Chapter 3

The Study of Cold Collisions Using Ion Guides and Traps

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3.1. Introduction

3.1.1. Cold Interstellar Clouds

It has been emphasized by Herbst and Millar in the first chapter of this book that studies of cold collisions in the gas phase and on grains are important for understanding the physics and chemistry of cold interstellar clouds. However, the experimental or theoretical determination of pure thermal rate coefficients may not be sufficient since the production and the destruction of matter is a complex result of many elementary processes. In general, the matter in interstellar or circumstellar space is not in thermal equilibrium. Klemperer\(^1\) likes to illustrate this with the conversion of hydrogen and carbon monoxide into methane and water. Simple thermodynamics predict an equilibrium ratio for \(\text{CO} + 3\text{H}_2 \leftrightarrow \text{CH}_4 + \text{H}_2\text{O}\) which differs from interstellar observation by more than 500 orders of magnitude. Another example is the population of the rotational states of \(\text{CH, CH}^+\), and \(\text{CN}\), the absorption spectra of which were already observed many decades ago. Usually rotational motion can couple efficiently via collisions to the translational temperature of the surrounding gas (5 K or higher); however, polar species can become colder since they interact efficiently with the cosmic background radiation of 2.73 K, an electromagnetic microwave field which is associated with the origin of the universe. Other examples include the non-thermal abundances of isomers (e.g. \(\text{HCO}^+\) and \(\text{HOC}^+\), see Smith \(\text{et al.}^2\)), heating of particles via cosmic rays, stimulated emission from the inversion transition of ammonia, or the role of \(\text{o-H}_2\) in creating non-thermal populations in cold environments.\(^3\) One of the conclusions from this is that for astrochemistry, often cold state specific cross sections are needed instead of thermally averaged rate coefficients.

3.1.2. Ultracold Collisions and Quantum Matter

For performing precision measurements of their properties, ultracold atoms and molecules are one of the central themes of current fundamental research in chemical and optical physics. Laser cooling of atoms allows micro-Kelvin
temperatures to be reached. Innovative techniques allow both the quantum-statistical behavior of condensates of dilute, weakly interacting atoms to be studied and coherent matter-waves to be produced, creating a new field of material science. Various approaches are being developed to produce ultracold molecular systems; however, molecules are much harder to manipulate with optical or other schemes. Today there are many activities in one subfield where the ultracold molecules are just homonuclear dimers, formed via photoassociation (see e.g. the chapter by Weiner). In addition, methods are under development and discussed in this book which allow ultracold molecules with a few atoms to be created; however, we are far from freezing all degrees of freedom of large molecules. The work described by the Rennes group in Chapter 2 and in this contribution is far from temperatures where coherent interaction of matter-waves plays a role. However, there is huge interest in the study of collisions under interstellar conditions and how to cool large biological molecules to a few K or below. Another interesting experimental method to cool molecular ions is based on sympathetic cooling by mixing them into a cloud of laser cooled atomic ions. Ions prepared in this way have been used successfully for spectroscopy and high-precision measurements in fundamental physics as discussed in more detail in Chapter 6. Below the question is raised whether these so-called ultracold ions really open up new routes for the study of state-selective chemical reactions at low collision energies.

3.1.3. Definition of “Temperature”, Coherent Motion

A key problem in many applications is to define what one means by “cold” or “ultracold”. What is the definition of temperature and what is a suitable thermometer? Presently the definition of the unit 1 Kelvin uses the triple point of water; however, in a few years, the Boltzmann constant $k_B$ will be fixed and the energy $k_B T$ will be the basis for defining the temperature scale. Most probably one will use the average translational energy associated with the disordered motion of Ar atoms in an acoustical gas thermometer. In most applications discussed in this book, the mean kinetic energy is used for defining the temperature; however, the velocity distribution of a beam of slowed particles or of an actively cooled ensemble is not necessarily a Maxwell-Boltzmann distribution. For trapped particles the boundary conditions lead to quantization of the translational degrees of freedom. The population of these states provides information on the mean translational energy of the system. In the case of a single trapped ion one can extract the information from a time-averaged measurement instead of using an ensemble average.
The definition of temperature in traps where ions are confined with time-varying external forces is problematic. A special case is a radio frequency quadrupole ion trap, in which ions are laser cooled into an ordered Coulomb crystal. This structure is characteristic of a temperature in the sub-mK range. Nonetheless the kinetic energy of the trapped ions is up to seven orders of magnitude higher, as discussed in detail by Schiffer et al.\textsuperscript{4} The explanation of this seeming contradiction is the separation of the motion into the fast coherent motion driven by the oscillating electric field and a superimposed random part. This definition of temperature is in good agreement with the observed phase transition and also with the Doppler width if the laser is oriented orthogonally to the secular motion; however, a collision between the so-called ultracold ion and a neutral target is very \textit{hot}, the mean translational energy may correspond to thousands of K. In addition, as will be discussed below, sympathetic cooling of molecular ions does not work for the internal degrees of freedom.

\subsection*{3.1.4. \textit{How to Obtain Low Collision Energies or to Prepare a Cold Ensemble}}

Progress in experimental science is closely related to experimental innovations. Starting in the 1980s, several groups have developed sophisticated instruments for studying ion-molecule and neutral-neutral reactions over a wide range of temperatures. Presently techniques are under development both for cooling ions below one K and for heating them with lasers to thousands of K.\textsuperscript{5} An introduction to the various methods used today in low temperature chemistry is given in Chapter 2. There are various strategies to prepare cold or slow ensembles of atoms or molecules. The traditional and rather general techniques are based on collisional cooling with cold buffer gas while modern techniques make use of laser cooling or slowing neutrals with suitable electromagnetic fields (see the chapter by van de Meerakker \textit{et al.}). The present chapter focuses exclusively on instruments which make use of inhomogeneous fast oscillating electric fields. Special ion guides and an innovative merged beam arrangement have opened up the meV collision energy range and are, in principle, capable of reaching sub-meV. The most successful and versatile solutions for reaching low ion temperatures are based on multi-electrode ion traps combined with cryogenic cooling. In order to overcome the limitations imposed by condensation of neutral species, traps also are combined with cold effusive or supersonic beams.

\subsection*{3.1.5. \textit{Reactions at Low Temperatures}}

Several aspects of the dependence of chemical reactions on temperature are discussed in other chapters of this book. For low relative velocities and
a long-range attractive interaction potential, it is common to use capture models (see Chapter 4 by Klippenstein and Georgievskii). The dynamics of complex formation in collisions of rotationally excited diatomic molecules with ions at very low collision energies and translational temperatures have been discussed recently. Special effects occur at very low collision energy where only a few partial waves contribute. Below a certain limit, s-wave scattering prevails. In general, lowering the total energies leads to an increase in the lifetime of the intermediate complex. This often allows for slow processes such as tunneling through barriers or emission of photons. As emphasized in Chapter 1, in the context of the astrochemically important process of deuterium fractionation, minor differences in zero-point energies caused by isotopic rearrangement can play a key role in low temperature chemistry. There are also several ion-molecule reactions which are nearly thermoneutral or which are influenced by small barriers. Excitation of reactants to low-lying fine structure or rotational states can change the outcome of a reaction significantly. In such cases it is advantageous if one can measure the rate coefficients for state specific reactions instead of working with a Boltzmann population. Combining ion traps with photoionization or optical pumping of stored ions with lasers opens up many related possibilities.

3.1.6. Preview

This chapter is organized as follows. After a short reminder of the basics of the ion guiding and trapping technique and a survey of the relevant kinematics, several instruments are described in detail together with characteristic measuring procedures. The versatility of the machines and modules is illustrated with a selection of experimental results, including meV collisions with cold polar molecules, cluster formation, radiative association, isotopic enrichment of deuterated molecules. Very recent activities aim at understanding reactions of cold ions with slow H atoms. In the outlook it will be mentioned that trapping charged objects is rather general. In principle there are no restrictions concerning mass, temperature or storage time. Present activities include cooling ions below one K or heating nanoparticles to very high temperatures.

3.2. Fast Oscillating Forces

3.2.1. Inhomogeneous Electric Fields

All experimental setups described in this chapter are based on the use of specific inhomogeneous, electrical fields \( E_0(r,t) \) which vary in space and
time. Usually one uses

\[ E_0(r, t) = E_0(r) \cos(\Omega t), \] (3.1)

i.e., a harmonic oscillation with the frequency \( \Omega \). The method to trap or guide ions, the basic theory, and a variety of applications in ion physics and chemistry has been thoroughly documented previously. In what follows more recent publications are reviewed. To better understand the method and its limitations, one needs some basic theory describing the motion of a particle under the influence of a fast oscillating force. The most important precondition is that, if the frequency is high enough, the main influence of the oscillatory force can be described by the so called effective potential

\[ V^* = \frac{q^2 E_0(r)^2}{4m\Omega^2}, \] (3.2)

where \( m \) and \( q \) are the particles’ mass and charge, respectively. In order to get a quantitative estimate of the range of validity of the high frequency or adiabatic approximation, one introduces an adiabaticity parameter defined by

\[ \eta = \frac{2q|\nabla E_0(r)|}{m\Omega^2}. \] (3.3)

This useful dimensionless parameter can be introduced in various ways; for example, by postulating that the change of the field over the oscillation must be much smaller than the field itself. Experience based on experimental tests and on numerical calculations has shown that one should use operating conditions such that \( \eta \) remains everywhere smaller than 0.3. This condition can always be achieved by using a high enough frequency.

The basic principle is quite general and can be applied in many fields. It is important to realize that \( V^* \) and \( \eta \) scale inversely with \( m\Omega^2 \). The effective potential \( V^* \) can be used for confining electrons (\( \Omega \) must be in the GHz range), ions (radio frequency range) and clusters (audio frequency). For trapping charged microscopic particles one can use AC voltages. Typical applications include strong focusing lenses in accelerator physics, the well-known Paul trap invented in the 1950’s or the Guided Ion Beam technique developed in the 1970’s. For a detailed review of the historical development and of specific applications see Ref. 7.

