The role of fine structure, rotational and zero point energy in slow collisions

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Abstract

In the physics and chemistry of cold interstellar gas **low lying fine structure and rotational states** as well as small **differences in zero point energies** caused by isotopic substitution play a key role. Often the coupling between these degrees of freedom via radiation and collisions is not efficient enough to thermally populate all these states during the evolution of interstellar matter. Examples include the ortho-H_2/para-H_2 ratio, the cooling via C^+ emission or the abundance of H_2D^+. In this project a 22pole ion trap (AB-22PT) is used to measure detailed ***state-specific* rate coefficients** for those ion-molecule reactions which influence the energy balance at kinetic temperatures between 10 and 300 K. Using REMPI schemes, optical pumping, chemical or physical quenching, or other suitable methods, specific ensembles of ions such as $N^+(^3P_j)$, $C^+(^2P_j)$, $CO^+(v=0,J)$, N_2^+, H_3^+, $C_2H_2^+$, and $C_3H_3^+$ will be prepared. As reactant gases p-H_2, n-H_2, and HD will be used, later also atomic targets (H, C, N, O) or molecules containing ^{13}C and ^{18}O.

Current Status of the Field

What makes the interstellar medium and its chemistry so special are the extreme conditions, i.e. **low temperatures** (10 K in dense molecular clouds) and **low densities** ($< 10^7$ cm^{-3}) of atomic and molecular species. The chemical networks of such clouds are vastly different from other regions because even small barriers or endothermicities as well as small excitation energies can change the outcome of such reactions in dramatic ways. As indicated in section 2.1 infrared emission from excited fine structure states of O and C^+ and rotational states of CO and, may be, also H_2, is the dominant cooling process of cold atomic and molecular gases. However, it is not known how fast the upper states are actually repopulated and whether the competition between heating and cooling processes really leads to a thermal equilibration of all degrees of freedom. In order to predict this balance with realistic models, state specific low temperature cross sections for a variety of inelastic and reactive collision processes are urgently needed. As also discussed in 2.1, an especially interesting sub-field of low energy (meV) collision dynamics is the process of isotopic fractionation. The enrichment D vs. H in molecules which is due to differences in zero point energies, is a complicated chemical process which is not at all understood with the required accuracy.

It is clear that special experimental techniques are necessary to study such systems under conditions relevant for interstellar conditions. The state of the art experimental techniques to investigate ion-molecule reactions in general have been explained in section 2.2.4. In the following we want to concentrate on the needs and recent developments which have been made with respect to the production of cold **state-selected ions** and neutrals

In most ion experiments the reactants are created simply by electron bombardment. Depending on the electron energy, this produces ions in many excited states (electronic states including fine structure, vibration, rotation). Since the degree of excitation depends on the time between creation and interrogation (e.g., spectroscopy, collision with a target or interstellar reaction), one way to get relaxed ions lies in the use of storage devices. In storage rings one usually waits for seconds (Amitay *et al.* 1999). In high pressure storage ion sources and rf-traps (Gerlich 1992a), ions may undergo enough collisions in order to relax all (!) internal degrees of freedom. The aim is that one reaches finally a thermal distribution, the temperature of which is defined by the walls or by the buffer gas. Another specific way of preparing cold ions is the use of supersonic expansion beam sources (i.e. corona discharges). It could be concluded from this short overview, that **creation of ground state ions** is simple; however, experience shows that quenching of very long lived states (e.g. excited fine structure) is not easy to achieve and to control.

Internal excitation (vibration, rotation) of the neutral collision partner needs to be controlled too in up-to-date experiments. H_2 is the most abundant molecule in space and therefore the dominant species in laboratory studies as well. Due to the very large spacing of the vibration as well as the rotation at low temperatures (10 K) only the lowest rotational states (J=0,1) are populated. Due to the different symmetry of the two nuclear spin species ortho-hydrogen (o-H_2, J=1,3,.) can not be relaxed to para-hydrogen (p-H_2, J=0,2,.) under normal conditions. It has been shown in many low temperature reaction experiments with hydrogen that the admixture of J=1 leads to drastically different results. Therefore it is necessary to **convert ortho into para hydrogen** using a gas inlet with a paramagnetic catalyst held at low temperatures. By varying the temperature of the converter the admixture of ortho hydrogen can be adjusted and the role of rotational energy can be studied.

One very well defined way to produce **state-selected ions** is multiphoton ionization (MPI) (for a review see (Anderson 1992)). With multiphoton excitation through various intermediate states it is possible to “tune” the ionization in order to produce state selected ions. A powerful feature of the resonantly enhanced multiphoton state selection (REMPI) is the ability to produce small polyatomic ions with controlled excitation in different vibrational modes. To date MPI has been successfully used in several groups for the production of rare gas atomic ions, diatomic ions, as well as for small polyatomic ions; however, according to our knowledge it has not yet been used to form atomic ions in selected fine structure states, e.g., N^+ and C^+.

