Buffer gas cooling of polyatomic ions in rf multi-electrode traps

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Cooling all degrees of freedom of a molecule, a cluster, or even a nanoparticle which is suspended in a vacuum, is an experimental challenge. Without suitable schemes, cold or ultracold chemical reactions are not feasible. Methods such as laser based preparation of very slow atoms, decelerating molecules to low velocities with electric fields or freezing molecular ions into Coulomb crystals, are generally not suitable to cool the vibrational or rotational motion of molecules. This contribution describes a new method in which a beam of slow atoms or molecules (H, He, H2, or D2) is used for cooling charged particles confined in a multi-electrode rf trap. For reaching sub-K temperatures, the fast part of a cold effusive beam is removed with a shutter before the slow remaining neutrals interact with the ion cloud. The development of a pulsed cold beam source is discussed as well as suitable methods for determining the ion temperature. A challenging application is to prepare internally cold CH5+ for spectroscopy or chemistry. New experimental results for hydrogen abstraction in collisions with slow H atoms are reported at energies of a few meV. For evaluating these measurements and for predicting effective rate coefficients at lower energies, the kinematic conditions of the slow neutral beam–ion trap arrangement have been analyzed in detail. The potential of cooling ions such as protonated methane or H3+ with slow energy selected H atoms is briefly mentioned. An interesting process is the formation of weakly bound ions such as H4+ or CH6+ via radiative or ternary association. Such ions are ideal candidates for preparing the corresponding collision complexes very close (μeV) to the dissociation continuum using infrared transitions.

1 Introduction

Several new instruments are currently emerging to study cold molecular ions and low-energy ion–molecule reactions. The majority of them are based on inhomogeneous rf fields either using 22-pole traps1,2,3,4 mounted onto a cold head or linear quadrupoles in combination with laser cooled atomic ions and sympathetically cooled molecular ions.5,6,7 The relevant methods have been summarized recently in the book, entitled Low temperatures and cold molecules.8 This interesting collection contains a variety of remarks concerning the meaning of cold, ultracold, slow etc. Generally accepted definitions of the temperature T such as “T is a measure of the average translational kinetic energy associated with the disordered microscopic motion of atoms and molecules” need to be reconsidered. In many innovative experiments the ensemble average is replaced by a time average. One also has to be aware that the language used in various subfields can lead to erroneous conclusions. For
example, laser cooled neutral atoms are really moving very slowly, *i.e.*, they are translationally ultracold, while the mK or μK ions in coulomb crystals oscillate in phase with the frequency of the storing rf field, usually with rather high kinetic energies. Another example is related to chemical reactions such as Ca\(^+\) + CH\(_3\)F → CaF\(^+\) + CH\(_3\), which has been studied with laser cooled Ca\(^+\) ions and a few K slow but internally 300 K hot neutrals.\(^7\) Since, especially at low collision energies, a collision complex usually utilizes the energy from all degrees of freedom, one should only call a bimolecular reaction *cold* if the *total energy* is a few meV or below. Another often overlooked fact is that the laser cooled ions or atoms spend quite some time in the electronically excited state. In order to differentiate between different aspects, it is useful to distinguish between *cold collisions*\(^9\) and the production and study of *cold molecules*.

The complexity of states and optical transitions does not allow one to directly laser cool molecules. One scheme used is laser stimulated association of two ultracold atoms. This is a very interesting process in itself; however, it is restricted to very few specific molecules. The effort to create these diatoms in the vibrational–rotational ground state is huge. Another strategy to produce ultracold neutral molecules is to slow them down in Stark decelerators.\(^11\) Although this method has become the subject of intense studies in recent years its applications are restricted to a small number of specific molecules. An advantage of the method is that the cold molecules are in selected states. In the case of molecular ions, a variety of single- and multiphotonization schemes has been developed to create them in specific states. Well-controlled but also complex is the creation of ground state ions using methods such as ZEKE (zero kinetic energy electrons), PFI (pulsed field ionization), or similar schemes. However, controlling the velocity of these ground state ions simultaneously is hard to achieve.

In this contribution to the Faraday Discussion on *Cold and Ultracold Molecules* we discuss recent progress in cooling polyatomic ions with buffer gas. For many years our main motivation was to investigate experimentally ion–molecule reactions relevant to interstellar chemistry as discussed several years ago\(^12\) and summarized recently.\(^9,13\) Therefore, most experiments have been performed at 10 K or above. However, the experimental scheme we use can be extended to relax ions to temperatures below 1 K, *i.e.*, to move towards the field of *ultracold ion chemistry*. The new method is based on the combination of ion trapping in suitable rf fields with very slow beams of neutrals.

