Deuterium Fractionation and Ion-Molecule Reactions at Low Temperatures

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Abstract. Understanding deuterium fractionation is currently one of the greatest challenges in astrochemistry. In this contribution deuteration experiments of the series CH_n^+, n = 2–5, in a low temperature 22-pole ion trap are used to systematically test a simple chemical rule predicting which molecular ion undergoes deuterium exchange in collisions with HD. CH_4^+ turns out to be a problem case, where prediction fails. The method of laser induced reaction (LIR) is used to determine the population ratio of the lowest ortho-to-para states of H_2D^+ relaxed in collisions with H_2. Preliminary results indicate that the ortho-to-para ratio of H_2D^+ is substantially reduced in para-H_2. This points at the important role of nuclear spin in deuterium fractionation, in particular at the destruction of ortho-H_2D^+ in collisions with ortho-H_2. More systematic LIR experiments are needed for a chemical model of deuterium fractionation including state-to-state modifications of the species involved.

Keywords. astrochemistry — ISM: molecules — molecular processes

1. Introduction

About 25 deuterated molecules have been found to date in the interstellar medium, Millar (2003). Much attention has been drawn to recent detections of doubly and even triply deuterated species in cold interstellar clouds. Triply deuterated ammonia (Lis *et al.* 2002) and methanol (Parise *et al.* 2004) show an isotopic enhancement (fractionation) which is up to twelve orders of magnitude larger than the simple predictions based on the cosmic D/H ratio of 1.5×10^{-5}. The recent detection of D_2H^+ (Vastel *et al.* 2004), stimulated new chemical modelling calculations for very cold dense clouds which find that even D_3^+ can be the dominant molecular species (Walmsley *et al.* 2004; Flower *et al.* 2004).

The main source of deuterium in molecular clouds is HD. Three primary molecular ions, H_3^+, CH_3^+ and $C_2H_2^+$, are known to transfer the deuterium in collisions with HD. These reactions are exothermic by a few hundred Kelvin due to differences in zero-point vibrational energies. Since typical cloud temperatures are much smaller than these exoergicities, isotopic enhancement of the singly deuterated ions can easily reach factors up to 10^4. Reactions in subsequent collisions of these ions lead to the deuteration of other molecules like HCO^+.

Due to the Arrhenius-type behavior of the back reactions (hydrogenation) the fractionation strongly depends on the temperature of the particular environment. Also the fractional electron abundance plays an important role for isotopic fractionation as dissociative recombination competes with deuteration. For the same reason the presence

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of atoms and molecules which react with the primary ions also reduce the isotopic enhancement. These species include almost all C, N and O bearing molecules. In contrast, freeze out of molecules on grains in very cold environments removes these species from the gas phase. As a consequence isotopic enrichment is found to be increased. Many of these dependencies are included in current chemical models for fractionation.

Another level of complication arises from collision systems with identical nuclei. This is for example the case in all three key initial deuteration reactions. Besides conservation of energy, momentum, angular momentum and parity, conservation of the total nuclear spin imposes further restrictions on the outcome of such reactions (Quack (1977)). Because of this, even more importantly, inelastic collisions with the most dominant H_2 molecule can influence the D/H ratio significantly. Thorough descriptions of appropriate theoretical methods to include nuclear spin effects as well as experiments to investigate the role of nuclear spin have been given by Gerlich *et al.* (2002a), Gerlich & Schlemmer (2002b), and Gerlich (2004).

Current laboratory challenges on understanding deuterium fractionation include (i) the search for more primary deuteration reactions, (ii) testing of theoretical predictions for possible deuteration reactions, and (iii) the role of nuclear spin conservation on the efficiency to replace H vs. D. More systematic studies on possible deuteration reactions of small hydrocarbons, CH_n^+, ($n = 3 - 5$), Asvany *et al.* (2004a), and of $C_3H_n^+$, ($n = 1 - 3$) have been carried out recently, Savic & Gerlich (2005), Savic *et al.* (2005). In this contribution the series CH_n^+ + HD will be used to compare the results to theoretical predictions worked out by Henchman *et al.* (1988) and modified by Maluendes *et al.* (1992).