Selective spin orbit effects have been demonstrated for the reactions of Br ($^2P_{3/2}$, $^2P_{1/2}$) with IBr (Haugen *et al.* 1985) and Al($^2P_{1/2}$, $^2P_{3/2}$) with O_2 (Chen *et al.* 1995) and Ar (LePicard *et al.* 1998). Very recently detailed experiments on nonadiabatic transitions in Na ($^2P_{3/2}$, $^2P_{1/2}$) in collisions with rare gases have been performed (Grosser *et al.* 1999). In case of ionic species $N^+(^3P_{0,1,2}) + H_2$ (Tosi *et al.* 1994) and Ar^+ ($^2P_{1/2}$, $^2P_{3/2}$) + O_2, N_2, H_2, have been investigated (Schweizer *et al.* 1994). In the latter case the charge transfer channel to form H_2^+ shows the strongest dependence on the fine structure state: at small collision energies, excited Ar^+ ions react an order of magnitude times faster than ground state ions. This strong fine structure dependence can be turned into an experimental tool, i.e., chemical probing. Some of the mentioned examples may not be of direct relevance for the astrophysical applications; however, the fundamental understanding of the involved non-adiabatic transitions at low temperatures is very important for predicting the efficiency of fine structure changing collisions.

In the case of photoionization one always has the problem that one works only with propensity rules. The best (especially in the case of preparing fine structure states) is to rely on resonant transitions to autoionizing states. This should be possible using a high resolution diode laser for the last excitation step.

An alternative route to vibrational and rotational state selection is the preparation of internally cold ions, e.g. ion formation in storage ion sources, which in a second step are laser excited by an IR photon. For a finite ensemble of molecular ions this leads to a selective preparation of the ground state species. Details are given in the subsequent section.

There are many other methods to modify the sample of stored ions in order to get information on the role of internal degrees of freedom. If FS transitions are optically allowed, **optical pumping** with circularly polarized light can be used to influence the fine structure population, one example being Rb. In order to change HFS states also radio- or microwave transitions may be used for inducing or impeding state specific reactions. As a non-radiative method charge transfer with a beam of spin polarized atoms has been used successfully in the sixties to prepare nonthermal samples of ions (Schuessler *et al.* 1969). Another very general method for state preparation is **chemical quenching**. Here the addition of a reactive buffer gas leads to a rapid disappearance of reactants in metastable excited states. The same technique can also be used for a selective detection of reaction products, i.e. **chemical probing**.

Own Contributions

In this section we discuss several recent studies of our group where state selection has played a role. In most of the experiments described in the following, trapping of ions in a low temperature environment is the fundamental experimental technique (Gerlich and Horning 1992, Gerlich 1993, Gerlich 1994). Since this method is well established and sufficiently documented in the literature (Gerlich 1992a), here emphasis is put on the special techniques involved to prepare the ions in selected states. Although we divide in the following the considered mechanisms into rotation, zero point energy and fine structure, one has to be aware of the fact that in most experiments a complex interplay between all states is involved.

Rotation

- $N_2^+ + Ar$

A system for which we demonstrated how state selection by optical pumping leads to detailed knowledge of the reaction dynamics is the charge transfer reaction (CT) $N_2^+ + Ar \rightarrow Ar^+ + N_2$ (Schlemmer *et al.* 1999). Due to a slight difference in ionization energy (endothermicity of the CT) for N_2 and Ar, the reaction $N_2^+ + Ar \rightarrow Ar^+ + N_2$ has a very small rate coefficient for ground state N_2^+. However it is well known that vibrationally excited N_2^+ (v>0) reacts in nearly every collision. In our low temperature trap experiment (TV-22PT) we used a diode laser for the excitation of the electronic state (X(v=0,J”)→A(v=0,J’)) with subsequent fluorescence back into the electronic ground state to prepare N_2^+ (v>0) which then reacts rapidly to Ar^+. As a first result we obtained action spectra of N_2^+ (v=0,J”) with Ar^+ as a monitor. The spectra are fully resolved with respect to the internal degrees of freedom of N_2^+: rotation, fine-structure (FS), and nuclear spin (HFS). This is on one side an example how the very sensitive technique of ***chemical probing*** can be used for spectroscopy, on the other side this experiment also indicates the power of our trapping method to extract information on state specific collisions.

More important than the spectral information is the fact that the process of laser preparation is the starting point of a complex kinetics of this seemingly simple system: N_2^+ + Ar. The primary elementary steps are laser excitation of a particular state, radiative decay of the excited states and reaction of the vibrationally excited species. The secondary processes are dealing with inelastic collisions of the ground state N_2^+. Relaxation of rotation, fine structure (FS) and hyper-fine structure (HFS) are involved. In our experiment we could determine quantitative rates and rate coefficients for all processes. For the primary steps our results are in good agreement with previous works. The trap experiment allowed for the first time to determine such data for the secondary steps too. It turned out that all three degrees of freedom are relaxing very slowly. One could have expected that for FS and HFS. However, a **slow rotational relaxation** comes as a surprise. It is a common believe that at temperatures (or collision energies) much lower than the binding energy of a stable molecule, $(ArN_2)^+$ in this case, a long lived $(Ar\text{-}N_2)^{*+}$ collision complex is formed in which energy is partitioned among rotation, vibration and translation according to the available phase space of the reaction products. This usually implies a very rapid rotational relaxation in almost every single collision. On the contrary we find that as many as 50 collisions are necessary for this process. Our study of this system shows how laser induced reaction serves as a tool for unraveling the elementary steps of a reaction system as well as classifying rate coefficients with respect to the role of different energy forms available.