### 2 Experimental

**High frequency multi electrode rf traps**

Since most methods of preparing cold molecules are rather inefficient, experimental studies usually rely on suitable traps where the slow objects can be collected and confined. Long storage times and a well-controlled environment provide ideal conditions for studying the trapped ensemble and its interaction with electromagnetic radiation, coolants, or reactants. For cooling ions and for studying low energy collisions it is necessary to understand the cooling process in detail and the impairment of the energy by the forces which are used for confinement. In general, random relaxation via multiple collisions works only in traps with real three-dimensional potential minima. Therefore, *dynamic* storage devices such as magnetic traps, where the Lorentz force plays a role, or electrostatic traps, in which centrifugal forces lead to quasi-periodic orbits, are not suitable for slowing particles down to zero velocity.

Our solution is based on rf ion traps with effective potential minima where the ions finally relax to. The method, which has been documented thoroughly in ref. 14 is based on inhomogeneous, electrical fields \(E_\text{in}(r,t)\), which vary in space and time. In most applications, the time dependence used is a harmonic oscillation with the frequency \(Ω\).
Although it seems to be contradictory to the aim of ion cooling, high frequency rf trapping makes use of iterative modulation of the kinetic energy. The success of our applications is to use, instead of quadrupoles, a wide nearly field free trapping volume created by multi-electrode arrangements such as a stack of rings or many parallel rods. In such structures the region where the kinetic energy is modulated, is very small. Of special importance for sub-K buffer gas cooling is the experimental fact that we use an atomic or molecular beam instead of filling the whole trap with neutrals. Restriction of the beam diameter passing through the ion cloud, already confines the relaxing collisions to regions of low field.

For semi-quantitative estimates of ion heating and cooling one can make use of the fact that the momentary energy never goes above 3 times the initial value and that, in time average, the energy is conserved. Mathematically, i.e., under ideal experimental boundary conditions, there is no limitation towards zero motion. In order to understand this, one can study numerically the equation of motion of a particle under the influence of such a field under inclusion of collisions.\textsuperscript{14} For heavy ions cooled with a light buffer gas it is sufficient to introduce a friction term. An analytical treatment of ion cooling in an rf field is based on the adiabatic approximation. As outlined in ref. 14 trapping ions without rf heating requires that the dimensionless parameter \( \eta \), defined by

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

must be very small in those regions where the ions are moving. If this condition is fulfilled, the time-averaged influence of the oscillatory force can be described by the effective potential

\[
V''(r) = \frac{q^2 E_0^2}{4m\Omega^2}.
\]

In these two equations \( m \) and \( q \) are the particles’ mass and charge, respectively. Usually it is sufficient, for practical applications, to postulate \( \eta < 0.3 \). For a mathematical treatment of ion cooling one makes use of the fact that, for many geometries, both \( V''(r) \) and \( \eta(r) \) are functions of the coordinate \( r \) and both go to 0 for \( |r| \rightarrow 0 \). In other words, the adiabatic approximation becomes better with decreasing kinetic energy \( E_k \). In the case of a linear multipole trap (2\( n \) pole) one can derive the relation

\[
\eta \sim E_k^{-(n-2)/(2n-2)}
\]

In practice, several technical problems restrict the efficiency of ion cooling in rf traps. One is due to so-called “patch effects”, i.e. potential distortions on the surfaces of electrodes. They can lead to local electrostatic fields, which pull slow ions into regions of strong rf fields. Superconducting electrodes may eliminate or reduce such surface effects. Another problem is caused by parasitic low frequency voltages, which can heat the motion of the ions. A high quality resonance circuit helps significantly to create a very pure sinusoidal field as described by eqn (1).

**Cooling in traps, buffer gas**

There are quite general schemes to cool a finite ensemble of charged particles in a trap. Examples include evaporation, optical pumping or chemically removing energetic ions. Interesting methods are resistive cooling or active-feedback cooling,\textsuperscript{15} which make use of the currents induced by the motions of the charges in suitable electrodes. If molecules are not exposed to any other interaction, long enough trapping finally equilibrates the internal excitation with the black body
radiation penetrating the ion cloud. Typical examples are the rotational temperature of polar molecules such as CH⁺ in dense interstellar clouds, which is given by the 2.7 K of the cosmic background radiation or the so-called ultracold HD⁺ ions in a Coulomb crystal which have a population of rotational states determined by the 300 K environment. This means that innovative instruments, which aim to reach temperatures of 1 K or below, either need an efficient cooling mechanism or the environment of the trap has to be operated at low enough temperatures.

Our strategy for contributing to the new interdisciplinary field of molecular matter at very low temperatures \( T < 1 \) K uses buffer gas cooling, i.e., elastic and inelastic collisions with very slow, velocity selected beams of non-reactive neutrals. It is based on the idea to take only the slow tail from a pulsed thermal beam of cold gas. Depending on the specific cross sections, collisions cool more or less all degrees of freedom efficiently, including complex ions. One of the restrictions of buffer gas cooling is that the ions must be capable of surviving multiple collisions. For example, clustering with the neutrals used for cooling should be avoided. In our experiment this process is significantly suppressed by operating at low enough densities that only radiative association plays a role. One favorable fact of cooling internal degrees of freedom of heavy ions (mass \( m_2 \)) via collisions with light buffer gas (\( m_1 \)) is that the internal temperature of the ions is determined by the collision temperature. Transformation into the center-of-mass system reveals that the ion motion contributes only with the fraction \( m_2/(m_1 + m_2) \). This means, for example, that very slow H atoms are well suited to get very cold CH₅⁺ (see below).