In order to detemine the role of nuclear spin conservation, state-to-state reactive and inelastic rate coefficients are needed. Experimentally this is very difficult. However, as described below, a method has been developed in recent years by Schlemmer *et al.* (1999), Schlemmer *et al.* (2002), Mikosch *et al.* (2004), Schlemmer *et al.* (2005), Asvany *et al.* (2005a), and Asvany *et al.* (2005b) to infer ro-vibrational spectra of a cloud of molecular ions in a trap experiment. Based on a few assumptions the rotational population of the ion cloud can be derived. First results on H_2D^+ using the free electron laser FELIX are presented.

2. Experimental

To measure the rate coefficients of low-temperature ion-molecule reactions, a 22-pole ion trap has been used. This apparatus has been developed and thoroughly described by (Gerlich & Horning 1992) and recent applications to isotopic fractionation are well documented by Gerlich & Schlemmer (2002b), Asvany *et al.* (2004b), Savic & Gerlich (2005), and Savic *et al.* (2005).

In brief, ions are produced in a storage ion source by electron bombardment, mass filtered in a quadrupole analyzer and then injected into the 22-pole ion trap, which is held at cryogenic temperatures: T > 10 K. On entrance, the ion temperature is adapted to the trap temperature by a short helium pulse. During the storage time of several seconds the ions can react with a neutral gas, here mainly HD, of known constant but adjustable number density. After the trapping period, the trap content is extracted, mass analyzed and the parent and product ions are counted with high efficiency. From this procedure, the rate coefficients of the involved processes are inferred by repeating the mentioned cycle of *trapping/reaction/detection* for all possible reaction products and different trapping times.
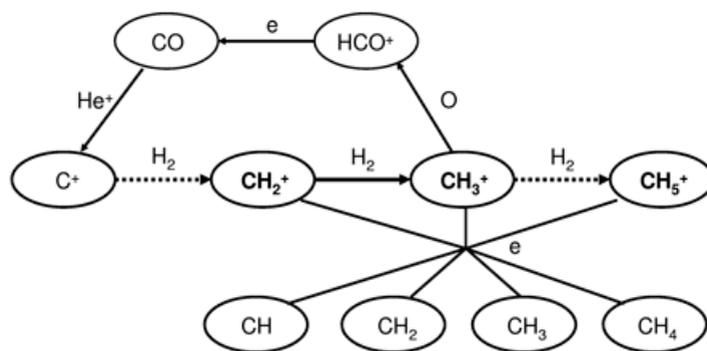
Figure 1. Formation routes for small hydrocarbon molecules in interstellar clouds as described by Black & Dalgarno (1977).

An extension of this technique is the method of laser induced reactions (LIR), in which an endothermic ion-molecule reaction (e.g. $H_2D^+ + H_2 \rightarrow H_3^+ + HD$, as presented below) is enhanced by resonantly exciting the trapped parent ions with a laser. This offers not only the possibility to record a spectrum by counting the product ions as a function of the laser wavelength, but LIR also yields information on state-selected rate coefficients, lifetimes of the excited states and the population of the pumped states (Schlemmer *et al.* 2002, 2005).

3. Results and Discussion

3.1. *Kinetic Studies*

Figure 1 shows the network of small hydrocarbon ions as proposed by Black & Dalgarno (1977) for diffuse interstellar cloud conditions. Similar schemes have been found also for cold dense clouds. In this scheme carbon is cycled between the small hydrocarbon ions, CH_n^+, $n = 0-3$, and CO. Thus these ions play an important role in molecular formation in interstellar clouds. Starting with C^+, hydrogen is either added via radiative association (adding H_2, dashed line) or in an abstraction reaction (adding H, solid line). Growth stops at CH_5^+, since CH_n^+ with $n > 5$, does not form a strongly bound molecule. Instead, dissociative recombination of this molecule is a major source for interstellar methane.