- $C_2H_2^+ + H_2$

As a second system along these lines we studied the reaction $C_2H_2^+ + H_2$, which is of importance for the formation of small hydrocarbons in dense molecular clouds. This work is funded by the DFG-SPP: *star formation*. At the low temperatures and densities of the ISM and in the trap it undergoes solely **radiative association** to form $C_2H_4^+$ (Gerlich and Horning 1992, Sorgenfrei 1994). $C_2H_4^+$ is a strongly bound molecule and $C_2H_2^+ + H_2$ is thus also thought to form a long lived $(C_2H_2 - H_2)^+$ complex. The rate coefficient for radiative association should therefore be governed by the lifetime of this complex. This has been confirmed by a comparison of the experimental data with the results of phase space calculations. The experiments have been performed with p-H_2 , which at T = 10 K is in the rotational ground state (J=0), and n-H_2, which is a mixture of 25 % of p-H_2 (J=0) and 75 % of o-H_2 (J=1). In the latter case a reduction of the reaction rate has been observed which could be explained by the reduced lifetime of the complex due to the additional rotational energy of the H_2 target. In fact a comparison with the phase space results shows that rotational energy is equivalent to translational energy in this reaction. Again state-selectivity revealed interesting insight into the details of an important astrochemical reaction mechanism.

Recently we extended these studies and employed the method of laser induced reaction to improve our knowledge about the system (Schlemmer 1999a). This time we used ro-vibrational excitation of the $C_2H_2^+$ in order to prepare the reactants. The additional energy of one quanta in the asymmetric C-H stretching mode is sufficient to overcome the endothermicity of the bimolecular reaction $C_2H_2^+ + H_2 \rightarrow C_2H_3^+ + H$. Therefore the appearance of $C_2H_3^+$ products serves as a monitor for the laser excitation, another example for chemical probing. This gave us the possibility to obtain an almost background free spectrum of the asymmetric C-H stretching mode of $C_2H_2^+$. The sensitivity of the method is given by the number of stored primary ions. A S/N ratio of better than 10 has be achieved so far with only 1000 $C_2H_2^+$ per wavelength step.

As in the case of the N_2^+ + Ar charge transfer, the spectroscopic part of this work is not directly correlated to astrochemistry. However, the secondary chemical and physical processes, following the specific depopulation of $C_2H_2^+$ rotational states, contain a lot of information on low temperature collision dynamics. First results indicate that rotational energy seems to hinder the reaction $C_2H_2^+ + H_2 \rightarrow C_2H_3^+ + H$. From a detailed analysis of data taken at low hydrogen densities we expect to extract state specific rate coefficients for the radiative association $C_2H_2^+ + H_2 \rightarrow C_2H_4^+ + h\nu$. Finally, also for this reaction the $C_2H_3^+$ production rate is expected to be fine structure dependent and compete with fine structure relaxation. Following in detail the kinetics under various trapping conditions will allow us to learn more about collision processes under interstellar conditions.

Fine Structure (FS)

- Ar^+ $(^2P_{1/2} \rightarrow {}^2P_{3/2})$

The versatility of our trapping technique has been demonstrated in a study of the relaxation of the fine structure of Ar^+ $(^2P_{1/2} \rightarrow {}^2P_{3/2})$ (Haufler *et al.* 2000). In this experiment (no laser!), Ar^+ ions from a storage source are injected into a 22pole trap at a temperature of 10 K. As a monitor of the FS-population we used the state specific reaction $Ar^+ + H_2 \rightarrow H_2^+ + Ar$ which has a 8 (±1.5) times larger rate coefficient for the excited parent ion.

This reaction may be taken as an example for the power of ***chemical probing***; however it also indicates the possibility to prepare ions in defined fine structure states utilizing the method of chemical quenching. Due to the transverse arrangement of the trap the trapping volume could be intersected with a pulsed molecular beam of H_2 (AB-22PT: (Schlemmer 1998)). By varying the time delay between the injection of Ar^+ and the monitor pulse of H_2, the temporal evolution of the $^2P_{1/2}/^2P_{3/2}$ ratio could be inferred. ***Collisional quenching*** of the $^2P_{1/2}$ state has been studied with He as a target gas. For this model system we find a rate coefficient of $(3.6\pm0.8)\times10^{-14}$ cm^3/s. Extrapolating the rates of $^2P_{1/2} \rightarrow {}^2P_{3/2}$ conversion at the zero pressure limit (p_{He} = 0 mbar) we find a **radiative lifetime** of about 17 seconds, a value which is in accordance with theoretical predictions. This measurement demonstrates the possibility and sensitivity of our experiments in determining lifetimes which are long from a point of view of laboratory techniques. More important for the present proposal is the fact that in our experiment we can measure rate coefficients for fine structure relaxation. Note that the exothermic process $Ar^+ (^2P_{1/2}) + He \rightarrow Ar^+ (^2P_{3/2}) + He + E_{kin}$ is extremely slow, the electronic structure of the ion is changed only in one out of 10^5 collisions.

