Chapter 6

The Production and Study of Ultra-Cold Molecular Ions

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6.1. Introduction

6.1.1. Cold Molecules

The late 20th century has seen significant experimental advances in cooling and trapping neutral atoms culminating in the successful formation of
Bose-Einstein condensates. Following the exciting progress with cold atoms the experimental challenge became to prepare ultracold molecules. Unfortunately the laser-cooling techniques applied to atoms are not directly transferable to molecules, since these methods rely upon cyclic absorption and spontaneous emission within an almost pure two-level system. The multi-level structure of the electronic states of molecules and the manifold of allowed transitions does not allow for simple iterative excitation with one single laser line.

With the invention of optical dipole traps and optical lattices for storing cold atoms, the association of two atoms opened up a field called ultracold molecules (see Chapter 9 by van de Meerakker et al.). Stimulating the association of two colliding atoms by a laser, cold molecules have been produced in atomic traps. In most cases, however, these molecules are just homonuclear diatomics made from alkaline metal, atoms which can easily achieve temperatures in the micro-Kelvin range due to the sub-Doppler cooling methods. Some efforts to extend these association techniques to heteronuclear molecules have been successful. However, besides being restricted to a few specific atoms, there is the problem that these molecules are only translationally cold. They have been formed from two atoms, which have been nearly at rest before they attracted each other; however the result is a more or less excited molecule. In order to get cold molecules for applications in chemical processes, it is not sufficient to lower the translational motion, one has to freeze also the internal degrees of freedom. Therefore it is necessary to distinguish between slow and cold. For some diatom systems, specific laser based strategies have been developed to transfer the slow molecules to low-lying vibrational rotational states, may be even to the ground state.

As described in other chapters of this book there are other strategies to produce ultracold neutral molecules, e.g. to decelerate polar molecules in pulsed electrostatic fields (see Chapter 9). Combining this method with suitable traps one can create and study ensembles of the molecules. Experimental advances have made it possible to cool selected molecules in well-defined states to temperatures below 1K and to trap them. Besides deceleration buffer gas cooling in cold $^3$He environments has also been utilized for loading magnetic traps with paramagnetic molecules. Although cooling and manipulating neutral molecules have become the subject of intense studies in recent years and although many research groups have contributed to this field, the activities with neutrals are still restricted to a small number of specific molecules. It is obvious that one needs more general strategies for contributing to the new interdisciplinary field of molecular matter at very low temperatures ($T < 1$K). In order to understand ultracold chemistry, e.g. needed for modeling dense interstellar clouds or for deposition of ultracold molecules on surfaces, one has to study the
quantum-mechanical details of the cold chemical systems including large polyatomic molecules, clusters, and cold nanoparticles. With charged particles and various cooling schemes, this is possible.

In contrast to neutrals, charged objects are much easier to trap because of their strong interactions with electromagnetic fields. As a consequence a wide variety of experimental set-ups for confining ions and charged particles has been developed ranging from small ion trap devices to large storage rings. One of the obvious advantages of deep potential wells is that it is possible to first trap externally created ions and to cool them afterwards. A nice review of cooling methods in traps has been given by Itano et al. As can be seen from that summary and as discussed below, the main driving force was and still is to increase the precision and accuracy in spectroscopy and metrology. Besides laser based cooling methods there are other quite general schemes to cool a finite ensemble of charged particles such as evaporation, optical pumping or chemically removing energetic ions. In addition there are interesting methods such as resistive cooling or active-feedback cooling. These methods make use of the currents induced by the motions of the charges in suitable electrodes. Note that, via the same coupling, parasitic voltages also can heat the motion of trapped ions.

Based on extremely sensitive detection schemes, sophisticated experiments on single objects became possible. Interesting results include the observation of quantum jumps in isolated atomic ions, ultrahigh resolution mass spectrometry on clusters or unstable nuclei, and extremely long time studies on single nanoparticles. Confinement of just one charge in a trap avoids space charge problems, which have to be accounted for if an ensemble of ions is to be cooled to low temperatures. An alternative strategy which has been discovered many decades ago and which has gained more and more attention in the last decade, is to work in a regime where space charge effects dominate. Progress in laser cooling trapped ions has made it possible to lower the temperature so far (typically a few mK; see below concerning the definition of temperature) that spatially ordered structures form. These so-called Coulomb crystals of ions have been observed in Penning and Paul traps. In such crystalline arrangements, which can be stored for hours, single specific ions can be addressed and manipulated. Strings of well-localized ions have become very attractive physical systems for studying multi-particle entanglement as well as for quantum computer research. For cooling of molecular ions, the subject of this chapter, the process of sympathetic cooling is of significant importance. As will be discussed in detail below, the motion of almost any molecular ion can be reduced below 100 mK in ion traps through Coulomb interactions with laser-cooled atomic ions.
6.1.2. Interaction with Radiation

A general problem in creating cold molecules is whether or how efficient the internal degrees of freedom couple to the cooling process. In the case of sympathetically cooled molecular ions, the vibrational or rotational motion is largely unaffected by the Coulomb interactions as explained below.\textsuperscript{7,8} If molecules are not exposed to another interaction, long enough trapping finally equilibrates internal excitation with the black body radiation penetrating the ion cloud. An example is the rotational temperature of the polar molecules CH, CH\textsuperscript{+}, and CN in dense cold interstellar clouds. As discussed in the introduction of Chapter 3, the observed population of the rotational states indicates that rotation is in equilibrium with the 2.7 K temperature of the cosmic background radiation. As a consequence of the permanent interaction with the black body radiation, innovative instruments, which aim at reaching temperatures of 1 K or below, either need an efficient cooling mechanism or the ion environment has to be operated at temperatures of a few K. With small traps this is rather easy to realize while operating a storage ring at low temperatures is a challenge.\textsuperscript{9}

Long time storage in a well-controlled environment provides ideal conditions for studying the interaction of the trapped objects with electromagnetic radiation. Several of the fundamental aspects of light-atom interactions such as spectroscopy at the limits and applications to novel frequency standards are meanwhile also extended to molecules, e.g. HD\textsuperscript{+}.\textsuperscript{10} One of the obvious conditions for obtaining high resolution is to reduce the Doppler effect. Orienting the micro-motion in rf traps transverse to the laser beam reduces the first-order Doppler effect, while elimination of the second-order Doppler effect requires getting the ions at rest. In the case of rf-based traps this means that one has to reduce the oscillatory motion. One general solution for that is to work with multi-electrode traps. One nice related illustration is a lamp-based Hg\textsuperscript{+} frequency standard which uses a linear rf 12-pole for ion trapping.\textsuperscript{11} Due to the improvement of the kinetic energy distribution in this trap, the second order Doppler fractional frequency shift has been reduced to $2.4 \times 10^{-13}$ with a stability of $<1 \times 10^{-16}$.\textsuperscript{11} If one works, however, with a single charged object, the harmonic potential of a quadrupole trap is the ideal solution for cooling the translational motion to the limits of the uncertainty principle. The extreme localization in space in such a system ($<1 \mu$m) even makes it possible to detect one single ion in absorption.\textsuperscript{12}

Traps are often used for accumulating ions, which are not so easy to produce, e.g. isotopes in nuclear physics applications. In the case of molecular ions this means that one may use also rather inefficient ways to create or to prepare them in specific states. So far photoionization schemes,
which allow molecular ions in specific states to be obtained, have been used rather seldom for creating a trapped ensemble. Using photons with an energy just at the ionization limit of the neutral, ions can easily be formed in their ground state. There are several multi- or multiple-photon based schemes for preparing ions in specific states. The state selective preparation of $\text{H}_2^+$ and $\text{CO}^+$ via resonance enhanced multi-photon ionization is mentioned in Chapter 3 (Sec. 3.5.5). Another strategy for preparing ions in specific states is to use optical pumping schemes including coherent manipulation of internal degrees of freedom. A partly destructive method, similar to evaporation of fast atoms, is to remove ions in unwanted states, e.g. by using photo-induced processes followed by a chemical reaction or by photo-fragmentation. Since the trapped ensemble is finite, the state population of the remaining ions becomes a hole, provided it is isolated. The most efficient and universal method which is available today is to use first buffer gas cooling and to start with excitation via electromagnetic waves from a few low lying states. Work is in progress in several laboratories to transfer an ensemble of ions to their ground state in collisions with He. An interesting question is whether such a sample, e.g. $\text{CO}^+$, can be used to perform infrared or micro-wave absorption spectroscopy.

6.1.3. Cooling Complex Systems

For systems that are more complex than diatomic ions, buffer gas cooling is today the only general way to relax all degrees of freedom. Already simple molecular ions with a few atoms can have very complex energy levels because of internal isomerization, pseudo-rotation, tunneling, etc. In such situation, standard methods of spectroscopy often fail and it helps if one can record spectra of ions which have been thermalized to well-defined low temperatures. The need of thermalizing polyatomic ions to a given temperature has been emphasized by Wang et al.\textsuperscript{13} who utilize high resolution photoelectron spectroscopy for studying anions. In their experiment vibrational cooling of $\text{C}_6\text{O}^-$ anions has been achieved via collisions with a cold buffer gas (70 K) in a Paul trap, which has been attached to a cold head. Relative to spectra taken at room temperature, vibrational hot bands have been completely eliminated, yielding well-resolved vibrational structures and an accurate electron affinity for neutral $\text{C}_6\text{O}$. Many more interesting results have been achieved within the past two years including spectra from several cold singly and doubly charged fullerenes.\textsuperscript{14} As discussed below and in Chapter 3 of this book, an rf quadrupole trap can be used rather successfully for collisional relaxation instead of a higher order multipole, provided that the ions are much heavier than the neutral buffer gas; however, a Paul trap should not be used if one intends to cool the ions to the limit
and if translational motion plays a role. A few selected examples for cooling complex molecular ions, e.g. protonated bio-relevant molecules are discussed below.

In recent years a lot of attention has been paid to the cation CH$_5^+$. Its potential energy surface is very flat near the various minima and the hydrogen atoms can change their location on a sub-ns time scale. This leads to very complex spectra especially if one does not cool the highly fluxional ion. As described by Davis et al., in Chapter 5, molecular ions such as protonated methane can be formed and cooled in supersonic jets. In this way high-resolution absorption spectra of CH$_5^+$ have been recorded in the 3000 cm$^{-1}$ range. Also a temperature variable 22-pole ion trap has been used successfully in combination with a free electron laser to record infrared spectra of CH$_5^+$. In this experiment the applied chemical probing scheme was based on laser induced proton transfer to carbon dioxide requiring the trap to be operated at and above 110 K. Both experiments have provided important spectral information; however, it is not yet sufficient to predict rotational spectra of CH$_5^+$ with the accuracy, required for detecting this important ion in space. It has been pointed out by Bunker et al. that the mm-wave spectrum of CH$_5^+$ is strongly affected by the large amplitude motion of the H atoms. From their simulated spectra, calculated at 300 and 77 K it is obvious that it is mandatory to cool the ions to much lower temperatures, especially if one intends to detect the J = 1 $\rightarrow$ J = 0 absorption spectrum which is predicted to be in the 220–235 GHz region. In principle, there are experimental techniques available today to cool complex ions such as CH$_5^+$ with buffer gas to 1 K or even below. The basics of these techniques are mentioned below.