Based on such a scheme, it is not obvious why only CH_3^+ should be a source for deuteration. Therefore more systematic studies of the deuteration of the CH_n^+, $n = 2-5$, ions have been conducted in recent years (Asvany *et al.* 2004a). The results of the kinetic measurements at a trap temperature of 15 K are summarized in Table 1. Various outcomes are possible in the collision of $CH_n^+ + HD$. CH_2^+ undergoes hydrogen or deuterium abstraction to form CH_3^+ or CH_2D^+. This process is so fast, that any deuteration, forming CHD^+, can hardly be detected, especially since the abstraction reaction product, CH_3^+, has the same mass as the deuteration product, CHD^+. Comparison of the measured total rate coefficient for the abstraction reaction to the limiting collisional rate coefficient, k_L, reveals that this process is happening practically in every collision. In fact the experimental value is about 20% larger than the predicted value. One possible reason for this discrepancy lies in the long-range attraction of HD.

Since abstraction is also very fast for CH_2^+ in collisions with H_2, the less frequent collisions with HD hardly yield a substantial fraction of CH_2D^+. Because of this reason

Table 1. Rate coefficients, branching ratios and reaction efficiencies (k/k_L) for the deuteration reactions of CH_n^+ + HD, $n = 2..5$, at $T = 15$ K.

Reaction		Branching ratio	k [$10^{-9} cm^3 s^{-1}$]	k/k_L
CH_2^+ + HD	$\rightarrow CH_2D^+$ + H	0.8	1.6	1.21
	$\rightarrow CH_3^+$ + D	0.2		
CH_3^+ + HD (+He)	$\rightarrow CH_2D^+$ + H_2		1.65	1.25
CH_3^+ + HD (+n-H_2)	$\rightarrow CH_2D^+$ + H_2		1.5	1.14
CH_3^+ + HD (+p-H_2)	$\rightarrow CH_2D^+$ + H_2		0.4	0.30
CH_2D^+ + HD (+He)	$\rightarrow CD_2H^+$ + H_2		1.59	1.21
CD_2H^+ + HD (+He)	$\rightarrow CD_3^+$ + H_2		1.5	1.15
CH_4^+ + HD	$\rightarrow CH_3D^+$ + H_2	<0.002	0.45	0.34
	$\rightarrow CH_5^+$ + D	0.68		
	$\rightarrow CH_4D^+$ + H	0.32		
CH_5^+ + HD	$\rightarrow CH_4D^+$ + H_2		$< 5 \cdot 10^{-9}$	0

CH_2^+ does not play a role in isotopic fractionation. Instead, only those ions are relevant for isotopic fractionation in collisions with HD which react very inefficiently with H_2. This is the case for CH_3^+, which forms CH_5^+ only very slowly via radiative association and for CH_5^+, which is effectively the end of the reaction chain. Therefore at least these two ions are reasonable candidates to contribute to isotopic fractionation. CH_4^+ is not shown in the network, see Figure 1, and will be considered separately.

For CH_3^+ sequential deuteration has been measured and rate coefficients for all individual steps have been determined at a trap temperature of 15 K, see Table 1. As in the case of CH_2^+ the rate coefficients are significantly larger than the capture rate coefficient. Moreover, each step of deuteration happens slightly faster. Besides these peculiarities, it turns out that deuteration of CH_3^+ is happening practically in every collision. It is quite surprising, that this process can be so fast, because simple statistics would predict a 40% chance to find the D-atom in HD and a 60% chance to find it in CH_3^+ after the collision. The deviation from this rather simple counting argument shows that the potential energy surface of the collision system has to be taken into account to understand the large deuteration efficiency.

