

CHAPTER I

INTRODUCTION

A. General motivation

The motion of a swarm of ions in a gas under the influence of an external electric field has been the subject of intense study both experimentally and theoretically for over 100 years. The birth of gaseous electronics can be traced to the discovery of X-rays in a cathode-ray tube by Roentgen in 1895. In drift tube studies, the charge of the ions provides a convenient “handle” that can be used by the external electric field to “drag” them through a buffer gas, often a noble gas. More precisely, the external drift field serves to vary the average center-of-mass collision energy of the ion-neutral pair. As ions undergo collisions with the buffer gas, a steady-state balance is achieved between the acceleration or energy imparted by the drift field and the energy or momentum lost to buffer gas collisions. The net result over hundreds of collisions is a steady-state anisotropic ion velocity distribution function $F(\mathbf{v})$, the precise character of which is determined by the ion-neutral interaction potential, mass ratio, and field strength. Additionally, the plane of rotation of a molecular ion can be altered by repeated directed collisions with the buffer gas, which is the phenomenon of collision-induced rotational alignment.

Mathematically, the ion velocity distribution $F(\mathbf{v})$ is described by integrodifferential equations. Much theoretical effort, dating from the initial work of Maxwell and Boltzmann, has been expended to find solutions to equations of this sort, and this theoretical work had been instrumental in developing many areas of

statistical physics. Experimentally, starting with work in the 1930's, drift tube experiments have focused on measuring the motion of ions in gases—i.e., their transport properties—in the hopes of obtaining a glimpse of the underlying ion velocity distribution.

There are several fundamental reasons why one would want to know $F(\mathbf{v})$. For one, knowledge of the ion velocity distribution function would in principle allow calculation of any ion transport property. More importantly for chemical physics, $F(\mathbf{v})$ is the key microscopic-to-macroscopic conversion entity, relating through its average, for example, a microscopic reaction cross-section to a macroscopic and observable rate constant. Because the ion velocity distribution function can “tailor” the observable outcome, manipulation of both ion and neutral velocity distribution functions is a subject of considerable technological interest, for example in kinetic-energy enhanced ion and neutral etching for semiconductor processing.

Traditionally, drift tube experiments, in which the external electric field strength is on the order of 1 V cm^{-1} , have bridged the energy gap of approximately 10 meV to 1 eV between “cold” supersonic jet expansion experiments and “hot” single-collision beam experiments. One of the primary motivations for the extensive research conducted on flow-drift apparatuses in the past 30 years has been to measure ion-molecule reaction rates. Drift tubes, which have an easily varied electric field that essentially plays the role of temperature, have permitted the study of ion-molecule reactions at above-thermal energies.¹ It was recognized by Wannier in 1953 that, by assuming a constant mean free time between ion-neutral collisions, the Boltzmann

equation can be solved exactly (in the high-field case) for the attractive r^{-4} potential characteristic of all ion-induced dipole interactions.² The resulting average lab-frame energy of the ion swarm is given by the surprisingly simple expression,

$$\langle KE_{lab} \rangle = \frac{1}{2} m \langle v_i^2 \rangle = \frac{3}{2} k_B T_{buffer} + \frac{1}{2} m v_d^2 + \frac{1}{2} M v_d^2 \quad (1.1)$$

where m is the ion mass, M is the buffer mass, and v_d the ion drift velocity. As can be seen from Eq. (1.1), superimposed on the purely thermal, isotropic energy are two additional terms. The first is associated with the directed motion of the ions in the buffer; the second accounts for the randomizing effect of collisions with the buffer. This expression turns out to work astonishingly well in yielding average kinetic energies provided that the *measured* values of ion drift velocities are used. This fact was the impetus for much of the ion transport work conducted in the 1970's.

Recently, there has been a resurgence of interest in these old methods. The technique of ion mobility spectrometry has been used to study cluster mobilities, which depend on the angle-averaged collisional cross sections of the clusters. For example, the mobilities of $\text{NO}^+(\text{CH}_3\text{CN})_n$ clusters drifted in He will monotonically decrease with increasing cluster size $n=0-3$ at a fixed field strength.³ Actual cluster structure information can be gleaned from differences in the mobility of isomers of various mass-selected species. The structure of silicon, germanium and aluminum clusters have been studied by injecting mass-selected clusters into a drift tube at various injection energies.⁴ Proposed formation mechanisms of fullerenes from cyclic carbon rings have been studied by this technique as well.⁵

It is hoped that the work presented here is in a similar spirit of “teaching a very old dog yet one more new trick”! The experimental technique of single-frequency laser-induced fluorescence (LIF) is employed in this work to study both transport properties and collision-induced rotational alignment of one particular ion, N_2^+ , drifted in helium in a drift-tube apparatus. The single-frequency ring dye laser beam can be thought of as a “delta function” in frequency space that selects out one laboratory ion velocity component along its propagation direction \hat{k} . This technique permits one to map out the steady-state ion velocity distributions more-or-less directly as a function of field strength and rotational state. Additionally, by measuring the polarization of the resultant LIF, the degree of rotational alignment of N_2^+ can be studied as a function of one component of laboratory-selected velocity.

