} B' \right] \psi(\vec{\rho}, z)' \] (3.36)
where $T$, $C$ and $L$ are constants defining the geometric relationships between the molecule and the field:

$$
T = 1 - 3(\hat{\rho} \cdot \hat{\mathcal{E}})^2 \\
C = 2(\hat{\rho} \cdot \hat{\mathcal{E}})(\hat{k} \cdot \hat{\mathcal{E}}) \\
L = 1 - 3(\hat{k} \cdot \hat{\mathcal{E}})^2
$$

(3.37)

The labels of the matrices are intended to suggest when each is dominant: $T$, the transverse, is primary during closest approach; $L$, longitudinal, at large separations; and $C$, the cross term, during intermediate parts of the trajectory.

Since the partial derivative with respect to $z$ on the left-hand side of (3.36) is taken with $\vec{\rho}$ held fixed, $\psi$ varies with $\vec{\rho}$ only parametrically. $\vec{\rho}$ may therefore be regarded as the classical impact parameter of a rectilinear trajectory [28]. A simple change of variables, $z = kt$, then reduces (3.36) to the familiar time-dependent Schrödinger equation

$$
i \frac{\partial}{\partial t} \psi(\vec{k}, \hat{\rho}, \tau, t)' = \left[ -\frac{2}{E_D} \Delta A' + \frac{T \tau^2 - 3Ct\tau + Lt^2}{k^3(\tau^2 + t^2)^{5/2}} B' \right] \psi(\vec{k}, \hat{\rho}, \tau, t)'
$$

(3.38)

where we have replaced $\rho$ by the collision time $\tau = \rho/k$, a measure of the width of the collision pulse. In the high-energy limit the time-dependent Schrödinger equation is derived from the time-independent one$^1$.

The time-dependent form of Schrödinger’s equation emphasizes the impulsive nature of the collision process. The pulse has a width $\tau$ and a height $1/(k\tau)^3$. The Massey criterion [43] suggests that the integrated contribution of the potential to the phase will peak when their product is unity (in scaled units), or when $\tau \sim 1/k^{3/2}$. In contrast, the phase contribution of the diagonal energy term in (3.38) will be of order $2\Delta\tau/E_D \sim (2\Delta/kE_D)/\sqrt{k}$. Comparing this with (3.32), it is clear that the assumption of a common wave number in all channels is consistent with neglecting the diagonal energy splittings in (3.38) during the collision process. We now obtain

$$
i \frac{\partial}{\partial t} \psi(\vec{k}, \hat{\rho}, \tau, t) = + \frac{T \tau^2 - 3Ct\tau + Lt^2}{k^3(\tau^2 + t^2)^{5/2}} B' \psi(\vec{k}, \hat{\rho}, \tau, t)'
$$

(3.39)

$^1$Most—if not all—quantum mechanics text books show the time-independent equation derived from the time-dependent one. In fact, Schrödinger himself began with the time-independent version, and the relationship between the two forms is still a matter of some interest. [50, 51, 52, 53]
Because the interaction in this simple model is separable in to spatial and internal factors, this equation is solved precisely by diagonalizing $B'$—that is, by transforming to the eigendipole basis, where it takes the diagonal form

$$i\frac{\partial}{\partial t} \psi(\vec{k}, \hat{\rho}, \tau, t)'' = + \frac{T\tau^2 - 3Ct\tau + Lt^2}{k^3\sin^2\gamma(\tau^2 + t^2)^{3/2}} B'' \psi(\vec{k}, \hat{\rho}, \tau, t)''$$  \hspace{1cm} (3.40)

with

$$B'' = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$  \hspace{1cm} (3.41)

Schrödinger’s equation can now be integrated, component by component

$$\ln \left[ \frac{\psi_i(t)}{\psi_i(-\infty)} \right]'' = -iB''_{i,i} \int_{-\infty}^{t} ds \frac{T\tau^2 - 3Cs\tau + Ls^2}{k^3\sin^2\gamma(\tau^2 + s^2)^{3/2}}$$  \hspace{1cm} (3.42)

with the result

$$\psi''(+\infty) = U''(+\infty, -\infty)\psi''(-\infty)$$  \hspace{1cm} (3.43)

where the time-evolution operator has the diagonal form

$$U''(+\infty, -\infty) = \exp \left[ -i\frac{2B''}{\tau^2k^3\sin^2\gamma} \left( 1 - (\hat{k} \cdot \hat{E})^2 - 2(\hat{\rho} \cdot \hat{E})^2 \right) \right]$$  \hspace{1cm} (3.44)

The geometric factors simplify upon introducing spherical-polar coordinates for the polarizing field direction

$$\hat{E} = \cos \theta \hat{k} + \sin \theta \cos \phi \hat{\rho} + \sin \theta \sin \phi (\hat{k} \times \hat{\rho})$$  \hspace{1cm} (3.45)

so that

$$U''(+\infty, -\infty) = e^{iB''\chi}$$  \hspace{1cm} (3.46)

where $\chi$ is simply the elastic eikonal phase (2.14) in the eigendipole representation

$$\chi = \frac{2\sin^2\theta \cos 2\phi}{k\rho^2\sin^2\gamma}$$  \hspace{1cm} (3.47)

Note that it differs from the eikonal phase for elastic scattering by the factor of $1/\sin^2\gamma$, an effect that can be traced to the occurrence of the intrinsic dipole moment, as opposed to the induced dipole moment, in 3.24. (Recall that $d = \mu/\sin \gamma$.)
Eigendipole states are a mathematical construct, not physical states. Experimentalists actually prepare and detect energy states, so (3.46) must be transformed back into the energy basis, with the result

\[
U'(\pm \infty, -\infty) = \\
\begin{pmatrix}
\cos \chi + i \sin \chi \sin^2 \gamma & \frac{i}{\sqrt{2}} \sin \chi \sin 2\gamma & i \sin \chi \cos^2 \gamma \\
\frac{i}{\sqrt{2}} \sin \chi \sin 2\gamma & \cos \chi + i \sin \chi \cos 2\gamma & -\frac{i}{\sqrt{2}} \sin \chi \sin 2\gamma \\
i \sin \chi \cos^2 \gamma & -\frac{i}{\sqrt{2}} \sin \chi \sin 2\gamma & \cos \chi + i \sin \chi \sin^2 \gamma
\end{pmatrix}
\tag{3.48}
\]

Thus, relatively complicated inelastic transition probabilities originate from a simple mismatch between the creation and detection of energy eigenstates and the free evolution of eigendipole states.