The CEB-22PT

The apparatus developed for sub-K cooling trapped ions with a beam of neutrals and for studying inelastic and reactive collisions is shown schematically in Fig. 1. The main parts (storage ion source, mass filter, temperature variable ion trap, and external detector) are standard and have been described in detail elsewhere (see ref. 9,10 and references therein). Briefly, externally created ions are injected into the 22PT via the electrostatic quadrupole bender (QP). There they are confined in a cylindrical volume (~8 mm diameter, 25 mm length) by the effective potential (eqn 3) and small dc voltages applied to the entrance and exit electrodes. Voltages of some 10 mV are sufficient for closing the trap if the ions are cold. For mass

![Fig. 1 Schematic diagram of the Cold Effusive Beam 22-Pole Trap Apparatus (CEB-22PT). This instrument has been developed for exposing trapped ions to an effusive beam of very slow atoms or molecules (H, He, H₂ or D₂). Primary ions are produced in a storage ion source (not shown), mass filtered, and injected into the ion trap via an electrostatic quadrupole bender (QP). For analysis, the ions are extracted, mass analyzed in a quadrupole mass spectrometer (QPMS) and detected. Large differential pumping capacity is provided using several turbomolecular pumps and a specially designed cryopump. For reaching the sub-K range, the neutral beam is pulsed such that only the slow part of the Maxwellian distribution is allowed to pass through the 22-pole trap. Hydrogen atoms are velocity selected using the transmission features of magnetic fields.](image-url)
analysis and detection, the ions are extracted (QPMS). A first description of this beam-trap arrangement and some preliminary results have been reported in ref. 16. Additional information and temperature dependent rate coefficients (above 10 K) for the interaction of cold CO$_2^+$ ions with slow hydrogen molecules and atoms can be found in ref. 17. More details concerning the preparation of a beam of cold H-atoms and their reactions with trapped hydrocarbon ions are published in ref. 18.

In this contribution, we discuss special features and modifications of this instrument needed for cooling trapped ions to sub-K temperatures. One module which is still under development is a special beam source for creating a cold effusive beam. As shown in Fig. 2, it is composed of a copper cylinder mounted onto a cryocooler (Sumitomo SRDK-101E). For producing a continuous beam, the inner cylinder is operated at such a temperature that the vapor pressure of the gas (usually He or H$_2$) is still high enough for getting a sufficiently dense cold effusive beam penetrating the trapped ion cloud. For producing intense cold gas pulses, the inner cylinder is operated at the lowest temperature (3.6 K) and the helium or hydrogen gas condenses on the walls. A short voltage pulse is used for locally raising the temperature of a thin substrate evaporating some gas (see left side in Fig. 2). Since this process takes place inside the cold tube, evaporation and cryopumping leads to a well directed pulsed beam emerging from the exit hole and to a very low overall gas consumption and gas load. For reducing the “temperature” of the gas pulse, time of flight selection is used, i.e., the fast part of the effusive beam is rejected and only the very slow neutrals are allowed to enter the trap. For this a fast UHV compatible shutter is needed, which is capable of being operated with ms switching time and at repetition frequencies of hundreds of Hz. Presently we perform tests with a rotating wheel and a tuning fork chopper.

Although molecular beams are well-described in the literature, most applications concentrate on high Mach numbers and high densities and almost nothing can be found on the slow velocity tail of an effusive beam. In order to test the idea, velocity

![Fig. 2](image)

**Fig. 2** Source for forming cold effusive beams (CEB) of helium or hydrogen molecules. The inner cylinder which is mounted on a cold head (SRDK-101E, lowest temperature 3.6 K) is operated at a temperature where the vapor pressure is sufficiently high that enough gas flows through the exit hole (2–5 mm). Alternatively, tests are underway to work at lower temperatures and to use a heating pulse for evaporating a short gas pulse on the left side of the cylinder. Cryopumping and an adequate temperature gradient for gas recycling significantly reduces the background gas load.
and density distributions of He atoms and D₂ molecules emerging from the source have been determined using time of flight measurements. A chopper wheel with 2 slits (2 mm wide) interrupts the beam on a 37 mm radius. For a chopping frequency of 200 Hz, one gets a time resolution of $\approx 20 \mu s$. The neutrals are detected at the location of the ion trap using an electron bombardment ionizer. The flight path is 37.5 cm. The data shown in Fig. 3 have been recorded at $T_{\text{CEB}} = 4.3 \text{ K}$ for He atoms. Comparison with a Maxwell–Boltzmann distribution, calculated for an effusive beam with $T_{\text{MB}} = 4.2 \text{ K}$, reveals good overall agreement. Cutting off the first half of the beam intensity, leads to a velocity distribution the mean velocity of which already corresponds to 1 K.