### 3.2.2. Multipole Fields

In any real experimental device, the electric field \( E_0(r) \) is determined by the boundary conditions imposed by suitable electrodes. For guiding and trapping ions, a variety of electrode arrangements have been applied. Many
theoretical and practical hints are given in Ref. 7. One of the best characterized examples is a linear multipole. The potential of a $2n$ pole is given by

$$\Phi(r, \phi) = \Phi_0 \hat{r}^n \cos(n\phi)$$  \hspace{1cm} (3.4)

where $\Phi_0 = U_0 - V_0 \cos \Omega t$ is the applied dc and rf potential, $2n$ corresponds to the number of poles, and $\hat{r} = r/r_0$ is a reduced radius. In most applications one operates a multipole “rf-only”, i.e., $U_0 = 0$. Calculating the electric field $|E_0|$ from $\Phi_0$ and using Eq. (3.2) one obtains the effective potential

$$V^* = n^2/4(qV_0)^2/(m\Omega^2 r_0^2)\hat{r}^{2n-2}.$$ \hspace{1cm} (3.5)

From Eq. (3.3) one gets the adiabaticity parameter

$$\eta = 2n(n-1)(qV_0)/(m\Omega^2 r_0^2)\hat{r}^{n-2}.$$ \hspace{1cm} (3.6)

For the case $U_0 \neq 0$ one has to add in Eq. (3.3) the dc term $qU_0 \hat{r}^n \cos(n\phi)$. The formula become even simpler if one introduces the characteristic energy $\varepsilon$,

$$\varepsilon = 1/2n^2m\Omega^2 r_0^2.$$ \hspace{1cm} (3.7)

For numerical calculations it is useful to work with the units cm, MHz, V, the atomic mass unit u, the charge unit e, and the energy unit eV. Using these units, $\varepsilon$ can be simply calculated from

$$\varepsilon = 1.036/2n^2m\Omega^2 r_0^2 \text{ (units: eV, u, cm, MHz).}$$ \hspace{1cm} (3.8)

### 3.2.3. Selecting Parameters

For selecting the proper ion guide and the optimum operating parameters for a special purpose, different criteria have to be taken into account. Parameters of the multipole include the number of poles, $2n$, the scale length $r_0$, the amplitude $V_0$, the frequency $\Omega = 2\pi f$, and eventually the dc component $U_0$. The ions are characterized by the charge $q$ and the mass $m$. Adiabatic conservation of energy ensures that safe transmission does not depend on the individual initial conditions, but only on the maximum transverse energy $E_m$. It is easy to show that a quadrupole ion guide is the optimum choice if one just intends to confine ions with a given $E_m$ to a specific maximum radius $r_m$ with a minimal amplitude $V_0$. From Eqs. (3.5) and (3.6) and $\eta < 0.3$, analytical formulas have been derived that permit one to calculate “safe operating conditions”. Using, for example, $n = 4$
and $E_m = 1\text{ eV}$, it is found that an amplitude $V_0 = 48.8\text{ V}$ is sufficient to guide a singly charged particle. This result is independent of $m$, i.e., it holds for electrons, protons, or charged nanoparticles. For simultaneously guiding ions with $E_m = 0.1\text{ eV}$ and masses ranging from $m_1 = 1\text{ u}$ to $m_2 = 100\text{ u}$, the values needed are $V_0 = 105\text{ V}$ and $f = 17.8\text{ MHz}$ for an octopole ($n = 4$, $r_0 = 0.3\text{ cm}$). It also can be shown that for a wider mass range, e.g., a factor of $10^4$, a decapole is preferred. More detailed examples can be found elsewhere.\textsuperscript{7}

### 3.2.4. Some Features

For $n = 2$ (a quadrupole), inspection of Eqs. (3.5) and (3.6) reveals that the effective potential $V^*$ is harmonic and that $\eta$ does not depend on $r$. This leads to special properties; e.g., focusing and phase space conserving transmission. Moreover, the equation of motion of an ion, moving in a quadrupole, can be solved without approximation by transforming it into the well-known Mathieu differential equation. This allows for a mathematically precise classification of stable and unstable operating conditions. A complete theoretical description of rf quadrupoles is given by Dawson.\textsuperscript{8} Concerning the use of a quadrupole as a mass filter or as an ion guide, it must be noted that this primarily depends on the stability parameter $\eta$ (called $q$ in the Mathieu equation). For mass-selective transmission, one operates usually with $\eta = 0.706$; whereas for guiding ions, conservation of the kinetic energy is desirable, i.e., one uses $\eta < 0.3$. This distinction is independent on whether one operates in the rf-only mode or with a superimposed dc field.

Some features of the motion of ions in an octopole are illustrated in Fig. 3.1. All sample trajectories start in the center with different initial conditions. First it can be seen that the ions move, rather unperturbed, on straight trajectories in the inner part. The three trajectories in the upper half illustrate the importance of selecting a small stability parameter. For $\eta_m = 0.1$ there are many oscillations during the reflection, i.e., the adiabatic approximation holds, while for $\eta_m = 0.7$ the ion absorbs energy from the rf field. The three examples on the lower right side illustrate that ions with a transverse energy of $E_m = 0.1\text{ eV}$ are safely stored while, using the same amplitude and frequency, $10\text{ eV}$ ions are also confined. However, the reflection law does not hold; i.e., impulse is transferred to the ion. The two examples in the lower left region compare two ions which are moving towards a rod or towards the gap between two rods. The effective potential (see Eq. (3.5)) is rotationally symmetric; however the oscillatory micromotion is different, in one case it is longitudinal in the other one transverse.
Fig. 3.1. Selected ion trajectories calculated for an octopole illustrating the influence of the rf field. The ions start in the center, but with different stability parameters $\eta_m$, initial energies $E_m$, and two directions (between and towards the rods). Details are explained in the text.

3.2.5. Cooling Ions

For cooling ions and for studying low energy collisions it is necessary to understand in more detail the impairment of the ion kinetic energy by the time varying forces acting on the stored ions. It is rather obvious that electrode arrangements with wide field-free regions are better suited for this purpose. The effective potentials plotted in Fig. 3.2 illustrate that a 22-pole has significantly steeper walls than a quadrupole; it is even superior to a ring electrode trap with similar electrode dimensions. More information is gained if one calculates the kinetic energy of a stored ion as a function of
Fig. 3.2. Comparison of the r-dependence of the normalized effective potentials of a linear quadrupole, a 22-pole and an arrangement of ring electrodes. In the limit of an extremely large number of electrodes one obtains a box potential.

Fig. 3.3 shows the modulation of $E$ in units of the initial energy $E_m$ if it approaches an electrode. The two results, one has been calculated numerically exact the other one in the adiabatic approximation, reveal that the energy reaches any value between 0 and $3E_m$. Comparison of the initial and final energy reveals that the system behaves on average like a conservative one if the conditions for the adiabatic approximation are fulfilled. In order to estimate the time averaged influence, energy distributions have been calculated over many rf cycles. Two typical results are given in Fig. 3.4. The distributions are very narrow peaking at the nominal energy $E_m$. This result confirms that the influence of the rf field on the kinetic energy of the stored ions is smaller the higher the number of electrodes.

An additional criterion comes into the play if one intends to cool ions with buffer gas or if one wants to study collision processes between neutrals and ions confined in rf fields. In this case one of the most important features is that, in general, both $V^\ast(r)$ and $\eta(r)$ are functions of the coordinate $r$ and that both go to 0 for $|r| \to 0$. This means that, with decreasing kinetic energy $E_m$, the adiabatic approximation becomes better. In the case of a multipole ($2n$ pole) one can derive the relation

$$\eta \sim E_m^{(n-2)/(2n-2)}.$$  (3.9)

During collisional cooling of ions, this reduction of $\eta$ reduces simultaneously more and more the impairment via the rf field. As mentioned above and
as can be seen from Eq. (3.9), there is only one example, the quadrupole. For $2n = 4$, the stability parameter $\eta$ is constant. Therefore a quadrupole trap is poorly suited for cooling ions to very slow motion. One has to use at least a hexapole. In other words: collisional relaxation is only efficient in higher order electrode arrangements.

Many numerical simulations have been performed for understanding in more detail the process of collisional relaxation in rf traps. A summary can be found in Ref. 7. In principle, an ion can always gain energy if it undergoes a collision during its interaction with the rf field. This effect depends strongly on the mass ratio. For example it is much easier to cool heavy ions in a light buffer gas than the other way around. Very problematic
are local potential distortions on electrodes ("patch effects") which can pull the ions into regions of strong rf fields. An innovative approach, which avoids collisions during the reflection of the ions from the rf walls and which is presently under development, is to use a cold skimmed beam of neutrals for collisional cooling. More details are discussed in Chapter 6.

3.3. Kinematics

The chapter by Strecker and Chandler is called *Kinematic cooling of molecules*. Their method relies on single, well-defined collisions in which just the correct amount of momentum is transferred for one of the particles to
Table 3.1.

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>(m_1, m_2)</td>
<td>mass (ion, neutral)</td>
</tr>
<tr>
<td>(M = m_1 + m_2 = m'_1 + m'_2)</td>
<td>total mass</td>
</tr>
<tr>
<td>(\mu = m_1 \cdot m_2 / M)</td>
<td>reduced mass</td>
</tr>
<tr>
<td>(v_1, v_2)</td>
<td>velocity in the LAB frame</td>
</tr>
<tr>
<td>(g = v_1 - v_2)</td>
<td>relative velocity</td>
</tr>
<tr>
<td>(v_C = (m_1 v_1 + m_2 v_2) / M)</td>
<td>velocity of the CM of the system</td>
</tr>
<tr>
<td>(u_1 = v_1 - v_C)</td>
<td>velocity of the CM frame</td>
</tr>
<tr>
<td>(\Lambda \leq (v_1, v_2))</td>
<td>intersection angle (v_1, v_2)</td>
</tr>
<tr>
<td>(E_1, E_2)</td>
<td>energy in the LAB frame</td>
</tr>
<tr>
<td>(E_T = \mu / 2g^2)</td>
<td>translational energy (collision energy)</td>
</tr>
<tr>
<td>(\Delta E_T = E'_T - E_T)</td>
<td>translational exoergicity</td>
</tr>
<tr>
<td>(E_{int})</td>
<td>internal energy (vib, rot, electr.)</td>
</tr>
<tr>
<td>(-\Delta E_0)</td>
<td>reaction exo-ergicity</td>
</tr>
<tr>
<td>(E_{int} + E_T - \Delta E_0 = E'_{int} + E'_T)</td>
<td>total available energy</td>
</tr>
</tbody>
</table>

remain at rest after the interaction. In more detail, they distinguish between slowing and cooling, to which one might add stopping. Our approaches to reach meV collision energies or sub-K collision temperatures are different. These latter methods rely on many collisions, either for preparing two cold beams or for cooling one trapped ensemble of ions, if necessary with thousands of collisions. In order to assess the capabilities and limitations of beam-beam and beam-cell arrangements in reaching meV or even sub-meV collision energies, a detailed analysis of kinematic averaging is required. In the following we treat the kinematics of a beam-beam and a beam-cloud arrangement. The second situation can be either an ion beam — neutral target cell arrangement (e.g. a standard guided ion beam apparatus) or a set-up where a neutral beam interacts with a cold ensemble of stored ions. The most important abbreviations used in this section are collected in Table 3.1.

### 3.3.1. Beam-Beam Arrangements

In a standard treatment of kinematics (see for example Ref. 9) one starts with two well-prepared beams of colliding partners which interact with each other in some spatial region. If the species in the two beams are characterized by individual velocity distributions, \(f_1(v_1)\) and \(f_2(v_2)\), one measures, instead of the elementary cross section \(\sigma(g)\), an effective cross section defined by

\[
\sigma_{eff}(\langle g \rangle) = \int_0^\infty \frac{g}{\langle g \rangle} \sigma(g) f(g) dg
\]

(3.10)
Here, $g = |g| = |v_1 - v_2|$ is the relative velocity and the distribution function $f(g)$ is defined by

$$f(g) dg = \int dV_1 \int dV_2 f_1(v_1) f_2(v_2) \quad (3.11)$$

The integration must be restricted to that subspace $(v_1, v_2)$ where $|v_1 - v_2| \in [g, g + dg]$. The mean relative velocity, $\langle g \rangle$, is defined via the integration

$$\langle g \rangle = \int_0^\infty g f(g) dg \quad (3.12)$$

Note that $\langle g \rangle$ and $\langle g' \rangle = \langle v_1 \rangle - \langle v_2 \rangle$ are not necessarily identical. The number of products, $dN_p$, produced per unit time in a small scattering volume $d\tau$ at location $r$ is given by

$$dN_p = \langle g \rangle \sigma_{\text{eff}} (\langle g \rangle) n_1(r) n_2(r) d\tau \quad (3.13)$$

To precisely determine absolute integral cross sections from measured quantities, the spatial overlap of the two reactant beams and their local densities must be known. Integration of $dN_p$ in accordance with the merged beam geometry leads, for weak attenuation of the primary beam, to

$$\sigma_{\text{eff}} = \frac{N_p}{N_1 \langle n_2 \rangle L} \frac{1}{\langle g \rangle} \quad (3.14)$$

where the ion density $n_1$ has been replaced by the ion flux $N_1 \sim n_1 \langle v_1 \rangle$, $\langle n_2 \rangle$ is the mean density of the neutral target, and $L$ the length of the overlapping region. In many experiments the product $\langle n_2 \rangle L$ can be determined with a known reaction, e.g., for hydrogen target one can use the $\text{Ar}^+ + \text{H}_2$ reaction. It is useful to compare Eq. (3.14) with the result for a beam — isotropic target arrangement where $\langle v_2 \rangle = 0$ and, therefore $\langle v_1 \rangle = \langle g \rangle$. This leads to

$$\sigma_{\text{eff}} = \frac{N_p}{N_1 n_2 L} \quad (3.15)$$

where $n_2$ is the directly measurable density of the target. The length of the overlapping region is in this case identical with the effective length of the scattering cell or of the ion trap.