Assuming that the molecules are polarized and trapped in the low-field seeking state \(|3\rangle\)', the probability for a single-flip transition, as a function of impact parameter \(\rho\), is then

\[
P_{3 \rightarrow 2}(\rho) = \left| -\frac{i}{\sqrt{2}} \sin \chi \sin 2\gamma \right|^2 \\
= 2 \sin^2 \gamma \cos^2 \gamma \sin^2 \left[ \frac{2 \sin^2 \theta \cos 2\phi}{k \rho^2 \sin^2 \gamma} \right]
\tag{3.49}
\]

while for a double-flip transition

\[
P_{3 \rightarrow 1}(\rho) = \left| i \sin \chi \cos^2 \gamma \right|^2 \\
= \cos^4 \gamma \sin^2 \left[ \frac{2 \sin^2 \theta \cos 2\phi}{k \rho^2 \sin^2 \gamma} \right]
\tag{3.50}
\]

The ratio of single to double flip cross sections is therefore

\[
\frac{\sigma_{3 \rightarrow 2}}{\sigma_{3 \rightarrow 1}} = 2 \tan^2 \gamma = \frac{8 \rho^2 \mathcal{E}^2}{\delta^2}
\tag{3.51}
\]

which indicates the propensity for double-flip transitions in weak fields owing to parity conservation, as discussed earlier.

Explicit estimation of the cross sections follows from an “incoherent” sum of probabilities over distinct classical paths, i.e.

\[
\frac{\sigma_{3 \rightarrow 2}}{D^2} = \int d\vec{\rho} P_{3 \rightarrow 2}(\rho) = \frac{2\pi}{k} \cos^2 \gamma \left( 1 - (\hat{k} \cdot \hat{E})^2 \right)
\tag{3.52}
\]
and

$$\frac{\sigma_{3\to1}}{D^2} = \int d\vec{\rho} P_{3\to1}(\rho) = \frac{\pi}{k} \cos^2 \gamma \cot^2 \gamma \left( 1 - (\hat{k} \cdot \hat{E})^2 \right)$$  \hspace{1cm} (3.53)

As with both the eikonal elastic scattering cross section (2.22) and the eikonal phase (3.47), these inelastic cross sections vanish when the incident axis is aligned with the polarizing field. However, as discussed in [27] the high-energy ansatz is weakest for this collision geometry because of the dominance of states having low magnetic quantum numbers about the field axis, resulting in severe diffraction of the $m = 0$ component of the incident wave.

We can also extract a formula for the elastic scattering cross section from (3.48) to find if the incorporation of inelastic channels causes it to deviate from the result of the eikonal approximation in [27] and Chapter 2. The amplitude can be rewritten

$$U_{3\to3} = e^{i\chi} - i \sin \chi \cos^2 \gamma$$  \hspace{1cm} (3.54)

and reduces to $e^{i\chi_{EI}}$ when $\gamma \to \pi/2$ (or $\delta \to 0$). However, the elastic cross section cannot be calculated from an incoherent sum of probabilities: since there is no way to distinguish scattered from unscattered trajectories in the beam, the result would be infinite. Accordingly, some analysis of the diffraction of the beam is required. This is accomplished by substituting $\Psi(\vec{r})$ into the integral equation for the scattering amplitude in the eikonal approximation as suggested in [31]:

$$f_{el}(\vec{k}_f, \vec{k}_i) = \frac{k}{2\pi i} \int d\vec{\rho} \ e^{i\vec{q} \cdot \vec{\rho}} \left[ e^{i\chi} - 1 - i \sin \chi \cos^2 \gamma \right]$$  \hspace{1cm} (3.55)

This differs from the elastic amplitude calculated using the eikonal approximation in two ways: the replacement of the eikonal phase with the eigen-dipole phase, and the addition of the last term.

The total cross section can then obtained from the optical theorem. Since the last term in the scattering amplitude is real, it does not contribute; the method for solving the integrals is the same as used in [27] and in the previous chapter:

$$\frac{\sigma_{3\to3}}{D^2} = \frac{4\pi}{k} \operatorname{Im}(f_{el}(\vec{k}_i, \vec{k}_i)) = 2 \operatorname{Re} \int d\vec{\rho} \left[ 1 - e^{i\chi} \right]$$

$$= \frac{4\pi}{k \sin^2 \gamma} \left[ 1 - (\hat{k}_i \cdot \hat{E})^2 \right] = \frac{\sigma_{EI}}{D^2 \sin^2 \gamma}$$  \hspace{1cm} (3.56)
Comparing with (3.52) and (3.53), the ratio of inelastic to elastic cross sections is independent of the direction of incidence, with \( \sigma_{3\rightarrow2}/\sigma_{3\rightarrow3} = \sin^2(2\gamma)/8 \) and \( \sigma_{3\rightarrow1}/\sigma_{3\rightarrow3} = \cos^4(\gamma)/4 \). In the limit of zero applied field, \( \gamma \to 0 \), and the double flip cross section is one-fourth of the elastic cross section.

Averaging the above results over the direction of the polarizing field, and expressing them as rate constants in conventional units, we find

\[
K_{3\rightarrow2} = v\sigma_{3\rightarrow2} = \frac{4\pi d^2}{3} \frac{\sin^2 \gamma \cos^2 \gamma}{\hbar},
\]

\[
K_{3\rightarrow1} = v\sigma_{3\rightarrow1} = \frac{2\pi d^2}{3} \frac{\cos^4 \gamma}{\hbar},
\]

\[
K_{3\rightarrow3} = v\sigma_{3\rightarrow3} = \frac{8\pi d^2}{3} \frac{\cos^4 \gamma}{\hbar},
\]

(3.57)

where \( v \) is the incident velocity. To set the scale, note that for a dipole moment of 1 Debye = 0.39 a.u., \( K_{3\rightarrow3} = 7.8 \times 10^{-9} \text{ cm}^3/\text{s} \). This corresponds to quite large cross sections: For example, for a zero-field energy splitting of \( \delta = 4 \text{ mK} \), at an impact energy of \( E' = 10\delta \), a molecule of mass 20 amu has a velocity of 3000 cm/s, corresponding to a cross section of \( 2.6 \times 10^{-4} (\mu \text{m})^2 \). Results with similar scaling, but different magnitudes, were obtained earlier by applying a unitarized version of perturbation theory [36, 37].

Importantly, the elastic rate constant \( K_{3\rightarrow3} \) differs from the result of the eikonal approximation (2.23) in that it depends on the intrinsic rather than the induced dipole moment. At high collision speeds, it is the intrinsic dipole moment that matters, and therefore the elastic rate constant is independent of the applied field. Moreover, even in the absence of a polarizing field the dipole-dipole interaction results in significant rate constants for both elastic and inelastic scattering over a broad temperature range, with the inelastic constant equal to one-quarter of the elastic constant. This is illustrated in Figure 3.2.