Using a calibrated ionizer, such measurements show in accordance with theoretical estimates that one can reach time averaged number densities of sub-K atoms of some $10^8 \text{ cm}^{-3}$ for the geometry shown in Fig. 1. Such densities require cooling times of several seconds, in specific cases several minutes. In principle, this is no problem with the rf trapping technique; however, one has to make sure that the background pressure in the trap is sufficiently low. In order to achieve this, a special cryopump has been constructed which is shown in Fig. 1. It consists of a 15 cm long porous carbon tube mounted onto a cold head (Sumitomo SRDK-101E, reaching 3.6 K). The geometry has been chosen such that only the directed beam coming from the beam source can pass this region without hitting the cold surface. In addition it is planned to use shutters on the differential wall for improving the separation of the vacuum chambers. Most important is finally to operate the ion trap itself at such low temperatures that the surrounding box adsorbs all gas with high efficiency, of course with the exception of the directed beam, which passes the ion cloud without hitting a surface. Presently, the ion trap is mounted onto a cold head which reaches only 10 K (Leybold RGD 210).

We are also exploring the possibility of using velocity selected hydrogen atoms not only for studying chemical reactions but also for cooling trapped ions. With the
setup shown in Fig. 1, mean H-atom number densities of some $10^9$ cm$^{-3}$ have been reached at 50 K. Fig. 4 shows a few velocity distributions measured for a beam of D atoms recorded at different temperatures of the accommodator. As explained elsewhere, the distributions are structured due to the transmission properties of the two guiding hexapole magnets used in this experiment. With this arrangement, the highest transmission obtained for D (and also H) atoms was at a kinetic energy of $(8.2 \pm 3.3)$ meV. Cooling the accommodator to 10 K leads to a beam in which the 3.6 meV part dominates with a half width smaller than 1 meV. Additional peaks appear at 1.5 and 1 meV. Comparison with the 10 K Maxwell–Boltzmann distributions (dashed line) reveals that weaker magnets should be used for favoring 1 meV atoms or slower ones. For velocity selection, it is also conceivable to change to other geometries such as deflecting magnets.

In order to test the cooling efficiency of the cold effusive beam and for determining the actual energy content (“temperature”) of the trapped ensemble, several methods are under development. Rather direct “thermometers” are based on in situ determination of rotational populations and translational distributions (Doppler profile). Related tests have been performed with diatomic ions such as the homonuclear N$_2^+$. Infrared active ions such as CH$^+$ and CO$^+$ are also interesting. N$_2^+$ is an ideal candidate because it can be excited with cheap but narrow bandwidth laser-diodes. Photoabsorption is detected via the slightly endothermic (179 meV) laser induced charge transfer N$_2^+$ + Ar $\rightarrow$ Ar$^+$ + N$_2$. So far this process has been used successfully by filling the ion trap with some Ar target gas; however, due to condensation, this limits the temperature range to above 35 K. In order to apply the method at lower temperatures, a skimmed Ar beam has to be integrated into the machine. Corresponding tests are ongoing; however,
operating two beams, one for cooling and the other one for chemical probing, has not yet been achieved.

Other methods for probing the temperature of an ultracold ion ensemble are based on the temperature dependence of collision processes such as weakly endothermic reactions (see below) or radiative association. One strategy is to follow the production of He–N₂⁺, a well-studied, weakly bound (12.5 meV) van der Waals molecule. If they are formed in sufficient numbers (conversion of a few %) laser induced fragmentation of the van der Waals bond can be used to determine rotational temperatures. Completely new methods are to combine sub-K trapping with the sensitivity of modern GHz and THz techniques. Ideal test cases are rotational transitions in cold molecular ions such as CO⁺, deuterated variants of H₃⁺, or CH₅⁺. These ions may be studied via suitable reactions or even via absorption spectroscopy.

**Kinematics**

In order to assess the capabilities and limitations of the present arrangement for cooling ions in elastic or inelastic collisions to temperatures below 1 K or for studying reactive collisions at total energies of a few meV or below, a detailed analysis of kinematic averaging is required. Some special aspects, e.g. how to reach very low relative velocities and how to cool efficiently the internal energy of molecular ions, have been discussed recently in ref. 9 and 10 respectively. Averaging over quantities like velocity or angular spread of the colliding partners is a quite general problem in gas phase experiments and many investigations have been devoted to such problems; however, the combination of ion traps and a molecular beam needs some special attention. An example is an experiment reported recently. In this arrangement, ions, confined in a Coulomb crystal, collide with a slow beam of neutrals. For large crystals, the collision energy distribution is dominated by the oscillatory motion of the ions imposed by the rf field. For ions sitting close to the center line of the trap, the distribution of the collision energy has to be calculated by integration over the velocity distributions of both reactants.