6.1.4. Preview

The following text concentrates on methods to cool molecular ions which are confined in traps. Concerning the use of inhomogeneous high frequency fields for guiding and trapping ions, this chapter is closely related to Chapter 3 in the center of which were experimental studies of collisions at low translational energies while here internal energies play a role. After a general introduction describing methods to prepare, detect and manipulate charged molecules in a trap, recent advances in laser based cooling methods are reviewed. Special emphasis is given to sympathetic cooling since this method can be applied to all kind of ions, as well as molecules. The main part deals with buffer gas cooling, i.e., inelastic collisions with a cold or slow non-reactive buffer gas, which is presently the most general scheme to cool all degrees of freedom of a complex molecule, a cluster or a nanoparticle. Selected instruments and results illustrate the wide range of applications
of cold ion traps ranging from fine structure states of atomic ions via di- and tri-atomic ions to complex molecules of astrochemical and biological interest. So far, buffer gas cooling in ion traps has been limited to typically 10 K; however, a new experimental strategy is presented which will allow trapped ions to be cooled to temperatures below 1 K.

6.2. Cooling Ions in Traps

6.2.1. Trapping, Probing, and Detecting

As already mentioned in Chapter 3, charged particles are easy to manipulate with electric and magnetic fields. Therefore, in comparison to neutral molecules, it is much simpler to confine positive or negative ions in specific regions of space. However, ions are also very sensitive to stray fields and space charge, making it simultaneously problematic to keep them cold. A variety of trapping devices has been described in the literature and been summarized in several review articles, see for example Refs. 2, 3, and 18–20. Many of the basic ideas have been developed already in the 1950s and 1960s as can be seen from a still very attractive paper written by Dehmelt or from the overview given by W. Paul in his Nobel lecture. In Penning and ICR traps (ion cyclotron resonance) confinement is achieved by a static magnetic field. These devices are well-suited for high resolution mass spectrometry and related studies; however, they cannot be used efficiently for buffer gas cooling since they belong to the class of dynamic traps where the confining force is based on the motion of the ion. The same obviously holds for storage rings or other electrostatic traps in which ions are moving on quasi-periodic orbits with rather high velocities. In contrast, traps that use inhomogeneous time varying fields in the adiabatic regime, have real three-dimensional potential minima and, therefore, can be used for buffer gas cooling. Many aspects of the technique and the basic theory, especially the limits of the effective potential approximation, have been explained in Chapter 3 with emphasis on applications in low energy collision dynamics. In this chapter the cooling process itself is discussed and in situ applications of the cold stored objects, especially spectroscopic applications, are described.

Dehmelt has stated in his article on Radiofrequency spectroscopy of stored ions that keeping a system at rest in space and free from any outside perturbation is of limited value unless one has dedicated methods for preparing, manipulating, and analyzing the stored objects. Interesting schemes for creating oriented, aligned or state-selected atomic ions have been discussed already before laser methods became integrated in such
experiments. As described in Chapter 3, many of today's applications of traps use the flexibility of external ion sources for filling the trap and also external detectors for counting each of the extracted ions. Mass selection is achieved by quadrupole or magnetic mass spectrometers. For mass analysis of a trapped ion cloud, the combination of pulsed ejection and time-of-flight mass spectrometry is ideal; however, the method is not yet fully developed as discussed in the conclusion of Chapter 3. There are also several non-destructive detection schemes, which leave the stored objects in the trap. Commercially established is the detection of the image current induced by the periodic motion of trapped particles in pick-up electrodes. The commonly used high resolution Fourier transform ion cyclotron resonance mass spectrometry (FTICR-MS) has been extended recently to an electrostatic trap, the Orbitrap.

Other methods to obtain information on the distribution of mass, or of mass to charge ratio in the case of multiply charged objects, are based on resonant excitation of periodic motions in magnetic traps or in suitable harmonic potentials, superimposing oscillatory electric fields. In the case of an rf quadrupole this method is know as a notch filter, if the excitation is used to eject specific ions. The method also can be applied to a linear multipole trap if one creates a harmonic potential along the axis with a set of ring electrodes (see Fig. 3.13 of Chapter 3). A significant advantage of such an arrangement is that the ions of a specific mass can be ejected towards the detector. As discussed below, mass selective in situ excitation also can be monitored via optical detection. For molecular ions, more information is desirable besides the mass over charge ratio. There are a variety of specific methods, e.g. for distinguishing different isomers or for analyzing the internal population of various vibrational or electronic states. Rather general is the method of chemically probing the trapped ions by exposing them to a pulse of suitable molecular reactants passing as collimated beam through the trap. As discussed in Chapter 3, atoms or radicals have also been used. Especially advantageous are chemical processes in which only the reaction products leave the trap while the prepared cold ion cloud remains stored, i.e., the product ions must be formed with additional kinetic energy in the laboratory frame. An example is the resonant proton transfer between a fast molecule and its protonated pendant. The probing of CH$_5^+$ with a beam of methane is mentioned below.

The combination of ion traps with lasers has opened up a wide range of innovative experiments. In addition to the information obtained from detecting reemitted or stimulated photons, there are many laser based schemes for probing or manipulating a trapped ensemble including optical pumping, laser induced dissociation, or light stimulated chemical reactions. Lasers are utilized for state specific creation of ions in the trap,
e.g. via resonance-enhanced multi-photon dissociation. It is important to note that, for testing cold ensembles, the Doppler profile of a transition provides information on translational motion. As summarized in what follows and illustrated with selected results, the majority of laser applications is still in high resolution spectroscopy, metrology, and fundamental quantum-electrodynamics; however, applying the sensitive optical manipulation and detection schemes to molecular ions allows for unique contributions to the emerging field of ultracold chemistry.

6.2.2. Laser Based Detection and Cooling

The methods of laser induced fluorescence (LIF) and laser based cooling has entered the field of ion trapping in the late 1970s as briefly mentioned in the Nobel lecture of W. Paul.\textsuperscript{22} The high sensitivity of various optical detection schemes has allowed individual trapped ions to be monitored over long times, resulting in interesting new experimental strategies. For example, information about the lifetime of metastable states has been deduced from \textit{not seeing} the stored ion, i.e., from the disappearance of the LIF signal, a process called shelving.\textsuperscript{2} A detailed understanding of the structure and dynamics of the stored system allows unique tests with photons including chemical shelving in the case of the reversible formation of a weakly bound molecule with a cold, inert buffer gas (see below the He–N\textsubscript{2}\textsuperscript{+} example). Permanent state-specific perturbation via optical pumping of a trapped low temperature ensemble with an infrared laser can avoid or reduce clustering with the cooling gas. The ability to monitor ions, be it a single one or a few thousands, in good isolation from the outside world has led to many improved spectroscopic measurements, and exquisite tests of QED, including the observation of quantum jumps, as mentioned above.

While laser cooling of a free particle is based on the Doppler effect and uses red shifted photons, for trapped ions one makes use of the fact that the translational motion is quantized by the boundary conditions. In a harmonic potential the oscillatory motion adds equidistant sidebands to optical transitions. Fig. 6.1 shows results from an interesting experiment\textsuperscript{23} where sideband cooling has been applied to one single Hg\textsuperscript{+} ion which has been confined in an rf quadrupole trap. The effective potential was set such that the eigenfrequency of the secular motion was $\omega/2\pi = 2.96$ MHz. Using a resolved sideband transition, based on the electric quadrupole transition $^{2}\text{S}_{1/2}^{\scriptscriptstyle -2}\text{D}_{5/2}$, the single mercury ion has been transferred almost completely into the ground state of its confining potential. Comparison of the absorption strengths of the upper and lower sideband (anti-Stokes and Stokes line) has confirmed that the ion was in the lowest state, $n_v = 0$, for 95% of the time. This corresponds to a time averaged temperature of
The quantum number $n_v$ characterizes the quantized motion of a single $^{198}\text{Hg}^+$ ion in the harmonic effective potential of the confining rf quadrupole trap (eigenfrequency $\omega/2\pi = 2.96$ MHz, $\hbar \omega = 12$ neV). Using side band laser transitions $\Delta n_v = -1$ transitions can be pumped. Analysis of side band resolved spectra reveals that the system can be cooled so far that it occupies the ground state $n_v = 0$ for 95% of the time, corresponding to a temperature of $47 \mu$K. As soon as the cooling laser is switched off, the ion motion is heated with a rate of $\langle dn_v/dt \rangle = 6/s$. After 2 s it reaches a mean value of $\langle n_v \rangle = 12$ corresponding to $T \sim 1.7$ mK.

$T = 47 \mu$K. In order to maintain such a low translational temperature, the ion has to be exposed continuously to the radiation field. Switching off the cooling laser leads to a heating rate, $\langle dn_v/dt \rangle$, of 6 vibrational quanta per sec, see Fig. 6.1. After 2s the mean expectation value of the vibrational quantum number is already $\langle n_v \rangle = 12$. This corresponds to a translational temperature of $T_T = 1.7$ mK of the 3-dimensional oscillator. For more details of this fundamental experiment see Ref. 23.

Besides sensitive and spectrally resolved detection of the light emitted from trapped ions, progress in the development of imaging devices (e.g. intensified CCD cameras) made it possible to record pictures of the trapped ensemble with high spatial resolution. This has allowed many tests to be performed on so-called Coulomb crystals. Trapped ions that are cooled with laser light below a translational temperature $T_T$, arrange themselves in spatial structures. A detailed analysis of regular arrays of a few laser-cooled Hg$^+$ ions which have been observed in an rf quadrupole trap has
been reported by Wineland et al. The ratio of Coulomb potential energy per ion to the thermal translational energy, \( k_B T \), has been estimated to be 120 in these clusters. The spectroscopy of such a pseudo-molecule is unique in that one can probe individual atoms of the structure separately due to \( \mu \text{m} \) distances. Order-chaos transitions in trapped ion clouds have been discussed for example by Blümel et al. Fig. 6.2 shows two typical pictures of two trapped \( \text{Ba}^+ \) ions taken by Hoffnagle et al. If laser cooling reduces the kinetic energy of the ion pair sufficiently they form a diatomic molecule in the trap. As can be seen from the left panel, the repulsion between the two positive charges, together with the confining force imposed by the trap, keeps them at an equilibrium distance of about 6 \( \mu \text{m} \). Sideband transitions allow vibrational transitions of such molecules to be probed. Reducing the cooling efficiency or heating the trapped ion pair leads to a phase transition: the molecule dissociates and the axial and radial motions of the two ions become uncoupled.