As described in detail in Asvany *et al.* (2004a), the results for collisions with pure HD have been compared to experiments, where the dominant collision partner is H_2. In the case of pure HD, CH_3^+ has been cooled in the trap to the ambient temperature via collisions with He. The value derived from this experiment is very similar to the value when CH_3^+ is cooled in n-H_2, which contains 1/4 p-H_2 and 3/4 o-H_2, as well as the terrestrial abundance of [HD]/[H_2] $= 3 \times 10^{-4}$. However, when conducting the experiment in p-H_2 with the natural abundance of HD (Gerlich & Schlemmer 2002b), the deuteration reaction is found to proceed about four times slower when compared with the other experiments, as shown in Table 1. The presence of the various collision partners changes the relaxation of the ion cloud. This result is linked to the influence that nuclear spin conservation imposes on the rotational state distribution when most collisions are with p-H_2 rather than with o-H_2 or HD. This finding will be discussed below in more detail.

As shown in Table 1, the collision of CH_4^+ with HD leads primarily to hydrogen abstraction, a process that has been described in a previous publication (Asvany *et al.* 2004b). The total rate coefficient for abstraction at 15 K, however, amounts to about 30% of the

collision limit. Interestingly, the experimental data show no indication of deuteration in this case. Although the detection of deuterated species has been limited by some spurious isotopomers coinciding with the mass of the products, an upper limit for the rate coefficient of deuteration could be derived. According to this result, shown in Table 1, more than 1000 collisions are necessary to exchange a hydrogen for a deuterium in CH_4^+ in collisions with HD. Another interesting result concerns the branching ratio in the abstraction reaction. The less exoergic product CH_5^+ is formed twice as often as compared to the energetically more favorable CH_4D^+ product. Moreover, the abstraction reaction shows a negative temperature dependence, meaning, that abstraction becomes more favorable at low temperatures. These results indicate that the dynamics of the CH_4^+ + HD collision system does not follow a simple downhill reaction without barrier.

Finally the collision system CH_5^+ + HD has been studied. As for CH_4^+, no indication for the exchange of a deuterium for a hydrogen atom has been found. In fact, product detection in this case is more sensitive than for the CH_4^+ measurements. Therefore the upper limit of deuteration has been determined to be much lower: $k \leqslant 5 \times 10^{-18} \, cm^3 \, s^{-1}$; see Table 1. As pointed out before and shown in Figure 1, CH_5^+ is the end of the hydrogenation route in interstellar clouds. The four valence electrons form a closed shell molecule. Therefore abstraction of D or H does not occur in collisions with HD. Since radiative association is a very slow process for this system, $k_r = 2 \times 10^{-16} \, cm^3 \, s^{-1}$, dissociative recombination dominates under interstellar conditions, leading to the various neutral small hydrocarbons depicted in Figure 1.

In summary, CH_n^+ exhibits fast deuteration in collisions with HD only for $n = 3$. All other molecular ions show a negligible chance for the exchange of a deuterium atom. Therefore no additional primary deuteration reaction has been found in these experiments. However, due to the systematic studies presented, the results can be compared to predictions or at least simple chemical rules. Such rules have been first formulated by Henchman *et al.* (1988). Here reactions are characterized distinguishing reactants with filled and unfilled valence shells. According to this work, no barriers inhibit deuterium exchange for exoergic reactions if at least one of the reactants has an unfilled valence shell. In contrast, barriers can inhibit the exchange if both reactants have filled valence shells. This simple rule is illustrated in Figure 2. Here the minimum energy path for an exoergic deuterium exchange, AH^+ + HD $\rightarrow$ AD^+ + H_2, is depicted. At the low temperatures of interstellar clouds the two reactants form an entrance complex $AH^+ \cdot \cdot HD$, where the two partners remain as distinct molecules. The H-D exchange needs a closer approach of the two reactants and occurs via a transition state. In case of closed shell species, this transition state is substantially higher in energy than the entrance channel. Therefore the exchange reaction is hindered. However, in case of one open shell reactant the complex formed is much stronger bound and the transition state is expected to be below the entrance channel, such that the exchange happens within the collision complex. Due to the exoergicity of the reaction the collision complex dissociates preferentially into AD^+ and H_2 based on statistical arguments counting the number of energetically accessible states. This simple classification is able to explain why H_3^+, CH_3^+ and $C_2H_2^+$ do undergo H-D exchange in collisions with HD, while HCO^+, N_2H^+ and NH_4^+, for example, do not.