- $N^+ + H_2$

A reaction system which is relevant for the **formation of ammonia** in interstellar clouds is $N^+ + H_2 \rightarrow NH^+ + H$. This reaction is the first of a chain of H-atom abstraction reactions which finally leads to NH_3 via dissociative electron ion recombination of NH_4^+. These reactions have been investigated at low temperatures by the CRESU technique (Marquette *et al.* 1988) and later in more detail in a concerted effort involving a crossed beam, a merged beam apparatus and a 22 pole trap experiment (Tosi *et al.* 1994 and Gerlich 1988). Variation of the temperature of the hydrogen/deuterium beam in the crossed beam experiment operated as a tool to change the rotational temperature of the neutral reactant. As a result it turned out rotational energy is equivalent to translational energy for driving the reaction. This effect was also found when using n-H_2 and p-H_2 in our trap experiment.

In the trap study (TV-22PT) also first hints to the role of fine structure energy were obtained. Since N^+ ions have been created by electron bombardment, it is safe to assume that the fine structure states $^3P_0$, $^3P_1$, and $^3P_2$ are populated statistically (high temperature limit 1, 3, and 5, respectively). After injection in the trap this distribution has to relax to the 15 K environment by inelastic collisions with cold gas or by radiation. If, however, hydrogen is present, fine structure relaxation competes with reaction. Two extreme assumptions can be made: (1) Assuming that fine structure energy is equivalent to rotation and translation, statistical calculations (Gerlich 1988) predict that excited $N^+(^3P_2)$ or $N^+(^3P_1)$ react much faster than the $N^+(^3P_0)$ ground state. For the temporal evolution of the initially injected parent ions this means that according to the FS-population there should be a rapid decrease following the injection of the ions which slows down when all the excited species have reacted. (2) Assuming, on the other extreme, that the energy of the excited FS-states cannot contribute at all to the reaction, all ions react with the same rate. As an experimental fact it is found that the parent ions disappear more or less with a mono exponential decay indicating a common rate coefficient of 3.8×10^{-11} cm^3/s. Note, however, that this result can also be explained with the assumption that only one of the FS states is reactive. In order to solve this problem, state-specific experiments are needed.

The use of p-H_2 enabled us then to measure the threshold behavior of the integral cross section. An analysis based on phase space theory reveals an activation energy for the endothermic $N^+ (^3P_0) + H_2(j=0) \rightarrow NH^+ + H$ reaction of 11 meV and 29 meV for $N^+ (^3P_0) + D_2(j=0) \rightarrow ND^+ + D$. On the one hand this investigation shows how detailed results can be obtained using the guiding and trapping fields to confine charged particles. On the other hand it demonstrates how complex the interpretation of the data can be with only three states and two competing channels (here reaction and relaxation) involved. It is obvious that the matter becomes simpler when only one state can be selected by laser methods rather than by an ensemble characterized by a thermal distribution.

Zero Point Energy

In cold environments where vibrations are relaxed to their ground state the difference in zero point energy for different isotopic variants plays an important role. In particular large differences in binding energies occur in deuteron-proton substitution which leads to the enrichment of deuterated species in the astrophysical environment. This process, called **isotopic fractionation**, has been verified by astrophysical detection of deuterated molecules. For example, the observed DCO^+/HCO^+ abundance ratios are between 100 and 1000 times larger than the overall D/H ratio (Walmsley 1999). However, quantitative evaluations require a detailed knowledge of the chemical processes, which are needed to substitute isotopes in molecules. It is often overseen that in chemical reactions where identical atoms are substituted by distinguishable isotopes symmetry selection rules may have a significant effect on the outcome. Also the o-H_2/p-H_2 ratio has a not yet fully understood influence on this chemical equilibrium. In most of our experiments with hydrogen, a D – H substitution has been observed.

Some quantitative analysis has been made in the case of the $C_2H_2^+ + H_2$ reaction in order to distinguish between $C_2H_3^+$ and C_2HD^+ ions (Gerlich and Horning 1992). Other examples include the very basic reaction $H^+ + H_2$ in various isotopic combinations or the deuteration of hydrogen clusters (Paul *et al.* 1996, Paul *et al.* 1995). Here we only briefly mention a particularly interesting case, the collision system $C_3H^+ + H_2$ (Sorgenfrei and Gerlich 1994).

- $C_3H^+ + H_2$

For this reaction and its isotopic variant $C_3H^+ + D_2$ it has been found that radiative association as well as bimolecular reaction to form $C_3H_2^+ + H$ is occurring at a very small rate. A barrier in the entrance channel has been inferred from these results. In addition extremely long complex life times have been found. A possible candidate for this intermediate being a H_2CCCH chain structure. A strong influence for isotopic variants of this reaction has been found which indicates that the barrier for the reaction with deuterium is considerably larger. Due to the measured branching ratios for radiative association compared to reaction it has also been concluded that the exit barrier in the $C_3H_2^+ + H$ channel is smaller in collisions with D_2.