By storing and cooling a cloud of many particles of the same sign of charge in a trap, large ion Coulomb crystals are formed and are the basis of many interesting experiments. Such an one-component plasma has been

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Fig. 6.2. Order (left side) and chaos (right side, note the difference in scale) of a pair of laser-cooled \( \text{Ba}^+ \) ions which are confined in a Paul trap. Laser cooling leads to the formation of a bound diatomic Coulomb molecule. At slightly higher temperatures, the bound is broken and the two ions move independently in the trap. The spatial confinement within a few tens of \( \mu \text{m} \) is determined by their mean energy and the effective potential.
first seen in a quadrupole trap for microscopic particles.\textsuperscript{21} There have been also activities to obtain regular structures of ions in storage rings; however, the cooling was obviously not efficient enough to reduce the average kinetic energy per ion sufficiently ($<\text{mK}$ in the moving frame) below the repulsive Coulomb energy for obtaining the transition from the liquid to the solid state phase. Many experimental and theoretical studies to understand the structure and the dynamics of ion crystals have been performed during the last few years; see for example Refs. 5, 26, and 27. The resulting structures, ranging from strings of a few ions via planar arrangements to complex multi-shell compositions, depend on the number of ions and the boundary conditions imposed by the trapping field. Today most experiments use linear quadrupole traps, which are closed in the axial direction by electrostatic barriers. It can be foreseen that higher order multipole traps will be used soon.

A few selected properties of Coulomb crystals are illustrated in Fig. 6.3. The left part shows a photo from the pioneering experiment performed by Wuerker \textit{et al.}\textsuperscript{21} An ensemble of 32 charged aluminum particles having a diameter of a few $\mu$m was stored in the effective potential of a three dimensional quadrupole trap operated with an ac voltage of some hundred Hz. Cooling of the translational motion was achieved by collisions with room temperature buffer gas. In this example the ions were confined in the plane of the ring electrode of the Paul trap leading to a radial oscillation with an amplitude that increases with the distance from the center. The other two panels of Fig. 6.3 show results from numerical simulations of a 1000-ion

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig63.png}
\caption{Motions and crystalline arrangements of trapped charged particles. The left figure is a photo of a cluster of 32 charged micro-particles stored in a Paul trap.\textsuperscript{21} The two other figures are results from a numerical simulation of a 1000-ion Coulomb crystal confined in a linear quadrupole trap.\textsuperscript{28} In the left and the center panel the micro-motion of the particles in the oscillatory electric field can be seen. The amplitude increases proportionally to the distance from the center. The time-averaged positions plotted in the right part for a selected sample shows that the ions remain well-localized. This is the basis for defining an effective translational temperature of the ion cluster by subtracting the periodic oscillation from the overall motion.}
\end{figure}
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Coulomb crystal confined in a linear quadrupole trap published by Schiffer et al. As in the picture on the left, the lines in the middle image indicate the micro-motion. Other than in the left picture, here the ions are stored in a linear quadrupole and the image shows the motion in a plane orthogonal to the axis of the rod system. As a consequence the direction of the rf field induced micro-motion is radial in front of the rods and tangential in between them. More details on the micro-motion can be found in Chapter 3 (see for example Fig. 3.1). The time-averaged positions plotted in the right part for a selected sample of ions shows that they remain well-localized. As discussed already in Chapter 3 and in more detail below, this observation is the basis for defining an effective translational temperature of the ion cluster.

6.2.3. Sympathetic Cooling in Traps

The early applications of ion Coulomb crystals have been restricted to single atomic species suitable for laser cooling; however, it is also possible to replace any single ion in the ordered structure by another one, including molecular ions. The strong coupling via the Coulomb repulsion, a process called sympathetic cooling, efficiently freezes the translation of all ions embedded in the crystal including those which do not interact directly with the cooling laser. There are some restrictions concerning the mass over charge ratio but a wide range can be covered if one uses for cooling an ion with a suitable mass. There are several atomic ions available with masses between $^9\text{Be}^+$ and $^{198}\text{Hg}^+$. Many applications have been reported including bi-crystals consisting of two different ions both of which can be imaged, isotopically mixed crystals created via isotope selective resonance-enhanced two-photon ionization or a cluster of 1000 laser cooled $\text{Mg}^+$ ions in which 95% have been converted into $\text{MgH}^+$ in reactions with $\text{H}_2$. The unique versatility of the method of sympathetic cooling has been demonstrated recently with two specific ions confined in a linear Paul trap, one $^{27}\text{Al}^+$ and one $^9\text{Be}^+$. The beryllium ion provides laser cooling and is used simultaneously for monitoring of the $^1\text{S}_0 \rightarrow ^3\text{P}_0$ transition in $^{27}\text{Al}^+$. In this arrangement the frequency of this clock transition could be determined with a fractional uncertainty of $5 \times 10^{-15}$.

Under ultrahigh vacuum conditions, ion clusters can last for several hours since loss or chemical modification is only caused by a collision with background gas. Such long storage times of sympathetically cooled clusters and a nearly 100% detection efficiency of individual ion events within that structure makes the technique very versatile. Therefore, recent years have seen many activities on two or more ion species crystals and new groups enter this field. Usually only one species in the crystal is laser
cooled and monitored while the other ones are dark, i.e., not seen by the detector; however, they are fixed at specific locations of the crystal. Various ion species usually segregate in the trap, one of the reasons being that the effective potential is weaker for higher masses. This means that detection and identification relies on the observation of changes in the spatial structure of the crystal. In order to understand and characterize the complex three-dimensional structures of the non-neutral plasmas, numerical simulations of the motion of up to several thousand species confined in a multi-species ion crystal have become routine.\textsuperscript{27,28,30} Such calculations are useful for extracting information from the observed CCD images. They also help to develop and quantify new schemes for identifying particles newly formed in the crystal. Very efficient is, for example, the nondestructive identification of species via resonant excitation with an oscillating electric field resulting in high mass-to-charge resolution. The secular frequencies of ions in the effective harmonic potential of the quadrupole trap are shifted and broadened by the Coulomb interaction.

Of special interest for the present chapter is the possibility that complex ions can be integrated into Coulomb crystals. The first detection of charged molecules in a laser-cooled Mg\textsuperscript{+} ensemble has been reported by Baba and Waki.\textsuperscript{31} Subsequent applications of forming and confining translationally cold molecular ions include MgH\textsuperscript{+}/MgD\textsuperscript{+},\textsuperscript{32} CaO\textsuperscript{+}, BeH\textsuperscript{+}, HD\textsuperscript{+}, and others. For a recent summary see the publications by Roth \textit{et al.}\textsuperscript{27,33} These authors have created large samples of ultracold (<20 mK) molecular ions including triatomic ones, e.g. N\textsubscript{2}H\textsuperscript{+}, H\textsuperscript{3}+, and deuterated variants by sympathetic cooling and crystallization via laser-cooled Be\textsuperscript{+} ions in a linear radiofrequency trap. Probably the largest ion, which has been so far integrated into a Coulomb crystal, was a protonated organic molecule with a mass of 410 u. The ions have been generated in an external electrospray ionization source and transferred and cooled to the sub-K range by Coulomb interaction with laser-cooled barium ions.\textsuperscript{34} In principle, these techniques allow a large variety of charged objects to be sympathetically cooled, including ions of much higher mass, such as protonated proteins. There is no doubt that these ultracold ions are interesting targets for a variety of high-precision measurements in fundamental physics. However it is not yet clear how to combine sympathetic cooling with other efficient schemes for really cooling both the translational as well the internal degrees of freedom, e.g. for applications in ultracold chemistry, for state-specific preparation of ions, or for absorption spectroscopy on internally frozen molecules.

The problem of the real kinetic energy of the ultra-cold ions has been discussed already in Chapter 3 and is illustrated in Fig. 6.3. Briefly, the effective temperature is just a practical parameter which describes surprisingly well the ordering process in a Coulomb crystal.\textsuperscript{28} Its definition
is based on the small random deviations of the ion trajectories from the coherent local periodic motion imposed by the oscillating electric field. Apparently there is only an extremely small coupling between this thermal energy and the orders of magnitude higher kinetic energy contained in the rf driven motion. So far no dependence of the ion temperature on the distance from the center line has been observed. As emphasized in Chapter 3, collisions with such ultra-cold ions are rather hot, since they occur with the full momentary relative velocity. One solution is to restrict collisional studies to strings of ions localized close to the axis of a linear multipole trap.

An experimental problem with ultra-cold molecular ions created in a crystal, which has not yet been solved, is how to control their internal energy. As already indicated in the introduction, the Coulomb interaction couples efficiently to the translational degrees of freedom while the internal degrees of freedom apparently are almost completely unaffected by the laser cooled environment. Without any other interaction the population of vibrational and rotational states is mainly determined by the production mechanism of the charged molecules and the following decay processes. Ionization with energetic electrons or formation via an exothermic reaction can lead to highly excited ions, while selective photoionization may be suitable for creating internally cold ions. If there is no other cooling process, after a long time molecular ions may come into equilibrium with the black-body radiation provided the coupling is efficient enough.

A special test case for internal relaxation is the cooling process of diatomic polar molecules. To investigate the efficiency of rotational relaxation, Bertelsen et al.\textsuperscript{35} used MgH\textsuperscript{+} ions which have been sympathetically cooled to a translational temperature below 0.1K. Information on the population of specific rotational states has been obtained using rotational resonance enhanced multiphoton dissociation. Although the MgH\textsuperscript{+} ion has a rather large permanent dipole moment of 3.6 Debye, no significant cooling of rotation via the laser cooled atomic ions could be found, indicating that the charge-dipole interaction is very weak. A similar experiment has been performed with HD\textsuperscript{+} ions which have been created by electron bombardment and which have been sympathetically cooled with laser-cooled Be\textsuperscript{+} ions.\textsuperscript{8} Also in this case destructive laser induced fragmentation has been applied to determine the rotational population of the trapped ions. While the translational temperatures were in the mK range, the effective rotational temperature has been found to be close to room temperature. The observed separation of rotation and translation led Koelemeij et al.\textsuperscript{8} to propose that such a system may be used as a thermometer for the ambient blackbody radiation.
6.2.4. Buffer Gas Cooling

In contrast to the specific process of laser cooling, which just reduces the translational energy, interactions with a cold buffer gas is a true cooling method. It can provide thermalization of all degrees of freedom through elastic and inelastic collisions. Gas friction has been used in the above mentioned trapping experiment for cooling the randomly moving aluminum particles so far (in this example 300K) that they arrange themselves into a Coulomb crystal.\textsuperscript{21} Cooling of molecules in supersonic beams is very efficient and can cool them to temperatures of a few Kelvin. Buffer gas cooling also has been applied successfully for loading paramagnetic atoms and molecules into a magnetic trap. In such experiments \textsuperscript{3}He buffer gas is employed to reach temperatures below 1K since the depth of the trap is rather shallow. Once loading has taken place the buffer gas is removed by cryopumping. While in this application the velocity of the injected atoms or radicals have to be slowed down sufficiently that the weak magnetic forces store them, ion traps have much deeper potential wells and are much easier to fill. Cooling to room temperature of ions produced by electron bombardment has been shown to be quite efficient in so-called storage ion sources, which also use rf fields for confining the ions. As described in Ref. 18 and in Chapter 3, the first liquid nitrogen cooled rf trap became operational two decades ago. Meanwhile there are several instruments that rely on buffer gas cooling in high order multipole traps. As already described in Chapter 3 (see Fig. 3.14) one can use long interaction times or an intense short gas pulse for thermalization.