Other important characteristics of the model are displayed in Figure 3.2, including (a) the suppression of single flip transitions at zero field due to parity conservation, (b) the dominance of single-flip transitions at high field strengths due to their smaller energy defect, (c) the rapid decline of inelastic processes with increasing field strength, and (d) a total inelastic rate constant, which peaks at one-quarter of the elastic rate.
Figure 3.2: The ratio of inelastic rate constant to the elastic rate constant, $K_{\text{elastic}}$, for various values of the aspect ratio, $2d\varepsilon/\delta$. 
constant. For reference, with an electric field of 300 V/cm and a dipole moment of 1 Debye, a molecule with a gap of $4 \times 10^{-3}$ Kelvin would have an aspect ratio of $2dE/\delta = 3.6$. 
Chapter 4

Inelastic Collisions of Cold Rotor Dipoles

This chapter describes cold inelastic collisions of molecules in a Σ state. This type of molecule is best modeled as a simple rigid rotor. The rotor description with $\vec{\ell} = 1$ has three different basis states and is considerably more complicated than the two-state case. In this chapter we introduce the theoretical structure for the rotor model, but calculations of cross sections and rate constants must be made numerically. The numerical analysis is presented in Chapter 5. Again, the content of this chapter was developed for inclusion in this dissertation although it was published in advance in [40].

4.1 Rotor Dipoles

Now consider a molecule in a Σ state. In this case the electron distribution is symmetric around the molecular axis, and opposite parity states are introduced due to the rotation of the molecule. Here we represent the molecule as a rigid rotor in a polarizing field [54, 55], with Hamiltonian

$$H = B\vec{\ell}^2 - d\hat{r} \cdot \vec{E}$$

(4.1)

where $\vec{\ell}^2$ is the squared angular momentum operator of the rotor, $B$ is the rotational constant in units of energy, $d$ is the intrinsic dipole moment of the molecule, and $\hat{r}$ is the direction of both the intrinsic dipole moment and the internuclear axis. $\vec{\ell}^2$ has eigenvalues $\ell(\ell + 1)$ ($\ell$ integral), and its eigenstates are the spherical harmonics, which we denote as $|\ell, m\rangle$. This Hamiltonian is invariant under rotations about the field axis, so that $\vec{E} \cdot \vec{\ell}$ is conserved, with integer eigenvalues $m$. $\ell$ is not a good quantum number. As in Chapter 3, we use the word “intrinsic” to describe the field-independent dipole moment of the molecule; in this case it corresponds to the charge separation along the molecular axis in a molecule-fixed reference frame.
Figure 4.1: A model rotor dipole constructed to second-order in the polarizing field $\mathcal{E}$, for a rigid rotor of rotational constant $B$. Red lines show states with $m = 0$, blue $m = \pm 1$, and green $m = \pm 2$. The three odd-parity states ($\ell = 1; m = 0, \pm 1$) form a polar multiplet of energy defect $\Delta$. The splitting is produced by electric field coupling states with different $\ell$ but the same $m$. 
The energy spectrum of (4.1) results from the Stark effect [28] and is readily constructed to second order in the polarizing field by elementary perturbative methods. The eigenstate corresponding to $\ell = 0$ as $\mathcal{E} \to 0$ does not show Stark splitting: for $\ell = 0$ there is only one possible $m$—namely $m = 0$—and it is conserved. The state remains nondegenerate, but molecules in this state are high-field seeking in the presence of an electric field. Since we require our trapped molecules to be in a low-field seeking state, we need to consider the states that correspond to $\ell = 1$ as $\mathcal{E} \to 0$. In the presence of an electric field the original odd-parity $\ell = 1$ state splits into three states which are a mixture of even and odd parity states. Because the magnetic quantum number $m$ is conserved, these states are denoted by $|m\rangle$. They consist of a single low-field seeking state

$$|0\rangle = |1, 0\rangle - \frac{d\mathcal{E}}{2B\sqrt{3}} \left( |0, 0\rangle - \frac{1}{\sqrt{5}} |2, 0\rangle \right) + \cdots$$ \hspace{1cm} (4.2)$$

with energy

$$E_0 = 2B + \frac{d^2\mathcal{E}^2}{10B} + \cdots$$ \hspace{1cm} (4.3)$$

and two degenerate (high-field seeking) states

$$| \pm 1\rangle = |1, \pm 1\rangle + \frac{d\mathcal{E}}{4B\sqrt{5}} |2, \pm 1\rangle + \cdots$$ \hspace{1cm} (4.4)$$

of energy

$$E_{\pm 1} = 2B - \frac{d^2\mathcal{E}^2}{20B} + \cdots$$ \hspace{1cm} (4.5)$$

In the presence of a field, these three states form a polar multiplet, with an energy gap of

$$\Delta = \frac{3d^2\mathcal{E}^2}{20B}$$ \hspace{1cm} (4.6)$$

as displayed in Figure 4.1. We will assume that collision energies are sufficiently low that transitions cannot be made to any states corresponding to $\ell = 0$ or $\ell = 2$ as $\mathcal{E} \to 0$. For illustration, the physical attributes of a few molecules are listed in Table 4.1 at a presumed electric field strength of 1kV/cm.
Let the electric field be aligned with the $z$-axis. Then the dipole operator in the basis of our three states (ordered $|1\rangle, |0\rangle, |-1\rangle$) is

$$\vec{d}' = d\hat{r}' = \mu \begin{pmatrix} 1/2 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1/2 \end{pmatrix} + \hat{\epsilon}_- \begin{pmatrix} 0 & 5/4 & 0 \\ 0 & 0 & -5/4 \\ 0 & 0 & 0 \end{pmatrix} + \hat{\epsilon}_+ \begin{pmatrix} 0 & 0 & 0 \\ 5/4 & 0 & 0 \\ 0 & -5/4 & 0 \end{pmatrix} \quad (4.7)$$

where we use standard polarization unit vectors $\hat{\epsilon}_\pm = (\hat{x} \pm i\hat{y})/\sqrt{2}$, and where

$$\mu \equiv \frac{d^2 \mathcal{E}}{5B} \quad (4.8)$$

is the magnitude of the induced dipole moment of the low-field seeking state $|0\rangle$. Note that

$$\mu' = -\frac{dH'}{d\mathcal{E}} \begin{pmatrix} \mu/2 & 0 & 0 \\ 0 & -\mu & 0 \\ 0 & 0 & \mu/2 \end{pmatrix} \quad (4.9)$$

These results indicate that rotor dipoles are both far more complex and far simpler than the two-state dipoles. They are more complex because the component matrices $d_x, d_y, d_z$ do not commute with one another: it is not possible to construct eigendipole states because the components of $\vec{d}'$ cannot be simultaneously diagonalized. (Compare 4.7 with 3.4.) As a result, the dipole-dipole interaction operator will not commute with itself at different times. To see why they are simpler, compare the energy representations of the dipole operators, (3.8) and (4.7). Since $\vec{d}'/\mu$ is entirely independent of the polarizing field for rotor dipoles, they will display universal behavior over a much larger range of field strengths, i.e. there is no analogue to the aspect ratio $\delta/2d\mathcal{E}$ for rotor dipoles.