The fact that the "filled valence shell" ions form only weakly bound complexes is related to the fact that electronic reorganization is hindered since empty AH^+ orbitals are energetically inaccessible due to a large HOMO-LUMO ("highest occupied molecular orbital", "lowest unoccupied molecular orbital") gap. Therefore the terms "filled" and "unfilled valence shells" have been replaced by Maluendes *et al.* (1992) for the chemically more precise terms of large and small HOMO-LUMO gap, respectively.
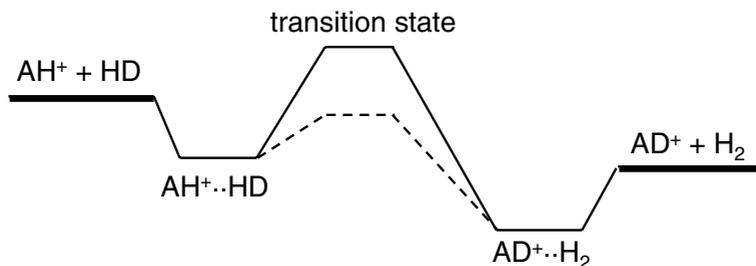
Figure 2. Energetics of an exoergic deuterium exchange reaction with barrier (solid) without a barrier (dashed).

HD has a very large HOMO-LUMO gap, therefore only the small hydrocarbon ions have to be considered in the present case. In the CH_n^+, n = 2–5, series, only CH_5^+ has a fully occupied valence shell with a very large HOMO-LUMO gap. The experimental result that more than 10^8 collisions are necessary for H-D exchange is in very good agreement with the prediction. For CH_2^+ the abstraction reaction is so fast, that deuterium exchange could not be detected. Therefore no comparison with the simple prediction can be made. H-D exchange is very fast for CH_3^+, which is in perfect agreement with the prediction. In fact, the CH_4D^+ complex which is formed is a strongly bound molecule in its ground state. Therefore the collision complex, the transition state and the complex in the exit channel are more or less the same entity. Apparently, the various H-atoms and the D-atom swap places in this complex very efficiently without substantial energetic hindrance. This process is known as *scrambling*. Thus the picture drawn in Figure 2 describes this case very well. Even the fact that deuteration is happening in almost 100% of the cases, rather than only in three out of five cases, as predicted by the statistical arguments given above has been explained by Maluendes *et al.* (1992). Upon forming the entrance channel complex the system can reach the transition state with a certain probability, x. In all other cases, probability $1 - x$, it re-dissociates back into the reactants. From the transition state the complex can fall back into the entrance channel again or react. From the entrance channel it can again form the transition state etc. In effect the chance of forming the deuterated product reaches almost unity.

In contrast, as an open valence shell ion CH_4^+ should undergo rapid H-D exchange, but does not, as shown above. Only little is known about the electronic structure of this molecule (Jacox 1994). Therefore the HOMO-LUMO gap cannot be quantified. This hampers a more quantitative comparison. Despite these limitations, as will be discussed in the following, deuteration is hindered even without a substantial barrier. The exoergic abstraction reaction in a CH_4^+ + HD collision proceeds faster by at least one order of magnitude at 10 K compared to 300 K. Such a behavior is associated with an extended lifetime of the collision complex in the entrance channel. This longer lifetime enhances substantially the chance to overcome the transition state and reaching the products. Even a small barrier can be surpassed via tunneling. Nevertheless, if the reaction is hindered by a barrier, higher temperatures will increase the reaction probability as well. Thus a reaction over a barrier (barrier height E_a) will follow the strongly positive temperature dependence of an Arrhenius type behavior, $\exp(-E_a/kT)$, in the high-temperature limit. In summary, the temperature dependence can be negative (collision complex) for low temperatures but will be positive (barrier) for high temperatures. For the CH_4^+ + H_2 system the negative temperature dependence prevails up to more than 1000 K based on the trap and selected ion flow drift tube (SIFDT) experiments (Asvany *et al.* 2004b; Federer *et al.* 1985). Such a behavior would imply a very high barrier, which makes it difficult for the reaction to occur at low temperatures at all. This is in contradiction to the