The situation in an ion trap is well-defined if the stored ions and the neutral reactants are in thermal equilibrium with the surrounding walls at a common temperature Tₑₑ. Adding non-reactive buffer gas for cooling does not change the situation as long as the densities are low enough to make ternary processes very scarce. In this case one extracts reaction rate coefficients from the measured temporal change of the number of ions, N₁(t) by fitting the parameters of an appropriate rate equation system. In the case of a simple two-channel process, the decay of the number of primary ions is described by

\[ \dot{N}_1 = \frac{dN_1}{dt} = -k n_2 N_1 \]  

where \( n_2 \) is the number density of the neutrals and \( k = k(T_{2\text{KPT}}) \) is the thermal rate coefficient (by definition). \( N_1(t) \) decreases exponentially with the time constant \( \tau = (k n_2)^{-1} \), while the number of product ions, \( N_2(t) \), augments complementarily. For slow reactions or low number densities (i.e., \( t \ll \tau \)), the linear approximation \( N_2 = N_1(0) \tau / \tau \) is often sufficient.

The situation is more complicated if one performs experiments with a beam–beam, beam–gas cell or beam ion–cloud arrangement. For deriving the relationships between measured quantities and rate coefficients (or cross sections), one usually starts with the ideal case of two well-collimated monochromatic beams with velocities \( v_1 \) and \( v_2 \), interacting in a scattering volume \( dt \). The number of products (or collisions) per unit time is given by

\[ d\dot{N}_2 = g \sigma(g) n_1 n_2 d\tau \]
Here \( g = |\mathbf{v}_1 - \mathbf{v}_2| \) is the relative velocity, \( n_1 \) and \( n_2 \) are the projectile and target densities, respectively. \( \sigma(g) \) is the elementary (or intrinsic) integral cross section. The corresponding elementary rate coefficient is obviously given by

\[
    k = g \sigma(g).
\]

In contrast to the ideal case, the conditions of a realistic experiment are less well defined. Therefore, the product rate actually obtained, \( d\tilde{N}_2 \), is an average over the velocity distributions of the reactants. Instead of eqn 6 one obtains the six-dimensional integral

\[
    d\tilde{N}_2 = \int_{v_1} dv_1 \int_{v_2} dv_2 \, g \sigma(g) n_1(r, v_1) n_2(r, v_2) d\tau \tag{8}
\]

Assuming that the velocity distributions are independent of the spatial coordinate \( r \), the density functions \( n_i(r, v_i) \) can be factored using normalized probability functions \( f_i(v_i) \) (\( i = 1, 2 \))

\[
    n_i(r, v_i) = n_i(r) f_i(v_i)
\]

With \( f_i(v_i) \) and \( f_2(v_2) \) we define \( f(g) \), the distribution of the relative velocity,

\[
    f(g) \, dg = \int_{v_1} dv_1 \int_{v_2} dv_2 \, f_1(v_1) f_2(v_2). \tag{10}
\]

The asterisk indicates symbolically that the integration must be restricted to that subspace \( (v_1, v_2) \) where \( |v_1/C_0 v_2| \leq [g, g + dg] \). \( f(g) \, dg \) denotes the probability that the relative velocity lies in the interval \([g, g + dg] \). With the mean relative velocity, given by

\[
    \langle g \rangle = \int_0^\infty g f(g) \, dg \tag{11}
\]

we define the effective cross section and the effective rate coefficient as

\[
    \sigma_{\text{eff}}(\langle g \rangle) = \int_0^\infty \frac{g}{\langle g \rangle} \sigma(g) f(g) \, dg, \tag{12}
\]

\[
    k_{\text{eff}} = \int_0^\infty g \sigma(g) f(g) \, dg. \tag{13}
\]

With this, we obtain a result that is very similar to eqn (8),

\[
    d\tilde{N}_2 = \langle g \rangle \sigma_{\text{eff}}(\langle g \rangle) n_1(r) n_2(r) d\tau \tag{14}
\]

For evaluating specific experimental results, the velocity and spatial distributions functions must be known. For the present experiment, we assume here for simplicity that the beam of hydrogen atoms is mono-energetic and that the ions are thermalized to the temperature of the trap. For this situation, eqn 10 can be evaluated analytically, resulting in the generalized Maxwell–Boltzmann distribution.\(^{14,21}\)

\[
    f(g) = \left( \frac{m_2}{2\pi k T_2} \right)^{1/2} \frac{g}{v_1} \exp \left( - \frac{m_2}{2k T_2} (g - v_1)^2 \right) - \exp \left( - \frac{m_2}{2k T_2} (g + v_1)^2 \right). \tag{15}
\]

In order to be consistent with the literature, we have used in this formula \( v_1 \) for the laboratory velocity of the H atoms and \( T_2 \) and \( m_2 \) for the ions, which play the role of
the target in this treatment. An approximation for the half width (FWHM) of this distribution is

$$\Delta E = \sqrt{11.1 \frac{m_1}{m_2} \frac{E_1 kT_2}{m_1}};$$

where $m_1$ and $E_1$ are the mass and the laboratory energy of the H atoms, respectively. The following example illustrates the importance of this result. For the H + CH₅⁺ system at $T_2 = 10$ K and $E_1 = 3.6$ meV, one obtains $\Delta E = 1.4$ meV, while the half width of the H atom peak (see Fig. 7) is only 0.75 meV. At low H atom velocities, the generalized Maxwell–Boltzmann distribution approaches a normal Maxwellian $f_M(g; T_C)$ with a reduced temperature $T_C = m_1/(m_1 + m_2) T_2$. This has the interesting consequence that, in the case of H + CH₅⁺, one can reach sub-K collision temperatures with 10 K ions, provided the H-atom beam is slow enough.