**4.2 The States of Two Rotor Dipoles**

Nine direct-product states can be formed from a system of two rotor dipoles. The eigenenergies of the noninteracting Hamiltonian

$$H^{(0)} = \left( B\vec{\ell}_1^2 - d\hat{r}_1 \cdot \vec{\mathcal{E}} \right) + \left( B\vec{\ell}_2^2 - d\hat{r}_2 \cdot \vec{\mathcal{E}} \right) \quad (4.10)$$
are displayed in Figure 4.2: The spectrum separates into states which are either even or odd under exchange of the locations of the two dipoles. The even states are

\[
|1\rangle = |0, 0\rangle \quad E_1 = 4B + 4\Delta/3 \\
|2\rangle = (1/\sqrt{2})(|1, 0\rangle + |0, 1\rangle) \quad E_2 = E_1 - \Delta \\
|3\rangle = (1/\sqrt{2})(| - 1, 0\rangle + |0, -1\rangle) \quad E_3 = E_1 - \Delta \\
|4\rangle = |1, 1\rangle \quad E_4 = E_1 - 2\Delta \\
|5\rangle = (1/\sqrt{2})(|1, -1\rangle + | - 1, 1\rangle) \quad E_5 = E_1 - 2\Delta \\
|6\rangle = |- 1, -1\rangle \quad E_6 = E_1 - 2\Delta
\]

while for the odd states:

\[
|7\rangle = (1/\sqrt{2})(|1, 0\rangle - |0, 1\rangle) \quad E_7 = E_1 - \Delta \\
|8\rangle = (1/\sqrt{2})(| - 1, 0\rangle - |0, -1\rangle) \quad E_8 = E_1 - \Delta \\
|9\rangle = (1/\sqrt{2})(|1, -1\rangle - | - 1, 1\rangle) \quad E_9 = E_1 - 2\Delta
\]

where \(|n\rangle\) is now an arbitrary label. Inelastic collisions can occur among the odd states, but the odd states are not coupled to the low-field seeking state \(|1\rangle\), which we choose as the initial state. We therefore consider transitions among the six even states. The energy gaps between \(|1\rangle\) and states \(|2\rangle\) through \(|6\rangle\) is either \(\Delta\) or \(2\Delta\). States \(|2\rangle\) and \(|3\rangle\) are degenerate with energy \(E_1 - \Delta\), and states \(|4\rangle\), \(|5\rangle\), and \(|6\rangle\) are degenerate with energy \(E_1 - 2\Delta\).

Since we will neglect transitions to states outside of the dipole multiplets, it will be convenient to shift all energies by \(E_1\), and so to remove it from the equations of motion which follow.

### 4.3 The Schrödinger Equation in Dimensionless Form

The Schrödinger equation for our system of two rotor dipoles can be written (in the energy representation)

\[
\left[-\frac{\hbar^2}{2M} \nabla_{\vec{R}}^2 - (E'\mathbf{1} + \Delta\mathbf{A}')\right] \psi(\vec{R})' = -\frac{\mu^2}{R^3} B'(\vec{R}) \Psi(\vec{R})' \quad (4.13)
\]
<table>
<thead>
<tr>
<th>Physical Parameter</th>
<th>NaF</th>
<th>KF</th>
</tr>
</thead>
<tbody>
<tr>
<td>mass (amu)</td>
<td>42</td>
<td>58</td>
</tr>
<tr>
<td>$d$ (debye)</td>
<td>8.16</td>
<td>8.59</td>
</tr>
<tr>
<td>$B$ (K)</td>
<td>0.625</td>
<td>0.401</td>
</tr>
<tr>
<td>$\mu$ (debye)</td>
<td>0.516</td>
<td>0.891</td>
</tr>
<tr>
<td>$\Delta$ (K)</td>
<td>9.38e-3</td>
<td>1.62e-2</td>
</tr>
<tr>
<td>$D$ ($\mu$m)</td>
<td>8.35e-2</td>
<td>3.44e-1</td>
</tr>
<tr>
<td>$E_D$ (K)</td>
<td>3.31e-6</td>
<td>1.41e-7</td>
</tr>
<tr>
<td>$\Delta/E_D$</td>
<td>2.83e+3</td>
<td>1.15e+5</td>
</tr>
<tr>
<td>$dE/B$</td>
<td>0.316</td>
<td>0.519</td>
</tr>
</tbody>
</table>

Table 4.1: Physical parameters of two molecules with rotor-like spectra. The last six entries for each molecule are field dependent; values are given assuming a field of strength $E = 1$ kV/cm.

![Diagram of energy levels](image)

Figure 4.2: The energy spectrum of two noninteracting rotor dipoles. The initial state, in which both dipoles are weak-field seekers, is labeled $E_1$. Only symmetric states are coupled to it by dipole-dipole interactions.
where $E' = E - 4B - 4\Delta/3$,

$$A' = \begin{pmatrix}
0 & 0 & 0 & 0 & 0 & 0 \\
0 & 1 & 0 & 0 & 0 & 0 \\
0 & 0 & 1 & 0 & 0 & 0 \\
0 & 0 & 0 & 2 & 0 & 0 \\
0 & 0 & 0 & 0 & 2 & 0 \\
0 & 0 & 0 & 0 & 0 & 2
\end{pmatrix} \quad (4.14)$$

and

$$B' = \frac{1}{\mu^2} \left( \bar{d}_1 \cdot \bar{d}_2 - 3(\bar{d}_1 \cdot \hat{R})(\bar{d}_2 \cdot \hat{R}) \right) \quad (4.15)$$

$B'$ is a cumbersome $6 \times 6$ matrix which can be calculated using (4.7); it need not be evaluated explicitly at this time. A key feature of the model, however, is that after the extraction of $\mu^2$ from the dipole-dipole interaction, $B'$ depends only on $\hat{R}$ and on the orientation unit vectors $(\hat{z}, \hat{\epsilon}_\pm)$ of the dipole states, where $\hat{z}$ is the direction of the polarizing field.

Transforming to dipole units, $\bar{R} = D\bar{r}$ and $E' = E_D\epsilon$, precisely as done in the previous chapter, gives the dimensionless form of the Schrödinger equation:

$$-\frac{1}{2} \nabla_r^2 - \left( \epsilon 1 + \frac{\Delta}{E_D} A' \right) \Psi(\bar{r})' = -\frac{1}{r^3} B'(\bar{r}) \Psi(\bar{r})' \quad (4.16)$$

When measurements are made in dipole units, and contributions from close approach of the molecules are neglected, the collision dynamics of a pair of rotor dipoles are independent of the reduced mass, and depend solely on the dimensionless ratio $\Delta/E_D$.

### 4.4 Application of the High-energy Approximation

Free relative motion of the rotors, far from the interaction region, is characterized by three distinct wave numbers

\begin{align*}
k &= k_1 = \sqrt{2\epsilon} \\
k_2 &= k_3 = \sqrt{2(\epsilon + \frac{\Delta}{E_D})} \approx k_1 + \frac{\Delta}{k_1 E_D} + \cdots \\
k_4 &= k_5 = k_6 = \sqrt{2 \left( \epsilon + \frac{2\Delta}{E_D} \right)} \approx k_1 + \frac{2\Delta}{k_1 E_D} + \cdots \quad (4.17)
\end{align*}

Again, the minimal requirement for the onset of the cold temperature regime is that
the kinetic energy of relative motion in the initial state (assumed to be the uppermost state with two weak-field seekers, |0, 0⟩) is

\[ E' > 2\pi^2 E_D \]  

(4.18)

To extract a common wave number in all channels, however, we make the more stringent requirement \( E' \gg \Delta \).