### 3.3.2. Collision Energy

Usually, measured effective cross-sections are reported as a function of the mean collision energy, $\langle E_T \rangle$. For two well-collimated monoenergetic beams crossing at an angle $\Lambda$, $E_T$ is given by

$$E_T = \frac{1}{2} \mu g^2 = \frac{1}{2} \mu (v_1^2 + v_2^2 - 2v_1 v_2 \cos \Lambda) \quad (3.16)$$
where $\mu = m_1 m_2 / (m_1 + m_2)$ is the reduced mass and $m_1$ and $m_2$ are the masses of the ion and the neutral, respectively. For a crossed beam arrangement ($\Lambda = 90^\circ$) the mean collision energy is related to the mean ion and neutral velocities by

$$\langle E_T \rangle = \frac{1}{2} \mu (\langle v_1 \rangle^2 + \langle v_2 \rangle^2)$$  \hspace{1cm} (3.17)

whereas for a merged geometry ($\Lambda = 0^0$) one obtains

$$\langle E_T \rangle = \frac{1}{2} \mu (\langle v_1 \rangle - \langle v_2 \rangle)^2$$  \hspace{1cm} (3.18)

Comparison of these two results reveals that the lowest accessible energy is limited by the mean energy of the neutrals for beams crossing at $90^\circ$ whereas a nominal energy $\langle E_T \rangle = 0$ can be obtained with the collinear arrangement. The lowest collision energy which can be obtained is determined by the energy spread of the two beams.

### 3.3.3. Energy Resolution

In general, the distribution of the relative velocity $f(g)$ must be determined by numerical integration. In many cases it is sufficient to approximate $f_1(v_1)$ and $f_2(v_2)$ with Gaussians, using experimentally determined parameters. For a coaxial beam-beam arrangement the six-dimensional integral over $(v_1, v_2)$ is reduced to a three-dimensional one over $(v_1, v_2, \Lambda)$. To make a quick analytical estimate of the attainable energy resolution, error propagation can be used. For the merged beam geometry one obtains:

$$\Delta E_T = \left[ \left( \frac{\mu g m_1}{v_1} \Delta E_1 \right)^2 + (\mu g \Delta v_2)^2 + \left( \frac{\mu}{2} v_1 v_2 \Delta \Lambda \cos \Lambda \right)^2 \right]^{1/2}$$  \hspace{1cm} (3.19)

where $\Delta E_1$ is the energy half-width of the ion beam, $\Delta v_2$ the velocity half-width of the supersonic beam, and $\Delta \Lambda$ the mean relative angular divergence between the two beams. For a crossed beam geometry one gets a slightly different result,

$$\Delta E_T = \left[ \left( \frac{\mu}{m_1} \Delta E_1 \right)^2 + (\mu v_2 \Delta v_2)^2 + (\mu v_1 v_2 \Delta \Lambda \sin \Lambda)^2 \right]^{1/2}$$  \hspace{1cm} (3.20)

Comparison of these two formulas reveals that, under identical beam conditions, the resolving power of the merged beam experiment is superior to that using crossed beams. This is partly due to the kinematic compression and partly due to the angular divergence, affecting $\Delta E_T$ in first-order in the crossed, but only in second-order in the merged, beam arrangement.
Fig. 3.5. Energy resolution in a merged beam arrangement for the collision system N$^+$ + H$_2$. The energy half width of the ion beam is $\Delta E_1 = 100$ meV, the speed ratio of the H$_2$ beam SR = 10 and the angular spread is $\Delta \Lambda = 10^\circ$. With these conditions collision energies as low as 1 meV have been achieved.

Two examples are used to illustrate the capabilities of a merged beam experiment in which a supersonic beam and a guided ion beam are superimposed. Fig. 3.5 shows the total energy resolution which has been obtained in a merged beam arrangement for the collision system N$^+$ + H$_2$. At low collision energies the ion beam half-width ($\Delta E_1 = 100$ meV) contributes most while at higher energies the neutral target beam (speed ratio SR = 10) determines the energy resolution. The angular spread of the intersecting beams ($\Delta \Lambda = 10^\circ$) is negligible. With these conditions, collision energies as low as 1 meV have been achieved. Another example is given in Fig. 3.6 for Ar$^+$ + H$_2$ and the conditions ($\Delta E_1 = 100$ meV, SR = 10, $\Delta \Lambda = 10^\circ$). The distributions of the collision energy $dN/dE_T$ have been obtained by numerical integration over the measured distributions. It can be seen that at the lowest energy, the mean energy is slightly larger than the nominal energy.

3.3.4. Slow Beam — Thermal Target

To describe the special case of a monoenergetic ion beam passing through a scattering cell containing target gas at the temperature $T_2$, the resulting integral can be reduced analytically, leading to the well-known generalized
Fig. 3.6. Distributions of the collision energy $dN/dE_T$ obtained by numerical integration over the measured distributions for the nominal collision energies 1, 10, and 100 meV (merged beam arrangement, collision system Ar$^+$+H$_2$, $\Delta E_1 = 100$ meV, SR = 10, $\Delta \Lambda = 10^\circ$). The functions are area normalized. At 1 meV the mean collision energy, derived from the mean relative velocity $\langle g \rangle$ is slightly larger than the nominal collision energy.

Maxwell-Boltzmann distribution

$$f(g) = f^*(g; v_1, T_2)$$

$$= (m_2/2\pi kT_2)^{1/2} \frac{g}{v_1} \left[ \exp \left( -\frac{m_2}{2kT_2} (g - v_1) \right) \right]$$

$$- \exp \left( -\frac{m_2}{2kT_2} (g + v_1) \right).$$

(3.21)

At low ion velocities, this function approaches a normal Maxwellian $f_M(g; \mu_2, T_C)$ with a reduced temperature $T_C = \{m_1/(m_1 + m_2)\} T_2$. In the majority of ion beam experiments this limit has only been reached for heavy ion masses, i.e., for $m_1 \gg m_2$. In such a situation the lowest attainable collision temperature is equal to the target temperature, $T_C \sim T_2$.

A special solution for obtaining very slow ions is the so-called trapped ion beam technique, a method which has been described in Ref. 10. Using an ion guide, e.g., an octopole, together with meV potential barriers, one can store nearly monoenergetic ions at meV laboratory energies. So far this method has been used only in a few cases, e.g., for He$^+$ stored in O$_2$. For this system, experiments have been performed with He$^+$ ions trapped at
laboratory energies as low as 9 meV. In the limit of very slow beams, one can reach a collision temperature of 33 K with 300 K oxygen (4/36 × 300 K).

3.3.5. Cold Effusive Beam — Trapped Ions

From a kinematic point of view, a similar situation is the combination of a cold effusive or supersonic neutral beam interacting with a stored ion cloud. If the trapped ions are thermalized to a temperature $T_2$, the collision energy distribution is also given by Eq. (3.21), if one assumes a monoenergetic beam. Otherwise one has to integrate in addition over the relevant distribution of $v_1$. This strategy is presently used for cooling trapped ions to temperatures below 1 K. More details are given in Chapter 6.

3.4. Experimental Methods

As already mentioned in the Introduction, several sophisticated technologies have been developed for cooling neutral or ionized gases. The evolution of the various methods and the techniques used today in low temperature ion and radical chemistry have been summarized and compared in Chapter 2. Many results have been obtained with ion drift-tubes, supersonic flows or free jet expansions. Other contributions to this book describe techniques which make use of laser cooling, slowing neutrals with suitable electromagnetic fields, or with just one single collision. In the following sections we describe first our strategy to prepare and utilize a slow beam of molecular ions. It is based on the guided ion beam technique. For reaching low collision energies these ion beams are superimposed to a cold neutral beam. Our approach to reach low temperatures is based on multi-electrode traps. As will be seen from the examples, the most important representative is the 22-pole trap.

3.4.1. Guided Ion Beam Merged with a Neutral Beam

In principle, it is easy to decelerate ions and, therefore, it seems to be straightforward to obtain a very slow ion beam. However, electric or magnetic stray fields, surface patch effects and space charge problems have held up progress in extending standard techniques towards meV collision energies. Another basic problem, which is often overlooked, is the Liouville theorem. Special rf ion guides and an innovative merged beam arrangement have contributed to overcome such difficulties. The first breakthrough to get near-thermal ion beams without buffer gas was due to the guided ion beam technique. Today there are many applications of this technique.
including the determination of differential cross sections.\textsuperscript{13} Despite all these technical advances, it is not straightforward to create an intense slow ion beam. Phase space conservation requires a well-defined ion ensemble to be prepared. There are many ion sources based on electron bombardment, corona-discharge followed by a supersonic expansion or state selective ionization via single or multiple photoionization. Nonetheless the most universal way for cooling and phase space compression is the use of rf traps.

There are several procedures to determine the kinetic energy of ions moving in an ion guide. An accuracy of sub-meV is possible. The elegant oscillating guided ion beam method uses on one side a reflecting wall and towards the detector a semi-transparent one. Fig. 3.7 shows as a typical example a trapped He\textsuperscript{+} beam. From the distance (in the example shown 32 mm) and the oscillation period the kinetic energy can be determined. The lowest laboratory energy obtained in this way is 2 meV. For more details see Ref. 10. The standard method to calibrate a pulsed guided ion beam is based on time of flight analysis. Usually one measures the mean kinetic energy $\langle E_1 \rangle$ as a function of the voltage U applied to the ion guide, see Fig. 3.8. The deviations from the linear dependence at low energies are due to the energy spread of the ion beam. For a detailed description of the calibration procedure see Ref. 7. Most of the guided-ion-beam (GIB) experiments have been performed by surrounding an octopole with a scattering cell. These arrangements allow one to determine integral cross sections with high accuracy and sensitivity. However, the influence of the random motion of the thermal target gas, usually 300 K, leads to a broadening of the

Fig. 3.7. Measured time distribution of a He\textsuperscript{+} ion beam which is trapped between two electrostatic barriers in an octopole (distance 32 mm). One of them is semitransparent leading to the shown distribution. The voltages on external ring electrodes have been set such that only ions with a kinetic energy close to 9 meV are oscillating. For a detailed description of the technique see Ref. 7.
collision energy (see Eq. (3.21)) and limits the lowest energy. Combinations of a well-characterized ion beam with a supersonic beam allow collisions at very low relative energies to be studied. Collision energies as low as 1 meV have been achieved, with the molecular beam and ion guiding techniques available today sub-meV energies are achievable.