Inspection of Fig. 4 reveals that our H-atom beam is not yet ideal and the assumption of a mono-energetic beam cannot be made. Therefore, further analysis requires to integrate the generalized Maxwell–Boltzmann distribution numerically over the velocity distribution of the H atom beam. An analytical approximation, describing the hydrogen atoms with the three Gaussians leads to rather good results.

3 Results

Preparing cold ions via photoionization

Photoionization has become a widely used technique for the preparation of state selected ions in the study of ion–molecule reactions in the gas phase. We have tested a variety of schemes to prepare internally cold and state selected ions. An example is the special photoionization source for mass-, energy-, and state-selected ions.

![Fig. 5](image-url)  
**Fig. 5** Multi- or multiple photoionization of acetylene for producing cold C₂H₂⁺ ions. The laser has been scanned in the wavelength region where the energy of three photons is equal to the ionization potential of C₂H₂⁺. It has been operated with 1 mJ per pulse corresponding to $2.5 \times 10^8$ W cm⁻². The upper scale indicates the maximum possible internal energy of the product ion, if one assumes absorption of three photons. Using chemical probing, the internal excitation has been determined at the wavelengths marked with arrows.
described in ref. 24. Low temperature applications of state-selective preparation of diatomic ions via resonance enhanced multi-photon ionization have been summarized recently. Another laser based strategy for getting ions in specific states is to use optical pumping schemes, e.g. to remove ions in unwanted states from the trap by using selective photo-fragmentation. In a well-isolated finite ensemble of trapped ions, this process (hole burning) can be used to tailor the population.

One of our attempts at creating a cold ensemble of C₂H₂⁺ ions via 3-photon ionization is shown in Fig. 5. The ionization energy (IP) of acetylene is 11.40 eV. Ionization with three photons of the same wavelength is energetically possible below 326.15 nm. As can be seen, the ion signal increases significantly above the threshold for 3-photon ionization. Energy conservation leads to a maximal internal energy of a few meV (see upper scale) provided no additional photon is absorbed. In this energy range no resonance enhanced multiphoton ionization has been observed. An investigation of the dependence of the ion intensity on the laser power did not show a significant change from below and above threshold, where 4 or 3 photons are needed, respectively. Most probably, there are some near resonant or predissociating states involved.

In order to get information on the internal energy of the product ions, chemical probing with H₂ has been used. As shown in Fig. 3.23 of ref. 9, the reaction C₂H₂⁺ + H₂ → C₂H₃⁺ + H strongly depends on the ion temperature. The rate coefficient with the ions produced at 326.3 nm (see arrow, four photons are needed for ionization) indicates a significant internal energy. For evaluating the reactivity of the ion ensemble at 325.8 nm (left arrow), it is assumed that the number of ions, created via 4-photon processes does not change in this range (extrapolated dotted line). The number of C₂H₃⁺ product ions revealed that, within statistical error, all products come from this part. So most probably the additional ions created just above the threshold, are internally cold; however, the multi photon scheme is not very useful since the portion of exited ions (~18%) is too large for most applications. A general conclusion from our photoionization studies is, that in almost all cases, collisional thermalization is superior if one works with traps.

CH₅⁺, a polyatomic test case

One of our motivations to develop new cooling methods and to extend our energy range towards the sub-meV range is the interesting cation CH₅⁺ and its interaction with H atoms. Many high quality calculations have shown in recent years (see ref. 25 and references therein) that the potential energy surface of protonated methane is very flat near the various minima. 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 to very low temperatures. This ion has been formed and cooled in a supersonic jet and high-resolution absorption spectra 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 CH₅⁺. 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 far from being sufficient to predict high resolution rotational transitions of CH₅⁺ with the accuracy required for detecting this important ion in space.