As mentioned earlier it is obvious that in complex situations such as in the last considered reaction the influence of all three forms of energy has to be taken into account. In order to extract the influence of ZPE in future experiments it will also be necessary to use rotationally state selected deuterium targets, i.e. o-D_2.

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Goals

It is the aim of this experimental project, to contribute to the understanding of physical and chemical collision processes which are (or are thought) to be important for the **thermal balance** of cold interstellar environments and which are urgently needed to **understand and evaluate** new observations, e.g. from ISO. From the point of view of energetics, mainly low lying states are involved. This means that our experiments have to study fine structure transitions, excitation of low rotational states and the influence of or slight differences in zero point energies at collision temperatures of 10 K and above. Typical open questions we want to answer are:

- **Population of IR emitting states**. We want to find out whether reactive or inelastic collisions at meV collision energies are fast enough to refill atomic or molecular states which have been depopulated by radiation. In the center of interest are N^+, C^+, H_2, CO.
- **Isotopic enrichment.** It is an open question whether isotopic fractionation actually results in an isotopic ratio, which is expected at the ambient low temperature from thermodynamical statistics. Special attention will be given to the influence of symmetry selection rules, nuclear spin constraints, and to the influence of a non-thermal ortho-para ratio. Systems of interest: H_2D^+, $C_3H_2D^+$, and other hydrocarbons.
- **State specific reaction dynamics at low temperature.** The fundamental goal of our activities is to understand reaction dynamics at low energies from first principles. In order to get more insight into non-adiabatic transitions we study processes such as Ar^+ + He, H_2^+ + H, and other ion molecule reactions. The role of rotational energy will be examined in collisions with state-selected ions such as CO^+, N_2^+, H_3^+, $C_2H_2^+$, and $C_3H_3^+$

In order to achieve these scientific goals, a variety of established experimental methods are available in our laboratory:

- **Temperature Variable Multipole Trap.** Despite the fact that meanwhile our low temperature 22pole trapping apparatus has reached a very high technical standard, we want to further develop this machine (AB-22PT) such that it becomes more and more an analytical tool. For future experiments we want this tool to become mobile such that a trapping experiment can be connected to immobile external light sources (IR-XUV, see also collaborations 3.7.3.).

- **Single beam experiments:** Some collision experiments will be performed in the cold environment of a single supersonic beam (REMPI).

In addition it is also a goal of this project, to improve the methods and to develop new schemes, especially for state-selective ion production:

- **Control of state distribution** of a stored ion cloud using chemical or physical quenching, optical pumping, and other suitable methods. A truly new opportunity for state preparation (pumping of fine structure or rotational states) arose since the advent of the free electron laser. Ways of use of this device in connection with trap experiments are under current discussion in a close cooperation with the group of Gerard Meier.
- **State-selective preparation of ions** using various one- or two-color REMPI schemes. Chemical ways for the production of state-specific atomic ions such as C^+ and N^+ involving chemical quenching will also be considered.
- As **target molecules,** mainly p-H_2, n-H_2, HD and D_2, and CO will be used (a para hydrogen generator is available). Other isotopes include molecules containing ^{13}C and ^{18}O, and may be also ^3H. Due to the importance of **atomic targets** (H, C, N, O), we will develop in cooperation with TP5 and TP7 efficient atomic beam sources. They can also be used as precursors for producing ions in selected fine structure states.

In the following we discuss in more detail some of the reactions which will be studied in this project:

Fine-Structure Energy

The reason that only a few results are available for fine structure selected species is the experimental difficulty of their preparation. Therefore one of the main experimental (technical) aims of this project is the preparation of atomic ions in a defined fine structure state. In general these ions are produced via REMPI excitation.

- $Ar^+(^2P_{1/2}, {}^2P_{3/2}) + H_2$

Ar^+ is an example that has been studied in our group before using REMPI. It has the great advantage that the atomic precursor is readily available. It is therefore a very good test case for all other studies. Results can be compared to the previous results in the guided-ion-beam apparatus (GIB), where only higher collision energies could be considered and also to earlier trap experiments where collisional quenching with He has been observed.

- $N^+(^3P_{0,1,2}) + H_2$

One of the tentative explanations for the observed abundance of ammonia in dense interstellar clouds is based on a chain of H-atom abstraction reactions (see section current status of the field). The $N^+ + H_2$ reaction is the first step in this chain and therefore very important in the ISM environment. It has been studied quite extensively by others and our group. N atoms can be produced (dissociated from N_2) in the same discharge source which will be used for the H atom production (see **TP5**). Possible REMPI schemes, especially from the $^4S^0$ ground state involve a 3+2 or 3+1 transitions in N at wavelengths around 360 nm which are accessible with the available laser system. In this way we plan to prepare **fine structure state selected N^+**.