In some ways, N_2^+ is a molecule ideally suited for study with the technique of single-frequency LIF. The ion can be made cleanly and easily in a flowing afterglow or plasma discharge. It has two fairly low-lying excited electronic states ($A\ ^2\Pi_u$ and $B\ ^2\Sigma_u^+$) that are optically accessible with visible photons. In particular, the $B\ ^2\Sigma_u^+$ state has a fluorescence lifetime (62 ns) short enough to insure that the molecule spends the majority of time in the ground $X\ ^2\Sigma_g^+$ state, but not so short that the natural linewidth of the transition must be taken into consideration in line shape analysis. Additionally, the Franck-Condon factors for the ground vibrational state of the $B\ ^2\Sigma_u^+ - X\ ^2\Sigma_g^+$ system are quite strong. The primary disadvantage of the molecule is its nonzero nuclear spin; the presence of unresolved hyperfine structure

underlying each rotational line somewhat complicates the data analysis for both the transport property and alignment experiments.

Because of these factors, N_2^+ is a natural “chromophore” for use in plasma environments. For example, N_2^+ has been studied via LIF in an electron cyclotron resonance (ECR) plasma to characterize transverse ion translational temperatures and obtain the “pitch angle” that determines the plasma etch anisotropy.⁶ Both translational and rotational ion temperatures were obtained by LIF in a pulsed RF-generated nitrogen plasma to study the transient plasma heating and cooling.⁷ Doppler shifts of the $B - X$ and $A - X$ emission of N_2^+ in a He glow discharge, measured by Fourier transform emission spectroscopy, are used as a probe of the plasma dynamics; the discharge electric field can be measured by this technique.⁸

Additionally, because of its atmospheric and interstellar importance, N_2^+ is a molecular ion of intrinsic interest. It is one of the major constituents of the F-region of the ionosphere (altitude > 120 km), and the $N_2^+ + O$ reaction is key in controlling the amount of O^+ and NO^+ in this region.⁹ Atmospheric models and measurements differ on the amount of N_2^+ in this region by a factor of greater than two, yet the $N_2^+ + O$ rate constants and branching ratios have been confirmed by several independent measurements.¹⁰ Work from this laboratory on a SIFT/LIF apparatus reveals a previously undetected channel of simultaneous charge and vibrational transfer between reactions of N_2^+ and neutral N_2 ,¹¹ which may provide clues to the solution of this puzzle.

However, this work concerns solely the nonreactive scattering properties of the N_2^+ -He system. Two basic categories of experiments will be discussed. The transport property experiments, covered in Chapter III, involve characterizing the ion velocity distribution function $F(\mathbf{v})$ as a function of field strength and attempting to understand some of the mechanisms leading to this behavior. The rotational alignment experiments, discussed in Chapter IV, seek to measure the degree of rotational alignment as a function of velocity subgroup and probe direction, and to understand the underlying dynamics.

B. Interaction potential

A distinguishing feature of ion-molecule interactions is that they are always dominated by the attractive, long-range r^{-4} ion-induced dipole term in the potential. Traditionally, the motivation for much of the older ion transport work was to obtain a more detailed picture of the interaction potential by extracting this information from the measured transport property data (i.e., the inversion problem). A more modern approach is to calculate what is believed to be an accurate *ab initio* interaction potential and then test the accuracy of this potential by calculating “forward” to transport properties that can be compared with actual measurements. For example, a recent calculation found good agreement between measured and theoretical mobilities derived from classical trajectory calculations run on an *ab initio* NO^+ -He interaction potential.¹² Unfortunately, there are still a small number of calculated ion-molecule interaction potentials for systems of interest.