Buffer gas cooling is very general, the only condition is that the ion is capable of surviving multiple collisions. It already has been observed in the case of weakly bound clusters that cooling of translation leads partly to dissociation. As will be discussed below the reverse mechanism can also play a role, clustering with the atoms or molecules used for cooling. Due to different efficiencies in removing specific forms of energy stored initially in the molecular ions, it may take many collisions before a real thermal ensemble is reached; however, the time can be varied from ms to min and the neutral’s number density from $10^7$ to $10^{16}$ cm$^{-3}$. In most ion trap experiments, He, n-H$_2$ or p-H$_2$ are injected into the trap effusively; however, there are also new initiatives to use very slow beams for cooling, e.g. also H atoms.

In an ideal situation both the trapped ions and the cooling neutrals reach a thermal equilibrium at a common temperature $T$ which is usually defined by the surrounding walls. Under such conditions the distribution of the relative velocity, $f(g)$ (definition see Eq. (3.10) of Chapter 3 and also Ref. 18) is given by

$$f(g) = f_M(g; \mu, T) = (4\pi^{1/2})(\mu/2kT)^{3/2}g^2 \exp \left( -\frac{\mu^2}{2kT}g^2 \right), \quad (6.1)$$
where $\mu$ is the reduced mass and $k$ the Boltzmann constant. In practice the translational temperature of trapped ions often deviates from the buffer gas temperature. If in such a situation the motion of the ions and the buffer gas can be approximated by two Maxwellians with different temperatures, $T_1$ and $T_2$, Eq. (6.1) still holds if one uses for $T$ the mass weighted collision temperature

$$T = \frac{m_1 T_2 + m_2 T_1}{m_1 + m_2}. \quad (6.2)$$

After a sufficient number of collisions, it is the collision temperature $T$, which determines the internal temperatures of stored ions, and not its translational temperature $T_1$. This means that one can cool efficiently internal degrees of ions even if they are translationally hot, provided one takes a light buffer gas. For example, the internal temperature of $\text{C}_{60}^-$ ions stored in a quadrupole trap by Wang et al.\textsuperscript{13} could be cooled to $T = 15.5 \text{K}$ with He at $T_2 = 10 \text{K}$, even if the ions had an energy distribution corresponding to $T_1 = 1000 \text{K}$. Another example illustrating the importance of Eq. (6.2) is shown in Fig. 6.4. In order to test the new low temperature ion spectrometer in Basel, $\text{N}_2\text{O}^+$ ions have been used in which predissociative rovibronic states are accessible through the absorption of a single UV photon.\textsuperscript{36} The ions have been cooled with 10 K He buffer gas. In Fig. 6.4 the measured spectrum, i.e., the number of NO\textsuperscript{+} fragments measured as a function of the wavelength, can be compared with three spectra simulated for rotational temperatures of 15, 25 and 35 K. The molecular constants used and more details of the experiment can be found in Ref. 36. In principle, it is also possible to assess the translational temperature of the $\text{N}_2\text{O}^+$ ions through the Doppler broadening of the rovibronic lines. However, in the present case the bandwidth of the OPO radiation ($\sim0.5 \text{cm}^{-1}$) was much greater than the Doppler width ($0.017 \text{cm}^{-1}$ at 25 K). On the other hand it also cannot be excluded that the kinetic energy of the $\text{N}_2\text{O}^+$ ions is much higher. Assuming that the rotational temperature $T_{\text{rot}} \sim25 \text{K}$ is equal to the collision temperature $T$ in Eq. (6.2) and using $m_1 = 44 \text{u}$, $m_2 = 4 \text{u}$ and $T_2 = 10 \text{K}$ one obtains for the translational temperature $T_1 = 190 \text{K}$. Possible reasons for heating the translational energy of the ions are discussed below.

Another test for the efficiency of buffer gas cooling is the study of the growth of weakly bound cluster ions until collision induced dissociation leads to a stationary state. The decreasing binding energy of ion clusters with increasing complexity allows one to use such equilibrium distributions for determining the trapping conditions. The dynamics of the growth and destruction of hydrogen cluster ions from $\text{H}_5^+$ to $\text{H}_{23}^+$ with para and normal hydrogen at 10 K has been reported by Paul et al.\textsuperscript{37} Figure 6.5 shows two typical mass spectra of cluster equilibria in the trap at a temperature of
Fig. 6.4. Rotational population as ion thermometer. The photofragmentation spectrum of \( \text{N}_2\text{O}^+ \) (lowest plot) has been measured in a recently completed machine which has been developed in Basel for ion spectroscopy.\(^{36}\) The ions have been cooled in collisions with 10 K He buffer gas. Comparison of the rotationally resolved intensities with the three simulated spectra (15, 25, and 35 K) indicates that the rotational temperature is about 25 K. As discussed in the text this indicates that there must be some parasitic heating.

10 K, \( \text{H}_5^+ \) ions have been injected into \( n\text{-H}_2 \) (upper panel) or \( p\text{-H}_2 \) (lower panel) and stored for 9.9 s at a hydrogen number density of \( 1.2 \times 10^{14} \text{ cm}^{-3} \). Since there is only a small chance of double deuteration, the odd masses correspond to \( \text{H}_n^+ \) while the even ones are \( \text{DH}_{n-1}^+ \). In both cases the maximum of the distribution is \( n = 19 \). With normal hydrogen one obtains a few more \( n = 21 \) clusters, while para hydrogen apparently favors the formation of deuterated clusters in collisions with the traces of HD in the hydrogen \( (3 \times 10^{-4}) \). This is an indication, that nuclear spin restrictions influence the thermodynamic equilibrium. Ortho-hydrogen, i.e., \( \text{H}_2 \) in the first rotational state at 10 K \( (E_{\text{rot}} = 14.4 \text{ meV}) \), also plays a specific role in heating the ensemble and there is the additional possibility that rotation leads to a dynamic stabilization of an attached \( \text{H}_2 \). A general conclusion is that the calibration of the size of hydrogen clusters as a thermometer is complicated by traces of \( o\text{-H}_2 \). A related problem, which has been discussed elsewhere, is the process of deuterium enrichment in \( \text{H}_3^+ \) ions.\(^{38}\)
Fig. 6.5. Hydrogen cluster ions as thermometer. The competition between cluster growth and fragmentation leads to a stationary equilibrium distribution, for typical densities after a few seconds. The plotted mass spectra (H\textsubscript{n+} in black and DH\textsubscript{n−1} in yellow) have been measured at 10 K with normal and para-hydrogen at a number density of 10\textsuperscript{14} cm\textsuperscript{−3}. In both cases the maximum of the distribution is n = 19; however, in n-H\textsubscript{2} more H\textsubscript{21}\textsuperscript{+} is formed while p-H\textsubscript{2} favors deuteration.

6.2.5. Heating of Stored Ions

Since the first application of multi-electrode traps, there have been several attempts to measure directly the actual kinetic energy distribution of buffer gas cooled ions using narrow bandwidth diode-lasers. In an early test with N\textsubscript{2}\textsuperscript{+} (see below), good agreement was found between the nominal and the translational temperatures between 300 K and 50 K. There is also one recent example where the temperature derived from the Doppler profile was in good agreement with the 10 K of the walls of the trap. On the other hand several recent publications report that ions trapped in a
22-pole trap have higher kinetic energies than expected from the buffer gas temperature.\textsuperscript{36,41,42} It is certainly necessary to localize and eliminate the mechanisms which heat the translational motion of stored ions.

Detailed numerical simulations have shown that the time-varying external force has a negligible effect on the energy distributions of a buffer gas cooled ensemble, provided some conditions are fulfilled.\textsuperscript{18} The basic requirement is that the electric field $E_0(r,t)$ (see Eq. (3.1) in Chapter 3) oscillates fast enough for working in the adiabatic limit, at least in those regions where the ion is confined. Note, however, that this condition has to be fulfilled for all frequency components of the time dependent electric field. Ions may be heated if the sinusoidal signal from the rf generator has some superimposed low frequency components. Another explanation for ion acceleration is that parasitic low frequency electric fields may penetrate into the trapped ion cloud from the entrance or exit electrode. One fundamental problem with rf traps is that rf-mediated heating always occurs if collisions take place in high field regions. This effect is significantly reduced if one uses traps with wide, nearly field-free regions and if one avoids space charge effects. In practice only a few thousand ion per cm$^3$ are used.

The biggest experimental problem which may hinder ion cooling is most probably caused by surface patch effects, i.e., local distortions of the work function of the electrodes. As discussed by Gerlich,\textsuperscript{18} local potential deviations from the average surface potential can be $\pm 100$ mV or higher. Such loci can pull ions into regions of large rf fields causing permanent heating. In practice, patch effects can only be reduced by cleaning the surfaces. Another strategy, which has not yet been tested, is to use superconducting surfaces. An important diagnostic tool is based on the external correction electrodes, surrounding the trap (see Fig. 3.13 of Chapter 3). Since this tool is of central importance for reaching low temperatures with buffer gas cooling, Fig. 6.6 shows the calculated influence of a ring electrode, surrounding an octopole. Using, for example, an external voltage $U_{\text{ext}} = +1$ V, the center line is raised by 2.5 mV. Such well-controlled local changes of the potential can be used to push ions away from critical regions. The barriers are also very practical for determining the homogeneity of the potential with time of flight methods (see Fig. 6.2 of Ref. 43). Other applications include the axial confinement of the ion cloud with very accurate barrier heights. In this way one also can eliminate influences from the entrance or exit electrode.

What are the consequences if a storage device is not operated with parameters which have been called in Ref. 18 safe operating conditions? In a recent publication, Mikosch et al.\textsuperscript{44} discussed some experience they made in the “unsafe” region, where the adiabaticity parameter $\eta > 0.3$ (see Eq. (3.3) in Chapter 3). They observed the evaporation of buffer gas thermalized Cl$^-$ anions out of a multipole rf ion trap. Working at conditions where the
adiabatic approximation is not anymore fulfilled, energy was transferred from the rf field to the ion motion. This resulted in a more or less controllable temperature dependent loss of ions explained with a parameter called trap depth. The interplay between rf based heating and confining makes this definition rather questionable. A more suitable method for determining the actual height of the effective potential is based on the use of a dc difference applied between the rods (see Figs. 12 and 37 of Ref. 18). If one really intends to measure the ion temperature via an evaporation rate it is much better to use an axial electrostatic barriers mentioned above. As can be estimated from Fig. 6.6, this method can be calibrated with an accuracy better than 0.1 mV. The combination of buffer gas cooling and collision induced heating in an “unsafe” rf region is — most probably — not suited for quantitative measurements. For low temperature applications it is recommended...
to confine ions in a region where the adiabaticity parameter $\eta$ is smaller than 0.1.