These assumptions lead, according to the prescription given in Chapter 2, to the time-dependent Schrödinger equation

\[
i \frac{\partial}{\partial t} \psi(\vec{k}, \hat{\rho}, \tau, t)' = \left[ -\frac{\Delta}{E_D} A' + \frac{T'^2 - 3C't\tau + L't^2}{k^3(\tau^2 + t^2)^{5/2}} \right] \psi(\vec{k}, \hat{\rho}, \tau, t)' \]  

(4.19)

where \( T', C' \) and \( L' \) are now matrices of the operators

\[
T = \frac{1}{\mu^2} \left[ \vec{d}_1 \cdot \vec{d}_2 - 3(\hat{\rho} \cdot \vec{d}_1)(\hat{\rho} \cdot \vec{d}_2) \right]
\]

\[
C = \frac{1}{\mu^2} \left[ (\hat{\rho} \cdot \vec{d}_1)(\hat{k} \cdot \vec{d}_2) + (\hat{k} \cdot \vec{d}_1)(\hat{\rho} \cdot \vec{d}_2) \right]
\]

\[
L = \frac{1}{\mu^2} \left[ \vec{d}_1 \cdot \vec{d}_2 - 3(\hat{k} \cdot \vec{d}_1)(\hat{k} \cdot \vec{d}_2) \right]
\]  

(4.20)

Using (4.7) these may be evaluated explicitly. They are independent of \( d, \mu, \) and \( \mathcal{E} \) and depend only on the orientations of the dipoles relative to the field and the incident direction.

The \( \Delta/E_D \) term is negligible at sufficiently high energies, at which point (4.19) has no remaining parameters and collisions of rotor dipoles become truly universal. The energy at which this occurs varies from one type of molecule to another. To illustrate this transition to the high-energy limit, we integrated (4.19) numerically for the specific collision geometry in which the angle of incidence relative to the polarizing field is 45°. For each impact parameter \( \vec{\rho} \), starting in state \( |1⟩ \), probabilities for transitions among the 6 states of the model were calculated using Runge-Kutta propagation (see Chapter 5). These were then integrated over all impact parameters to obtain inelastic cross sections and rate constants. Results for single-flip and double-flip transitions are shown in Figures 4.3 and 4.4, respectively, where they are compared with similar calculations that neglect the \( \Delta/E_D \) term in (4.19). Note that
at sufficiently high incident energies the $\Delta/E_D$ term in (4.19) is indeed negligible. Then

$$i \frac{\partial}{\partial t} \psi(\vec{k}, \hat{\rho}, \tau, t) = + \frac{\mathbf{T}'\tau^2 - 3C't\tau + L't^2}{k^3(\tau^2 + t^2)^{5/2}} \psi(\vec{k}, \hat{\rho}, \tau, t) \equiv V'(t)\psi(\vec{k}, \hat{\rho}, \tau, t)' \quad (4.21)$$

which is parameter-free within the three-state rotor model.

We can see now how the inability to construct an eigendipole representation leads to more complicated dynamics than in the case of the two-state dipoles. While we can still express $\psi(\vec{k}, \hat{\rho}, \tau, t)'$ as

$$\psi'(\vec{k}, \hat{\rho}, \tau, +\infty) = U'(+\infty, -\infty)\psi'(\vec{k}, \hat{\rho}, \tau, -\infty) \quad (4.22)$$

because the time dependence of the interaction does not separate from geometric factors, $V'(t)$ cannot be rendered in diagonal form at all times, and it is no longer meaningful to write the solution as

$$U'(+\infty, -\infty) = \exp \left[-i \int^{+\infty}_{-\infty} dt \; V'(t) \right] \quad (4.23)$$

Results of a numerical solution to (4.21) will be presented in the following chapter. At this point we will present an approximation method that not only closely approaches the exact results, but also illustrates the impulsive nature of the collision process.

4.5 Sudden limit

One approach to the solution of (4.21) is to construct the Magnus [56] expansion to the time-evolution operator

$$U'(t, t_0) = \exp M'(t, t_0) \quad (4.24)$$

in which $M'$ is a matrix that is expressed as a series

$$M'(t, t_0) = -i \int^{t}_{t_0} dt_1 \; V'(t_1) - \frac{1}{2} \int^{t}_{t_0} dt_1 \int^{t_1}_{t_0} dt_2 \; [V'(t_1), V'(t_2)] + \cdots \quad (4.25)$$

and where higher order terms in the series involve higher order commutators of the potential matrix with itself at different times. The expansion is predicated upon the
Figure 4.3: The sum of the rate constants for single flip transitions plotted versus the collision velocity for KF molecules in a 1 kV/cm electric field. The calculation is for a particular collision geometry (the incident beam and the polarizing field form an angle of 45°), and shows the high-velocity convergence to similar calculations which neglect the energy gap between the target states.
Figure 4.4: The sum of the rate constants for double flip transitions plotted versus the collision velocity for KF molecules in a 1 kV/cm electric field. The calculation is for a particular collision geometry (the incident beam and the polarizing field form an angle of 45°), and shows the high-velocity convergence to similar calculations which neglect the energy gap between the target states.
notion that for interactions that are strongly pulsed or for short periods of propagation
\((t - t_0)\) successive terms in the expansion are of one higher order in the pulse width.
That allows the expansion to be terminated at a specified order without compromising
the unitarity of \(U'\).

Consider now evaluating the Magnus series over the entire duration of the collision
process, from \(t = -\infty\) to \(t = +\infty\). The scaling of successive terms is elementary: The
\(N^{\text{th}}\) term contains \(N\) powers of the potential, and \(N\) factors \(dt\). After setting \(t = \tau \sigma\)
for each time variable and extracting all powers of \(\tau\) and \(k\) from the various integrals,
one finds that the \(N^{\text{th}}\) term is proportional to \((1/k\rho^2)^N\). Since we are interested here
only in the high-energy limit, this suggests retaining only the first term in the series,
which is known as the sudden approximation \[56\], given by

\[
U'(-\infty, \infty) = \exp \left\{ -i \int_{-\infty}^{\infty} dt \, V'(t) \right\}
\]

\[
= \exp \left\{ -i \frac{2(2T'(\theta, \phi) + L'(\theta, \phi))}{3k\rho^2} \right\}
\]

(4.26)

where we note explicitly the dependence on the direction of the polarizing field (3.45).

Within the sudden approximation, we see that complicated transition probabilities
result because the sudden eigenstates evolve freely in time while energy eigenstates
are prepared and detected in experiments. Accordingly, \(U'\) is first evaluated by
diagonalizing and exponentiating the \(2T' + L'\) operator for each orientation of the
field. The eigenvectors of the diagonalization are then used to transform back to
the energy representation for the calculation of transition amplitudes, precisely as
indicated in Section 2.