Merging two beams for reaching low relative velocities with high energy resolution is a powerful method. However, despite many advances in technologies, such experiments remain a challenge due to their complexity. Pioneering work started in the 1960s. A recent review explains the fundamental principles of the method and summarizes the worldwide efforts in atomic and molecular physics. In all the instruments described by Phaneuf et al., two fast beams, with parallel velocity vectors having nearly the same magnitude, are superimposed to obtain very low relative energies. It is usually emphasized that kinematic compression allows meV collision energies to be

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**Fig. 3.8.** Calibration of the laboratory energy of an ion beam using the retarding field (upper curve) and the time of flight method. Over a wide range the mean kinetic $\langle E_1 \rangle$ is proportional to the voltage $U$ applied to the ion guide. $\Delta U$ is an usually small additive correction accounting for space or surface charges. At low energies, the energy spread of the ion beam plays a role (Liouville theorem). For a detailed description of the technique see Ref. 7.
reached, even with beam energy spreads of several eV, if one operates at keV laboratory energies; however, the critical dependence of the energy resolution on the angular spread is often overlooked (see Eq. (3.19)). Owing to the high laboratory energies, it is necessary to create the fast neutral target beam via charge exchange neutralization of an ion beam. All this leads to a number of difficulties and problems, ranging from low reactant densities, a small and uncertain interaction volume, short interaction times, to unknown internal excitation of the reactants. All these drawbacks have impeded widespread use of this method.

Instead of two fast beams, combining a supersonic neutral beam with a slow guided ion beam solves many problems. The two situations are compared in Fig. 3.9 for $\text{H}_3^+$ colliding with $\text{D}_2$ at a relative energy of 10 meV. In order to reach the required velocity difference of 1.1 km/s, the pair 1.8 km/s and 2.9 km/s is used on the left side while 547.7 and 548.8 km/s in the case of fast beams. The 5 orders of magnitude higher target density and the 100 times longer interaction time makes the slow merged beam technique very efficient. Despite the low laboratory energies involved, the kinematic compression resulting from the merged-beam geometry leads to surprising results. For advantageous systems collision energies below 1 meV can be obtained. The first realization of a merged guided ion and neutral beam apparatus has been described in some detail elsewhere, together with typical results measured for $\text{H}_3^+ + \text{D}_2$ and $\text{D}_3^+ + \text{H}_2$. Later improvements include a variable-temperature ion trap for separately cooling the primary ions before they enter the reaction region and an intense continuous supersonic beam, which can be chopped mechanically (see Fig. 3.3 of Ref. 15).

![Fig. 3.9. Schematic comparison of two merged beam arrangements for studying collisions between $\text{H}_3^+$ and $\text{D}_2$ at a selected relative velocity of 1.1 km/s, corresponding to a collision energy of 10 meV. On the left side the laboratory energy of the ion is 0.13 eV, on the right side 4518 eV. The low target density and the short interaction time makes the fast merged beams method very inefficient while the use of a supersonic beam superimposed to a slow guided ion beam can allow to convert a few % of the primary ions into products.](image-url)
For rotational relaxation of hydrogen, a para-hydrogen generator has been used and the nozzle temperature has been cooled down to 10 K. Several differential pumping stages are used to maintain a sufficiently low background pressure of the target gas in the interaction chamber. Unfortunately, it is not straightforward to develop in an university laboratory routines and strategies for operating and maintaining such a complex instrument in a professional way.

A rather simple version of a slow merged-beam apparatus is depicted in Fig. 3.10. Here the slow ion beam is guided in a wire quadrupole. With such a multi-electrode structure the electrodes of which are at large distances, extremely slow and narrow ion beams can be prepared. For creation
of the supersonic beam a pulsed valve is used. Two differential pumping stages maintain a sufficiently low background pressure of the target gas in the interaction chamber. The well-collimated neutral beam has a density of up to $10^{11}$ cm$^{-3}$ and an angular divergence of much less than $10^\circ$. For preparing ions the standard combination of a storage ion source and focusing quadrupole is used. The ions are pulsed synchronously with the neutral beam. The mass- and energy-selected ions are deflected by $90^\circ$ in a weak magnetic field of less than 1 kG and then injected at the desired energy into a weak rf guiding field. There, they propagate in the same direction as the neutral beam and react at low relative energies. Calibration of the ion axial energy, $E_1$, and determination of the energy distribution is performed using the method described above. To measure the mean velocity $\langle v_2 \rangle$ and the spread of the neutral beam (FWHM, $\Delta v_2$), an additional differentially pumped ionization detector is mounted subsequent to the ion detector at a distance of about 1 m from the nozzle. For this application, a quadrupole ion guide is preferred over a higher order multipole, since the harmonic effective potential confines the ion beam so close to the axis that full overlap with the neutral beam can be achieved. The impairment of the collision energy is negligible since only the transverse velocity is modulated. In such an arrangement one can operate routinely with ion laboratory energies down to 50 meV. For many mass ratios a nominal relative velocity of zero can be obtained. In some cases, it is advantageous to seed the neutrals in order to operate at higher laboratory velocities.

As a typical set of raw data recorded with a merged beam arrangement, Fig. 3.11 shows an H$_2$O$^+$ signal produced via electron transfer from H$_2$O to Ar$^+$. The uncorrected, directly measured product intensity increases very steeply at an Ar$^+$ laboratory energy of 0.62 eV. At this energy the ion beam and the H$_2$O beam move with the same velocity. In the present example the steep increase of the product rate versus zero relative velocity, $|g| = 0$, depends very critically on the operating conditions of the supersonic beam. The reason is that the high pressure expansion not only leads to a well-defined collision energy, characterized in our kinematic considerations with the speed ratio, but also to rotational cooling of the target molecules. In order to analyze such results quantitatively, the resulting rotational distribution of the H$_2$O in the beam has to be known. First attempts have been made.$^{17}$ Since cooling of molecules to translational temperatures around 1 K has become routine in supersonic jets, collisions in the sub-meV range are possible.

Much effort has been put into the development of special merged beam arrangements which allow one to study the interaction between electrons and cold ions at meV collision energies. One example is the ion storage ring TSR where fast ions are cooled with an intense cold electron
Electron transfer from $\text{H}_2\text{O}$ to $\text{Ar}^+$. The uncorrected, directly measured product intensity increases very steeply at an $\text{Ar}^+$ laboratory energy of 0.62 eV. As can be seen from the upper scale, this corresponds to a nominal collision energies of 0 eV, e.g. the two beams move with the same velocity. The steepness depends critically on the expansion conditions since it influences the rotational population of the $\text{H}_2\text{O}$ molecules in the beam.\(^\text{17}\)

beam and where they can interact with a separate electron target. In the recombination of electrons with hydrogen molecular ions, rovibrational resonances have been measured down to a few meV.\(^\text{18}\) Electrons with translational temperatures of a few K have been created using a cryogenic photocathode. To cool the ions, e.g. $\text{H}_3^+$, internally a low temperature 22-pole trap has been used as ion source. First steps towards state selective measurements of dissociative recombination rate coefficients have been made, more work is in progress. The set-up also allows for an \textit{in-situ} diagnostic of the population of low-lying rovibrational states using chemical probing in the radiofrequency multipole ion trap.\(^\text{19}\)

3.4.2. \textit{RF Ion Traps, Buffer Gas Cooling}

Various ion traps have been used since the 1960’s for studying ion-molecule reactions. With suitable electric or magnetic fields, ions can be confined
for long times and, with the use of buffer gas, thermal conditions can be attained. The most common techniques used in chemistry are the ion cyclotron resonance (ICR) machines and Paul traps. Much of our own work has been stimulated by the liquid helium-cooled Penning ion-trap experiment of Dunn and co-workers.\textsuperscript{20} Despite the fact that magnetic confinement is a dynamic trap, i.e., kinetic energy is needed for trapping, collision temperatures below 10 K have been reached for collisions between hydrocarbon ions and hydrogen; i.e., for favorable mass ratios.\textsuperscript{21}

As emphasized above, fast oscillating forces on the boundary of a wide field free region are the best solution for confining and cooling charged particles. In contrast to storage rings, fast beams trapped between electrostatic mirrors or Penning traps, the most important feature of such traps is the possibility of relaxing ions by collisions with buffer gas. Very important in this context is Eq. (3.9). Since the principle is very general, one can tailor the device to specific boundary conditions imposed by neutral or laser beams, by optical detectors. An example for a specific geometrical solution is the U-shaped storage ion source.\textsuperscript{7} Very successful and versatile solutions utilize multi-electrode arrangements, such as stacks of ring electrodes or linear multi-poles traps, combined with cryogenic cooling. For many applications, the work horse has become the 22-pole ion trap (22PT). First results from this device have been reported in a review on radiative association.\textsuperscript{22} A thorough description has been presented at the Nobel Symposium 91 on Trapped Charged Particles and Related Fundamental Physics.\textsuperscript{23} As shown in Fig. 3.12 the trapping electrodes are mounted onto a closed cycle helium refrigerator in order to obtain a cold environment. When the trap is surrounded by two radiation shields, temperatures as low as 3.6 K have been reached with modern cold heads.

Today some ten 22-pole traps are in operation worldwide. They are used for reaction dynamics,\textsuperscript{24,25} laser induced reactions,\textsuperscript{26} or as an ion source for preparing cold ions for the electrostatic storage ring in Aarhus. As already mentioned above, a 22PT is used to cool H$_3^+$ ions at the ion storage ring TSR in Heidelberg for measuring state specific rate coefficients for dissociative recombination.\textsuperscript{19} In a new 22PT machine, absolute photodetachment cross sections of negative ions have been determined.\textsuperscript{27} Two 22PT based instruments became operational recently aimed at measuring spectra of large cold ions of relevance to astronomical observations\textsuperscript{28} or of very cold protonated biomolecules.\textsuperscript{29} One typical arrangement of an ion-trapping machine is shown schematically in Fig. 3.13. In such a “standard arrangement” the primary ions are created externally by electron bombardment and pre-thermalized in a high-pressure storage ion source. For selecting the mass of the primary ions a quadrupole filter is used. It is best to operate this filter in the high frequency, low mass filter mode to avoid rf heating of the kinetic
energy of the ions. There is also progress with \textit{in situ} synthesis of reactants within the trap. Most trapping machines are optically transparent in the axial direction, at least from one side, for facilitating applications of laser methods.

Upon entering the trap, the ions are thermalized by injecting them together with a very intense, short He or H$_2$ gas pulse directly into the inner box (see Fig. 3.12). It is also possible (but not efficient) to operate at very low number densities and to wait long enough for the trapped ions to be internally cooled by radiation. As can be seen from Fig. 3.14 a fast piezo-valve makes it possible to raise the pressure in less than 1 ms. Peak number densities up to $10^{15}$ cm$^{-3}$ have been reached. With higher pumping speed or with mechanical shutters closing the trap, one can go much higher. The dense buffer gas leads to thousands of collisions in a few ms and, therefore, to a very efficient relaxation of all degrees of freedom of the stored ions.
Fig. 3.13. Construction details of the combination of a temperature variable 22-pole ion trap and a pulsed supersonic beam. Primary ions are produced in a storage ion source and mass selected in a quadrupole mass filter (from the bottom, not shown). After deflection in an electrostatic quadrupole bender the ions are injected into the trap (see Fig. 3.12). There the ions are confined in radial direction by the rf field and in axial direction with dc voltages applied to the entrance and exit electrodes (less than 100 mV). Buffer gas is used, usually He, for thermalizing the ions. From the left a skimmed molecular beam traverses the trap without colliding with the cold surfaces. For detection, the stored ions are extracted to the right, mass selected and counted via a Daly detector. A laser beam can be injected via the detector tract for state selective excitation of the trapped ions.

