Dynamical constraints and nuclear spin caused restrictions in $H_mD_n^+$ collision systems

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This contribution summarizes a variety of results and ongoing activities, which contribute to our understanding of inelastic and reactive collisions involving hydrogen ions. In an overview of our present theoretical knowledge of various $H_mD_n^+$ collision systems ($m+n\leq5$), it is emphasized that although the required potential energy surfaces are well characterized, no detailed treatments of the collision dynamics are available to date, especially at the low energies required for astrochemistry. Instead of treating state-to-state dynamics with state of the art methods, predictions are still based on: (i) simple thermodynamical arguments, (ii) crude reaction models such as H atom exchange or proton jump, or (iii) statistical considerations used for describing processes proceeding via long-lived or strongly interacting collision complexes. A central problem is to properly account for the consequences of the fact that H and D are fermions and bosons, respectively.

In the experimental and results sections, it is emphasized that although a variety of innovative techniques are available and have been used for measuring rate coefficients, cross-sections or state-to-state transition probabilities, the definitive experiments are still pending. In the centre of this contribution are our activities on various $m+n=5$ systems. We report a few selected additional results for collisions of hydrogen ions with $p$-H$_2$, $o$-H$_2$, HD, D$_2$ or well-defined mixtures of these neutrals. Most of the recent experiments are based on temperature variable multipole ion traps and their combination with pulsed gas inlets, molecular beams, laser probing or electron beams. Based on the state-specific model calculations, it is concluded that for completely understanding the gas phase formation and destruction of $H_mD_n^+$ in a trap, an in situ characterization of all the experimental parameters is required with unprecedented accuracy. Finally, the need to understand the hydrogen chemistry relevant for dense pre-stellar cores is discussed.

Keywords: $H_3^+$; interstellar chemistry; reaction dynamics; state-specific rate coefficients; deuterium fractionation; ion traps

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1. Introduction

(a) $H_n^+$: from atoms via molecules to collision dynamics

In fundamental atomic and molecular physics, the hydrogen atom, the diatomic molecules $H_2$ and $H_2^+$, and the simplest polyatomic molecule $H_3$ play a central role in understanding the basics of quantum theory. Present challenges in spectroscopy are, for example, a detailed comparison of the anti-hydrogen atom with $H$ or ultrahigh resolution spectroscopy of the three centre Coulomb system $HD^+$. As clearly proven by this discussion meeting, many spectroscopic features of $H_3^+$ and deuterated analogues are understood in great detail. However, there are still many open questions concerning this triatomic molecule, e.g. the chaotic behaviour in the vicinity of the $H^+ + H_2$ continuum or all the $H_3^+ + e^-$ states required to understand fragmentation of the excited states of neutral $H_3$ or the process of electron ion recombination also occurring via $H_3^+$ states.

In the field of bimolecular collision dynamics, the three protons two electrons system, $H_3^+ + H_2$, certainly is a prototype reaction. In addition to absolute differential and integral state-to-state cross-sections, specific results such as ortho–para conversion via proton exchange have been reported. An interesting process is the radiative association of $H_3^+$ and $H_2$ leading from the collision continuum to a stable $H_3^+$ via spontaneous emission of a photon (Gerlich & Horning 1992). Not yet completely explored is the non-adiabatic coupling in low-energy $H_3^+ + H$ collisions, occurring on the first excited potential energy surface of $H_3^+$. In this class of collision systems also belongs the interaction of $H^+$ Rydberg atoms with $H_2$ (Dai et al. 2005).

Many additional possibilities and complications come into the game if one goes to the four- and five-centre systems, $H_4^+$ and $H_5^+$, which are the focus of this contribution. The reaction of $H_2^+$ with $H_2$ has been studied in the past with a variety of experimental methods (Glenewinkel-Meyer & Gerlich 1997), and in principle, it is accessible to detailed quantum mechanical studies. Nonetheless, there are many open questions, e.g. the role of the charge exchange during the approach, the branching into o- and p-$H_3^+$ products, the reverse endothermic reaction $H_3^+ + H$ or scrambling in $H_3^+ + D$ collisions. Experimental studies of $H_3^+ + H_2$ and deuterated variants have been discussed recently by Cordonnier et al. (2000) and Gerlich et al. (2002); however, there are many open questions if one wants to use laboratory results for simulating astrochemical environments, e.g. very cold pre-protostellar cores (Walmsley et al. 2004).

(b) Importance for astrochemistry

It has been discussed very often that detailed information on the low-temperature hydrogen and deuterium ion chemistry is of basic importance for tracing the chemical and the physical processes occurring in the early universe or in dense interstellar clouds (Roberts et al. 2004; Walmsley et al. 2004). $H_3^+$ ions and deuterated variants act as important proton and deuteron donors initiating myriads of chemical reactions and leading to ions with significant dipole moments. Many details of isotopic fractionation must be known in order to correlate the D/H abundances observed in molecular clouds with the cosmic D/H isotopic abundance ratio, which itself is correlated to the isotopic abundance produced in big-bang nucleosynthesis.
In order to understand quantitatively the observed abundance, e.g. specific states of H$_2$D$^+$, the actual populations of all energetically accessible states are needed. This requires detailed information on many elastic, inelastic, radiative and reactive processes. Typical examples include the role of $\text{o-H}_2$ heating or the conversion of gained zero-point energy into translation or internal excitation. As discussed by Gerlich et al. (2002), such heating processes are responsible for the destruction of H$_2$D$^+$ with a rate coefficient that is orders of magnitude larger than the value presently used in interstellar chemistry. These rate coefficients are still based on the assumption that isotope enrichment via gas phase ion–molecule reactions is thermodynamic rather than kinetic in origin. Some more remarks concerning the determination of equilibrium coefficients can be found later.

(c) Nuclear spin restrictions

The overall situation, both in space and in most experiments, is that a simple thermodynamical equilibrium is seldom reached. One of the reasons is that the chemistry of H$_m$D$_n^+$ systems is complicated by the fact that H and D atoms are fermions and bosons, respectively. The exchange symmetry in such polyatomic molecules or collision systems leads to rather stringent restrictions if the total nuclear spin is a good quantum number. The best-known example is the existence of two very different forms of hydrogen molecules, $p$-H$_2$ and $\text{o-H}_2$. A second one is that certain rotational states of H$_3^+$ are forbidden, e.g. the groundstate. This affects the partition function and must be accounted for in a correct way for calculating the energy gain in an H–D exchange. A third example is that one can show that the reaction $p$-H$_3^+ + p$-H$_2$ leads exclusively to $p$-H$_3^+$. Note, however, that subsequent $p$-H$_3^+ + p$-H$_2$ collisions can produce rather quickly $\text{o-H}_3^+$ if the energy is available. Since many of these facts including the way to treat nuclear spin selection rules in chemical reactions are not yet fully worked out, this subject will be discussed later.

(d) Experimental challenges

In the last decades, many experiments have been performed on H$_m$D$_n^+$ collision systems in order to understand H–D scrambling, ortho–para conversion, and the destruction of these ions via proton transfer to other molecules or via electron capture (e.g. Cordonnier et al. 2000; Farnik et al. 2002; Gerlich et al. 2002; Schlemmer et al. in press; and contributions in this issue). Nonetheless, the relevant subset of the fractionation reactions used in the new models of interstellar deuterium chemistry (Roberts et al. 2004) is still based on rate coefficients extrapolated from more than 20-year-old measurements which have been performed at high pressure in a swarm experiment, at temperatures above 80 K, and using just n-H$_2$. As stated by Roberts et al. (2004), it is necessary to get more detailed measurements and theoretical justifications for making the required huge modifications on the established astrochemical models. One step forward is the model described by Walmsley et al. (2004) in which, for each lowest state of the ortho and para manifold of each molecule and ion, the reactivity has been treated separately. In the present contribution, we will come to the conclusion that one has to go one step further. In a realistic model, one must include a set of state-to-state or state-specific rate coefficients for correctly describing the o-H$_2$ induced non-equilibrium conditions prevailing both in the low-temperature ion traps and in

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interstellar clouds. Even if not all final states are relevant for astrochemistry due to radiative decay, memory of an exothermic reaction is transferred to the next reaction via the translational exoergicity.