- $C^+(^2P_{1/2}, {}^2P_{3/2}) + H_2$

C^+ is not only the starting point of the carbon chemistry in cold dense clouds but it also acts as the dominant cooler via transitions between the two indicated fine structure states. From the point of view of chemical development, the two reactions $C^+ + H_2 \rightarrow CH^+ + H$ and $C^+ + H \rightarrow CH^+ + h\nu$ play a negligible role in the ISM environment, since hydrogen abstraction is endothermic by almost 0.4 eV and radiative association is to slow. Thus the only important chemical process occurring at low temperatures is radiative association of C^+ with H_2. This system has been studied extensively in our group (Gerlich 1994). **Radiative lifetimes** have been derived from the experimental data using several assumptions, e.g. Langevin rate coefficient for the collision process. These lifetimes are much larger than expected from theoretical estimates. Therefore it has been suggested that electronic transitions contribute to the radiative stabilization considerably. In order to address this question further experiments have been carried out with the heavier D_2 target. As expected the higher density of states of the CD_2^+ complex leads to an increase of the complex lifetime. On the one hand this indicates that nuclear motion is involved in the stabilization. On the other hand it is not clear whether indeed vibrational transitions are involved or a vibronic coupling of the corresponding potential energy surfaces is responsible for the experimental findings.

In order to obtain an even more detailed picture of this key reaction, C^+ ions should be prepared selectively with respect to their fine structure state. This is a very challenging task, because it involves the concerted action of the C atom source which will be developed in close cooperation with TP7 and a REMPI scheme for state selective ionization. Here the splitting of the $^2P_{1/2}$ and $^2P_{3/2}$ is small. Other preparation methods such as photofragmentation of precursor hydrocarbon molecules followed by REMPI will be investigated too.

In case that $C^+(^2P_{1/2}, {}^2P_{3/2}) + H_2$ shows a strong specificity with respect to reaction (as is the case for $Ar^+(^2P_{1/2}, {}^2P_{3/2}) + H_2$), this reaction can serve for chemical probing of collisional excitation and relaxation of the C^+ fine structure. In distant future this technique might be used to probe IR excitation (with the free electron laser) of $C^+(^2P_{1/2})$.

Rotation

- Collisions with $p\text{-}H_2$ or $n\text{-}H_2$

At low temperatures, when most (if not all) internal degrees of freedom are relaxed to the lowest state, rotational energy is „stored“ in $o\text{-}H_2$. Scrambling collisions (ortho-para transitions) serve as an effective heat bath in non-reactive collisions. The heating effect then usually depends on the number of „active“ degrees of freedom of the **collision complex**. This has been demonstrated for various examples. The reduction of the radiative association in $C_2H_2^+ + H_2$ collisions is but one example. More experiments along these lines should give more insight into this phenomenon, one example being the important $N^+ + H_2$ reaction which will also be mentioned in connection with the role of fine structure energy.

Para hydrogen (p-H_2) will be produced using a cold paramagnetic catalyst. Changing the temperature of the cold head the o-H_2 content in H_2 can be varied between 75 and 0 %. This setup is already available in conjunction with one of the trap experiments (TV-22PT).

- $C_2H_2^+ + H_2 \rightarrow C_2H_3^+ + H$

Preliminary results for the kinetics of the vibrationally induced bimolecular reaction indicate that the bimolecular reaction does not occur in every collision although the excess energy of one quanta of ν_3 is almost 400 meV and the barrier to be surmounted to produce $C_2H_3^+$ is only 48 meV. This indicates that vibrational energy might not be available in the reaction coordinate but rather „heat up“ the collision complex. Therefore it will be interesting to see whether additional energy in form of rotation (collisions with p-H_2 and n-H_2) leads to a significant change in reactivity. This will be even more interesting in view of other preliminary results for the same reaction which indicate that rotational excitation of the $C_2H_2^+$ parent ion reduces the reactivity of the vibrationally excited species.

Zero Point Energy (ZPE)

Reactions which involve solely the scrambling of isotopes are close to being thermoneutral. Only the changes in the zero point energies of the involved molecules lead to a slight gain in energy in one direction or hinder the exchange in the opposite direction. Differences in ZPE are responsible for the astrochemical effect of **isotopic fractionation** which leads to the enrichment of heavier isotopes in molecules found in astronomical observations. Since the comparison of the abundance of D containing isotopes such as HD, H_2D^+, DCO^+ , DCN, or larger hydrocarbons with the H / D abundance contains a lot of information, it is important to understand the details of the dynamics of forming these molecules.

The reaction $D^+ + H_2 \rightarrow H^+ + HD$ or other isotopic modifications are rather well understood in both directions. Not yet known, however, is today the outcome if one starts with low kinetic energies on the upper surface, e.g., with $HD^+ + H$. It is obvious that the situation is more complicated if one has a larger number of identical but not necessarily equivalent atoms in a collision complex. It is also not easy to predict the influence of zero point energy on reactions which are hindered by a small barrier. Related experimental observations have been made for the reaction $C_3H^+ + H_2$ and its isotopic variants where H-D exchange competes with hydrogen abstraction and radiative association (see current own contributions).