Results of these sudden approximation calculations are discussed below, where
they are compared with exact results obtained by direct numerical integration of
(4.21) for each impact parameter and collision geometry.

### 4.6 Results

The universal characteristics of collisions of rotor dipoles emerge not from the high-
energy limit, but directly from the dimensionless form of (4.13), which indicates that
our calculated cross sections depend only on the ratio \(\Delta/E_D\). Furthermore, even this
Figure 4.5: Universal dimensionless angular distributions of inelastic rate constants of rotor dipoles, plotted as a function of the angle of incidence relative to the field axis. The dashed curves were calculated in sudden approximation, while the solid curves are exact numerical results. Rate constants are obtained by multiplication of these curves by $\mu^2/\hbar$ for the dipole of interest.
dependence vanishes in the high-energy limit. Let us consider what this high-energy universality implies for our calculated cross sections and rate constants. By changing variables to \( t = \tau \sigma \), one can see directly that (4.21) depends only on the combination \( k \rho^2 \). Since cross sections are obtained by integrating dimensionless probabilities over \( d\hat{\rho} = \rho \, d\rho \, d\phi \) a change of variables \( s = k \rho^2 \) yields \((1/2k) \int ds \, P(s)\). Accordingly, all cross sections must scale as \( 1/k \) at sufficiently high velocities, either in the exact solutions of (4.19) or in the sudden approximation; i.e. for \( E' \gg \Delta \)

\[
\frac{\sigma_{1\rightarrow j}}{D^2} = \frac{C_{1\rightarrow j}(\cos \theta)}{k} \tag{4.27}
\]

where \( C \) is a dimensionless function of the angle between the polarizing field and the beam, \( \cos \theta = \hat{k} \cdot \hat{z} \). This implies rate constants (for final states \( j \neq 1 \)) in conventional units (with dimensions \([L^3/T]\))

\[
K_{1\rightarrow j} = \frac{\hbar K}{M} \sigma_{1\rightarrow j} = \frac{\mu^2}{\hbar} C_{1\rightarrow j}(\cos \theta) = \frac{d^2}{25 \hbar} \left[ \frac{d\mathcal{E}}{B} \right]^2 C_{1\rightarrow j}(\cos \theta) \tag{4.28}
\]

Note that the rate constants all vanish in the absence of a polarizing field, in contrast to the two-state dipoles of Section 2. For the molecules listed in Table 4.1, assuming a polarizing field of 1 kV/cm, \( \mu^2/\hbar \) in (4.28) is \( 2.6 \times 10^{-10} \text{ cm}^3/\text{s} \) for NaF and \( 2.75 \times 10^{-10} \text{ cm}^3/\text{s} \) for KF.

The variation of inelastic rate constants with angle of incidence relative to the field, embodied by universal dimensionless coefficients \( C_{1\rightarrow j}(\cos \theta) \), is shown in Figure 4.5. The sum of the coefficients for single-flip and for double-flip transitions is plotted versus the angle of incidence, revealing a preponderance of double-flip processes for all geometries. Note that the sudden approximation agrees qualitatively with the exact numerical results, and agrees quantitatively within 10% when averaged over the angle of incidence; thereby illustrating the impulsive nature of these inelastic processes.

Figure 4.5 also reveals another qualitative difference with the two-state dipoles discussed in Chapter 3. While all cross sections (elastic and inelastic) vanish when \( \hat{k}_i \cdot \hat{\mathcal{E}} = 1 \) for two-state dipoles, the two-flip cross section for rotor dipoles actually peaks for this collision geometry.
Chapter 5

Computational Methods and Results for Rotor Dipoles

As discussed in the previous chapter, since the Hamiltonian for the rotor model cannot be diagonalized at all times, an exact solution requires numerical methods. Well-established techniques were employed to calculate cross sections and rate constants. We elaborate here on the methods and compare the results from exact, integrated solutions of equations (4.19) and (4.21), the sudden approximation, and a unitarized perturbation approximation. The vast bulk of the author’s efforts in the work for this dissertation was expended on numerical analysis.

5.1 Preliminaries

To facilitate the solution, we first express (4.19) in the interaction picture where

$$\psi_I(\vec{k}, \hat{\rho}, \tau, t)' = \exp \left\{ i \frac{\Delta E}{E_D} A' t \right\} \psi(\vec{k}, \hat{\rho}, \tau, t)'$$

(5.1)

This leads to the interaction Hamiltonian

$$H_I(t) = e^{-i \frac{\pi}{E_D} A'} \left[ \frac{T' \tau^2 - 3C't\tau + L't^2}{k^3(\tau^2 + t^2)^{5/2}} \right] e^{i \frac{\pi}{E_D} A'}$$

(5.2)

and the modified Schrödinger equation

$$i \frac{\partial}{\partial t} \psi_I(\vec{k}, \hat{\rho}, \tau, t) = H_I(\vec{k}, \hat{\rho}, \tau, t)\psi_I(\vec{k}, \hat{\rho}, \tau, t)$$

(5.3)

The interaction picture is appropriate for an impulsive potential such as the dipole-dipole interaction. Expressed in this way, all amplitudes will be constant in time before and after the collision "pulse", i.e. \((d/dt) \langle \cdot \cdot \cdot | \psi_I(t) \rangle \rightarrow 0\) as \(|t| \rightarrow \infty\).

It is also useful to use the collision angle

$$\alpha = \arctan t/\tau,$$

(5.4)

$$-\pi/2 \leq \alpha \leq \pi/2$$
rather than the time as the independent variable. Schrödinger’s equation becomes

$$i \frac{\partial}{\partial \alpha} \psi_I(\alpha) = \mathbf{H}_I \psi_I(\alpha) = \frac{1}{k^3 \tau^2} e^{-i \frac{\Delta}{E_D} A' \tan \alpha} h(\alpha) e^{i \frac{\Delta}{E_D} A' \tan \alpha} \psi_I(\alpha)$$  \hspace{1cm} (5.5)$$

$$h(\alpha) = \cos \alpha \left[ T \cos^2 \alpha - 3C \cos \alpha \sin \alpha + L \sin^2 \alpha \right]$$  \hspace{1cm} (5.6)$$

Note that $h(\alpha)$ is independent of both $\tau$ and $k$. When we neglect the $\Delta/E_D$ term this equation simply becomes

$$i \frac{\partial}{\partial \alpha} \psi_I = \frac{1}{k^3 \tau^2} h(\alpha) \psi_I(\alpha)$$  \hspace{1cm} (5.7)$$

The resulting dimensionless probability amplitudes will be functions of $\tau, \phi,$ and $\theta$.