### 6.2.6. Specific Instruments

Many applications prove that ion traps are versatile tools for preparing, confining, and cooling molecular ions. A selection of instruments and their applications in studying low energy collisions has been presented in Chapter 3. In specific experiments, e.g. in some of the Coulomb crystals, the ions are produced and characterized \emph{in situ} while in other instruments, the ion trap is integrated in a complex arrangement containing additional external ion sources, molecular beams and various detectors for ions and photons. In some applications, a low temperature ion trap is operated just as a source for cold ions. One example is the installation of a cryogenic 22-pole ion trap on a high-voltage platform for preparing cold $\text{H}_3^+$ and for injecting them with high kinetic energies into the Test Storage Ring.  

The excellent phase space of the cold ion cloud has allowed a transfer efficiency of almost 50% to be reached. Effects of molecular rotation and evidence for nuclear spin effects have been reported for dissociative recombination of this astrophysically important ion with electrons. In another experiment a 22-pole ion trap has been used in combination with an electrospray source for cooling and injecting bunches of protonated biomolecules into an electrostatic ion storage ring. There the time dependence of the fragmentation of protonated amino acids and peptides after absorption of a 266 nm photon has been measured. Another example of ion cooling in an rf trap is the photo detachment experiment mentioned in the Introduction to this chapter. In this instrument a Paul trap has been used successfully as a source for cold $\text{C}_{60}^-$ ions. As discussed above the favorable mass ratio between light buffer gas and heavy ions allows the use of such a trap. In general, however, a linear 2n-pole with $n > 2$ is better suited because the stability parameter $\eta$ is r-dependent, i.e., the adiabatic approximation becomes better if the ions get colder. In addition a linear electrode arrangement makes injection and extraction of ions much easier.

The first 22-pole trap based apparatus has been described in detail elsewhere. Most of the early applications concentrated on the study of low temperature ion-molecule reactions (see Chapter 3). Of course in all these applications it is mandatory to have control over, or to get information on, the actual temperature of the stored species. Especially flexible are methods based on laser induced processes as discussed above. Selected laser induced reaction (LIR) schemes which can been performed with trapping machines have been summarized recently by Schlemmer \emph{et al.} The sensitive method provides spectral information and rate coefficients for several competing
processes including reactions of the excited species, collisional relaxation, and radiative decay. Sophisticated LIR applications use today several pulsed gas inlets or pulsed effusive or supersonic beams (see Fig. 3.13 of Chapter 3). The first 22-pole trap based instrument for studying cold anions has been completed recently. As a first application, absolute photodetachment cross sections of cooled OH\(^-\) ions have been determined. As discussed in the results section below, variation of the temperature will provide state specific photodetachment cross sections.

Using a 22-pole trap and cryogenic cooling with helium gas, a special instrument has been developed in Basel for measuring electronic transitions to bound exited states for large cations of relevance to astrochemistry. For directly comparing electronic spectra with astronomical observations, it is mandatory in the case of large molecules to cool their vibrational and rotational temperatures to those found in the interstellar medium. Previous studies have employed pulsed molecular beam methods to produce cold polyatomic cations. While these methods have proven useful in rotationally cooling the created species, spectral congestion is still present due to the fact that vibrational modes are often not fully relaxed. First test measurements on N\(_2\)O\(^+\) have been mentioned above (see Fig. 6.4). Further applications of the new instrument are mentioned below. A general strategy of this instrument is to use two or multiple photon fragmentation for detecting the absorption of the first photon. A rather important observation made with this machine is, that polyatomic ions can become transparent to VUV radiation if they are cooled to low temperatures. This results in very low background two-color spectra since the VUV photon only leads to fragmentation if the first resonantly absorbed photon has heated the ion.

Another 22-pole based instrument recently became operational in Lausanne aimed at recording electronic and vibrational spectra of cold closed-shell biomolecular ions. Representative of such types of machines, Fig. 6.7 shows the Lausanne apparatus, a tandem quadrupole mass spectrometer the central element of which is the rf ion trap cooled to less than 10 K. The ions of interest are produced in the gas-phase by electrospray, mass-selected in a quadrupole, and then injected into the trap where they are cooled via collisions with cold helium. After irradiating the ions with IR and/or UV laser pulses, the content of the trap is ejected and sent through an analyzing quadrupole before being detected. Spectra are generated by monitoring the appearance of a particular fragment ion mass as a function of the laser wave number.

An ion trapping apparatus for sub-K cooling of ions is close to completion in Chemnitz. It is based on the simple idea to take for buffer gas cooling only the slow tail from a thermal beam of cold neutrals. The important parts of this instrument, which is based on the apparatus shown
Fig. 6.7. The Lausanne photofragment-spectrometer for measuring spectra of cold biomolecular ions as well as their clusters with solvent molecules.\textsuperscript{50} In the center of the tandem quadrupole mass spectrometer is a 22-pole ion trap which can be cooled to temperatures below 10 K. The ions of interest are produced by an electrospray source, mass-selected in a quadrupole, and then injected into the trap where they are cooled via collisions with cold helium. After irradiating the ions with IR and/or UV laser pulses, the contents of the trap are ejected and sent through an analyzing quadrupole before being detected. Spectra are generated by monitoring the appearance of a particular fragment ion mass as a function of the laser wave length.

in Fig. 3.15 of Chapter 3, are shown in Fig. 6.8. The ions are pre-cooled in the ion trap in the usual way, i.e., with a pulse of He buffer gas. A special cold head (Oerlikon Leybold 4.2 GM), in principle, allows temperatures as low as 3.5 K to be obtained; so far 5.8 K has been reached, indicating an overall heat load of 2 W. The very low temperature in the surrounding of the trap is also important for cryo-pumping and for reducing the blackbody radiation. Further cooling of stored ions is achieved in collisions with a pulsed beam of slow atoms ($^3$He, $^4$He, may be also H) or molecules (H$_2$, HD, D$_2$).

The construction of a special pulsed effusive beam source, which is based on a two-stage cryocooler (Sumitomo SRDK-101E-A11C), is indicated schematically on the left side of Fig. 6.8. An efficient method for getting a cold gas pulse is to evaporate adsorbed gas inside a cold tube with a short voltage pulse from a thin substrate that can be cooled down
Fig. 6.8. Ion trapping apparatus for sub-K cooling of ions. A pulsed, cold effusive beam is produced via desorption of helium, hydrogen, or deuterium from a cold 3.6–8 K surface. Using fast shutters with sub-ms switching time and operating at a repetition frequency of typically 100 Hz, only the slow part of the Maxwellian distribution is allowed to pass through the 22-pole trap. Large differential pumping capacity is provided using several turbomolecular pumps and efficient cryo-pumping. In addition it is planned to separate the various chambers with shutters operating synchronously.

to 3.5 K. Of basic importance for the method is the integration of UHV compatible fast shutters which are able to operate with ms (better sub-ms) switching time and at repetition frequencies of some hundred Hz. Magnetically driven shutters have been tested; however they are not yet fast and reliable enough. Other ideas to solve this technical problem are based on piezo actors. Rotating wheels or tuning fork choppers also can be used; however, they are less flexible. A special role has the shutter at the entrance of the ion trap. It is synchronized with the pulsed beam and delayed such that only the slow part of the Maxwellian distribution passes through the ion cloud. As indicated in Fig. 6.8 shutters are also used for improving the separation of the various vacuum chambers, which are differentially pumped by magnetically suspended turbo pumps and by cryopumping.

Although molecular beams are well-described in the literature, most applications concentrate on high Mach numbers and high densities and not so much on the slow velocity tail of an effusive beam. In order to test the idea, the beam source shown in Fig. 3.15 of Chapter 3 has been utilized in combination with a mechanical chopper and a universal detector. The arrangement, which has been optimized for forming a cold effusive beam of H atoms, is described in detail in Ref. 51. In Fig. 6.9 the measured time of flight distribution of an effusive D₂ beam, which has been produced with the accommodator set at 10 K, is compared with a 10 K Maxwell-Boltzmann distribution (solid line). The flight path was 37 cm. The differences at long flight times indicate that the long channel of the accommodator already leads to some acceleration of the slow D₂ molecules towards the mean velocity. Avoiding the long channel and restricting the gas flow to a few mbar l/s will lead to a rather unperturbed cold tail of an effusive beam.
Fig. 6.9. Measured time of flight distribution of an effusive beam of D$_2$ created with the apparatus shown in Fig. 3.15 of Chapter 3. The flight path was 37 cm. Comparison of the experimental distribution with a Maxwell-Boltzmann distribution (solid line) indicates that the long channel of the accommodator leads to some acceleration of the slow molecules towards the mean velocity.

Based on the geometry shown in Fig. 6.8 and assuming a source — trap distance of 23 cm, the resulting number densities have been estimated which can be reached in the trap with the cut-off beam. A typical result is shown in Fig. 6.10 for a 5 K He beam with a flow of 0.5 mbar l/s. Cutting away half of the beam leads already to a velocity distribution with a mean velocity corresponding to 1 K. The reduction of the time averaged number density due to the duty cycle (pulse length $<$ 1 ms, frequency typical 100 Hz) may require cooling times of several seconds, in specific cases minutes; however this is no problem with the rf trapping technique. One very important advantage of cooling ions in a linear rf multipole with a slow beam of neutrals is that the collisions are restricted to the nearly field free region of the trap.

6.3. Selected Results

6.3.1. Fine Structure Relaxation in Atomic Ions

One important question in many low energy collisions is the role of fine structure energy. It is therefore important to create ions in specific states
or to cool them from an initially high temperature population to a low temperature equilibrium. In the following, typical test procedures and some problems are discussed with reference to the two atoms Ar\(^+\) and N\(^+\).

Due to spin-orbit interaction the electronic ground state of Ar\(^+\) splits into two fine structure states, the \(^2\text{P}_3/2\) ground state and the 0.178 eV higher lying \(^2\text{P}_1/2\) state. In a fully thermalized ensemble already 99.95% of the ions are in the ground state at room temperature, while at 20 K the probability to find an ion in the excited state is not measurable (<10\(^{-45}\)). This simple two state system has been selected as an example to illustrate the method of buffer gas relaxation and for briefly mentioning the experimental method of chemically probing specific states of a trapped ensemble of ions with a pulsed supersonic beam of reactant gas. Here the fact is used that, in comparison to the ground state, charge transfer from H\(_2\) to Ar\(^+\) is significantly faster for the \(^2\text{P}_1/2\) excited state \((k_{1/2} \sim 7.5 \times k_{3/2}\) at a collision energy of 0.1 eV, see Ref. 52 for more details).