The FWHM of the gas pulse is 5 ms and, within 20 ms, the number density drops with a fast time constant of 3.5 ms by 2 orders of magnitude. The subsequent decay has a larger time constant of 23 ms; however, in most cases the rates of ternary processes involving the buffer gas atoms are negligible after 100 ms.

In typical experiments, reactions are studied by periodically filling the trap with ions, buffer gas and reactants. Depending on the process to be studied, repetition periods between ms and many minutes are chosen. After a certain storage time, primary and product ions are extracted from the trap, mass analyzed, and detected with a scintillation detector. The delay of the extraction pulse can be varied within the repetition period, i.e., from \( \mu \)s to min or longer. In the absence of target gas, the mean decay
Fig. 3.14. Time dependence of the intense gas pulse injected into the ion trap using a piezo valve. During their transfer into the trap, ions are cooled with buffer gas, in most cases He. The width of the pulse (FWHM = 5 ms) and the two decay times (3.5 ms and 23 ms) are determined by the geometry of the small housing surrounding the trap, the volume of the vacuum chamber and the pumping speeds of the pumps.

time of the number of specific ions is determined by reactions with background gas, the pressure of which can be below $10^{-12}$ mbar, especially at low temperatures. For the study of specific collision processes, target gas is added continuously or in a pulsed mode at number densities varying from below $10^9$ cm$^{-3}$ to above $10^{14}$ cm$^{-3}$. By choosing a suitable combination of number density and interaction time, the rates of rather fast as well as very slow bimolecular reactions can be measured. The wide range of operating parameters makes the trapping device unique. For example, very slow radiative association processes have been separated from ternary association. For comparing forward-backward reactions, e.g. in the case of isotopic enrichment, a special feature of the trapping technique is that one can choose a well-defined gas mixture and evaluate the stationary equilibrium reached after a sufficiently long storage time. At very low collision rates and long storage times, the coupling of the internal degrees of freedom to the low temperature black-body radiation field has also been observed in some cases.

A state of the art trapping machine, the Atomic Beam 22-Pole Trap (AB-22PT) is shown schematically in Fig. 3.15. This instrument has been
developed for exposing cold trapped ions to a slow effusive beam of H atoms. A first description of this set-up can be found in a conference proceedings.\textsuperscript{24} The crucial part of this machine is the differentially pumped effusive target beam. In the machine shown in Fig. 3.15, hydrogen atoms are produced via an rf discharge. After their precooling to 100 K, the atoms are thermalized in an accommodator to a temperature which can be as low as 10 K. As tested by time of flight measurements, the final velocity distribution of the hydrogen atoms is strongly influenced by the transmission features of the two hexapole magnets. A publication describing this sophisticated instrument in detail is in preparation.\textsuperscript{30}

### 3.4.3. How to Determine Temperatures

As discussed above, there is always a competition between buffer gas cooling and rf heating if one uses oscillatory fields for trapping the ions. Many collisions or long storage times lead to a stationary equilibrium but not necessarily to the temperature of the ambient buffer gas or the black-body radiation field penetrating the ion cloud. Therefore one has to provide tools for measuring the actual temperature of the trapped ions. It is well known from experiments in Paul-traps that ion-neutral collisions lead to a significant transfer of energy from the radio-frequency field to the motion of the ions. One of the proofs has been the appearance of products from reactions with rather high endothermicities. As discussed above the heating process is significantly reduced in traps with steep rf potential, e.g. defined by a stack of ring electrodes or high order multi-poles. In addition, the wide field free regions support cooling collisions to the temperature of the buffer gas. Numerical simulations and experimental tests quantitatively support these considerations.
Various experimental tests have been performed to determine the translational energy distribution of the trapped ions or the population of internal states. One of them is based on temperature dependent rate coefficients. Since in almost all cases helium is used as buffer gas, the formation of He$_2^+$ dimers via the ternary association reaction

$$\text{He}^+ + 2\text{He} \rightarrow \text{He}_2^+ + \text{He}$$

(3.22)

is a good test reaction for characterizing a low temperature trap. This reaction has been studied over a wide temperature range in a selected ion drift tube (SIDT) apparatus by Böhringer et al.$^{31}$ Their measurements, plotted in Fig. 3.16 as open squares, have been extended towards lower temperatures operating the 22-pole trap at [He] number densities in the range of $10^{14}$ cm$^{-3}$. The results have been fitted with the function

$$k_3 = 1.4 \times 10^{-31} (300K/T)^{0.6} \text{cm}^6\text{s}^{-1}.$$  

(3.23)

Presently this temperature dependence is used as a calibration standard above 10 K. However, for extending it towards lower temperatures, more precise experiments are needed in order to separate the influence of ion temperature, density of the neutrals and the temperature dependence of the ternary association reaction.

![Fig. 3.16. Temperature dependence of the ternary rate coefficients for the reaction He$^+ + 2$He $\rightarrow$ He$_2^+$ + He. The filled circles are data obtained with a 22-pole trap, the open squares have been measured using a selected ion drift tube.$^{31}$ The fit $k_3 = 1.4 \times 10^{-31} (300K/T)^{0.6} \text{cm}^6\text{s}^{-1}$ is used as a “thermometer”. Note, however, that more precise experiments are needed in order to separate the influence of ion temperature, density of the neutrals and the temperature dependence of $k_3$.](image-url)
The in situ growth of weakly bound clusters, e.g. hydrogen clusters $\text{H}_n^+$, also depends on the temperature. A related sensitive quantity is the final cluster size distribution as discussed in Ref. 23. Problematic is that the thermodynamics of weakly bound clusters are only known from high pressure measurements and more studies are needed at low temperatures and low pressures. Other possible processes include the formation and decay of protonated or deprotonated water clusters or the enrichment of ions with isotopes, e.g. H-D exchange. First tests have been made with isotope exchange using $^3\text{He}/^4\text{He}$ or $^{12}\text{C}/^{13}\text{C}$. In general, there is not yet any ideal chemical reaction with a well-characterized low temperature behavior. Even the process of deuteration, where the energetics are best known from the differences of zero point energies, causes problems. An interesting collision system with a strong temperature dependence is $\text{N}^+ + \text{H}_2$. However, as discussed below, the formation of $\text{NH}^+$ is not yet suitable for ion thermometry. At the moment this reaction is used as a sensitive probe for minor traces of ortho-hydrogen.

In order to determine ion temperatures more directly, laser based techniques have been used and new schemes of "action spectroscopy" are under development. The Doppler profile of an observed transition provides direct information on the ion velocity distribution along the laser beam. In addition a quantitative analysis of the population of rotational or other suitable internal states can provide information about how cold the ions are internally. The first successful application based on the laser induced reaction

$$\text{N}_2^+ + h\nu + \text{Ar} \rightarrow \text{Ar}^+ + \text{N}_2$$

has been discussed in detail by Schlemmer et al. In order to determine the translational temperature of the ion cloud the line shapes of several ro-vibrational transitions were recorded and fitted with Gaussians. The temperature of the fitted Maxwell-Boltzmann velocity distributions has been in good overall agreement with the nominal temperature of the trap. Also the rotational population of the $\text{N}_2^+$ ions was in accord with the wall temperatures. So far, these measurements have not been extended to temperatures below 50 K because of condensation of the Ar gas on the walls; however, work is in progress to use target beams for chemical probing.

The first Doppler profile at the present temperature limit of the trapping technology, 10 K, has been recently reported by Glosik et al. In this experiment an overtone transition in $\text{H}_2\text{D}^+$ ions, which have been trapped in hydrogen, has been excited at 6536.317(8) cm$^{-1}$. This additional energy allows the $\text{H}_2\text{D}^+$ ions to reconvert in collisions with $\text{H}_2$ into $\text{H}_3^+$ ions, an endothermic process. The kinetic temperature, derived from the Doppler profile was $(9 \pm 4.5)$ K. More details and examples are given in
chapter 6 which describes the production, control and study of ultra-cold molecular ions.

3.4.4. Sub-Kelvin Cooling of Trapped Ions

It has often been stated that an experimental limitation of low temperature ion traps is condensation of the neutral species on the walls. Since usually only very low number densities are required one can operate the trap — at least in principle — at such a low temperature that the resulting vapor pressure is just sufficient. The example shown in Fig. 3.17. illustrates that one can operate a trap at 38 K and simultaneously maintain a nitrogen number density of $10^9 \text{ cm}^{-3}$ by leaking a stationary gas flow of $3 \times 10^{-8} \text{ mbar l s}^{-1}$ into the trap. In this test, the dissociative charge transfer $\text{He}^+ + \text{N}_2 \rightarrow \text{N}^+ + \text{He} + \text{N}$ has been used to follow *in situ* the time dependence of the nitrogen density. The example shows that it takes about 1 hr to reach stationary conditions. At the beginning of the experiment pumping of the cold clean surfaces maintains a stationary number density below $10^7 \text{ cm}^{-3}$. From the constant flow one can conclude that cryopumping has a pumping speed of a few l/s.

![Graph](image)

Fig. 3.17. The dissociative charge transfer $\text{He}^+ + \text{N}_2 \rightarrow \text{N}^+ + \text{He} + \text{N}$ has been used to follow the time dependence of the nitrogen density in the trap at a temperature of 38 K. The gas flow has been hold constant gas at $3 \times 10^{-8} \text{ mbar l s}^{-1}$. At the beginning of the experiment, the pumping speed of the cold clean surfaces maintains a rather low stationary density. With increasing time, saturation reduces the sticking efficiency.
A more versatile solution to extend the ion trapping method towards lower temperatures and to use also condensable gases for reactions is to combine linear traps with skimmed beams of molecules, atoms or radicals. Geometrical arrangements are similar to those shown in Figs. 3.13 and 3.15. Presently special beam sources are under development for cooling trapped ions to temperatures below 1 K. The method is based on the simple idea of using only the slow Boltzmann tail of a cold effusive beam (e.g. He or p-H₂ at a few K). This can be achieved by pulsing the beam and chopping the entrance of the trap. Simple calculations show that there are still enough cooling collisions if one cuts off 90% of the thermal distribution. The remaining distribution is very cold. For specific purposes and depending on the mass ratio, supersonic beams may also be used to collisionally cool the ions. As already mentioned above, a unique advantage of the skimmed beam is that cooling collisions take place only in the field free region. With efficient cryopumping there are practically no collisions during the interaction of the ions with the rf wall of the trap. Another strategy is based on a cold effusive H-atom beam (see for example Fig. 3.15) in combination with a weak magnetic field which guides slow H atoms. The ultimate solution is to superimpose a magnetic trap for ultracold H atoms with the multipole ion trap.