One possible strategy to get more direct spectral information on the CH₅⁺ ground state is to detect the J = 1 ← J = 0 absorption spectrum, which is predicted to be in the 220–235 GHz region. Spectra in the mm-wave range will contain a lot of information on the large amplitude motion of the H atoms. One possible basis for such an experiment is to cool the ions to a few K. This can be achieved in the present experiment using the continuous or pulsed beam of He. Another very attractive method is to use a slow beam of H-atoms. The scheme is illustrated in Fig. 6, which shows a part of the potential energy surface relevant for H–CH₅⁺ collisions. The data
Based on these results, the reaction

\[ \text{CH}_5^+ + \text{H} \rightarrow \text{CH}_4^+ + \text{H}_2 \]  

(17)

is 12.7 ± 5.2 kJ mol\(^{-1}\) endothermic at 0 K. As a consequence, there should be no competition between inelastic cooling with slow H atoms and the hydrogen abstraction reaction, provided one starts with cold enough ions. However, first experimental studies performed with the ion trapping apparatus, resulted in rate coefficients for the reaction CH\(_5^+ + \text{H} \rightarrow \text{CH}_4^+ + \text{H}_2\) that are only weakly dependent on \(T_{22\text{PT}}\), i.e., on the internal excitation of the ions. The ions are cooled in more than 10\(^4\) collisions with He buffer gas. Lowering \(T_{\text{ACC}}\) from 92 K (open circles) to 12 K (filled circles) leads to smaller rate coefficients; however, the observed reactivity is not at all in accordance with the known energetics (see Fig. 6). The solid lines are the result of a detailed analysis of the data, using an analytical ansatz for the rate coefficient and accounting for the kinematic broadening. The dashed lines are predictions from the model assuming a monoenergetic beam of H atoms with the indicated kinetic energies \(E_{\text{H}}\).
coefficients which are in contradiction to this.\textsuperscript{16} In these studies, the ions have been pre-cooled with an intense pulse of He to the temperature of the walls surrounding the trap, 10 K. These results ($T_{ACC} = 92$ K) are shown together with new measurements ($T_{ACC} = 12$ K) in Fig. 7. It is obvious that the reaction rate decreases if one uses slower H atoms; however, the measured data are in contradiction to the calculated endothermicity.

In order to account for the kinematic conditions, the data have been evaluated using the measured velocity distributions shown in Fig. 4 and accounting in detail for the thermal motion of the ions as discussed above. Some assumptions have been made concerning the elementary rate coefficients in order to calculate the effective rate coefficients from eqn (13). The threshold for reaction (17) has been used as a free parameter, $E_0$. Various assumptions have been made concerning the influence of the internal excitation of the CH$_5^+$ ions. After several tests, the experimental results have been reproduced successfully using the following \textit{ansatz} for the elementary rate coefficient
\begin{equation}
k(E_t) = k_0 ((1 - E_0/(E_t + \alpha kT_{22PT}))^{0.3}. \end{equation}

$E_t$ is the translational energy of the relative motion. The internal energy of the stored ions is described just by the temperature $T_{22PT}$. The factor $\alpha$ weights the internal energy of the CH$_5^+$ ion relative to the translational energy in helping to overcome the endothermicity. In a more sophisticated evaluation, and if more data are available, we will start with elementary state to state rate coefficients $k_{i\ell} = g\sigma_{i\ell}(g)$, accounting at least for the rotational population. Fitting the experimental data (solid lines in Fig. 7) results in a very low value for the threshold, $E_0 = 3.5 \pm 0.1$ meV. This is in obvious contradiction to the established energetics of reaction (17). Very surprising is also the fact, that internal energy is very inefficient, which can be seen from the value $\alpha = 0.1 \pm 0.1$. The scaling factor $k_0 = (3.2 \pm 0.2) \times 10^{-11}$ cm$^3$ s$^{-1}$ is not so critical and has been adjusted for overall agreement. An obvious conclusion from these results is that we need colder H atoms in order to really probe the threshold onset of reaction (17). Predictions for monoenergetic H atom beams with 1, 2, or 3 meV are shown in Fig. 7 as dashed lines. In principle the preparation of a colder beam of H-atoms by operating the accommodator at the limit of H-atom condensation and by using a weaker hexapole magnet is straightforward. First velocity distributions of a thermal 8 K H-atom beam have been obtained recently.

Although very high number densities of He buffer gas have been used (1.5 $\times$ 10$^{13}$ cm$^{-3}$) and storage times up to 1 s, we cannot completely exclude the possibility that there are some metastable excited ions in the trap which react. Therefore, new measurements will use higher He number densities and extend the storage time up to 100 s. This would also allow us to remove possible exited ions chemically towards CH$_4^+$ + H$_2$. For such studies and for cooling CH$_5^+$ directly with H atoms, our corrected potential (guessed, thin line in Fig. 6) has several attractive features. For example, it would allow us to synthesize cold CH$_5^+$ ions just by a collision of cold CH$_4^+$ with H$_2$. The very small exoergicity will result in a cold ensemble of CH$_5^+$ since the internally exited ions react away to CH$_4^+$. Even more attractive is the possibility that rotationally exited CH$_5^+$ ions react faster with H atoms than non-rotating ions. Such behavior would allow us to record directly rotational spectra by using cold H atoms not only as cooling atoms but also for chemical probing.