The N_2^+ -He system is unusual in this regard because high-level interaction potentials have been calculated several times. In an early calculation from the group of H.-J. Werner, Miller *et al.*¹³ performed an *ab initio* calculation using multi-configuration self-consistent field, configuration interaction (MCSCF-CI) wave functions to determine the 2-D interaction potential as a function of the N_2^+ -He internuclear distance R and angle θ between the diatomic bond and R . The calculations were carried out for the equilibrium N_2^+ bond length of 2.11 bohr radii (a_0) and for three discrete angles, $\theta = 0, 45$ and 90 degrees with R varying from 3.5 to $25.0 a_0$. The resulting energies were then fit to an interpolating function to obtain an analytic interaction potential $V_{\text{int}}(R, \theta)$ as a continuous function of the two coordinates, as shown in Fig. 1.1. Note that the depth of the well minimum (approximately 140 cm^{-1}) is almost independent of orientation, but the position of both the minimum and the repulsive wall of the bare potential vary considerably with angle. Qualitatively, it is this angular variation that produces rotational alignment in the collision dynamics of N_2^+ -He. Additionally, the well is sufficiently deep to give rise to a number of bound rovibrational states of the N_2^+ -He complex.

In a more recent and detailed calculation, Berning and Werner¹⁴ use multireference configuration interaction (MRCI) expansions to calculate 3-D adiabatic N_2^+ -He potential energy surfaces for the first three electronic ground states of N_2^+ as a function of R , θ , and bond length r . A grid of four discrete values of $\theta = 0, 30, 60,$ and 90 degrees, and three values of $r = 1.90, 2.11,$ and $2.65 a_0$ were

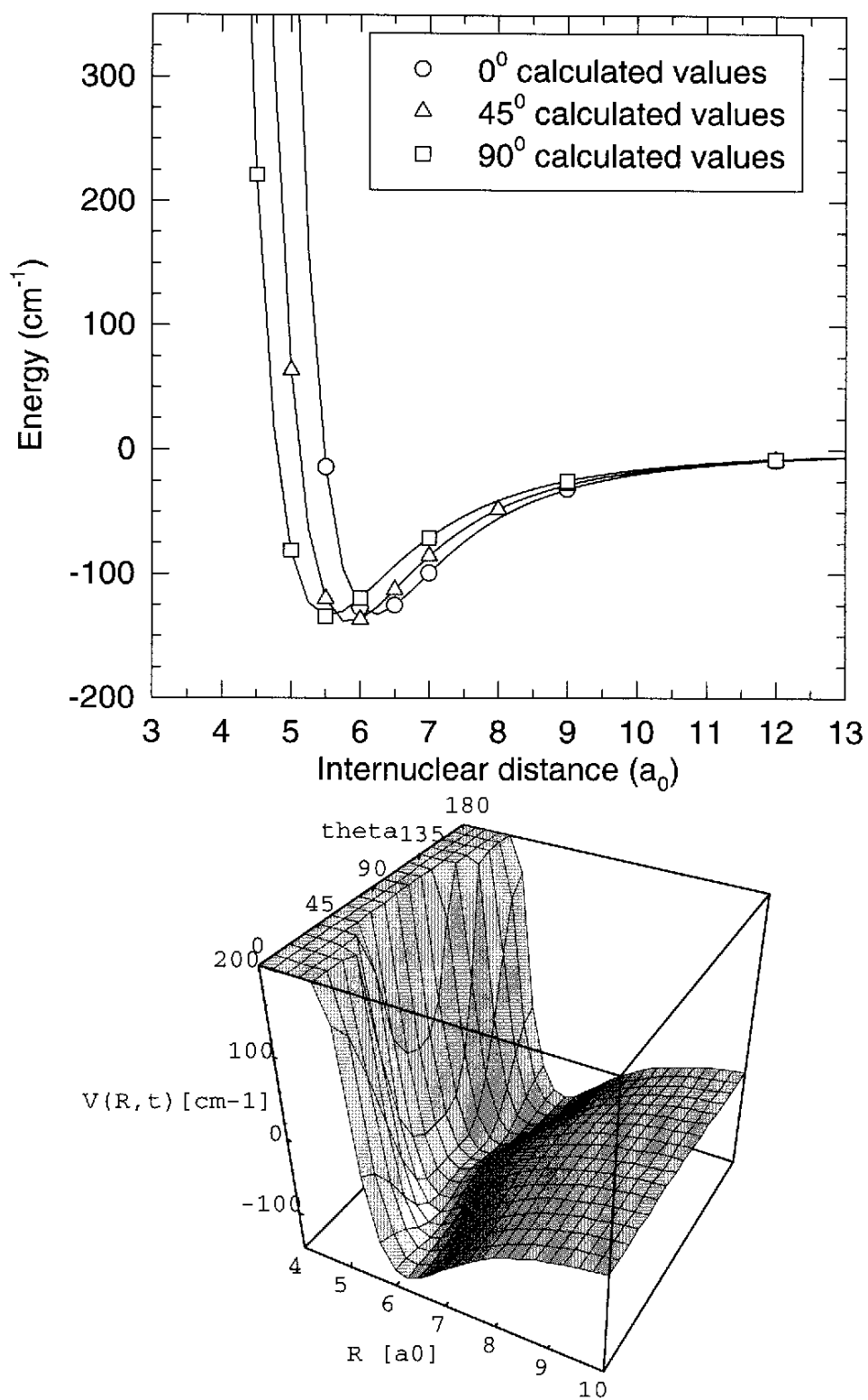


Fig. 1.1: N_2^+-He *ab initio* interaction potential of Miller *et al.* in Jacobi coordinates.