There are a variety of in situ experiments (spectroscopy) planned which are of fundamental importance for characterizing such a trap for creating brilliant beams of ultracold molecular ions, including biomolecules (e.g. from an electrospray ion source). It is also possible to synthesize directly in the trap special ions such as clusters or molecules with van der Waals bound ligands. More details, e.g. how to record a pure rotational spectrum of ultracold CH₅⁺ ions, are discussed in Chapter 6.

3.4.5. Collisions in a Sympathetically Cooled Ion Crystal

Another strategy to reduce the translational energy of ions in traps is based on laser cooling. For more than 20 years atomic ions, which are confined in Penning traps or radio frequency quadrupole ion traps, have been cooled with lasers to such low temperatures that they form regular structures. This process, called Coulomb crystallization, has attracted a lot of experimental and theoretical interest. As already mentioned in the Introduction, the condensation to such structures is characteristic for temperatures in the sub-mK or even μK range. With the discovery of sympathetic cooling of other ions mixed into the cloud of atomic ions the application of Coulomb crystals has been significantly extended. Some more aspects of this very interesting subject are discussed in Chapter 6. Here we just want to mention
briefly that this fascinating technique is able to observe ion-neutral reactions with single-particle resolution as described recently by Roth \textit{et al.};\textsuperscript{38} however it is misleading to call such processes ultracold collisions.

There has been significant progress in recent years in using sympathetically cooled ions in linear quadrupole traps.\textsuperscript{39,40} An interesting publication discusses the production of ultracold diatomic and triatomic molecular ions of spectroscopic and astrophysical interest.\textsuperscript{41} With clever experimental detection schemes in combination with molecular dynamics simulations one can study chemical reactions without seeing the reactants or the products. The information is derived from images of the fluorescent atomic ion ensemble and their perturbation by the dark ions. The localization of these ions in specific regions together with mass selective excitation of the secular motion of the trapped ions allows one to follow chemical reactions. For small Coulomb crystals changes in the ion cloud can be detected at a single-ion level. For example, formation of localized MgH\textsuperscript{+} and MgD\textsuperscript{+} molecules in collisions of Mg\textsuperscript{+} ions with hydrogen and deuterium has been reported.\textsuperscript{39} A recent publication reports rate coefficients for reactions of H\textsubscript{3}\textsuperscript{+} ions with various neutrals.\textsuperscript{38}

Despite the fact that in all these examples so-called \textit{ultra-cold} ions are involved in the reactions, the chemistry occurs at rather high collision energies and most probably with hot reactants. The problem is that one has to distinguish between the \textit{collision temperature}, i.e., the energy distributions in the center of mass frame which is determined by the rf driven motion of the ions and the temperature of the neutrals and the \textit{optical temperature}, derived from the first order Doppler effect. It seems to be contradictory but in certain processes, e.g. absorption of a photon, the ions confined in a Coulomb crystal can be characterized with mK or even \(\mu\)K temperatures, while in other processes, e.g. chemical reactions, they contribute energy which is equivalent to several 1000 K. The explanation is the huge kinetic energy associated with the oscillating motion. This velocity component is not seen in the optical transitions as long as it is orthogonal to the laser beam and if there is no coupling of the radial and axial motion of the ions. An example illustrating nicely the overall situation is the recent high-resolution detection of rovibrational infrared transitions in HD\textsuperscript{+}.\textsuperscript{42} A Doppler width corresponding to 0.2 K has been achieved with ions which have been sympathetically cooled by Be\textsuperscript{+} to 20 mK.

A quite different problem impeding the study of \textit{cold chemical reactions} in ion crystals is the internal energy of the stored ions. While Coulomb interactions are very efficient at sympathetically cooling translation, the internal degrees of freedom of molecular ions are not coupled to the laser cooled atomic ions. The creation of ultracold ions in rf traps is further discussed in Chapter 6.
3.5. Selected Results

The various methods described above, and also in Chapter 2, have been used to study a large number of ion-molecule reactions over a wide range of densities, temperatures or energies. The first application of a temperature variable multi-electrode trap, consisting of a stack of ring electrodes, has been the study of the association reactions of C$^+$ and H$^+$ with H$_2$ at 230 and 320 K.\textsuperscript{43} Results from an early version of the merged beam apparatus have been mentioned in Ref. 7. Evidence for the unique sensitivity of ion traps is provided by the systematic studies performed on radiative association, a reaction mechanism of astrochemical importance.\textsuperscript{22} Examples such as NHe$^+$ formation in N$^+$ + 2He collisions have illustrated that one can measure extremely small rate coefficients with a few hundred ions.\textsuperscript{44} An interesting application of traps is to study the dynamics of the growth of clusters. Starting from H$_3^+$, hydrogen cluster ions up to H$_{23}^+$ have been formed in collisions with para- and normal-hydrogen at 10 K. Ion trapping allows one to perform a systematic study of the dynamics of the association, cooling and fragmentation processes under well defined thermal conditions.\textsuperscript{32} Especially important is that the choice of an adequate density enables one to stretch the time scale for the growth processes such that individual steps can be traced in great detail. Establishing stationary equilibria in a trap, thermodynamic data can be determined. A typical result has been published for protonated and deprotonated water cluster ions.\textsuperscript{33}

A first low temperature study of reactions between stored ions and condensable gases, the formation of protonated methanol via radiative association, has been reported.\textsuperscript{45} The trapping method also allows for a lot of additional tests. For example the method of chemical probing has been used to determine the rate coefficient for isomerization of HOC$^+$ in collisions with H$_2$. The resulting rate coefficient obtained at 25 K is surprisingly large, $3.8 \times 10^{-10}$ cm$^3$ s$^{-1}$.\textsuperscript{2} Some very recent applications for addressing key problems in laboratory astrochemistry have been summarized by Gerlich and Smith.\textsuperscript{25} In the following, a few selected topics are discussed in more detail.

3.5.1. The Role of Fine-Structure, Rotational, and Zero Point Energy

Chemistry at low temperatures can be significantly influenced by the excitation of low lying electronic states, e.g. fine-structure or even hyperfine-structure levels, by rotational and soft vibrational motions, and by gain or loss of a small amount of energy caused by isotope substitution. The interpretation of low energy collisions often suffers from the fact that one does
not know how these different forms of energy help to promote the reaction in the endothermic direction. It is also often unclear whether the formation of a new product really needs energy or whether a small activation barrier has to be overcome. Quantum chemical calculations are not yet sufficiently accurate to predict the energies which are required for understanding collisions at a few K. A typical example is the hydrogen abstraction reaction

\[ \text{N}^+ + \text{H}_2 \rightarrow \text{NH}^+ + \text{H}. \]  

Since this simple triatomic reaction is of fundamental importance and since formation of interstellar ammonia occurs via this process and subsequent hydrogen abstraction reactions, it has been studied very often. Nonetheless, there are still many open questions. It is hard to believe that one does not yet knows the energy balance, although one could get it with spectroscopic accuracy just by measuring the dissociation energy of \( \text{NH}^+ \). The best value which is presently available for the endothermicity of reaction (3.25) is \( \Delta H = 11 \text{meV} \) for \( \text{H}_2 \) and \( \Delta H = 29 \text{meV} \) for \( \text{D}_2 \). Note that the differences of the two values are not in accord with the differences of the asymptotic zero point energies. This indicates that there are intermediate barriers slowing down the reaction. The \( \Delta H \)-values have been derived from a variety of low temperature measurements most of which are more than 10 years old. According to the best of our knowledge there are no recent measurements or new calculations.

As explained in Ref. 44, the temperature dependence of rate coefficients can be measured rather quickly during the cooling of the trap, which typically takes 1 hr. Fitting experimental results measured for \( \text{n-H}_2 \) and \( \text{p-H}_2 \) has resulted in temperature dependent rate coefficients,

\[
\begin{align*}
\text{k(n-H}_2) &= 1.1 \times 10^{-11} \exp\left(-26 \text{K/T}\right) \text{cm}^3\text{s}^{-1}, \quad (3.26) \\
\text{k(p-H}_2) &= 1.4 \times 10^{-9} \exp\left(-230 \text{K/T}\right) \text{cm}^3\text{s}^{-1}. \quad (3.27)
\end{align*}
\]

The lowest rate coefficient, which has been measured with \( \text{p-H}_2 \) at 15 K \( (k(15 \text{K}, 99\% \text{ p-H}_2) = 1.4 \times 10^{-13} \text{cm}^3\text{s}^{-1}) \), has been explained with an \( \text{o-H}_2 \) impurity of \( \sim 1\% \). For pure para-hydrogen calculations predict \( 1 \times 10^{-14} \text{cm}^3\text{s}^{-1} \).

The interpretation of such thermal rate coefficients is complicated by the fact that the endothermicities \( \Delta H \) or the barriers involved are comparable with the rotational energy of \( \text{H}_2 \) \( (14.4 \text{meV for } j = 1) \) and with the fine structure energy of \( \text{N}^+ (3\text{P}_0 0\text{meV}, 3\text{P}_1 6.1\text{meV}, 3\text{P}_2 16.2\text{meV}) \). As long as there are no measured state specific cross sections, assumptions have to be made about the role of these different energy forms in driving the reaction. Therefore, the best evaluation one can perform is based on state specific cross sections determined with a statistical theory.\textsuperscript{46} The situation
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Fig. 3.18. Phase space calculation of state specific cross sections for the reaction $N(3P_0)^+ + H_2(j) \rightarrow NH^+ + H$. The endothermicity which is not yet known with the required accuracy, has been assumed to be $\Delta H = 17.5$ meV and 15 meV. For more details see the text.

is illustrated in Fig. 3.18 where calculated state-specific cross sections are plotted as a function of the collision energy. It is obvious that, ideally, one would have to perform state specific experiments at meV collision energies.

In order to study separately the influence of translational, rotational and fine-structure energy on the threshold onset of a few meV, guided ion beam experiments have been performed for $N^+ + D_2 \rightarrow ND^+ + D$. High-energy resolution has been achieved by combining a slow guided ion beam with a supersonic deuterium beam, in one case by crossing the two beams, in the other case by merging them. Fig. 3.19 shows a typical result from the merged beam arrangement. In these measurements every effort has been made to approximate “ultracold” conditions; i.e., to prepare both reactants exclusively in their ground state. For the neutral target, para-hydrogen has been expanded from a liquid-nitrogen cooled nozzle, the $N^+(3P_j)$ ions have been relaxed in a trap using a 20 K He buffer. As can be seen from the figure, the reduction of rotational energy has a significant influence while
no changes in the reactivity could be detected as a function of the “ion temperature”.

This is a hint that the N\(^+\) fine structure energy may not be available for promoting the reaction. A careful trapping experiment corroborates this. In this experiment the N\(^+\) ions have been created by electron bombardment in a 350 K ion source. Under such conditions it is safe to assume that this leads to a statistical population of the three fine-structure states \(^3\text{P}_0\), \(^3\text{P}_1\), and \(^3\text{P}_2\), i.e. to the ratio 1 : 3 : 5. If the excited ions react faster, one would get two breaks in the slope of the reaction decay curve. In the experiment the number of N\(^+\) ions decreases with a single time constant over several orders of magnitude. Also the competition between collisional relaxation and reaction has been excluded.\(^{47}\) For more critical tests, experiments with state selectively prepared N\(^+\)(\(^3\text{P}\)) reactants are needed or one has to find an independent method to prepare and test a low temperature fine structure ensemble (see Chapter 6).