There have been many experimental studies on fine structure changing collisions with argon ions, most of which have been performed at collision energies high in comparison to the excitation energy of the \(^2\text{P}_1/2\) state. With the exception of the following unpublished data, which are from the PhD thesis of E. Hauffler\(^52\) there have been so far no experimental studies determining the fine structure relaxation

\[
\text{Ar}^+ (^2\text{P}_{1/2}) + \text{He} \rightarrow \text{Ar}^+ (^2\text{P}_{3/2}) + \text{He} \quad (6.3)
\]
at low temperatures. Figure 6.11 shows some typical data measured at 20 K with a 22-pole ion trap. The experimental set-up was similar to that shown in Fig. 3.13 of Chapter 3. Ar$^+$ ions have been created by bombardment of argon with energetic electrons in an external ion source. It is rather safe to assume that the two states have been initially populated with their statistical high temperature ratio $^2\text{P}_{1/2} : ^2\text{P}_{3/2} = 1 : 2$. These ions are injected into the trap containing He buffer gas at different number densities in the range of $10^{13}$ cm$^{-3}$ (see Fig. 6.11) and stored there for times varying between 0 and 4 s. After this time a pulse of hydrogen passes the ion cloud and a few H$_2^+$ ions are formed by electron transfer. The total number of H$_2^+$ products decreases as a function of time. Besides a minor loss of Ar$^+$ ions due to reactions with hydrogen background gas this is mainly due to fine structure relaxation, i.e., due to the lower reactivity of the Ar$^+ (^2\text{P}_{3/2})$ ground state ions.

The lines in Fig. 6.11 are fits accounting for the various competing mechanisms. A detailed analysis of the kinetic system reveals that the final experimental result, the relaxation rate coefficient $k^*$, is independent of the initial population and of the ratio of the two rate coefficients for charge
Fig. 6.12. Effective $\text{Ar}^+(2P_{1/2}) \rightarrow \text{Ar}^+(2P_{3/2})$ relaxation rate $k^*$, measured through the fine structure dependent $\text{Ar}^+ + \text{H}_2$ charge transfer for various He densities. The parameters of the linear fit are given in the text, for $[\text{He}] \rightarrow 0$ one obtains the radiative rate $k_r = 1/\tau_r = (0.06 \pm 0.04) \text{s}^{-1}$.

A collection of measured data is plotted in Fig. 6.12 as a function of the helium number density $[\text{He}]$. This dependence has been fitted with

$$k^* = k_{\text{rad}} + k_{\text{col}}[\text{He}].$$

(6.4)

It is obvious from the very small relaxation rate coefficient, $k_{\text{col}} = (3.6 \pm 0.8) \times 10^{-14} \text{cm}^3 \text{s}^{-1}$, that one has to take very large He densities for getting a thermalized sample of $\text{Ar}^+$ with He as buffer gas. The deduced radiative relaxation rate $k_{\text{rad}} = (0.06 \pm 0.04) \text{s}^{-1}$, corresponding to a radiative lifetime of 17 s, is in good agreement with a lifetime of 19.0 s calculated for the magnetic dipole transition.

A second example of fine structure relaxation at low temperatures is the three state system $\text{N}^+(3P_1)$. Here spin-orbit coupling leads to the three states $^3P_0$ (0 meV), $^3P_1$ (6.1 meV), $^3P_2$ (16.2 meV). The numbers in brackets give the excitation energy relative to the $^3P_0$ ground state. In the following the question is raised how one can prepare a nearly pure $\text{N}^+(^3P_0)$ ensemble in collision with He or $\text{H}_2$. Note that at 20 K an ensemble at equilibrium would still contain 8% of $^3P_1$. The experiment was based on the idea that hydrogen is an ideal quencher since the low temperature relaxation process

$$\text{N}^+(^3P_J)^+ + \text{H}_2 \rightarrow \text{N}^+(^3P_{J'})^+ + \text{H}_2$$

(6.5)
with $J' < J$ is supported by the weakly endothermic reaction

$$N(3P_J)^+ + H_2 \rightarrow NH^+ + H.$$  \hspace{1cm} (6.6)

Some remarks concerning the reaction of $N^+(3P_J)$ with $H_2$ have been made in Chapter 3, more details can be found in Ref. 53 and references therein. Using reaction rate coefficients from phase space theory in which it has been assumed that translation, rotation and fine structure energy are equivalent, the competition between reactions 6.5 and 6.6 has been modeled. A few examples are plotted in Fig. 4 of Ref. 53. For the unknown relaxation rate coefficients $k(3P_J \rightarrow 3P_{J-1}) = 10^{-n}$ cm$^3$/s has been assumed with $n = 9$, 10 or 11. None of the calculated curves could reproduce the data measured in a 22-pole trap.

Fig. 6.13 shows the decline of the relative $N^+$ intensity as a function of storage time due to the $NH^+$ formation. The measurements have been performed with $[n-H_2] = 3 \times 10^{12}$ cm$^{-3}$ at a trap temperature of 15 K. The $N^+$ ions, created externally by electron bombardment, must include species in excited states. Most probably one starts with the high temperature statistical population of the fine-structure states, i.e., $3P_0 : 3P_1 : 3P_2 = 1 : 3 : 5$. Simulations with different assumptions concerning relaxation show that the competition between relaxation and reaction of $N^+$ ions always leads to a curved decay of primary ions. The perfect mono-exponential decay, in Fig. 6.13 extending over four orders of magnitude, is a strong indication that all three $N^+$ fine structure states react with the same rate coefficient. This, on the other hand, impedes the observation of relaxation processes. Note that the rate coefficient, here $k = 5.0 \times 10^{-11}$ cm$^3$/s, strongly depends on the ortho — to para ratio of the hydrogen gas. For critical tests, experiments with state selectively prepared $N^+(3P)$ reactants are needed or another probing gas than hydrogen has to be found.

**6.3.2. Rotation of Diatomic Molecules**

One of the diatomic molecular ions very often used for testing low temperature environments is $N_2^+$, most probably because it can be easily probed via exciting the A state with cheap laser-diodes. This allows one to determine the rotational and translational temperature of stored $N_2^+$ ions with the method of laser induced charge transfer. The slightly endothermic (179 meV) charge transfer with Ar is used in the following way. In a first step photons induce the transition

$$N_2^+(X, v = 0) + h\nu \rightarrow N_2^+(A, v = 2).$$  \hspace{1cm} (6.7)

The excited ions undergo radiative decay within $\mu$s; however, due to the Franck-Condon-factors, the majority of the $N_2^+(X)$ formed is vibrationally
Fig. 6.13. Test measurement for preparing $\text{N}^+(3\text{P}_0)$ ground state ions via inelastic collisions (fine structure relaxation) or chemical quenching at 15 K in a 22-pole trap. $\text{N}^+(3\text{P}_1)$ ions which have been produced by electron bombardment with the high temperature population of the three fine structure states ($3\text{P}_0$; $3\text{P}_1$; $3\text{P}_2 = 1 : 3 : 5$) are stored in normal hydrogen at a number density of $3 \times 10^{12} \text{cm}^{-3}$. The mono-exponential decay over 4 orders of magnitude indicates that the reaction rate coefficient for forming $\text{NH}^+$ is independent on the fine-structure state. For more details see text, Chapter 3 and Ref. 53.

Excited. Therefore, the ions have sufficient internal energy to react with Ar via the charge transfer process

$$\text{N}_2^+(X, v > 0) + \text{Ar} \rightarrow \text{Ar}^+ + \text{N}_2. \quad (6.8)$$

Fig. 6.14 shows an early measurement of the translational temperature, derived from the Doppler profile, as a function of time after turning on the cold head.$^{39}$ The light source was a 10 mW single-mode cw laser-diode (Sharp LTO24 MDO, 783–787 nm). The line width was better than 250 MHz as determined with an etalon (free spectral range 2 GHz, finesse 200). This derived translational temperature is in good overall agreement with the
nominal temperature that has been measured with a thermistor directly at the cold head. The slight deviation can be partly explained by a temperature gradient caused by heat conduction or by uncertainties of the temperature calibration. Also rf heating of the ions may have been partly responsible for the deviation in this early experiment. Many more details including the determination of the rotational temperature of the stored ions can be found in the publication by Schlemmer et al.\textsuperscript{54}

Filling the trap with Ar target gas limits the temperature by the onset of condensation. At 35 K the vapor pressure of Ar is $10^{-4}$ mbar. One method for using reaction (6.8) for probing $N_2^+$ also at very low temperatures is to use a skimmed Ar beam instead of the effusive gas inlet. Although straightforward with a set-up such as shown in Fig. 3.13 of Chapter 3, corresponding experiments have not yet been reported. Another method is based on the use of He buffer gas and the formation of He--$N_2^+$, a weakly bound (12.5 meV) van der Waals cluster. Ionic clusters of nitrogen and helium have been investigated in detail by Bieske et al.\textsuperscript{55} For various clusters He\textsubscript{n}--$N_2^+$ spectra have been reported between 390 and 392 nm, very close to the $N_2^+$ (B$\leftarrow$X) band origin. The absorption of one of the near UV photon is detected via dissociation of the cluster ion. A third method to detect stored $N_2^+$ ions is LIF. There have been some successful activities; however, only large ensembles of $N_2^+$ ions have been seen via LIF.
So far there has been no experimental detection of a single molecular ion such as $\text{N}_2^+$ via LIF, although conservative estimates reveal that this should be possible with today’s techniques at a few K where only the ground rotational state is populated under thermal conditions. For efficient LIF-detection, the cycle (i) laser excitation, (ii) photon emission has to be closed with (iii) relaxation. This means, the multi-level system has to be coupled efficiently to a low temperature bath, the method of choice being He buffer gas at high densities. Such a single molecular ion experiment has a lot of interesting applications. For example the sequence excitation, fluorescence, and collisional relaxation can be followed time resolved. Other interesting applications are the observations of the formation of the He–$\text{N}_2^+$ cluster (reactive shelving) or the detection of the unlikely event that the homonuclear molecule changes its nuclear spin in a collision with He.

Cold, trapped HD$^+$-ions are ideal objects for direct spectroscopic tests of quantum-electrodynamics, relativistic corrections in molecules, or for determining fundamental constants such as the electron-proton mass ratio. It is also of interest for many applications since it has a dipole moment. The potential of localizing trapped ions in Coulomb crystals has been demonstrated recently with spectroscopic studies on HD$^+$ ions with sub-MHz accuracy.$^{10,56}$ The experiment has been performed with 150 HD$^+$ ions which have been stored in a linear rf quadrupole trap and sympathetically cooled by 2000 laser-cooled Be$^+$ ions. IR excitation of several rovibrational infrared transitions has been detected via selective photodissociation of the vibrationally excited ions. The resonant absorption of a 1.4 $\mu$m photon induces an overtone transition into the vibrational state $v = 4$. The population of the $v = 4$ state so formed is probed via dissociation of the ion with a 266 nm photon leading to a loss of the ions from the trap. Due to different Franck-Condon factors, the absorption of the UV photon from the $v = 4$ level is orders of magnitude larger than that from $v = 0$.