Cross sections are generally defined in terms of the scattering of a uniform beam of molecules by a fixed target. This requires integrating the probabilities $P = |\psi|^2$ over the area elements $d\vec{\rho} = \rho \, d\rho \, d\phi = k^2 \tau \, d\tau \, d\phi$. To get a total cross section that accounts for collisions from all directions in a trapped ensemble then requires an average over $\theta$. Thus

$$\sigma = \frac{k^2}{\pi} \int \tau \, d\tau \, d\phi \, d\theta \, P$$  \hspace{1cm} (5.8)$$

### 5.2 Exact Numerical Integration

At this point it is possible to proceed to a numerical solution. The first method attempted was fourth-order Runge-Kutta propagation [57]. In this method the interval $-\pi/2 \leq \alpha \leq \pi/2$ is divided into a sufficient number of steps. For each geometry and for each value of $\tau$, the computational routine then propagates the solution at each step in the interval beginning in the initial state $|1\rangle$ at $\alpha = -\pi/2$. In practice it was found that the solution was very erratic at small $\tau$, and it was necessary to manually adjust the number of steps in $\theta$ from a maximum of 40,000 at very small $\tau$ to a minimum of 1,000 at large values of $\tau$. This produced data of probability amplitude versus collision time $\tau$ for both (5.5) and (5.7).

Figures 5.1 and 5.2 show results for dimensionless wave numbers $k = 4600$ and 46,000, which correspond to velocities of 2900 and 29,000 cm/s or collision energies...
Figure 5.1: $\tau \cdot$ probability vs. $\tau$ for $k = 4600$. Results are from the exact numerical solution of Schrödinger’s equation with $\Delta/E_D = 1.15 \times 10^5$ and $\Delta$ set artificially to 0. The collision geometry used is for the incident beam 45° from the polarizing field and the impact parameter at an azimuthal angle of 45°.
Figure 5.2: $\tau^*$ probability vs. $\tau$ for $k = 46,000$. Results are from the exact numerical solution of Schrödinger’s equation with $\Delta/E_D = 1.15 \times 10^5$ and $\Delta$ set artificially to 0. The collision geometry used is for the incident beam 45$^\circ$ from the polarizing field and the impact parameter at an azimuthal angle of 45$^\circ$. 

![Graph showing probability vs. $\tau$ for $k = 46,000$. The graph includes lines for different scenarios: Exact, single flip, Exact, double flip, Exact $\Delta=0$, single flip, and Exact $\Delta=0$, double flip.](image)
of about 1 K and 100 K. The results shown are for $\Delta/E_D = 1.15 \times 10^5$ and for $\Delta$ set artificially to 0. The collision geometry used is for the incident beam 45° from the polarizing field and an azimuthal angle for the impact parameter of 45°. The results are plotted as $(\tau \cdot P)$ vs. $\tau$. This form allows one to visualize the function that is actually integrated to produce the cross section. Realize that the probability alone diverges for small $\tau$, but because smaller impact parameters make a correspondingly small contribution to the cross section, the integrand does actually converge for $\tau \to 0$.

Figure 5.2 is above the high-energy limit discussed in Chapter 4. Universal collision behavior is evident at this energy, and one can see that there is no difference between the results for finite $\Delta$ and $\Delta = 0$. The preponderance of double over single flip transitions is clearly noticeable in the plot. Notice that there is a distinct peak for both one and two-flip transitions after which the probability decays exponentially. Prior to the peak value, the probability oscillates rapidly below the unitarity limit, i.e. $P = 1$ as $\tau$ becomes small. It is this rapid oscillation that makes the numerical solution difficult and time consuming.

Figure 5.1 is included for reference. Here, the collisions are below the high-energy limit, and one can see that there is a difference between the finite $\Delta$ and $\Delta = 0$ cases. As expected from figures 4.3 and 4.4, peak single flip transitions increase and double flip transitions decrease as collision energy decreases below the high-energy limit.

After calculating the probability amplitudes, results were integrated over tau and the azimuthal angle using Simpson’s Rule for the $\Delta = 0$ case in the high-energy limit. When divided by the square of the dipole length $D$ and multiplied by $k$, these results give $C$, the universal dimensionless coefficient discussed in Chapter 4 and shown in Figure 4.5.

### 5.3 Sudden Approximation

The sudden approximation discussed in Chapter 4 offers two advantages over exact numerical solution. First, it significantly reduces computing time with relatively minor qualitative and quantitative differences in results. Secondly, it demonstrates the impulsive nature of dipole-dipole collisions at cold temperatures.
Computational analysis using this approximation is straightforward. The requirement is to use the time evolution operator \( 4.26 \) to find the probability amplitude for each state at \( t = \infty \) given the initial state \(|0\rangle\) at \( t = -\infty \)

\[
\langle i | \psi(\infty) \rangle = \langle i | U(-\infty, \infty) |0\rangle \quad (5.9)
\]

If we let \(|\nu\rangle\) be the basis of eigenstates of the argument of the time evolution operator

\[
\langle \nu | \int_{-\pi/2}^{\pi/2} d\alpha \, H_I(\alpha) |\nu'\rangle = \nu \delta_{\nu \nu'} \quad (5.10)
\]

then

\[
\langle i | \psi(\infty) \rangle = \sum \langle i | \nu \rangle e^{-i\nu \langle \nu |0\rangle} \quad (5.11)
\]

We proceed by diagonalizing \( \int_{-\pi/2}^{\pi/2} d\alpha \, H_I(\alpha) \) to find the eigenvalues \( \nu \) and eigenvectors \(|\nu\rangle\). The computation of \( \langle i | \psi(\infty) \rangle \) then consists of converting the initial state \(|0\rangle\) to the basis \(|\nu\rangle\) and multiplying each term by \( e^{-i\nu} \). Translating the resulting vector back into the original basis gives the probability amplitude for each state, \( \langle i | \psi(\infty) \rangle \).

We then follow the same procedure as in the exact case to calculate \( C \) as a function of incident angle.

Figures 5.3 and 5.4 compare results respectively for sudden approximation with \( \Delta/E_D = 1.15 \times 10^5 \), the sudden approximation with \( \Delta = 0 \), and the exact solution. The figures show single-flip and double-flip cases respectively. The calculations are for \( k = 46,000 \), which is above \( 2\pi^2 E_D \), the minimal energy for the onset of the cold temperature regime. One can see that, as with the exact solution, at high energies the energy gap \( \Delta \) makes a negligible contribution to the probabilities. Although the exact solution and the sudden approximation do not give identical results, as noted in Chapter 4, they are both qualitatively and quantitatively similar. Double flip transitions predominate in both cases, and the exact and sudden probability plots share the general shape of a distinct peak with exponential decay at high \( \tau \) and rapid oscillation below the unitarity limit at low \( \tau \).

Figures 5.5 and 5.6 show the dependence on the angle between the incident direction and the electric field for one-flip and two-flip cases respectively in the sudden
Figure 5.3: Sudden approximation for single flip transitions. The sudden approximation solution with $\Delta/E_D = 1.15 \times 10^5$ and $\Delta$ set artificially to 0 are compared to the exact solution. $k$ is 46,000.
Figure 5.4: Sudden approximation for double flip transitions. The sudden approximation solution with $\Delta / E_D = 1.15 \times 10^5$ and $\Delta$ set artificially to 0 are compared to the exact solution. $k$ is 46,000.
Figure 5.5: Single flip transitions in the sudden approximation with varying angle of incidence $\theta$ relative to the electric field direction. $k$ is 46,000.
Figure 5.6: Double flip transitions in the sudden approximation with varying angle of incidence $\theta$ relative to the electric field direction. $k$ is 46,000.
approximation. Notice that the sudden approximation gives exactly 0 probability for single flip transitions for \( \theta = 0 \) when the incident direction is aligned with the field direction while the double flip case is maximum. As the angle between \( \vec{k} \) and \( \vec{E} \) increases from 0 to \( \pi/2 \) the probability of one flip transitions increases while the probability for double flip transitions decreases. This reproduces the angular dependence seen in Figure 4.5.