Isotope exchange has often been used in experiments in order to get detailed information on the microscopic dynamics. Since most of such experiments have been performed at high energies, it was assumed that the minor differences in zero point energies could be ignored. At low temperatures, however, these differences become important, especially if one replaces an H atom by a D atom in a molecule. This can lead to isotope enrichment, a
special field which has attracted a lot of interest in recent years. The relevance for astrochemistry has been emphasized in Chapter 1. In addition to D, important isotopes which are routinely detected in interstellar molecules are $^{13}$C, $^{15}$N. In order to correlate quantitatively isotope ratios in molecules with the isotope ratios of the elements one has to know in detail the kinetics and dynamics of a variety of processes including chemical reactions, inelastic collisions and radiative transitions.

Low temperature ion traps are ideal tools for studying such processes and have been used rather often in recent years. Selected ion trap studies on deuterium fractionation have been reviewed by Gerlich and Schlemmer. Recent results for the fundamental H$_m$D$_n^+$ collision systems have been discussed by Gerlich et al. and are briefly mentioned below. Many laboratory studies have concentrated on the deuteration of hydrocarbon ions in collisions with HD. For example, sequential deuteration of or CH$_3^+$ or C$_2$H$_2^+$ in collisions with HD has been found to be rather fast, although there are deviations from simple statistical expectations. In collisions of CH$_4^+$ with HD, the CH$_5^+$ product ion (68% at 15 K) prevails over CH$_4$D$^+$ (32%). The scrambling reaction

$$\text{CH}_5^+ + \text{HD} \rightarrow \text{CH}_4\text{D}^+ + \text{H}_2,$$  \hspace{1cm} (3.28)

is extremely slow if it occurs at all. For the rate coefficient an upper limit of $5 \times 10^{-18}$ cm$^3$ s$^{-1}$ has been determined, a nice illustration of the sensitivity of the 22PT based instruments.

Early ion trap studies of isotopic variants of the C$_3$H$^+$ + H$_2$ reaction have indicated that this system is very complicated. More detailed studies of C$_3$H$_n^+$ colliding in a trap with HD have been performed recently. Many surprises have been found. For example the rate coefficient for the reaction

$$\text{C}_3^+ + \text{HD} \rightarrow \text{C}_3\text{D}^+ + \text{H},$$  \hspace{1cm} (3.29)

$k = 9.3 \times 10^{-10}$ cm$^3$ s$^{-1}$, is six times larger than assumed in astrochemical models. Surprisingly, direct production of C$_3$HD$^+$ via radiative association,

$$\text{C}_3^+ + \text{HD} \rightarrow \text{C}_3\text{HD}^+ + h\nu,$$  \hspace{1cm} (3.30)

has been observed to be fast ($k_r = 6.0 \times 10^{-11}$ cm$^3$s$^{-1}$). Another unexpected result is the branching in

$$\text{C}_3\text{H}^+ + \text{HD} \rightarrow \text{C}_3\text{HD}^+ + \text{H} \quad \text{and} \hspace{1cm} (3.31)$$  
$$\rightarrow \text{C}_3\text{H}_2^+ + \text{D}. \hspace{1cm} (3.32)$$

Forming the deuterated ion (3.31) is over hundred times faster than channel (3.32). A final example is the exothermic H-D exchange reaction

$$\text{C}_3\text{H}_3^+ + \text{HD} \rightarrow \text{C}_3\text{H}_2\text{D}^+ + \text{H}_2. \hspace{1cm} (3.33)$$
A careful analysis of the data reveals that the 15 K rate coefficient is smaller than $4 \times 10^{-16}$ cm$^3$ s$^{-1}$. This is in accord with theoretical predictions. All these C$_3$H$_n^+$ + HD ion trap studies have been thoroughly discussed by Savic et al.\textsuperscript{53}

3.5.2. Reactions with Significant Temperature Dependences

It is still generally assumed that the rate coefficients for exothermic ion-molecule reactions are almost independent of temperature; however, experimental studies at low temperatures often reveal more and more exceptions. One typical example is the reaction

\begin{equation}
\text{CH}_4^+ + \text{H}_2 \rightarrow \text{CH}_3^+ + \text{H}
\end{equation}

which has been discussed by Asvany et al.\textsuperscript{50} another one is

\begin{equation}
\text{C}_3^+ + \text{H}_2 \rightarrow \text{C}_3\text{H}^+ + \text{H}.
\end{equation}

Although exothermic, reaction (3.35) is rather slow at room temperature but becomes faster with decreasing temperature.\textsuperscript{53} In addition to the increasing lifetime of the collision complex, this behavior may be caused by the floppy structure of C$_3^+$. It is well known, at least qualitatively, that the rate coefficients for ions colliding with polar molecules increase with decreasing collision energies. Fig. 3.20 shows a result measured in a merged beam arrangement for the charge transfer reaction

\begin{equation}
\text{Kr}^+ + \text{H}_2\text{O} \rightarrow \text{H}_2\text{O}^+ + \text{Kr}.
\end{equation}

The H$_2$O beam has been seeded in He, the nozzle temperature was 300 K. Comparison of the two energy scales (lower scale: laboratory energy of the ion, $E_1$, upper scale: collision energy $E_T$) reveals that the Kr$^+$ ions have been accelerated to 1.3 eV in order to match the velocity of the seeded H$_2$O molecules. The Gaussian-like curves show two distributions of the collision energy. They have been determined numerically for the nominal collision energies 0 and 50 meV. The dashed curve is an empirical fit indicating that the rate coefficient increases proportional to $E_T^{-0.5}$. Accounting for the energy resolution of the experimental set-up leads to the solid line. This simulated curve is in good agreement with the measured data. The minor deviations at laboratory energies below 0.5 eV are probably due to experimental difficulties, such as changes in the ion beam shape.

Another reaction where the rate coefficient exhibits an interesting temperature dependence is the charge transfer process

\begin{equation}
\text{Ar}^+ + \text{N}_2 \rightarrow \text{N}_2^+ + \text{Ar}.
\end{equation}
The rate coefficient is plotted as a function of the laboratory energy of the ion, $E_1$ (lower scale). Accounting for the velocity of the water beam which has been seeded in He, one obtains the collision energy $E_T$ (upper scale). The two Gaussian-like curves represent the numerically determined energy distributions at the nominal energies 0 and 50 meV. The dashed curve is an empirical fit.

It has been studied very often and in great detail, both experimentally and theoretically; however, the low temperature behavior is not yet understood. Although it is 0.179 eV exothermic, it proceeds very slowly at collision energies below 100 meV as can be seen from Fig. 3.21. The merged beam results (open circles) have been measured with a supersonic beam. Above 100 meV the merged beam data are in good agreement with GIB and temperature variable DRIFT tube data (see Refs. 17 and 54). The low energy points are from a free jet\textsuperscript{11} and a CRESU experiment (see Chapter 2). The increase of the rate coefficient at low temperatures may be taken as an indication that the longer lifetime of the collision complex allows for non-adiabatic transitions. A similar reaction mechanism, where the increasing lifetime of the collision complex allows for tunneling, has been discussed for the temperature dependence of the reaction

\[ \text{NH}_3^+ + \text{H}_2 \rightarrow \text{NH}_4^+ + \text{H}. \]  

(3.38)
Fig. 3.21. Energy dependence of the effective rate coefficients for the exothermic charge transfer reaction \( \text{Ar}^+ + \text{N}_2 \rightarrow \text{N}_2^+ + \text{Ar} \). Above 100 meV the merged beam data (open circles) are in good agreement with results which have been obtained with the Guided Ion Beam technique (GIB: crosses) and a temperature variable DRIFT tube (open triangles, see Ref. 54). The increase of the rate coefficient with increasing energy coincides with the energy needed for forming \( \text{N}_2^+ \) in the first vibrational state, \( v = 1 \). The points at low energies are from a free jet\(^{11}\) and a CRESU experiment (see Chapter 2).

A short summary of this reaction and some ion trap results can be found in Ref. 44.

### 3.5.3. Formation and Destruction of Hydrocarbons

Elementary steps in forming and destroying small hydrocarbons in the ISM include collisions of \( \text{C}^+ \) ions with \( \text{H} \) and \( \text{H}_2 \), proton transfer from \( \text{H}_3^+ \) to \( \text{C} \) or collisions of \( \text{CH}_n^+ \) with \( \text{H} \) atoms. In the last few years, many relevant studies have been performed using ion traps. Of fundamental importance is the radiative association reaction

\[
\text{C}^+ + \text{H}_2 \rightarrow \text{CH}_2^+ + h\nu.
\]  

This reaction has been studied several times in rf ion traps with increasing accuracy. The results are summarized in Fig. 3.22 (see also Refs. 15 and 55). For p-\( \text{H}_2 \) the rate coefficient for radiative association is \( 1.7 \times 10^{-15} \text{ cm}^3 \text{ s}^{-1} \) at 10 K, while the value for n-\( \text{H}_2 \) is 2.5 times smaller. As discussed in detail in Ref. 22, much more has been learned about such processes, e.g. the competition between complex lifetime and radiative decay, by comparing ternary and radiative association and by isotopic substitution.
An interesting hydrocarbon system, where different low temperature experiments have resulted in quite different results, is the reaction
\[
\text{C}_2\text{H}_2^+ + \text{H}_2 \rightarrow \text{C}_2\text{H}_3^+ + \text{H}.
\] (3.40)

This reaction is already slow at room temperature and the rate coefficient falls below \(10^{-13} \text{ cm}^3 \text{ s}^{-1}\) at 100 K as determined with the 22-pole ion trap. Evaluation of several measurements has lead to an endothermicity of \((50 \pm 20) \text{ meV}\) in good accordance with earlier conclusions. The question whether this endothermicity is in reality a barrier was raised by measurements performed with a low temperature flow reactor (for details see Ref. 55). In this instrument a rate coefficient of \(10^{-12} \text{ cm}^3 \text{ s}^{-1}\) was measured.
Fig. 3.23. Temperature dependence of the rate coefficient for the reaction $\text{C}_2\text{H}_2^+ + \text{H}_2 \rightarrow \text{C}_2\text{H}_3^+ + \text{H}$. As discussed by Gerlich,\textsuperscript{55} there is some disagreement between the free jet and the ion trap experiments. While, at low temperatures, the high pressure experiments seems to indicate an increasing rate coefficient, the 10 K ion trap results proof that the rate coefficient for the abstraction reaction is much smaller than $10^{-13}$ cm$^3$s$^{-1}$. A possible explanation is the fast radiative association process ($k_r(\text{p-H}_2) = 5 \times 10^{-12}$ cm$^3$s$^{-1}$), which has been observed in the ion trap experiment (open circle and triangle). The phase space calculations (solid line) have used adjusted parameters for getting the low temperature behavior.

at 10 K and an increasing tendency towards $10^{-11}$ cm$^3$ s$^{-1}$ was observed when the temperature was lowered to 1 K. This increase was interpreted with a tunneling mechanism. None of the ion trap studies could corroborate these conclusions. The main fraction of mass 27 products could be attributed to $\text{C}_2\text{HD}^+$ which are formed via isotope enrichment in collisions with the natural abundant HD. One of the possible explanations for the signal found in the free jet experiment is based on the large radiative association rate coefficient detected in the trap. This process together with ternary association occurring in the high pressure flow can lead to highly excited $\text{C}_2\text{H}_4^+$ products which are fragmented during the extraction and detection. Studying the reverse reaction $\text{C}_2\text{H}_3^+ + \text{H}$ will shed some more light onto the energy balance of this system.