calculated, for distances R between 3 and 11 a_0 . These adiabatic surfaces were then transformed into a diabatic representation to study electronically inelastic scattering dynamics of N_2^+ -He. Although not explicitly compared to the first calculation, diagrams of the ground-state adiabatic potential indicate it is quite similar to the earlier potential.

C. Ion transport properties

Although the study of ion transport properties is a mature field, ongoing experimental work continues to yield surprises. For example, the mobilities of O^+ and O^- in He are considerably different over the same range of effective temperatures, due to the different interaction potential well depths of the HeO^+ and HeO^- systems.¹⁵ New techniques are continually being developed that enhance the field. For instance, a recent modification of the zero-kinetic energy photoelectron spectroscopy technique promises the possibility of near-complete rotational and vibrational state molecular ion preparation for the investigation of state-selected ion-molecule reactions.¹⁶

The single-frequency LIF transport property experiments in this work are primarily concerned with measuring N_2^+ mobilities and translational temperatures as a function of rotational state and field strength. The advantages of the LIF technique are that it provides a state-selective, non-obtrusive, *in situ*, direct measurement of velocity component distribution functions. Additionally, the LIF technique can reveal information—such as translational temperatures and a relative measure of local ion number densities—that can not be obtained from other techniques traditionally used to measure ion transport properties.^{17,18}

Mobility is the phenomenological proportionality “constant” between applied electric field and observed steady-state drift velocity. This constant in general depends on field strength and contains structure information about the interaction potential. In this technique, measured mobilities are directly proportional to the Doppler shift in line center or first moment of a LIF transition for a given field strength. Translational temperatures are an indicator of how the resultant randomizing energy of the ion-buffer gas collisions is being disposed of, on average, between the directions parallel and transverse to the field. For LIF, measured translational temperatures are proportional to the square of the linewidth or the second central moment of the line shape. Higher line shape moments, such as the third central moment, which reveals skewness information, can be studied as well. Details of these measurements and results are presented in Chapter III.

D. Collision-induced rotational alignment

Alignment phenomena are ubiquitous in chemical physics. Their appearance in such a diversity of experiments makes alignment a simultaneously fascinating and frustrating subject to study. Rotational alignment, the preferential arrangement of the angular momentum vector associated with a molecule’s rotation, can be created in a variety of ways. For example, the intense electric fields associated with a pulsed laser can be used to induce a dipole in the molecule that effectively “traps” the molecule into pendular motion around the polarization vector of the laser. Pendular motion of the linear molecules CO_2 and CS_2 has been demonstrated by examining the angular distribution of O^+ or S^+ fragments relative to the electric field of the laser.¹⁹ The “brute force technique” of orienting polar molecules with a strong DC electric field

(linear Stark effect) has recently been applied to orient the asymmetric top molecule C_6H_5I and study steric effects in the reaction $K + C_6H_5I \rightarrow KI + C_6H_5$.²⁰ Gas-phase chemical reactions can create alignment. To cite just one example from the vast field of stereochemistry, a strong steric effect is observed for the “benchmark” reaction $O(^1D_2) + H_2(v=0) \rightarrow OH(X^2\Pi_i, v'=0, N', f) + H$ when the final states are resolved.²¹ Reactive scattering with surfaces can also generate alignment. For example, D_2 exhibits strong preference for desorption from a Cu (111) surface in a helicopter alignment, indicating a smaller activation barrier for adsorption onto the surface for this approach.²²

This particular work is concerned with collision-induced rotational alignment in a drift tube environment. It has been known for many years that there is an intimate relationship between transport properties and molecular alignment. The so-called Senftleben-Beenaker effect²³ historically refers to the change in thermal conductivity of neutral paramagnetic gases in the presence of an external magnetic field. However, to the best of this investigator’s knowledge, collision-induced rotational alignment has not been previously reported in any ion-molecule system outside of this group. Chapter IV covers the details and results of alignment experiments on the $N_2^+ - He$ system, with the unique twist of partial velocity selection. Indeed, evidence presented there suggests a hypothesis that velocity-subgroup alignment is the “generic” behavior of any gas phase system in which there is some sort of anisotropic (i.e., non-Maxwell-Boltzmann) velocity distribution.

References for Chapter I

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