The relative accuracy of the transition frequencies, which can be achieved within a sympathetically cooled ensemble, is in principle better than with buffer gas cooled ions or with fast ion beams. Molecular dynamics simulations of the motion of the trapped HD$^+$ ions lead to an estimate of a Doppler broadening of only 10 MHz under ideal conditions, whereas a thermal 10 K ion ensemble leads to a Doppler width (FWHM) of 280 MHz. In reality the reported line broadening was 40 MHz indicating an effective temperature of 0.2 K.$^{56}$ Note that this temperature describes only the axial motion of the HD$^+$ ions, the radial motion does not lead to a first-order Doppler effect. The explanation given by the authors is based on a non-linear coupling between the axial and radial motion of the ions via Coulomb interaction. In a more detailed analysis, Koelemeij $et\ al.$$^{10}$ distinguish between translational (secular) temperature of 50 mK resulting
in 20 MHz Doppler broadening and an axial micro-motion caused by field
imperfections. In the case of HD⁺ cooled by ⁹Be⁺, the ions of interest are
confined close to the centerline of the linear trap because of their lower
mass. Nonetheless one has to be aware that, already 10 μm away from the
trap axis, the radial micro-motion energy corresponds to 0.5 K.

It can be foreseen that, in the near future, the method of sympathetic
cooling is going to lead to outstanding new measurements. For extending
the method several improvements are possible. In the HD⁺ example the
detection is based on a combination of mass-specific excitation and laser
based destructive of the ions. If one finds non-destructive detection schemes
it will become possible to work with a small number of ions arranged along
the axis of a linear multipole where the micro-motion is close to zero. A nice
example for permanent monitoring is the ²⁷Al⁺⁻⁹Be⁺ pair confined in a
linear Paul trap. An extension of the method towards larger ions and
spectroscopic applications will require the internal degrees of freedom of the
ions to be cooled. One obvious method is to transfer the linear multipole
trap into a cryogenic environment.

As third diatomic example, which illustrates the need for cooling ions,
as well as demonstrating the potential of low temperature ion traps, is
the negative ion OH⁻. The absolute cross section for the photodetachment
process

\[ \text{OH}^- + h\nu \rightarrow \text{OH} + e^-, \]

has been measured in the 22-pole based machine mentioned above at a
rotational and translational temperature of 170 K. This machine, which is
described in detail in Ref. 49, has been developed for investigating funda-
mental questions concerning negative ions, such as reaction rates or life-
times. As light source a He-Ne laser has been used. The photon energy
(1.96 eV) is sufficient to expel the electron from OH⁻ (electron affinity
1.8 V). Figure 6.15 shows the loss of OH⁻ ions with and without laser radi-
ation present. Absolute cross sections are obtained from the laser induced
decay constant. Using a tomography scan of the photodetachment laser
through the trapped ion cloud, the derived cross section is independent on
assumptions concerning the radial ion distribution and thus features a small
systematic uncertainty. The tomography also yields the column density of
the OH⁻ anions in the 22-pole ion trap in good agreement with the expected
trapping potential of a large field free region bound by steep potential walls.

Photodetachment of electrons from negative ions is a fundamental
destruction process in chemical environments such as the upper atmosphere
or interstellar space. In comparison with previous results, the measured
cross sections seems to indicate that the cross section is proportional to
(2J + 1), where J is the rotational quantum number of OH⁻. Since such
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6.3.3. Preparing Ultracold $H_3^+$

$H_3^+$ ions and deuterated variants play an important role in interstellar chemistry. Various aspects of the importance of these ions at low temperatures have been recently discussed by Oka, Gerlich et al., and Asvany et al. There are many motivations for studying this simplest triatomic ion at low temperatures including ultrahigh resolution spectroscopy, the role of nuclear spin in collisions, fermionic and bosonic behavior in chemical reactions, or the relevance of the ion for dense interstellar clouds.

One fundamental collision process is the interaction of $H_3^+$ with slow electrons. There have been several efforts in recent years to measure the dissociative recombination rate coefficients for state selected ions. One of the approaches, installed at the ion storage ring in Heidelberg (see above), is to
use a 22-pole trap in which the $\text{H}_3^+$ ions are relaxed at different temperatures before injection into the TSR, using either normal- or para-hydrogen or also helium. The diagnostic tools for extracting information about the state populations have been reviewed by Krekel et al. As can be seen in Fig. 6.16 there are only a few rotational states populated in $\text{H}_3^+$ at low temperatures. In order to determine their actual population the method of laser induced chemical probing has been used by Mikosch et al. The detection scheme is based on the reaction

$$\text{H}_3^+ + \text{Ar} \rightarrow \text{ArH}^+ + \text{H}_2$$

(6.10)

which is very slow for ions in the vibrational ground state since it is endothermic with $\Delta H_0 = 0.57 \text{eV}$. Laser excitation to the third vibrational bending level provides enough energy for reaction (6.10) to proceed. The used transitions are indicated in Fig. 6.16. As already mentioned above in the $\text{N}_2^+$ study, the use of argon for chemical probing limits the lowest temperature because of condensation. In the present case the trap was operated at 55 K. The absorption profiles, recorded as gain in $\text{ArH}^+$ as a function of the laser wavelength can be found in Fig. 3 of Ref. 41. The product signal count rate was typically 0.1 ions per trap filling.

From the so obtained spectra, the frequencies of the three transitions have been determined with experimental errors of only $\pm 0.017 \text{cm}^{-1}$, increasing the accuracy by about a factor of 4 in comparison with earlier results. The relative intensities and the widths of the three line profiles

![Energy levels of $\text{H}_3^+$ used for chemical probing.](image)

Fig. 6.16. Energy levels of $\text{H}_3^+$ used for chemical probing. The population of the three lowest rotational states of $\text{H}_3^+$ has been determined via overtone transitions to the third vibrational bending level $(0,3^1)$ followed by a chemical reaction with Ar. The states $(J, G) = (0, 0)$ and $(2,0)$ are forbidden.
provide three important experimental parameters, the translational temperature (170 K), the rotational temperature of the para-\( \text{H}_3^+ \) ensemble (150 K) and the ortho to para ratio (\( \sim 1:1 \)). The large Doppler widths of 470 MHz is unexpected. It leads to the conclusion that the ions have been heated by some of the effects mentioned above. In addition the rotational energy of o-H\(_2\) may play an important role in heating.\(^{38}\)

A very important process involving \( \text{H}_3^+ \) is the H-D exchange reaction

\[
\text{H}_3^+ + \text{HD} \leftrightarrow \text{H}_2\text{D}^+ + \text{H}_2. \tag{6.11}
\]

State specific rate coefficients in both directions are needed to fully understand the process of deuteration in low-temperature interstellar clouds. So far it is generally assumed that, at low temperatures, the rules of equilibrium thermodynamics adequately describe the outcome of a bimolecular proton-deuteron-exchange reaction. In a thermal equilibrium where all states are coupled efficiently enough, the equilibrium constant for reaction (6.11) is proportional to \( \exp(231.8\, K/T) \) (see Fig. 1 of Ref. 38). In reality, however, the actual equilibrium constants obtained in ion traps are orders of magnitude lower due to traces of o-H\(_2\). As discussed by Gerlich \textit{et al.},\(^{38}\) this is not so much caused by the average energy contributed by a few H\(_2\)(J = 1) molecules but more by nuclear spin restrictions which allow for accumulating non-thermal amounts of energy in the H\(_2\)D\(^+\) ions. In order to confirm these predictions, it is necessary to measure precisely the population of H\(_2\)D\(^+\) at very low temperatures and for very clean para-H\(_2\). One possible method is to induce reaction (6.11) in the backwards direction with a laser.

Recently the LIR-trapping machine in Köln\(^{48}\) has been used to make the first steps towards the determination of the state populations under the conditions described in the previous paragraph. Laser induced D-H exchange in collisions of H\(_2\)D\(^+\) and D\(_2\)H\(^+\) with H\(_2\) has been used to obtain high-resolution IR spectra.\(^{42}\) The nominal temperature was 17 K; however, as already discussed above, some unexplained heating effects lead to a translational temperature of 27 K. In addition just normal-hydrogen has been used. Despite these \textit{hot} conditions nice spectra could be recorded. In total, line positions of 27 new overtone and combination transitions have been detected. Comparison to high accuracy \textit{ab initio} calculations revealed some minor mode-dependent differences. As reported by Asvany \textit{et al.}\(^{42}\) populations have not yet been extracted from these measurements. Future activities in this direction must reach temperatures below 10 K, use pure para-H\(_2\), and test the influence of traces of ortho-H\(_2\). It may also be better to use a pulsed beam of Ar or O\(_2\) for \textit{in situ} probing of the state populations.

For studying nuclear spin restrictions in great detail and for obtaining a \( \text{H}_3^+ \) ion ensemble in a real thermal equilibrium, it is planned to use the
exchange reaction

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

(6.12)

for thermalization. At a temperature of 5 K the (1,1) ground state (see Fig. 6.16) is already populated with 99.7% probability; lowering the temperature to 4 K reduces the population of the competing \(22.9\text{ cm}^{-1}\) higher lying (1,0) state to \(5 \times 10^{-4}\). An instrument similar to that shown in Fig. 3.15 in Chapter 3 is going to be used for such studies, including measurements of rate coefficients for ortho-para transitions or reaction of \(\text{H}_3^+\) with \(\text{D}\).\(^{51}\)

A very cold H atom beam is prepared by operating the accommodator at the lowest temperature possible and using weak magnetic guiding fields for transferring slow hydrogen atoms into the 22-pole trap. Similar to Fig. 6.8 cryopumping removes efficiently warmer background gas. The ideal solution would be to trap cold H atoms in the region of the 22-pole trap. The idea of such a nested trap is not new and it is technically possible; however, it requires significant modifications of the trapping region. The use of superconducting electrodes for creating both the electric rf field and the magnetic field may allow a rather simple set-up to be constructed.