In addition to the methane cation\textsuperscript{29} and the protonated methane\textsuperscript{30} the CH$_6^+$ collision complex belongs to the class of fluxional molecules. Its synthesis \textit{via} radiative or ternary association followed by collisional cooling is also within the reach of the present experiment. Threshold IR photofragmentation of this ion is a real challenge for preparing the ultracold CH$_5^+$ + H collision complex (or also CH$_4^+$ + H$_2$) in the vicinity of the dissociation limit. Finally there are many possibilities to perform experiments with partial deuteration or with the bosonic system CD$_5^+$ + D.
Ultracold $\text{H}_3^+$ and $\text{H}_4^+$

$\text{H}_3^+$ ions and deuterated variants play an important role in interstellar chemistry. Various aspects of the importance of these ions at low temperatures have been discussed recently.$^{3,31,32}$ 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 deuterated ion for dense interstellar clouds.

Very challenging are studies of the ultracold $\text{H}_4^+$ ion or the collision complex with various H–D ratios. The relevant potential energy surface is shown schematically in Fig. 8. The indicated energies (well depth and barrier height) have been taken from ref. 33. For studying the cold $\text{H}_4^+$ ion itself in more detail, the potential energy surface needs to be known with spectroscopic accuracy, a challenge for quantum chemistry. For predicting ortho–para transitions in $\text{H–H}$ exchange or deuteration in $\text{H–D}$ exchange, the energies in the vicinity of the $\text{H}_4^+$ transition state need to be characterized with very high accuracy, a challenge for quantum chemistry.

![Diagram](image)

**Fig. 8** Schematic illustration of the $\text{H}_4^+$ potential energy surface in the $\text{H}_3^+ + \text{H}$ region. The indicated well depth and the barrier height have been taken from ref. 33. The much higher lying $\text{H}_2^+ + \text{H}_2$ part (not shown here) is well characterized; however, in order to understand scrambling in low energy $\text{H}_3^+ + \text{H}$ collisions such as ortho–para transitions or $\text{H–D}$ exchange in partly deuterated combinations, the energies in the vicinity of the $\text{H}_3\text{D}^+$ transition state need to be characterized with very high accuracy, a challenge for quantum chemistry.

One of the present projects with the cold H-atom beam is to obtain an ensemble of $\text{H}_3^+$ ions in a real thermal equilibrium via a sequence of exchange reactions

$$\text{H}_3^+ + \text{H} \leftrightarrow \text{H}_3^+ + \text{H}. \quad (19)$$

Already at a temperature of 5 K, the (1,1) ground state of $\text{H}_3^+$ (see Fig. 2 of ref. 32) would be populated with a probability of 99.7%. Lowering the temperature to 4 K reduces the population of the competing, 22.9 cm$^{-1}$ higher lying (1,0) state to $5 \times 10^{-5}$. However, nuclear spin restrictions and traces of ortho-$\text{H}_2$ make it very hard to get to these limits with cold molecular hydrogen as buffer gas. Collisions with He do not change the total nuclear spin. Therefore reaction (19) is used for cooling $\text{H}_3^+$. The actual state population can be determined using laser probing as already shown in previous experiments.$^{34,35}$ Such detailed experiments will allow us to study
the influence of nuclear spin restrictions in great detail. Looking at the barrier, it may take many collisions to really get into thermal equilibrium with the cold H-atom beam. It is an interesting question whether the lifetimes of the collision complex become long enough at low energies that tunneling leads to full scrambling.

4 Conclusions

For many years, and many applications, buffer gas cooling in rf traps has been based on cryogenically cooling the trap and the surrounding walls. In order to overcome the limitation imposed by condensation of neutral species, our trapping method has now been combined successfully with cold effusive beams. First tests with a 4.3 K He beam have been performed. The temperature regime below 1 K for ion chemistry is within our reach. Chopped very slow beams of He as coolant appear particularly promising at the frontier of cooling all degrees of freedom in the laboratory frame. Another interesting method is based on slow H-atoms. Attractive and technically possible is the combination of our ion traps with a trap for ultracold H atoms; however, there has not yet been any attempt to develop such an instrument. The use of superconducting electrodes for creating both the rf and the magnetic field may allow one to construct a rather simple setup. As already mentioned above, the use of superconducting materials can also reduce potential distortions on surfaces. It certainly will create less heat and improve the quality of the resonance circuit needed for getting an rf field without parasitic oscillations.

An alternative strategy in ultracold ion chemistry which has gained a lot of attention in the last decade, is to work with Coulomb crystals in rf ion traps. Especially attractive are linear strings of ions localized along the axis of a linear multipole trap. For working with cold molecular ions the process of sympathetic cooling is of significant importance. In addition one has to use specific methods such as photoionization for preparing internally cold or state selected ions. A unique feature of this method is that single specific ions can be addressed and manipulated in the crystalline arrangements.

All these methods are still far from producing an ionic ensemble in the quantum degenerate regime. However, many recent results, such as spectra for large molecules of biological and astrochemical relevance or the examples discussed in this contribution, show that there is a lot to do between room temperature and the sub-K regime. Applying, in addition to buffer gas cooling, optical manipulation and detection schemes to the stored molecular ions will allow us to make unique contributions to the emerging field of cold and maybe also ultracold chemistry.

References