This paper is organized as follows. We first summarize a few theoretical facts, ranging from equilibrium coefficients via nuclear spin restrictions on statistical theories to dynamical consequences, which can be presupposed from inspection of the potential energy surfaces. The experimental section discusses specific technical problems, which are important for low-temperature ion trap studies including buffer gas cooling and radiofrequency (RF) heating, in situ calibration of traces of HD and o-H₂, and laser-based diagnostics. In addition to the recently reported data (Gerlich et al. 2002), the results section reports additional evidence corroborating our present understanding of the chemistry of hydrogen ions. A final section summarizes first results from simulations describing the H₃⁺D_H collision on a state-specific level. The outlook gives some hints how to include H- and D-atom beams or collisions between ions and charged grains into the next generation experiments.

2. Theoretical considerations

Much theoretical work has been done to explore the dynamics in H⁺+H₂ and H₃⁺+H₂ collisions based on potential energy surfaces, non-adiabatic coupling and classical or semi-classical treatments of the nuclear motions. Less information is available for the reaction systems H₃⁺+H, H₄⁺+H and especially H₅⁺+H₂. Some early calculations to understand the scrambling cross-sections in H₃⁺+D₂ and D₃⁺+H₂ measured in the first guided ion beam apparatus were performed three decades ago by Ahlrichs (1975). Later ab initio studies of the stationary points of the H₅⁺ potential energy surface have been determined with high accuracy, while only recently, a global surface became available which also includes the asymptotic scattering regions (Xie et al. 2005).

In principle, it is possible today to treat the collision dynamics of the hydrogen systems we are interested in, e.g. H₂D⁺+H₂, with adequate methods although it is still not at all straightforward to treat a five-atom system with quantum mechanical methods. In classical or semi-classical calculations, tunnelling and the fact that proton–deuteron exchange is significantly influenced by zero-point energies can be treated only approximately. The problem has been discussed by Xie et al. (2005) in an attempt to predict the branching ratio in the unimolecular decay of H₄D⁺. So far, there are no detailed calculations that could be of use for predicting quantitatively the isotopic enrichment in H₅⁺. Therefore, the data used in model calculations are based on simple models and speculations (Roberts et al. 2004; Walmsley et al. 2004).

(a) Thermodynamics: applicable? Simple?

It is generally assumed that, at low temperatures, the rules of equilibrium thermodynamics adequately describe the outcome of a bimolecular proton–deuteron-exchange reaction. The situation is illustrated for the reaction

\[ \text{H}_3^+ + \text{HD} \leftrightarrow \text{H}_2\text{D}^+ + \text{H}_2, \]  

(2.1)

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which is exothermic by 161.1 cm$^{-1}$ (231.8 K) in the left-to-right direction. In the past, no temperature dependence has been accounted for the exothermic reactions. To describe the endothermic backwards process, a simplified purely exponential temperature dependence was assumed. With this, the destruction rate of H$_2$D$^+$ in collisions with H$_2$ was estimated to be many orders of magnitude that of the formation rate of this ion at a temperature of 10 K (Adams & Smith 1981; Herbst 1982; Millar et al. 1989; Giles et al. 1992). The thermodynamic predictions have been improved in several iterations using molecular properties from sophisticated ab initio calculations (Sidhu et al. 1992; Ramanlal & Tennyson 2004). By explicitly summing over many rotation–vibration energy levels of the respective species, partition functions have been calculated for temperatures up to 800 K. For high temperatures, extending into the energy region, where the linear H$_3^+$ potential surface becomes lower than the triangular, interesting results have been obtained; however, the low-temperature behaviour has been the subject of a few rather trivial errors such as omitting a factor $(2J+1)$, the treatment of the nuclear spin statistical weights in a consistent way, or accounting twice for the rotational zero-point energy of H$_3^+$.

In order to clarify the situation, we present in figure 1 the equilibrium coefficient $K$ for reaction (2.1). We have performed a few test calculations based on the state of the art energy levels. The results (dots) show that the curve presented already in Herbst (1982; solid line) can be used as a reliable reference if one really reaches a thermodynamical equilibrium in a cold environment. They are also in good agreement with the values presented in table 4 of Sidhu et al. (1992). Note that the low-temperature limit of $K$ is proportional to $\exp(231.8K/T)$ and that at 10 K, a temperature change of $\Delta T$=1 K changes $K$ by approximately one order of magnitude.

In Ramanlal & Tennyson (2004), the rotational zero-point energy has mistakenly been accounted for both in the enthalpy of 161.1 cm$^{-1}$ (231.8 K) and in the H$_3^+$ partition function, since it has been calculated relative to the rotational groundstate, $0_0$. For the relevant energy levels, see figure 2. It is certainly logical to treat vibrational and rotational zero-point energies in the same way, and therefore, to use the lowest accessible H$_3^+$($1_1$) state as a reference point. A similar argument holds for the calculation of the equilibrium constant in a hypothetical environment of pure ortho-hydrogen. The dashed line in figure 1 marked with $o$-H$_2$ has been calculated by accounting exclusively for odd rotational states of H$_2$ relative to the $J=1$ ‘groundstate’. In such a situation, the enthalpy of reaction (2.1) would be 161.1–118.4 cm$^{-1}$ (231.8–170.4 K). The line, $1.5 \times \exp(90K/T)$, is the extrapolation derived from experimental data measured at 80 K and above in a flow tube with $n$-H$_2$ (Adams & Smith 1981). A comparison of the calculated and measured equilibrium constants can be found later.

(b) Symmetry selection rules

Of central importance, for all low-temperature H and D involving reactions, is that restrictions are imposed by the exchange symmetry. A rigorous theoretical description how to obtain in such a situation selection rules for state-specific or state-to-state reactions has been presented by Quack (1977). In general, molecular systems change their quantum numbers under the influence of an external interaction. Depending on the symmetry of the Hamiltonian of the
unperturbed system and the strength and the properties of the perturbation, there can be correlations between the set of quantum numbers before and after the interaction. Well-known examples include the rather stringent selection rules in a bound–bound transition via emission or absorption of a photon or the propensity rules governing autoionization. The interaction of two molecules during a collision is more violent, especially if they undergo a chemical reaction. Nonetheless, there are good quantum numbers in a bimolecular collision, e.g. the total energy, the total momentum, the total angular momentum and the parity. In addition, one can assume that the nuclear spin is conserved separately. In this ‘frozen nuclear spin’ approximation, restrictive selection rules are found to occur in systems involving identical nuclei, a consequence of permutation symmetry.

Experimental and theoretical results for collision systems, involving just two hydrogen atoms, have been reported in the literature by Gerlich et al. (1987) and Gerlich (1989). It is evident that in such simple cases, the selection rule, $\Delta J=\text{even}$, is nearly rigorous. A more sophisticated illustration of nuclear spin caused constraints is the triatomic $H^+ + H_2$ system (Gerlich 1990). There is
Experimental evidence that at collision energies above a few thousand per centimetre, rotationally inelastic collisions are direct, and therefore, characterized by the propensity rule $\Delta J = \text{even}$, while at low-temperature reactions proceed via long-lived collision complexes. In this case, all the three atoms are or become equivalent. Nonetheless, there are rather stringent restrictions if the total nuclear spin $I = 3/2$ or $1/2$ is conserved. Detailed results from a dynamically biased statistical model, especially ortho–para transition probabilities in reactive $\text{H}^+ + \text{H}_2$ collisions, can be found in Gerlich (1990).