### 6.3.4. Electronic Spectra of Ions of Astrophysical Interest

A special ion trap based spectrometer for recording electronic spectra of large ions at low vibrational and rotational temperatures has been constructed in Basel.\(^{36}\) It has been described above together with first results, e.g. the single-photo-fragmentation of \(\text{N}_2\text{O}^+\) (see Fig. 6.4). These rotationally resolved spectra are demonstrating the power and the limits of such an instrument. A variety of additional interesting results have been reported recently.\(^{59-61}\) As an example, Fig. 6.17 shows in the upper part a spectrum of the 2,4-hexadiyne-cation isomer of \(\text{C}_6\text{H}_6^+\). As described in detail in Ref. 59, the ions were vibrationally and rotationally relaxed to around 30 K by collisions with cryogenically cooled helium in a 22-pole trap. The fragments are dominantly \(\text{C}_6\text{H}_5^+\) with minor amounts of \(\text{C}_6\text{H}_4^+\) and \(\text{C}_4\text{H}_4^+\). Measured breakdown curves show that the yield of these two ions remains constant, around 20% and 5%, respectively. Comparison of the spectrum recorded with cold ions with the room temperature spectrum reveals that the origin band at 486 nm becomes very narrow and that there is no evidence of hot bands in the upper spectrum. The analysis of the well resolved vibrational pattern and of the rotational K-structure indicates that the vibrational and rotational degrees of freedom are equilibrated to around 30 K.

Another application of the instrument in Basel has been to study for the first time electronic spectra of cold protonated polyacetylenes \(\text{HC}_2\text{H}_2^+\)
Fig. 6.17. One photon dissociation spectrum of the 2,4-hexadiyne-cation isomer of C₆H₆⁺ in the Basel 22-pole ion trap. In the upper panel, the vibrational and rotational degrees of freedom of the ions were cooled to ∼30 K in collisions with helium. Comparison with the 300 K spectrum (lower panel) reveals that the origin band at 486 nm becomes very narrow and that there is no evidence of hot bands. For more details see Ref. 59.

(n = 3, 4) in the gas phase. In this case, the detection of the spectra was based on photodissociation with two lasers. A tunable laser promotes the cold ions to an electronically excited state. A subsequent UV photon is then used to initiate fragmentation of the excited ions. For optimum signals the two laser beams must be overlapped both in time and space. Cooling dynamics of excited ions has been observed by varying the delay between the pump and the probe lasers while monitoring the intensity of the fragment ions. These protonated systems were chosen due to their astrophysical significance; however, no correspondence between experimental bands in the electronic spectra and features listed in the diffuse interstellar band (DIB) literature has been found.
In a recent paper, Dzhonson et al.\textsuperscript{61} have reported the gas-phase origin bands of different polyacetylene cation chains. Also in this application a two-color two-photon pump-probe scheme was applied to dissociate the polyatomic species in the low temperature ion trap. The observed bands are not rotationally resolved because the rotational constants vary from 0.15 cm\textsuperscript{-1} for HC\textsubscript{4}H\textsuperscript{+} to less than 0.01 cm\textsuperscript{-1} for species larger than HC\textsubscript{10}H\textsuperscript{+}. Figure 6.18 shows the rotational profile for the A\textsuperscript{2}Π\textsubscript{g}–X\textsuperscript{2}Π\textsubscript{u} transition of HC\textsubscript{6}H\textsuperscript{+}. The laser resolution was limited to 0.3 cm\textsuperscript{-1}. In addition, lifetime broadening might occur as a result of intramolecular processes. Simulating this spectrum with known spectroscopic constants and the laser line width led to the conclusion that the ions were cooled to 30 K. Interest in these species stems from the observation of hydrocarbons in combustion and interstellar environments. Since microwave spectra of these linear cations are not available due to their centrosymmetric nature, electronic spectroscopy offers a means of identification in diffuse clouds. Also for the polyacetylene cation chains no distinct matches between experimental and observed spectral features could be found.

### 6.3.5. Spectroscopy of Cold Biological Molecules

A very successful installation of a temperature variable 22-pole trap has been made in Lausanne for the investigation of biologically related...
molecules in the gas phase. It is important to study ionic species since biological molecules are charged in solution, and the presence of a nearby charge can strongly influence their photophysics. The aim, to use spectroscopic tools as a probe of the structure and dynamics of molecular architectures of biological interest, significantly profits from cooling the ions to very low temperatures. The instrument that is shown in Fig. 6.7 uses electrospray ionization (ESI) as a soft ionization technique to bring large thermally labile, bare molecular ions into the gas phase directly from solution. There is almost no limit to the size of molecules that can be transferred into the gas phase and stored in the trap. As a first demonstration of the potential of this innovative tool, cold protonated tyrosine, TyrH$^+$, and tryptophan, TrpH$^+$, have been studied by Boyarkin et al.$^{50}$

In Fig. 6.19 one can compare electronic photofragmentation spectra of TyrH$^+$ measured at room temperature (upper panel) and of ions stored in

![Image](image_url)

Fig. 6.19. Electronic spectra of room temperature and 6 K cold TyrH$^+$ measured in the Lausanne 22-pole ion spectrometer.$^{50}$ The lower spectrum shows only the small section indicated by the arrow in the upper part. The product fragment corresponding to m/z 136 u was monitored in each case.
a 22-pole ion trap, the walls of which have been cooled to 6 K. In both cases fragment ions with \( m/z = 136 u/e \) have been recorded as a function of the laser wavenumber. The absence of hot-bands in the lower electronic spectrum demonstrates that the trapped ions attain a vibrational temperature of \( \sim 10 \text{ K} \). Features in the spectra arising from distinct conformations of the molecules clearly appear. Using an IR-UV double-resonance technique different conformers have been identified via their vibrational spectra.

Fig. 6.20. Electronic photofragment action spectrum of protonated tryptophan with 0, 1, and 2 attached water molecules. The three spectra have been measured at 10 K using the Lausanne 22-pole ion spectrometer. The broad overall band observed for the bare, protonated tryptophan (top panel) becomes slightly narrower when one water molecule is added. Attaching a second one leads to sharp lines indicating a significant reduction of the decay rate of the excited state.
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The second example is tryptophan, which is widely used as a test case for protein structures and dynamics. Mercier et al.\textsuperscript{62} used the low temperature trap to cool TrpH\textsuperscript{+} to 10 K and to study its spectrum with a controlled number of water molecules. The results presented in Fig. 6.20 reveal a very surprising microsolvation effect for TrpH\textsuperscript{+}–(H\textsubscript{2}O)\textsubscript{n} going with \(n\) from 0 to 2. Even at low temperatures, the bare TrpH\textsuperscript{+} exhibits a broad electronic spectrum, implying ultrafast, nonradiative decay of the excited state. Comparison of the two upper spectra reveals that the band becomes slightly narrower when one water molecule is attached. The addition of a second water molecule apparently leads to a substantial lengthening of the excited state lifetime and a fully vibrationally resolved electronic spectrum is obtained. Quantum chemical calculations gave important hints as to how the interaction with the water molecules destabilizes the photodissociative states and increases the lifetime of the excited intermediate state.\textsuperscript{62}

6.4. Conclusions

There are many innovative ways to explore the fundamental principles that govern low temperature chemistry. This chapter has concentrated on ions. All the discussed experimental approaches to produce and to study cold molecular ions are based on trapping. It is obvious that the long storage times which can be achieved under extremely good vacuum conditions, allow for experiments with unprecedented sensitivity and accuracy. Besides ultrahigh resolution spectroscopy one can observe very rare processes such as radiative association, spin changing collisions or spontaneous isomerization. There are interesting applications of the trapped ions in quantum optics, frequency metrology and quantum information processing.

Some experimental strategies are based on permanent interrogation of one single ion, other technique use a small ensemble of ions to reduce space charge effects, while several new approaches are based on a strongly interacting plasma. Many interesting experiments have been made with sympathetic cooling and there are several proposals to use laser-based schemes for manipulating the population of the internal states.\textsuperscript{7} However, there is presently no general method to get really ultra-cold molecular ions for chemical applications, besides coupling to a low temperature black body radiation field. This is certainly sufficient for some applications, especially if one makes use of non-destructive detection schemes and extremely long storage times. For simple molecular systems such as HD\textsuperscript{+} or H\textsubscript{3}\textsuperscript{+} such a set-up will allow unique experiments, especially if one arranges these ions in a chain along the axis of a linear multipole. One fascinating possibility
for non-destructive detection of molecular ions is the application of an ion in the neighborhood. It can be foreseen that one finds a suitable atomic transition for distinguishing between a rotating or non-rotating polar ion in the neighborhood of the sensing ion.

Many remarks have been made in this chapter concerning the meaning of cold, ultracold, slow etc. It is by no means straightforward to define thermodynamic quantities such as temperature or equilibrium constant in a strongly correlated Coulomb system where the cooling ions heavily oscillate in space and spend quite some time in the electronically excited state. The concepts of temperature and equilibrium are not well defined in systems of particles that are confined by time-varying external forces. Indeed, the adiabatic approximation described in Chapter 3 helps to transfer such a system into a conservative one; however, there are limitations. Very serious, from a practical and technical point of view are the problems of parasitic heating of ions via “noise” and local deviations from an ideal equipotential surface imposed by the conductors the ion traps need. Working at low temperatures and introducing superconducting materials may reduce surface patch effects, will create less heat, and certainly can be used to improve the quality of the resonance circuit needed for the creation of the rf field. Simultaneously, parasitic oscillations can be reduced.

The methods described to obtain cold molecular ions are far from producing an ionic ensemble in the quantum degenerate regime. However, the spectra recently recorded for large molecules of biological and astrochemical relevance have shown that there is a lot to do between 300 and 10 K in order to learn more about their structure and dynamics. A “polyatomic” test case is the CH$_5^+$ ion which has been mentioned in the introduction. It is the mm-wave spectrum that will most directly provide the experimental information needed to understand the large amplitude motion of the molecule. Attempts to detect the $J = 1 \leftrightarrow 0$ spectrum which is predicted to be in the region 220–235 GHz. At 3 K already more than 99.5% are in the rotational ground state (mean rotational constant $B = 3.7 \text{cm}^{-1}$). Using a supersonic beam of methane, it may be possible to distinguish between different states via the large distance proton transfer reaction: $\text{CH}_4 + \text{CH}_5^+ (J, K) \rightarrow \text{CH}_4\text{H}^+ + \text{CH}_4$.

Finally the temperature regime below 1 K for ion chemistry is within our reach. Chopped very slow beams of non-reactive coolers appear particularly promising at the frontier of cooling of all degrees of freedom in the laboratory frame. Combination of ion trapping in high order rf fields with cold neutrals confined in magnetic fields are an ideal solution for specific experiments. Attractive, and technically possible, is the combination of a trap for H atoms with a multi-electrode rf trap; however, there have not yet been any attempts to deploy such an apparatus. The sub-K range
opens up many interesting experiments. One example is the formation and study of a deuterated variant of the H$_4^+$ ion confined in the shallow H$_3^+$–H van der Waals potential. Efficient buffer gas cooling may create ensembles of ions where a significant fraction is always in the ground state. With the sensitivity of modern GHz and THz techniques this may allow cold, well localized molecular ions, such as CO$^+$ or H$_3^+$, to be studied via absorption spectroscopy.

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