- $H_3^+ + HD$

The thermal equilibrium of $H_3^+ + HD \rightarrow DH_2^+ + H_2$ has been and still is the matter of an ongoing debate (McCall *et al.* 1998, Gerlich 1998). It has been seen in preliminary experiments that the relative fraction of H_3^+ / DH_2^+ is an extremely sensitive function of several parameters. In order to finally solve this problem the reaction will be further investigated in our cold 22-pole ion trap (TV-22PT) under well defined conditions. Especially important is a systematic study of the rate coefficients and the equilibrium constant as a function of the parameters temperature and various concentrations ([HD], [o-H_2], [p-H_2]). Also traces of the D_2 and hydrogen containing background gases have to be accounted for. Even the hydrogen, (n-H_2 or p-H_2) which has been used for producing the initial H_3^+ has an influence on the outcome of the reaction due to the two different nuclear spin states 1/2 and 3/2 of the ion.

For the H_5^+ system and deuterated variants, many experimental and theoretical studies have been performed already. Simple statistical models show that the outcome of the experiment will depend on the relative probability of the competing channels where on the one hand a proton hops from H_3^+ to HD or on the other hand two protons are exchanged, i.e. proton scrambling. While the first process is a more direct transfer mechanism the latter process obviously requires more complicated rearrangements and in particular the formation of a longer lived complex. The lifetime of such a complex and thus the probability of an exchange is strongly dependent on the total available energy. Unfortunately in a system as big and as light as H_3^+ + HD several states contribute their energy. In a 10 K 22-pole trap experiment, HD can be relaxed to J=0 and H_3^+ carries also only very little energy. Since the kinetic energy is also small the difference in ZPE will be the largest contribution to the total energy. Therefore it seems feasible to unravel the dominant mechanism in the process of isotopic fractionation not only for this particularly interesting case.

- $CDH_4^+ + H_2 \rightarrow CH_5^+ + HD$

This system is interesting for various reasons. Preliminary data are available on the rate coefficients for the forward as well as the backward reaction at 10 K. Due to conventional analysis these quantities refer to a barrier of about 10 (2.7) meV for forward (backward) reaction. The structure of the CH_5^+ molecule is under long debate. It serves as a prototype of a strongly bound molecule which, however, is very floppy, due to its three center two electron (3c-2e) bonding of the proton to methane. This molecule is thought to undergo very rapid „internal“ scrambling motions. These internal motions may play an important role in the process of isotopic fractionation. And it may well be the case that not the barrier height but rather dynamical restrictions are responsible for the reduced forward reaction rate. Several other molecules which play an important role in the chemical networks of the ISM such as $C_2H_3^+$, fall into the same class of floppy molecules. Therefore the planned studies of the CH_5^+ test case are of general importance.

The studies will be carried out in a 22-pole trap (TV-22PT). CDH_4^+ will be formed in the trap starting from CH_3^+ or CH_5^+ precursor molecules. Laser induced reaction is used as an analyzing tool of the CDH_4^+ parent molecule. The spectrum of the molecule in the range of the C-H stretching vibration will tell us whether the incorporation of the heavier (distinguishable) isotope leads to a reduction of the „internal“ scrambling motions.

Research Program

First year:

- Collisions between ions and HD

Hydrocarbonic ions will be studied in the temperature-variable 22-pole trap apparatus (TV-22PT) right after the beginning of the project. Today the machine is operated by a senior graduate student on another project (DFG-SPP: star formation). During the investigation on various isotopic exchange reactions he will train the new graduate student on this project on the technique of electrodynamical trapping.

- $N^+ + H_2$

The previous experiments on $N^+ + H_2$ performed in our group using the electron bombardment ion source will be repeated very carefully. Special emphasis will be put on a detailed analysis of the competing processes. This work includes a training of the student in the use of the para- hydrogen generator.

- $Ar^+(^2P_{1/2}, ^2P_{3/2}) + H_2$

One of the major tasks of the graduate student in this project is the operation of the nanosecond laser system which will serve as a tool for the production of fine structure state selected ions. Because Ar is readily available in form of a nozzle beam and because there is substantial experience in the group with the production of $Ar^+(^2P_{1/2}, ^2P_{3/2})$ this system serves as another training object for the student to become familiar with the techniques necessary. These ions are produced in the single beam/guide ion beam apparatus (REMPI) which is fully available to this project. It consists of the beam source, a quadrupole ion guide and an ion counting detector. The home-built quadrupole is an open design which is intersected with an electron gun as well as with the optical path of a nanosecond high power (IR-UV) laser system. As a first collisional system the reaction with H_2, which will be added to the beam of Ar, will be studied. First results are expected hopefully within the first half year.

Second year:

- Formation of spin-orbit selected N^+

From the experience with the atomic hydrogen beam we expect it to be only a minor step to the formation of atomic nitrogen. All our experiments are designed in a modular fashion. After the design and testing in the single beam experiment the atomic beam source will be moved to the trap apparatus with the transverse arrangement in order to investigate collisions with H-atoms in TP5. In this project (TP4) a second discharge source will be designed and tested within the first year and should go in operation in the second year, again first on the single beam apparatus. The characterization of the source includes the determination of (1) the degree of dissociation, (2) the degree of ionization and (3) the degree of internal excitation due to the discharge.

In contrast to the atomic hydrogen beam the atomic nitrogen beam has to be ionized by a REMPI scheme. On the one hand this makes things easier because molecular nitrogen will not be ionized by the laser and therefore the degree of dissociation is not as critical as it may be for most of the experiments with atomic hydrogen. On the other hand the stability of the discharge source is a critical quantity in these experiments because fluctuations in the degree of dissociation add up to the fluctuations of the degree of ionization due to laser power fluctuations which could degrade the quality of the data. Therefore great care will be focussed on a stable operation of the discharge source.