(c) Oka: angular momentum algebra

In order to explain the interesting kinetics observed in a para- and normal-hydrogen plasma with laser diagnostics, Oka and co-workers have developed a method to make predictions for ortho–para transitions in collision systems involving four of the five hydrogen atoms (Uy et al. 1997; Cordonnier et al. 2000). The selection rules derived for these reactive collisions have been corroborated using an elegant mathematical description based on angular momentum algebra (Oka 2004) rather than group theory (Quack 1977). A typical result, the probabilities for forming either $p$-$\text{H}_3^+$ or $o$-$\text{H}_3^+$ in collisions of $o/p$-$\text{H}_2^+$ with $o/p$-$\text{H}_2$, is given in Table 1a. Easy to understand is that $p$-$\text{H}_2^+$ can produce only $p$-$\text{H}_3^+$ if the nuclear spin is conserved during the collision. For the derivation of the other numbers, see Oka (2004).

In a more realistic theoretical treatment, both the nuclear spin and the asymptotically accessible rovibronic states have to be considered; however, it is not straightforward to weight them properly. The outcome depends on the coupling of the channels in the collision complex and it is most probably different for peripheral or violent scrambling trajectories. Inspection of the potential energy curve along the reaction coordinate (Eaker & Schatz 1986) reveals that $\text{H}_2^+$ reacts with $\text{H}_2$ most probably in a rather direct way. Nonetheless, the symmetric long-range charge transfer may not allow one to talk about a simple...
Table 1. Probabilities for forming $o/p$-$H_3^+$ in collisions of $o/p$-$H_2^+$ with $o/p$-$H_2$. The row on the left denotes the four possible combinations of reactants, while the two possible products are indicated in the upper line.

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<thead>
<tr>
<th></th>
<th>$o$</th>
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<td>(a) angular momentum algebra (Cordonnier et al. 2000; Oka 2004)</td>
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<tr>
<td>$oo$</td>
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<td>$po$</td>
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<td>$pp$</td>
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<td>(b) high-temperature approximation</td>
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<td>$oo$</td>
<td>$13/18$</td>
<td>$5/18$</td>
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<td>$op$</td>
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A still open question is the $o/p$-$H_3^+$ equilibrium, which is established if both the $o/p$-$H_2$ ratio and the translational temperature are fixed. The model discussed by Walmsley et al. (2004) gives a tentative answer (discussed later). In addition, the transition probabilities reported by Oka (2004), which are printed in table 2a and illustrated in figure 3a can be used to make predictions; however, comparison with table 2b,c reveals that one can get quite different answers. All the three calculations account correctly for the conservation of nuclear spin, but make different assumptions concerning the decay of the collision complex. The results in table 2b are based on the high-temperature $p$-$H_3^+$ to $o$-$H_3^+$ ratio, while the numbers in table 2c (see also figure 3b) have been calculated for a fixed collision energy equivalent to $7 \text{ cm}^{-1}$ (approx. $10 \text{ K}$). The method used (conservation of nuclear spin and microcanonical equilibrium distribution) is described in more detail in §5. It is obvious that, for energetic reasons, a $pp$ collision cannot lead to excited $o$ products. Also interesting is the strong propensity for the $op \rightarrow op$ transition and the fact that the predictions for the energetic $oo$ collisions are similar to the results in figure 3a.

Under the assumption that the predicted transition probabilities describe properly the ortho–para changes in collisions, a conclusion can be drawn which is of practical importance for a storage ion source or for plasma. If one uses pure $p$-$H_2$, only pure $p$-$H_3^+$ is formed via electron bombardment and the following $H_2^+ + H_2$ reaction. If, however, additional $p$-$H_3^+ + p$-$H_2$ collisions follow at high temperatures ($100 \text{ K}$ are...
already sufficient), subsequent scrambling can lead to \( o-H_3^+ \). Sequential applications of the conversion probabilities from Table 2 lead already to 49\% \( \text{ortho} \)-hydrogen after two collisions while the numbers of Table 2 lead to 26\% after one additional collision and reach a stationary \( o:p \) ratio of 5 : 2.

\( (e) \) Potential energy surface: dynamical restrictions

The differences in the results presented in Table 2 for \( o/\text{para} \) transitions in \( H_3O + H_2 \) collisions are due to differences in the assumptions made for the decay of the \( H_3O^+ \) collision complex; however, it is rather sure that the real outcome cannot be predicted using any of these simple statistical assumptions, maybe even at very low energies. The reason is that, in contrast to the deep \( H^+ + H_2 \) potential energy surface where all atoms become rather quickly equivalent, the topology of the \( H_3O^+ \) surface is more complicated, hindering the scrambling of the atoms. In addition, nuclear spin restrictions of internal motion in the collision complex, e.g. a propeller-like rotation of \( H_2 \) relative to the \( H_3O^+ - H_2 \) molecular axis, may reduce the \( o: \text{para} \) scrambling efficiency.

An accurate global potential energy surface for \( H_3O^+ \) has been reported recently by Xie et al. (2005), which has full permutational symmetry with respect to interchange of \( H \) atoms. It also dissociates correctly to \( H_3O^+ \) and \( H_2 \). As can be seen from fig. 2 of Xie et al. (2005), the \( H_3O^+ \) ion can be described as an \( H_3O^+ - H_2 \) cluster ion with a rather large binding energy of 6.3 kcal mol\(^{-1}\). Internal motions are not hindered by barriers that are extending over the dissociation limit, but a closer inspection of the stationary points reveals that there can be significant dynamic constraints, especially if the collision complex is formed with a large total orbital angular momentum. In Gerlich et al. (2002), the slowness of deuteration of \( H_3O^+ \) in collisions with HD has been taken as a hint that scrambling is hindered by steric...
or angular momentum constraints. Note that replacement of H by D not only changes the asymptotic zero-point energies, but also increases or lowers the centrifugal barriers due to different moments of inertia.

In a preliminary classical calculation, Xie et al. (2005) have used their potential energy surface (PES) to study the decay of a collision complex starting from different configurations and with total angular momentum 0. These results support

Figure 3. Schematic illustration of ortho–para conversion probabilities in H$_3^+$+H$_2$ collisions calculated with two models (see also table 2a,c). In the model shown in (a), exclusively angular momentum algebra has been accounted for (Oka 2004), while in (b), additional dynamical restrictions have further limited the mixing of the states (see text). Rigorously forbidden are $pp \leftrightarrow op$ transitions.
the interpretation that the central proton plays a specific role and that an exchange with a peripheral atom is less probable than jumping back and forth (see figure 4). This is most probably due to the fact that in-plane rotation of the H$_3^+$ subunit requires a significant amount of energy (see structure (e) 5-\(C_{2v}\) in Xie et al. (2005)).

It is common to discuss chemical reactions using the terms: (i) proton transfer, (ii) H atom exchange, or sometimes (iii) H$^-$ transfer. In the present case, it is rather certain that all products are exclusively formed via proton or deuteron transfer and that the electron charge is localized on the two sides of the H$_3^+$–H$_2$ complex. More complex rearrangements, which may look like an atom exchange, are in reality a sequence of proton or deuteron jumps. This is illustrated schematically in the upper part of figure 4, while the graph presents a time dependence calculated with a simple statistical model. The assumptions of this model are explained in figure 4. In order to get quantitative insight into how realistic such a model is and how fast the scrambling of H and D in the triatomic subunit really can be, trajectory calculations are a suitable tool. They may also allow one to define a subspace of initial collision conditions in which the statistical approximations are applicable. The experimental results presented in the next section provide evidence for incomplete scrambling, even in an exothermic reaction at 10 K.