### 5.4 Perturbation Theory

An additional analysis of the dipole-dipole collision problem was made using a unitarized perturbation method [36]. The sudden approximation was applied because the collision process between polar molecules was anticipated to be impulsive. The sudden approximation appears to give good results, but to be thorough, we wished to confirm that indeed the interaction was indeed more impulsive than perturbative in nature.

Perturbation theory relies on the idea that the interaction term \( V \) of the full Hamiltonian is small in comparison to the kinetic and internal energy terms. Then the actual wave function varies little from the initial state at any time during the collision process and we can take the solution at \( t = \infty \) to be

\[
\langle i | \psi(\infty) \rangle = \langle i | -i \int_{-\pi/2}^{\pi/2} d\alpha \ H_I(\alpha) | 0 \rangle
\]

where \( H_I \) is defined in 5.5. As can be seen from the form of \( H_I \), the probability \( P \) will be proportional to \( 1/\tau^2 \), so \( \tau \cdot P \) will be divergent as \( \tau \to 0 \). To avoid this violation of unitarity, when the calculated probability exceeded 1, it was simply replaced by 1. This choice would be expected to yield poor results at small impact parameters (small \( \tau \)) and to overestimate scattering by a factor of at least two. While an arbitrary choice, it has precedent in [36]. This method at least provides an upper bound on the probability amplitude for small \( \tau \) and demonstrates the exponential decay of amplitude at higher energies where the potential does become perturbative.

Figure 5.7 compares plots of \( \tau \cdot P \) at \( k = 46,000 \) for the perturbation method and for the sudden approximation. Perturbation theory gives correctly the exponential
Figure 5.7: Perturbation theory approximation for single and double flip transitions. The perturbative solution with $\Delta/E_D = 1.15 \times 10^5$ is compared to the sudden solution with $\Delta = 0$. $k$ is 46,000.
decay at large $\tau$, but as expected, gives a large overestimation of transition probability at small $\tau$. This results in cross sections approximately twice as large as those given by the exact solution and the sudden approximation. This can be seen in the plot of $C$ vs. incident angle shown in Figure 5.8. On the other hand, perturbation theory still demonstrates many of the qualities of the other methods. Double-flip transitions are still found to be dominant except near $\theta = \pi/2$ where perturbation theory shows that single flip transitions become slightly dominant. At $\theta = 0$ as with the sudden approximation, perturbation theory shows that only double flip transitions occur.
Figure 5.8: Universal dimensionless angular distributions of inelastic rate constants of rotor dipoles, plotted as a function of the angle of incidence relative to the field axis. The dashed curves were calculated in sudden approximation, the solid curves are exact numerical results, and the dotted lines give perturbation theory results. Rate constants are obtained by multiplication of these curves by $\mu^2/h$ for the dipole of interest.
Summary and Conclusions

It is the complexity of real molecules that makes them exciting from a scientific point of view and gives them so much promise for practical applications. The two simple models presented in this dissertation do not even begin to do justice to reality. They are, however, a starting point.

We began this investigation in the hope that a simple model would produce a simple result useful to experimentalists as a rule of thumb. There was no intent to supply detailed results about a particular type of molecule to be used in a particular experiment. Close-coupling calculations could be, had been, and will continue to be applied to the problem of molecular scattering to give accurate results for particular molecular species under particular conditions, but they are time consuming, unwieldy, and give unique results highly tailored to precise circumstances. Experimentalists sometimes just wish to have a way to determine approximate scattering rates. They want general results to help them choose among different molecular species when planning an experiment, to give them a sense of how difficult it might be to keep a sample stable in a trap, to provide guidance in deciding if a new idea is worth pursuing.

Initially, though, the project was intractable. The equations depended upon a lot of parameters, and it was difficult to identify which variables were responsible for different behaviors. Simplicity was elusive. Yet as the volume of numerical data began to pile up, we recognized similar patterns, tantalizing clues that there was indeed universal behavior hidden beneath the complexity. Eventually it became clear that translating the equations into dimensionless form was even more important than applying the high-energy limitation for cold temperatures.

We initially began working with the somewhat more complicated rotor model; the two-state model was added much later. We recognized that the description of the
two-state model would be different but that having fewer basis states, it would be easier. The simplicity of the solution to the two-state molecule and the magnitude of the difference in scattering behavior at cold temperatures depending on the types of molecules were surprising, however. Most importantly, the two-state model, with its explicit solution, shows that cross sections depend on the permanent dipole moment for the two-state model and that inelastic scattering is greatest at zero field. For the rotor molecule, rate constants increase as the square of the applied field and the dependence is upon the field-dependent induced dipole moment, which means that no inelastic scattering occurs at zero field. In addition, the angular dependence of the cross sections is totally different for the two models.

It would be interesting to see if the results of these calculations are useful for the purpose intended. In experiments with molecules whose Stark spectrum is accurately described by the models, the rate constants and cross sections described in this dissertation should be accurate. Many molecules will have more complicated spectra, however, and it is possible—perhaps even likely—that the complex internal structure of most molecules is, in fact, not negligible even for gross calculations of scattering behavior. No doubt, caution should be exercised in accepting the utility of the results even as a general guide. It would be worthwhile to explore the effects of increasing layers of complexity such as adding more rovibrational states or including fine or hyperfine structure. Will it be possible to assign different molecular species to groups that share certain general behaviors, or when it comes down to it, is every molecule unique and unclassifiable for the purpose of low temperature inelastic collisions?

Perhaps the most important conclusion to be drawn from this work is that the magnitude of a molecule’s dipole moment is not the only characteristic that should be considered when an experiment is being planned. Molecules can be divided into at least two categories—those with a Λ-doublet and those in a Σ electronic ground state—and perhaps others. In regard to inelastic collisions, molecules in the two categories studied in this dissertation behave very differently at cold temperatures. Inelastic cross sections and angular distributions for the two types of molecules are very unlike each other regardless of the dipole moment, so it is to be expected that
cooling and trapping methods will have to be different for the different categories of molecule.

One hopes that the basic method applied here will turn out to have application to more complex and realistic systems. It is expected that a considerable amount of research will still be done at cold temperatures where the high-energy limit will apply. Furthermore, the method of dimensional analysis can be expected to ferret out universal behavior that might otherwise be hidden under a multitude of parameters. Ultimately, it is the methods that have been applied here rather than the models themselves that hold the most promise for the problem of cold dipolar scattering.
References


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