The fine structure splitting in atomic nitrogen is considerably large (> 2.38 eV). Therefore it is a reasonable assumption that a large fraction of NI will be in the $^4S_{3/2}$ ground state. From here five photons with a wavelength shorter than 426 nm are sufficient to ionize NI. In order to employ a resonant step to enhance the probability of ionization substantially three photons of 360.2 nm (360.1 nm, 359.8nm) are sufficient to pump NI into the $^4P_{1/2}$ ($^4P_{3/2}$, $^4P_{5/2}$) state. The experiences gathered for the nitrogen system are an investment for future applications such as the spin-orbit selected production of CII. During the time of the technical development (REMPI mechanisms), the graduate student will be involved in further experiments on isotopic fractionation, e.g. the $CDH_4^+ + H_2 \rightleftharpoons CH_5^+ + HD$ system. The possibility of laser induced reaction will be investigated for various isotope exchange reactions. For that purpose the lead salt diode laser (high resolution) and the nanosecond laser in its IR configuration (survey scan) are available. The UV- and IR-option on the pulsed laser can not be operated at the same time. Therefore time slots for the different experiments will be planned in advance.

- $N^+ + H_2$

Experiments on the reactive system $N^+ + H_2$ will be undertaken in the single beam experiment (REMPI) first. In close cooperation with TP5 it will then be moved to the transverse trap apparatus where collisions with cold H_2 will be studied. In the latter case fairly high collision energies (75 meV) are involved due to the initial velocity of NI. In order to reduce this energy below the differences in spin-orbit energies of N^+ ($^2P_0$, $^2P_1$, $^2P_2$; 0 meV, 6.1 meV, 16.2 meV) the experiments in the single beam might be better suited. Here energy from the dissociated nitrogen atom might be taken via collisions with He which is coexpanded with D_2 (same mass as He). In this case atomic as well as ionic nitrogen will most likely travel at the same laboratory speed as the hydrogen target (here D_2). Therefore the collision energy varies as the spread in velocity in the beam (parallel temperature of the beam). This might reach values well beyond 10 K and thus the goal of this experiment might become achievable. Crucial for this experiment is therefore good differential pumping between the source chamber and the guided ion beam chamber because reactions originating from thermal D_2 gas (at much larger collision energies) in the second stage of the experiment can defeat the whole idea of the experiment.

Third year:

- Reactions with atomic target: $H_2^+ + H$

After these initial steps the project should proceed to the challenging task of the formation of fine structure state-selected ions from molecular precursors. At this stage the discharge source for the production of atomic hydrogen in TP5 should be in operation. Together with the graduate student of TP5 a beam of hydrogen will be plugged to the single beam/guided ion beam (REMPI). The discharge source will give a beam of H with an admixture of H_2. Following an ionization scheme for H_2 the reaction of $H_2^+ + H \rightarrow H^+ + H_2$ will be studied. Whereas the back reaction has been studied quite extensively the forward reaction has not attracted a lot of attention due to the experimental difficulties. Besides the fact that these reactions are also important in the astrophysical environment the forward reaction is a particularly interesting system because charge transfer as well as hydrogen abstraction can contribute to the reaction.

- $C^+(^2P_{1/2,3/2}) + H_2$ and/or $C^+(^2P_{1/2,3/2}) + X$

A very important task in this project is the investigation of excitation or quenching of fine structure states. In a first step we want to understand the role of collisions. Therefore various reaction systems $C^+(^2P_{1/2,3/2})$ + X will be studied. In the course of these studies we will search for reactants X (perhaps H_2), such that the outcome of the reaction strongly depends on the FS state of C^+. This behavior will be identified by an exponential decay of C^+ with two different time constants referring to two different rate coefficients. These results will then be used in the transverse ion trap apparatus (AB-22PT), where a molecular beam of X will be used to interrogate the population of $C^+(^2P_{1/2,3/2})$ in collisions with another ambient target gas, Y. It might also be feasible from these experiments to extract a lifetime for the excited state of C^+.

Beyond the first funding period:

The program of this project is quite challenging because new grounds will be broken especially in the field of state-selective preparation of ions. On the basis of these new approaches several other directions are at hand which might be studied after the first three years in the *FGLA*:

- optical pumping of fine structure states may become feasible

- H-D isotopic fractionation in larger molecules is of interest

- Experimental studies involving molecules with other isotopes such as ^{13}C , ^{18}O are another important issue for the interstellar environment

- ro-vibrational state selectivity. This field of research which is currently funded in the DFG SPP: *star formation* shows a lot of very interesting results with respect to the role of rotational and vibrational energy and will therefore be continued beyond the end of the SPP.

- infrared spectroscopy: With the possible use of the free electron laser (FELIX) many applications to interstellar chemistry come to mind because this device opens up the wavelength regime of 5-250 µm. In this range for example fine structure states of cold ions may be directly populated or rotational transitions in H_2 (previously observed with ISO) may be excited.