3. Experimental remarks

(a) Symmetry selection rules

So far, only a few experimental studies could actually prove the influence of symmetry selection rules in chemical reactions. As already mentioned in §1, high-resolution crossed-beam experiments provided related results for C$^+$, N$^+$ and H$^+$ interacting with H$_2$ (Gerlich 1990) and for the neutral system H$^+$+H$_2$.
using Rydberg tagging (Dai et al. 2005). These experiments are technically rather complicated. The laser-based methods are more versatile and provide results on a state-specific level required for observing such effects. An interesting study based on the absorption of an infrared laser beam in hydrogen plasma has been reported by Uy et al. (1997) and Cordonnier et al. (2000). Observing the relative intensities of selected $\text{H}_3^+$ lines, ortho–para conversion via $\text{H}_3^+ + \text{H}_2$ collisions has been monitored experimentally. Using pure $p$-$\text{H}_2$ and $n$-$\text{H}_2$ as discharge gases, some evidence for the influence of nuclear spin selection rules has been obtained. In another plasma experiment, Farnik et al. (2002) have used a pulsed slit jet supersonic discharge for studying cold $\text{H}_2\text{D}^+$ and $\text{D}_2\text{H}^+$ molecular ions via overtone transitions. Additionally in this case, observations could be described by steady-state kinetics in the slit discharge expansion. Such experiments have sufficiently high densities of ions for probing them via absorption; however, the complex kinetics in the plasma make it difficult to extract reliable results, especially due to the extremely high number densities of electrons and radicals, which also have a net effect on the ortho:para ratio of the neutral gas.

(b) Laser-induced reactions

More detailed information can be obtained by combining low-temperature trapping methods with suitable lasers. Applications of this method to stored $\text{H}_3^+$ and isotopologues is described thoroughly in the contribution of Glosik et al. (2006). The feasibility of the chemically probing laser excited $\text{H}_3^+$ with Ar has already been demonstrated in a compact trapping arrangement by Mikosch et al. (2004). Another application, the combination of a trap with the free electron laser for infrared experiments (FELIX), will be mentioned later (Schlemmer et al. in press).

Meanwhile, we are using near infrared high-power continuous wave (CW) diode lasers to pump enough energy into the ions in a controlled way (e.g. 6536 cm$^{-1}$ in the case of $\text{HD}_2^+(1_{11})$) for efficiently probing this subgroup with a variety of suitable neutral reactants. The high resolution of these lasers allows us to resolve the Doppler profile of the cold ions, providing direct information on their velocity distribution. Various strategies for deriving kinetic information are possible ranging from a dedicated perturbation of a stationary low-temperature equilibrium via laser-induced reactions (LIRs) and hole burning to two-colour pump–probe experiments. Especially important at the moment is the determination of the population of the low-lying $\text{H}_2\text{D}^+$ states shown in figure 2 and the $o/p$ ratio of $\text{H}_3^+$ stored at different $\text{H}_2$ $o/p$ ratio and temperatures. A planned extension is to apply the method to high-resolution overtone fragmentation of ultracold $\text{H}_3^+$.

(c) Low-temperature radiofrequency ion traps

The various RF ion traps used in most of the low-temperature studies are based on the design described in Gerlich (1995). A few recent improvements, typical tests and problems are mentioned in Glosik et al. (2006). As discussed by Wolf et al. (2006), the ion trap used in Heidelberg has been primarily constructed for injecting a well-characterized cold ion beam into the Test Storage Ring. However, it also allows for in situ analysis using chemical probing. First,
experimental results of ion–electron recombination rates with cold H$_3^+$ ions have been reported by Kreckel et al. (2005). Our new 22-pole instrument, which is mounted on a 4 K cold head (4K-22PT), has been especially constructed for performing specific experiments on stored ions at very low temperatures (Gerlich & Smith 2006). In this experiment, the method of LIRs can be utilized with much higher flexibility than in the previous experiments, since the gas used for chemical probing can be injected as a skimmed effusive or supersonic beam. For detailed experiments on H$_m$D$_n^+$ ions, a special in situ para-hydrogen converter is under construction.

A very important and unique feature of RF traps is the possibility to relax ions by collisions with buffer gas, the temperature or velocity distribution of which can be controlled in various ways. Helium peak number densities above $10^{15}$ cm$^{-3}$ have been reached leading to millions of collisions in a second, and therefore, to very efficient relaxation of all degrees of freedom. The temperature of the walls surrounding the trap is measured with an accuracy of ±2 K; however, the final determination of the ion temperature is still a problem. If very high RF amplitudes are applied, the RF coil and multipole electrodes may become several degrees warmer. Careful tests are required in order to exclude RF heating of the ion cloud via potential distortion or via parasitic low-frequency components in the RF voltage. There is a variety of methods to determine parameters characterizing the energy content of the ion cloud, ranging from the Doppler profile and populations of low-lying states to temperature-dependent chemical test reactions. Very sensitive is the ternary association with He. In the case of H$_3^+$ + H$_2$ reaction system, isotopic enrichment and growth of hydrogen clusters have been measured simultaneously (discussed later). Ternary rate coefficients usually have a steep temperature dependence and are therefore excellent thermometers.

(d) In situ calibration of HD and o-H$_2$ number densities

The specific role of traces of both o-H$_2$ and HD in the hydrogen gas has been mentioned several times. It affects in a similar way the chemistry occurring either in cold dense clouds or in trapped ion ensembles. It is therefore very important to determine in situ their concentrations and all critical parameters with unprecedented accuracy in situ. Isotope enrichment in H$_3^+$ is certainly an ideal detector; however, it first needs to be calibrated. The present standard test reaction for determining very small fractions of o-H$_2$ is the endothermic reaction N$^+$ + H$_2$ → NH$^+$ + H (Gerlich 1993). Unfortunately, this reaction is also not yet completely understood, especially the role of the three low-lying fine structure states of the nitrogen ion. For obtaining a real thermal o/p equilibrium in the trap, it is planned to use an in situ catalyst. This reduces the risk of re-conversion in the gas inlet system and distortion from background normal hydrogen gas in the vacuum chamber. It is our aim to reach p-H$_2$ purities of more than 99.999%. In principle, it should be possible to attain the 10 K thermodynamic o/p equilibrium of 3.6×10$^{-7}$. If this is achieved, addition of traces of n-H$_2$ via a skimmed effusive beam allows for very sensitive tests.

Most of our deuteration experiments use just the natural admixture of HD and it is assumed that the gas containers are filled with the global terrestrial abundance of [HD]/[H$_2$] = 3×10$^{-4}$. Note that due to the mass dependence of
diffusion, the number density in the trap is 1.5 times larger. For careful studies at temperatures below 15 K, one has to account for fractionation caused by isotope-dependent condensation on the walls.

4. Selected experimental results

(a) $H^+ + H_2$, $H_2^+ + H_2$

The classical example for a gas phase conversion of ortho-hydrogen into its para-form is the reaction

$$H^+ + o-H_2 \rightarrow H^+ + p-H_2. \quad (4.1a)$$

It is, although exothermic, rather slow (Gerlich 1990). The details of this reaction and of isotopic variants are understood in great detail both from crossed-beam and ion-trap experiments and from a dynamically biased statistical theory (Gerlich 1982, 1990). The prototype reaction for understanding H–D scrambling and the influence of small energy differences is the reaction

$$D^+ + H_2 \rightarrow H^+ + HD. \quad (4.1b)$$

It is exothermic by 258.9 cm$^{-1}$ (372.5 K) from left-to-right as a result of the difference in the zero-point energies of H$_2$ and HD, 288.7 cm$^{-1}$ (415.4 K) and the difference in the ionization potentials of H and D, 28.8 cm$^{-1}$ (42.9 K). As summarized recently by Gerlich & Schlemmer (2002), this simplest of chemical reactions has been studied extensively both experimentally and theoretically. In the context of the subject of this paper, it must be added that the theoretical prediction for the outcome of reaction (4.1b) depends on the treatment of the nuclear spin although there are no restrictions on the right side. All the accessible states of HD can be populated. The reason is that the decay of the collision complex back to reactants which competes with product formation, has to fulfil the selection rules $\Delta J=$ even, if the nuclear spin remains unchanged.