Ion traps also have been combined with beams of radicals. For studying collisions between small neutral carbon molecules $\text{C}_n$ ($n = 1$–3) and stored ions a special experimental setup has been developed.\textsuperscript{56} In this instrument ions are confined in a ring electrode trap (RET) at temperatures between 80 K and 600 K. There they interact with an effusive carbon beam, which is produced via high-temperature vaporization of a carbon rod. For the
reaction

\[ \text{D}_3^+ + C \rightarrow \text{CD}^+ + \text{H}_2 \]  \hspace{1cm} (3.41)

the importance of which is mentioned in chapter 1, first results have been obtained. The reaction rate coefficients measured for forming \( \text{C}_n\text{D}^+ \) are almost a factor two smaller than values presently used in astrochemical models. Another important class of reactions concerns the growth of pure carbon chains via radiative association,

\[ \text{C}_m^+ + \text{C}_n \rightarrow \text{C}_{m+n}^+ + h\nu. \]  \hspace{1cm} (3.42)

First results have indicated that the rate coefficients are slower than generally assumed in astrochemical models; however, all the experiments have to be extended towards lower total energies. While it is easy to change the temperature of the ions, the neutral carbon target needs to be cooled, especially in the case of the dominating \( \text{C}_3 \) molecule. This is only possible by the high temperature vaporization carbon source with a high pressure laser ablation source.

One of the most important radicals is the hydrogen atom. Hydrogen is the most abundant baryonic species in the universe and it plays therefore, in both its atomic and molecular form, a central role in many regions of the ISM. It was therefore a challenge to combine a low temperature ion trap with a beam of \( \text{H} \)-atoms the velocity distribution of which can be varied. A first version of the experimental setup is shown schematically in Fig. 3.15.

Collisions of hydrocarbon ions with \( \text{H} \) often lead to dehydrogenation. One example is the reaction

\[ \text{CH}_5^+ + \text{H} \rightarrow \text{CH}_4^+ + \text{H}_2 \]  \hspace{1cm} (3.43)

The rate coefficients for this reaction, which have been presented at a conference,\(^{24} \) are compared in Fig. 3.24 with those for the reverse reaction which also has been mentioned above.\(^{50} \) A detailed discussion of all results together with a critical analysis of the kinematics is in preparation.\(^{57} \) A question which is related to reaction (3.43) is whether catalytic cycles such as \( \text{XY}^+ + \text{H} \rightarrow \text{XYH}^+ \) followed by \( \text{XYH}^+ + \text{H} \rightarrow \text{XY}^+ + \text{H}_2 \) can contribute to the formation of molecular hydrogen under interstellar conditions.

### 3.5.4. Pure Hydrogen Chemistry

One motivation for studying pure hydrogen chemistry, i.e., reactions between hydrogen ions, atoms, molecules and deuterated variants, originates from cold pre-protostellar cores. As described for example by Walmsley \textit{et al.},\(^{58} \) such processes become of central importance if, at very
Fig. 3.24. Temperature dependent rate coefficients for the CH$_6^+$ collision system. The reaction CH$_5^+$ + H$_2$ → CH$_5^+$ + H has been reported by Asvany et al.$^{50}$ First results for the CH$_5^+$ + H collision system have been presented on a conference.$^{24}$ The results depend critically on the energy distribution of the H-atom beam. A detailed analysis is in preparation.$^{30,57}$ The dashed line predicts the rate coefficient as a function of the ion temperature, T$_{22PT}$, for an hydrogen beam with 1 meV kinetic energy.

For example, the reaction

$$H_3^+ + HD \rightarrow DH_2^+ + H_2 \quad (3.44)$$

is still intriguing.$^{35}$ An experimental difficulty is that, at low temperatures, very small traces of o-H$_2$ have a significant but rather unknown influence on the measured H$_3^+$/DH$_2^+$ ratio.$^{59}$

Another motivation for studying reactions involving several H and D atoms at low temperatures is connected with the fact that they are fermions and bosons, respectively. The question is whether, at low enough energies, one can detect experimentally consequences from what one could call Bose- or Fermi-chemistry. “Simple” consequences of the exchange symmetry in low temperatures, all heavy elements become integrated into ice layers on dust grains, i.e., vanish from the gas phase. In a recent summary of our present knowledge of various H$_m$D$_n^+$ collision systems, it has been emphasized that systems with $m + n \leq 3$ are reasonably well understood, while much more work needs to be done on systems involving more than three atoms.$^3$
molecules containing identical atoms and the rather stringent restrictions of the conservation of the total nuclear spin in a scrambling collision have been discussed by Gerlich et al.³ So far only statistical models have been used for making predictions although it must be expected that dynamical constraints may also play a role. Special effects can be expected for the reaction

\[ \text{H}_3^+ + \text{H} \rightarrow \text{H}_3^+ + \text{H}. \] 

The relevant H\(_3^+\) potential energy surface is shown schematically in Fig. 3.25. The H\(_2^+\) + H\(_2\) part (right side) is probably characterized well enough for understanding formation of H\(_3^+\) + H.

However, in order to model scrambling in sub-K H\(_3^+\) + H collisions correctly, a very precise potential energy surface is required on the left side. Astrochemically important variants of reaction (3.45) are H-D exchanges, e.g. in H\(_3^+\) + D, or ortho-para conversion of H\(_3^+\) via H atom scrambling. In all these cases a very good potential energy surface is needed in order to distinguish between effects caused by the van der Waals type interaction, the zero point energies and the dynamics of the mixed 4-center fermion/boson system. Corresponding experiments involving cold ions and slow H or D atoms are in preparation.
3.5.5. **State Specific Reactions**

There have been so far only a few approaches for studying ion-molecule reactions at collision energies of a few meV with state selected reactants. One of the early studies at low temperatures was the association reaction

\[ \text{CO}^+(v = 0, j) + 2\text{CO} \rightarrow (\text{CO})_2^+ + \text{CO}. \]  

(3.46)

The experiments have been performed in a free CO expansion using multiphoton ionization for preparing \( \text{CO}^+(v = 0, j) \) ions.\(^{61}\) Propensity rules favor the formation of specific rotational states. Several aspects of the kinematics in single beam and merged beam arrangements have been discussed in Ref. 62. In addition to integral cross sections which have been measured for the reaction

\[ \text{H}_2^+ + \text{H}_2 \rightarrow \text{H}_3^+ + \text{H} \]  

(3.47)

at collision energies between 5 meV and 5 eV with a merged beam arrangement, state specific information has been obtained at meV energies by preparing \( \text{H}_2^+ \) ions in different rotational states via \((3 + 1)\) REMPI (resonance enhanced multi photon ionization).\(^{62}\) REMPI also has been used to create \( \text{NO}^+ \) ions directly inside an rf trap; however, no reactions have been studied.

In recent years, there have been several successful attempts to use lasers for re-exciting ions after they have been cooled down. Since the ion cloud consists of a limited number, various strategies are possible for deriving information on state specific collision dynamics. The methods range from a dedicated perturbation of a stationary low temperature equilibrium via burning a hole into the state population to two colour pump — probe experiments. Most of such activities are used for spectroscopy or for understanding the low temperature populations of trapped hydrogen ions. They are discussed in Chapter 6.

One example for a low temperature state specific reaction is the hydrogen abstraction reaction

\[ \text{C}_2\text{H}_2^+ + \text{H}_2 \rightarrow \text{C}_2\text{H}_3^+ + \text{H}, \]  

(3.48)

which has been measured in a trap by infrared excitation of the acetylene ion.\(^{63}\) From the measured intensities and their dependence on parameters such as storage time, laser fluence and target gas density, information on state specific rate coefficients has been obtained. Vibrational excitation of \( \text{C}_2\text{H}_2^+ \) increases the rate of reaction (3.48) by more than three orders of magnitude, while rotation hinders the reaction. The fine-structure state of the parent ion does not affect its reactivity.
Important contributions towards a detailed state specific understanding of H-D exchange reactions in collisions of $\text{H}_3^+$ with H or $\text{H}_2$ in all possible deuterated variants have been made in the last years in several laboratories. The activities, which all use low temperature 22-pole traps in combination with the method of laser induced reactions, have been summarized in Ref. 3. The feasibility of analyzing cold $\text{H}_3^+$ via laser excitation, followed by proton transfer to Ar, has been first demonstrated in a compact trapping machine which has been mainly developed as an ion source.$^{64,65}$ Meanwhile high power CW diode lasers are applied to excite $\text{H}_3^+$ ions and isotopic variants in specific states via overtone transitions.$^{35}$ Also the first spectra with a free electron laser have been reported.$^{26}$

In order to extract from such laser induced processes quantitative information such as state populations or reliable state specific rate coefficients, it is mandatory to separate relaxation, reactions and laser induced processes. This is possible by combining the flexible trapping method with short gas pulses, chopped or modulated CW lasers, and pulsed effusive or supersonic beams.

### 3.6. Conclusions and Outlook

Trapping techniques have been and still are the basis of many new experiments in physics and chemistry. All these experiments make use of inherent advantages such as extremely long interaction times, the possibility to accumulate weak beams, phase space compression, laser cooling or interaction with buffer gas. This contribution has focused on the use of rf fields to explore collisions at low temperatures or with low relative velocities. The examples have shown that it is now possible to study collisions at energies of 1 meV or at temperatures of 10 K. As already mentioned, there are activities to cool ions in traps to temperatures below 1 K using the slow tail of a cold effusive beam for buffer gas cooling. There are also efforts to heat ions with a laser in order to access temperatures above 2000 K.$^5$

There are many technical improvements and innovative applications possible. Especially important is the development of methods for non-destructive detection of the stored objects, e.g. based on image current or optical methods. More work needs to be done in order to optimize the combination of an ion trap with a time of flight mass spectrometer.$^{66}$ Low temperatures collisions also could be used successfully in several fields of analytical chemistry. As proposed recently for applications in elemental analysis,$^{67}$ the dependence of ternary association on the collision temperature and the number of internal degrees of freedom can be used efficiently for distinguishing between atomic ions and molecular ions with the same mass which otherwise create a background. The addition of helium to
trapped seed ions is possible if one uses a chopped beam of very slow He atoms or He clusters. Among many interesting questions concerning sub-K cooling, such experiments can provide results similar to those of the He droplet experiments described by Slenczka and Toennies in Chapter 7. The extension of the rf trapping technique toward anions is obvious and causes no problems with rf trapping since the effective potential is proportional to the square of the charge, $q^2$. Nonetheless such activities have been started only very recently.$^{27}$ For astrochemistry more laboratory data are needed in order to understand and model the formation and destruction of matter in a variety of environments, ranging from very cold dense interstellar clouds via planetary atmospheres to the high temperatures of circumstellar environments. At the University of Arizona, a new instrument, the central part of which is a temperature variable multi-electrode trap, is close to completion. In combination with radical sources, complex gas phase reactions can be studied over a wide range of temperature. Based on the fact that the effective potential can be tailored for many purposes, special traps can be designed for observing and characterizing one single nanoparticle over long times. This opens up the possibility of studying cold or also hot interstellar grain equivalents.

Cooling all degrees of freedom of molecular ions down to a few K or even in the sub-K range has many obvious applications in spectroscopy. One example is to study rotational transitions in floppy molecular ions such as CH$_5^+$. Applications of rf traps in the analysis of molecular structures together with planned extensions towards infrared or microwave absorption spectroscopy on ultracold ions are discussed in Chapter 6.

References


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