Of great importance for forming H$_3^+$ ions is the four-centre reaction

$$H_2^+ + H_2 \rightarrow H_3^+ + H. \quad (4.2)$$

Most of our today’s experimental and theoretical knowledge has been summarized by Glenewinkel-Meyer & Gerlich (1997). For astrophysical applications, it is important to note that the rate coefficients measured with a merged beam experiment confirm that the reaction occurs with the capture limit at collision energies below 40 cm$^{-1}$. However, there is no experimental or theoretical information about the $o/p$ branching ratio of the formed H$_3^+$ ions. If statistical arguments hold (described earlier), this ratio is 0.5 : 0.5 as assumed by Walmsley et al. (2004); however, it is quite possible that this direct reaction is controlled by some dynamical features (resonances) leading to the preference of specific product states. Important for astrochemical applications is the four-centre scrambling reaction

$$H_3^+ + D \rightarrow H_2D^+ + H, \quad (4.3)$$
which is exothermic by 860.1 cm\(^{-1}\) (597.8 K). So far, there are no measurements available with cold ions. This process occurs on a very weakly interacting potential energy surface, which is not yet well enough characterized (Eaker & Schatz 1986). There are many interesting open questions related to the H–D scrambling on the van der Waals type potential energy surface. It can be expected that there are significant differences if there are mainly fermions involved as in reaction (4.3), or if bosons dominate as in HD\(_2^+\) + D.

\[(b) \quad \text{H}_3^+ + D_2\]

An isotope combination, which allows us to further explore nuclear spin and other restrictions in a low-temperature H\(_m\)D\(_n^+\) collision complex is the reaction of H\(_3^+\) with D\(_2\) leading to

\[
\text{H}_3^+ + D_2 \rightarrow \text{HD}_2^+ + \text{H}_2, \quad (4.4a)
\]

\[
\rightarrow \text{H}_2\text{D}^+ + \text{HD}. \quad (4.4b)
\]

Both the channels are exothermic \((a, 489.5\text{ cm}\(^{-1}\) (340.2 K); \(b, 220.1\text{ cm}\(^{-1}\) (153.0 K)). The reaction has been studied at low collision energies by means of the traditional merged beam technique (Dougless et al. 1982) and in the slow merged beam apparatus (see fig. 55 in Gerlich (1992)). Both sets of results agree well with each other indicating that internal excitation plays no significant role. Figure 5 shows the results measured in the 22PT trap at a nominal temperature of 10 K using a rather low number density of n-D\(_2\). As in most of the ion-trapping experiments, the ions have been cooled in the first 10 ms with an intense pulse of He. The derived rate coefficients are given in table 3. As can be seen from a comparison with 300 and 80 K results published by Giles et al. (1992), there is almost no temperature dependence and all values are in excellent agreement. The sum of the two rate coefficients is close to the Langevin value of 1.6\(\times\)10\(^{-9}\) cm\(^3\) s\(^{-1}\). There is a strong preference for a single proton transfer, dominating with almost 80%. Assuming the validity of the model shown in figure 4, one can conclude from the branching ratio that the interaction time is only 50% of the mean time for a proton jump, \(t_0\). Another possibility for explaining the dominance of channel 5a is its larger phase space due to the larger exothermicity. The reactions with D\(_2\) are now also included in astrochemical models; however, the propensity for proton transfer in reaction 5 is not accounted for by Walmsley et al. (2004).

\[(c) \quad \text{D}_3^+ + \text{H}_2\]

An isotopic variant where scrambling dynamics can be studied in the endothermic direction is

\[
\text{D}_3^+ + \text{H}_2 \rightarrow \text{H}_2\text{D}^+ + \text{D}_2, \quad (4.5a)
\]

\[
\rightarrow \text{D}_2\text{H}^+ + \text{HD}. \quad (4.5b)
\]

The first channel is 492.4 cm\(^{-1}\) (342.2 K) endothermic and the second is 336.4 cm\(^{-1}\) (233.8 K). The rate coefficients are given in table 3. It has already been discussed by Gerlich (1993) and Gerlich & Schlemmer (2002) that a simple

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Figure 5. Reactions of $\text{H}_3^+$ with $\text{D}_2$ at a nominal temperature of 10 K and a deuterium number density of $2.8 \times 10^9 \text{cm}^{-3}$. The experimental data have been fitted with the rate coefficients given in table 3. Note the large preference for the $\text{HD}_2^+$ channel which can be reached via a single proton jump.

Table 3. Reaction rate coefficients measured for the indicated reactions at room temperature, 80 K and at $15 \pm 5$ K. Rate coefficients $k = a \times 10^{-b}$ are presented as $a(-b)$. The values are given at the indicated temperature $T$.

<table>
<thead>
<tr>
<th>reaction</th>
<th>$k$/cm$^3$ s$^{-1}$ (300 K)</th>
<th>$k$/cm$^3$ s$^{-1}$ (80 K)</th>
<th>$k$/cm$^3$ s$^{-1}$ (15 K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{H}_3^+ + n\text{-D}_2 \rightarrow \text{H}_2\text{D}^+ + \text{HD}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>→ $\text{HD}_2^+ + \text{H}_2$</td>
<td>$2.6(10)^a$</td>
<td>$3.5(10)^a$</td>
<td>$1.1(-9)$</td>
</tr>
<tr>
<td>$\text{H}_2\text{D}^+ + n\text{-D}_2 \rightarrow \text{HD}_2^+ + \text{HD}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>→ $\text{D}_3^+ + \text{H}_2$</td>
<td>$6.5(-10)^a$</td>
<td>$7.0(-10)^a$</td>
<td>$3.0(-10)$</td>
</tr>
<tr>
<td>$\text{HD}_2^+ + n\text{-D}_2 \rightarrow \text{D}_3^+ + \text{HD}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>→ $\text{D}_2\text{H}^+ + \text{HD}$</td>
<td>$5.2(-10)^a$</td>
<td>$8.7(-10)^a$</td>
<td>$1.0(-9)$</td>
</tr>
<tr>
<td>$\text{D}_3^+ + p\text{-H}_2 \rightarrow \text{D}_2\text{H}^+ + \text{HD}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>→ $\text{DH}_2^+ + \text{D}_2$</td>
<td>$9.0(-10)$</td>
<td>$6.0(-11)$</td>
<td></td>
</tr>
<tr>
<td>$\text{D}_3^+ + n\text{-H}_2 \rightarrow \text{D}_2\text{H}^+ + \text{HD}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>→ $\text{DH}_2^+ + \text{D}_2$</td>
<td>$2.9(-10)^a$</td>
<td>$3.6(-10)^a$</td>
<td>$0.7(-11)$</td>
</tr>
<tr>
<td>$\text{D}_2\text{H}^+ + p\text{-H}_2 \rightarrow \text{DH}_2^+ + \text{HD}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>→ $\text{H}_3^+ + \text{D}_2$</td>
<td>$5.0(-10)$</td>
<td>$0.5(-11)$</td>
<td></td>
</tr>
<tr>
<td>$\text{D}_2\text{H}^+ + n\text{-H}_2 \rightarrow \text{DH}_2^+ + \text{HD}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>→ $\text{H}_3^+ + \text{D}_2$</td>
<td>$5.7(-10)^a$</td>
<td>$4.8(-10)^a$</td>
<td>$0.7(-11)$</td>
</tr>
<tr>
<td>$\text{DH}_2^+ + p\text{-H}_2 \rightarrow \text{H}_3^+ + \text{HD}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{DH}_2^+ + n\text{-H}_2 \rightarrow \text{H}_3^+ + \text{HD}$</td>
<td>$9.0(-10)$</td>
<td>$1.2(-10)^a$</td>
<td></td>
</tr>
</tbody>
</table>

$^a$Results determined with a variable-temperature selected ion flow tube (Giles et al. 1992).

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statistical model based on counting identical atoms, fails completely. At low energies, the reaction (4.5b) is favoured due to the lower endothermicity. As soon as the total energy gets larger than 400 cm\(^{-1}\), the branching ratio is determined by the fact that reaction (4.5a) can proceed via a direct deuteron jump, while (4.5b) requires more complicated rearrangements. Figure 6 shows an ion-trap result, performed at 300 K with \(p\)-H\(_2\). It can be seen that at this temperature, the deuteron transfer channel, although more endothermic, already has almost the same weight as channel (4.5b).

\[
(d) \quad H_3^+ + HD
\]

The H\(_2\)D\(^+\) ion formed in reaction (2.1) is probably the most important deuteron donor in the chemistry of dense interstellar clouds although recent models now include all deuterated isotopologues of H\(_3^+\) (Roberts et al. 2003). Recently, the first low-temperature experimental results measured at a nominal temperature of 10 K have been published (Gerlich et al. 2002). The rate coefficient for the forward direction of reaction (2.1), \(3.5 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}\) at 10 K, has been found to be significantly smaller than the value previously assumed in models, \(1.5 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}\). In order to dispute the sceptical remarks made in Roberts et al. (2004), a few experimental facts are repeated here. It is important to realize that H\(_3^+\) undergoes in the trap a mono-exponential decay over three orders of magnitude. This clearly indicates that the rate coefficient for the H\(_3^+ + HD\) reaction is really measured with ions thermalized with the intense He pulse of several milliseconds. Note that the ortho : para ratio after relaxation with He is 1 : 1, while the slow subsequent thermalization occurring in the ambient HD reactant gas may finally convert the remaining H\(_3^+\) ions into their lowest para state. In addition to state-specific studies, there is certainly a demand for theoretically justifying the low rate coefficients measured for reaction (2.1).
In the same experimental set-up, additional information for the backward reaction has been derived from a stationary equilibrium which has been reached in the trap after 100 ms at rather high hydrogen number densities. In addition, these results have led to some discussions in the literature culminating in the statement that the experiment deviates from calculations by 12 orders of magnitude (Ramanlal & Tennyson 2004). Certainly, the experimental results published by Gerlich et al. (2002) deviate significantly from the thermodynamical equilibrium; however, the discrepancy is much smaller. The experimental equilibrium constant $K$ can be directly derived from the measured data. Accounting for the experimental HD/H$_2$ ratio, one obtains from the measured H$_2$D$^+$/H$_3^+$ enrichment directly $K(15 \pm 5 \text{K}) = 390$. This result is shown in figure 1 with the experimental uncertainties. Note that the actual ion temperature is assumed to be slightly higher than the nominal temperature of $T_n = 10 \text{K}$ which is the temperature of the trap housing. The deviation of this result from the calculated curve is due to the influence of ion heating by traces of o-H$_2$.

The central role o-H$_2$D$^+(1_{11})$ in both isotopic enrichment and also in astrophysical observations has already been mentioned by Pagani et al. (1992). As emphasized by Gerlich et al. (2002), it is very important to understand the inelastic and reactive collisions of H$_2$D$^+$ with o-H$_2$, especially the two processes

$$p\text{-H}_2D^+ + o\text{-H}_2 \rightarrow o\text{-H}_2D^+ + p\text{-H}_2,$$

$$o\text{-H}_2D^+ + o\text{-H}_2 \rightarrow H_3^+ + \text{HD}.$$  

From the measured equilibria (Gerlich et al. 2002) and the forward rate coefficients, effective back reaction rate coefficients for reaction (2.1) have been calculated. For n-H$_2$, a value of $k_{-1} = 4.9 \times 10^{-11}$ cm$^3$ s$^{-1}$ has been deduced, while for almost pure p-H$_2$ (purity 99 ± 1%) the value drops to $k_1 = 7.3 \times 10^{-13}$ cm$^3$ s$^{-1}$. Based on a simple model, a rate coefficient $k_{oo} = 1.4 \times 10^{-10}$ cm$^3$ s$^{-1}$ has been derived from the two mean values measured with two different conditions (Gerlich et al. 2002). It is rather certain that this rate coefficient is mainly determined by reaction (4.7). A more detailed analysis follows in §4e.

As discussed by Gerlich et al. (2002) and Walmsley et al. (2004), the H$_3^+$/DH$_2^+$ ratio one obtains finally in a stationary equilibrium is, in addition to the ion temperature and the HD concentration, an extremely sensitive function of the o/p ratio of the neutral hydrogen gas. In order to prove the results presented previously, additional experiments have been performed using an increased HD number density. In addition, the ion trap has been operated at such high pressure that a stationary equilibrium could be reached already after 10 ms. Two typical results are shown in figure 7. The experiments have been performed with n-H$_2$, more detailed experimental parameters are given in figure 7. In figure 7a, it can be seen that the stationary equilibrium obtained for H$_3^+:H_2D^+:HD_2^+:D_3^+$ is about 1 : 0.1 : 0.01 : 0.001. The H$_2$D$^+/H_3^+$ equilibrium constant is $K = 5.4$. The data shown in figure 7b have been obtained at higher pressure. This leads to a weak, but obvious linear increase of mass 5 and 6 caused by formation of H$_5^+$ and H$_4$D$^+$ via three body association. From a comparison with the horizontal line, it also can be seen that there is a slight decay of H$_2$D$^+$ due to ternary association. The ternary rate coefficients, $k_3 \approx 5 \times 10^{-29}$ cm$^6$ s$^{-1}$ can be

---

used as an independent \textit{in situ} measure for the actual collision temperature. Such measurements are a critical test of the overall consistency and sensitivity of RF ion traps and are used in the present experiments with high-purity \textit{para}-hydrogen.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure7.pdf}
\caption{Equilibrium (nearly stationary) of an $H_3^+$, $H_2D^+$, $HD_2^+$ and $D_3^+$ ion cloud trapped in two different $n$-H$_2$/HD mixtures (a) $9.3 \times 10^{11}$ cm$^{-3}$/1.4$ \times 10^{13}$ cm$^{-3}$ and (b) $5.7 \times 10^{13}$ cm$^{-3}$/1.9$ \times 10^{14}$ cm$^{-3}$. The higher pressure leads to an additional linear increase of mass 5 and mass 6 via three body association to $H_3^+$ and $H_4D^+$. The ternary rate coefficient, $k_3=5 \times 10^{-29}$ cm$^{-6}$ s$^{-1}$ is an independent \textit{in situ} measure for the actual collision temperature.}
\end{figure}

\textbf{(e) Laser-induced reactions with $H_2D^+$}

All the results, discussions and questions shown and raised in this paper clearly prove that one needs state-specific information for accurate modelling of the low-temperature behaviour of $H_3D_3^-$ collision systems. At the moment, one of the most interesting questions is the stationary rotational population of low-lying $H_2D^+$ states in the ion trap. Inspection of figure 2 reveals that one should probe at least the four lowest rotational states, although it will be shown below that also the $J=2$ manifold is probably ‘pumped’ in 10 K collisions with \textit{o}-H$_2$.
There have been several successful initiatives to combine ion trapping techniques with the flexibility a free electron laser can offer. Figure 8 shows a spectrum of $^{2}H_{2}D^{+}$ recently recorded with FELIX using the temperature variable ion-trapping machine in the standard configuration (Gerlich 1995). Some details of this preliminary experiment have been reported by Schlemmer et al. (in press).

Briefly, externally produced hot $^{2}H_{2}D^{+}$ ions have been mass selected and injected into the trap at an ambient temperature of 25 ± 5 K. There occur several competing processes: (i) relaxation with He and $^{2}H_{2}$, (ii) reactions with $^{2}H_{2}$, and (iii) LIRs with $^{2}H_{2}$. It is rather certain that the trap temperature was already so high that back-deuteration of the $^{3}H_{2}^{+}$ products in collisions with traces of HD plays no role. Unfortunately, it is not known whether the number of collisions with He buffer gas was sufficient to relax the $^{2}H_{2}D^{+}$ primary ions to the trap temperature. Assuming full thermalization and conservation of the initial high-temperature $o/p$ ratio, collisions with the buffer gas populate almost exclusively the four lowest states with probabilities of 0.21, 0.04, 0.50 and 0.24. A difficulty in analysing the results is that the probing gas, $n$-$^{2}H_{2}$, has been leaked in as a continuous flow. This leads to additional modifications of the state population, especially to loss of $o$-$^{2}H_{2}D^{+}$ via reaction (4.7). As discussed by Schlemmer et al. (in press), additional complications may be due to saturating the transitions with the high intensity of the picosecond pulses from the free electron laser FELIX.

The differences between the measured intensities and the simulation shown in figure 8 are most probably caused by such effects. In summary, the FELIX results show, in addition to the first $^{3}H_{3}^{+}$ LIR data reported by Mikosch et al. (2004), that laser-induced probing of trapped hydrogen ions is feasible. These preliminary results also must be taken as a hint that such experiments have to be performed under well-defined conditions.

Figure 8. Laser-induced acceleration of the reaction $^{2}H_{2}D^{+} + ^{2}H_{2} \rightarrow ^{3}H_{3}^{+} + ^{3}HD$ at a temperature of 25 ± 5 K and a hydrogen number density of $7 \times 10^{10}$ cm$^{-3}$ measured in a 22-pole trap. It is obvious that all the four states, shown in the upper right corner (see also figure 2), are significantly populated. Some more information concerning the simulation (thin line) and how the experimental data (histogram) have been recorded may be found in the original report (Schlemmer et al. 2005).
For extracting useful information on populations, it is mandatory that the relaxation phase with He, the laser excitation and the following chemical probing phase are well separated in time. With pulsing separately the He and H₂ gas inlet, this is certainly possible. In our dedicated set-up (Glosik et al. 2006), we additionally use a pulsed effusive or supersonic beam for chemical probing (i.e. Ar) and a chopped or modulated CW diode laser for overtone excitation. All this opens up a wide range of experiments dedicated to understand the low-temperature populations of trapped hydrogen ions and their state-specific interaction with all forms of hydrogen neutrals including HD, p-H₂, o-H₂, p-D₂, o-D₂ and also H and D.

5. Towards state-specific understanding

The second section has summarized the present status of our theoretical understanding of the formation and destruction of H₅⁺ and its deuterated analogues. It is clear now that one has to go beyond simple models and assumptions. We hope, for example, that trajectory calculations on the new H₅⁺ surface will replace or quantify pictures such as ‘proton transfer’, ‘H-atom exchange’ or ‘scrambling’ as shown in figure 4. In addition, theories have to provide state-specific information. Finally, full quantum mechanical calculations are needed to properly account for zero-point energies and exchange symmetries in the H₅D₅⁻ collision complexes.

Although we are not completely convinced, it may be justifiable to calculate state-to-state cross-sections using statistical simplifications, especially at low energies. It may be possible that the interaction on the H₅⁺ surface is strong enough and the lifetime of the reactive intermediate is long enough that in a complex |c> the information on the initial state |i> gets lost. For predicting the decay to the final states |f> only the conserved quantum numbers (E, total energy; J, total orbital angular momentum; I, total nuclear spin; P, parity, i.e. |c> = |E, J, I, P, … >) have to be considered (Miller 1970). Trajectory calculations similar to those reported for H⁺ + D₂ by Gerlich et al. (1980) may help to test such assumptions. A complete dynamically biased statistical calculation using the formulation given by Gerlich (1989) is in preparation.

In the following, a very simple approach is described and used. It is based on the assumption that the intermediate complex |c> = |E, I> is characterized only by the total energy and the total nuclear spin. Since there is no dynamical coupling between the nuclear spin and all the other degrees of freedom, a complex is formed with the statistical weight (2I+C), provided the density of complex states is high enough. It is clear that the spin I must be accessible from the initial nuclear spin states. For the decay of |c> into various competing product channels, we take the microcanonical equilibrium distribution P(f) = gₑ√Eᶠ, where gₑ is the statistical weight of the final state |f>, e.g. (2J+1; 2I+1) in most cases, and Eᶠ is the kinetic energy after the reaction.

Based on these model assumptions, detailed transition probabilities have been calculated. One typical result, ortho–para transitions in H₅⁺ + H₂ collisions at 10 K, can be found in table 2 and in figure 3b. Comparison with the predictions from Cordonnier et al. (2000) reveals similarities, but also significant differences. While in all cases nuclear spin selection rules forbid the transitions op → pp and

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Only the microcanonical equilibrium distribution accounts properly for the fact that a $p$-$H_3^+ + p$-$H_2$ collision cannot lead to excited products for energetic reasons. The slightly larger value in the $oo \rightarrow po$ transition probability is due to the fact that an $o$-$H_3^+ + o$-$H_2$ encounter has enough energy (see energy levels in figure 2) to populate the $2_s$ state.

Another set of typical results is plotted in figure 9 showing three different exothermic collision processes leading to excited $H_2D^+$. The collision energy has been set to $E_t = 10$ K. The black bars represent the population resulting from an inelastic collision of $o$-$H_2D^+$ ground-state ions with $o$-$H_2(1)$. The other two distributions are obtained in the $H_3O + HD$ reaction. Obvious is the preference for forming $o$-$H_2D^+$ if one starts with $o$-$H_3^+$. This is mainly a consequence of the conservation of the nuclear spin in the complex $|e\rangle = |E, I=5/2\rangle$. The reaction of $p$-$H_3^+$ with HD leads to a more uniform population of the energetically accessible states. The model also allows one to predict the fraction of the total available energy which is converted into translation. With $p$-$H_3^+$, 33% of the available energy is converted into translation, with $o$-$H_3^+$ only 14%. Such information is very important for astrochemical models since there is a big difference whether the energy gained, e.g. via deuteration, leads to a rotationally excited ion followed by infrared radiation or to translational heating of the cloud.

As a final example, the statistical model has been used to calculate the relative state-specific rate coefficients presented in the upper line of table 4, while the lower line shows the absolute rate coefficients (in $10^{-11}$ cm$^3$ s$^{-1}$) taken from table 1 of electronic supplementary material from Walmsley et al. (2004). In order to get absolute values from our statistical theory, one has to make assumptions concerning the complex formation cross-section. Using at the moment for simplicity the canonical value $10^{-9}$ cm$^3$ s$^{-1}$, the unit of our results is also $10^{-11}$ cm$^3$ s$^{-1}$. It is certainly too early to make detailed conclusions from these simple calculations. Nonetheless, we want to emphasize that some of the rate coefficients coincide surprisingly well, while other predictions are significantly off, e.g. the formation of $o$-$H_2D^+$ and $p$-$H_2D^+$ in an $o$-$H_3^+$ + HD reaction.

All this detailed information can be used as well to simulate in great detail the processes occurring in an ion trap. A variety of typical situations have been calculated three of which are shown in figure 10. In all the three cases, the HD/H$_2$ abundance has been fixed to $3.7 \times 10^4$ which is expected to prevail in the trap with natural hydrogen (terrestrial abundance). Figure 10a illustrates the ideal isotope enrichment experiment. It starts at $t=0$ with an $H_3^+$ ensemble the o/p ratio of which is equilibrated at 10 K. In addition, the o/p ratio of H$_2$ has been assumed to be fully thermalized. It is obvious that under these conditions, $H_3^+$ disappears mono-exponentially in the depicted time window. A stationary equilibrium will be reached much later. The time constant $t_0$ is given by the actual value of the rate coefficients and the number density. In the trap experiment, it can be varied between 100 ms and minutes. Figure 10b illustrates the huge changes if the o/p ratio of H$_2$ is increased from the 10 K value to 0.001 and if one starts with n-$H_3^+$ thermalized in a 10 K He buffer gas. Figure 10c shows a simulation of an experiment with externally prepared $H_2D^+$ ions, similar to the one discussed in figure 8. The decay of the deuterated ions depends critically on the amount of o-$H_2$. Here, 10% has been assumed. Note that the time-scale had to be changed in order to show the details of the conversions of the $H_2D^+$ ions.

Figure 9. Calculated populations of the seven lowest rotational states of H$_2$D$^+$ formed in various exothermic reactions at a collision energy of 7 cm$^{-1}$ (approx. 10 K). Black, inelastic collision of o-H$_2$D$^+$(111) with o-H$_2$(1); grey, reaction of o-H$_3^+$(10) with HD(0); and hatched, reaction of p-H$_3^+$(11) with HD(0). The values have been calculated using a microcanonical equilibrium distribution with ‘memory’. Inspection reveals that conservation of nuclear spin leads to an ortho–ortho propensity if one starts with o-H$_3^+$. 

Table 4. Relative rate coefficients for inter-conversion of the indicated ions in collisions with HD or o-H$_2$. The first value in each cell has been derived from the decay of the indicated collision complexes, assuming a microcanonical equilibrium distribution at energy of 7 cm$^{-1}$ (approx. 10 K). The second values are rate coefficients from Walmsley et al. (2004) in 10$^{-11}$ cm$^3$ s$^{-1}$.

<table>
<thead>
<tr>
<th></th>
<th>o-H$_3^+$</th>
<th>p-H$_3^+$</th>
<th>o-H$_2$D$^+$</th>
<th>p-H$_2$D$^+$</th>
</tr>
</thead>
<tbody>
<tr>
<td>o-H$_3^+$</td>
<td>—</td>
<td>o-H$_2$</td>
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<td>17.5</td>
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<tr>
<td>o-H$_2$D$^+$</td>
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<td>o-H$_2$</td>
<td>—</td>
<td>o-H$_2$</td>
</tr>
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<td>p-H$_2$D$^+$</td>
<td>—</td>
<td>—</td>
<td>o-H$_2$</td>
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<tr>
<td></td>
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</table>

Figure 10. Simulation of ortho–para transitions and H–D exchange reactions in an ion cloud stored in an ideal 10 K ion trap. In all the three cases, the HD/H$_2$ abundance has been set to $3.7 \times 10^{-4}$, which is expected to prevail in the trap with natural (terrestrial) hydrogen. The rate coefficients used are presented in table 4. In (a), the ortho–para ratios of both H$_3^+$ and H$_2$ have been assumed to be fully thermalized at the beginning, $t=0$, to the ambient temperature. In (b), the $o$-H$_2$/$p$-H$_2$ ratio was increased to 0.001 and it was assumed that $n$-H$_3^+$ has been initially thermalized to 10 K in collisions with He buffer gas. (c) Simulation of the LIR experiment with externally prepared H$_2$D$_2^+$ ions. The decay of the deuterated ions depends critically on the amount of $o$-H$_2$; here 10% has been assumed. Note the change in the time scale. More details concerning the various initial conditions are described in the text.

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6. Conclusions and outlook

The material presented in this paper shows that we already know a lot about the interaction of hydrogen ions with hydrogen molecules, but it also indicates that there are many complications which are not yet fully under control, both in theory and experiments. The new generation of low-temperature machines combining traps with lasers and beams of molecules or radicals will hopefully provide the required state-specific information soon. Polyatomic systems like $\text{H}_5^+$ or $\text{CH}_5^+$ have recently attracted the attention of several theoretical groups and it can be foreseen that this will contribute to our fundamental understanding of these basic systems. The first step in the development of a dynamically biased statistical theory has been made. It is simple to write down general formulae as given by Gerlich (1989); however, one needs more information to define complex formation and decay. A detailed study of state-selected rate coefficients for the capture of hydrogen-containing ions colliding with $\text{H}_2$, $\text{HD}$ or $\text{D}_2$ in rotational states $J=0$ and $1$ has been published recently (Dashevskaya et al. 2005).

A large fraction of the motivations to study $\text{H}_m\text{D}_n^+$ originates from astrophysics, but many of the questions raised also can be extended from H and D to T (tritium) and are of importance for understanding fusion plasma. Very stimulating for performing more studies between 5 and 30 K is the hypothesis that a pre-protostellar core can be completely depleted, which means that all heavy elements including C, N and O vanish from the gas phase and become integrated into ice layers on dust grains. In such a situation, the hydrogen chemistry gets a huge weight as illustrated by the calculations carried out by Walmsley et al. (2004). Inspection of the table of reactions they use in their model reveals that many of the rate coefficients are based on pure speculations. Examples include the catalytic formation of $\text{H}_2$ or low-temperature collisions with H or D atoms. The experimental and theoretical tools are available today to study in great detail the fundamental reactions of $\text{H}_2^+$ or $\text{H}_3^+$ with H and we hope to present some results soon. It will take much longer until someone really understands the formation of hydrogen molecules on dirty ice layers or measures a rate coefficient for processes with negatively charged grains g, such as $g^- + \text{H}_3^+ \rightarrow g^0 + 3\text{H}$. Nanoparticles in low-temperature RF traps may be a solution.

The work summarized in this contribution involved the cooperation and assistance of many researchers in Freiburg and Chemnitz. We thank them all. Part of the project has been supported by the German–Israeli Foundation (grant no. I707-55.7/2001) and via the DFG Forschergruppe Laboratory Astrophysics (FOR 388).

References


Discussion

T. Oka (University of Chicago, USA). Perhaps a conference is not the right place to discuss discrepancies between numbers. So I would like to look at your paper of 2004 and think about it after I go back to Chicago. Please let me know the reference.

D. Gerlich. It was not the aim of the comparison of the two tables (see supplementary material) to emphasize on the discrepancies between the numerical results of your and my calculations. Primarily I intended to indicate that there are strict selection rules for certain transitions (marked in yellow). In a complete statistical theory describing the decay of $H_3^+$ collision complexes with given total nuclear spin one has to sum over all accessible product states. The table I have shown for the first time at a conference in 2004, is just a high-energy limit (see (iii)).

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S. Schlemmer (*University of Cologne, Germany*). What is the motivation that $P_{\text{decay}}$ is given by the high-temperature probabilities? Is this perhaps because of an exothermicity?

D. Gerlich. The $\text{H}_3^+ + \text{H}_2$ scrambling reaction is of course thermoneutral, and therefore, the high-temperature approximation should not be used at low temperatures ($<50 \text{ K}$). However, in our 300 K storage ion source or in an 80 K plasma, the $o/p$ conversion probabilities can be described in good approximation by my table, provided that the reaction really can be treated using a statistical model.

D. Schwalm (*MPI Nuclear Physics, Heidelberg, Germany*). What is the difference in the assumption for the table of Cordonnier et al. (2000) and your table for the transition probabilities $o/p-\text{H}_3^+ + o/p-\text{H}_2 \rightarrow o/p-\text{H}_3^+ + \text{H}^+$?

D. Gerlich. Oka’s calculations account exclusively for the nuclear spin states and ignore any dynamical restrictions or whether some states are accessible with the available energy. My table has been calculated in the high-temperature approximation, i.e. it is assumed that the number of open $o-\text{H}_3^+$ states is equal to the open $p-\text{H}_3^+$ states.