fact that abstraction proceeds in about 1/3 of the cases. In fact, abstraction of CH_4^+ + H_2 occurs about 100 times faster than in the isoelectronic NH_3^+ + H_2 system, which shows a turnover to a positive temperature dependence already at 150 K. Therefore it is concluded that a barrier is not hindering the abstraction reaction of CH_4^+ + H_2. Rather, the transition state seems to form a dynamical bottleneck that is hard to surpass. Note, that for the abstraction an atomic species has to be liberated to form CH_5^+ + D or CH_4D^+ + H, indicating a very intimate chemical interaction along this path. Apparently, this path can be followed without a substantial barrier. The products of a hypothetical reverse reaction, e.g., CH_4D^+ + H → CH_3D^+ + H_2 are energetically accessible when starting from a low temperature CH_4^+ + HD collision. Therefore deuterium exchange is obviously not hindered by a barrier. Nevertheless it does not occur. This finding is in sharp contrast to the simple model made by Henchman *et al.* (1988), where the hinderance of the H-D exchange is associated with a barrier in the transition state.

3.2. *Laser Induced Reactions*

In the series of small hydrocarbon ions only CH_3^+ undergoes rapid H-D exchange. It has been found in the kinetics studies above that the speed of this exchange depends on the nature of inelastic collision partners, p-H_2, o-H_2 or He, see Table 1. It is the aim of this section to (i) understand the possible reasons for this, as well as the consequences on isotopic fractionation and (ii) to describe an experiment, which allows a derivation of rotational populations of a low temperature ion cloud.

Inelastic collisions with H_2 are much more frequent in space than collisions with HD. Thus CH_3^+ relaxes to the lowest rotational states accessible. Due to the Pauli exclusion principle antisymmetric/symmetric rotational states of this Fermion are linked to the symmetric/antisymmetric nuclear spin state. The population of these states therefore depends on the H_2 temperature and the ortho-to-para ratio of H_2. As a consequence, the two nuclear spin configurations can be treated as separate molecules when dealing with inelastic collisions, which do not change the nuclear spin state of CH_3^+. In contrast, there is an interchange between the two configurations when nuclear spin changing collisions are permitted. Still in the latter case restrictions are imposed by the conservation of the total nuclear spin in those collisions. The fast deuteration of CH_3^+ shows that scrambling of the protons (and the deuteron) is a common process in the CH_4D^+ collision complex. This complex decomposes into different nuclear spin configurations, thus allowing for nuclear spin changes. It has been worked out by Bates (1991) for the CH_5^+ system that conservation of the total nuclear spin is one restriction for the possible outcome of such collisions. As a consequence, relaxation of CH_3^+ in H_2 leads to different rotational states of CH_3^+, depending on the ortho-to-para ratio of the H_2 collision partner. Apparently this must be the reason why deuteration is slower when CH_3^+ is relaxed in p-H_2 rather than in He or n-H_2.

Determination of the rotational population of such an ion cloud would yield direct insight into the role of the nuclear spin configurations. Such an experiment has been described recently by Mikosch *et al.* (2004). In this work a 22-pole trap experiment has been devised to determine the rotational population of an H_3^+ ensemble at $T = 55$ K by means of action spectroscopy. For this purpose H_3^+ is excited with more than two quanta of vibration in the ν_2-mode using a diode laser. Chemical probing in collisions with Ar is used to detect the excitation. The number of ArH^+ products is a direct measure for the number of H_3^+ found in the rotational state prior to excitation. Three rotational lines have been detected. From the relative intensities of the absorption lines the rotational temperature and from the Doppler width the kinetic temperatures have been derived. As a result H_3^+ is found to be thermalized.

$H_3^+ + HD$ $H_2D^+ + H_2$

2_2

1_0

1_1

0_0

100 K

1_{10}

1_{11}

1_{01}

0 K

0_{00}

p-H_3^+ o-H_3^+ p-H_2D^+ o-H_2D^+
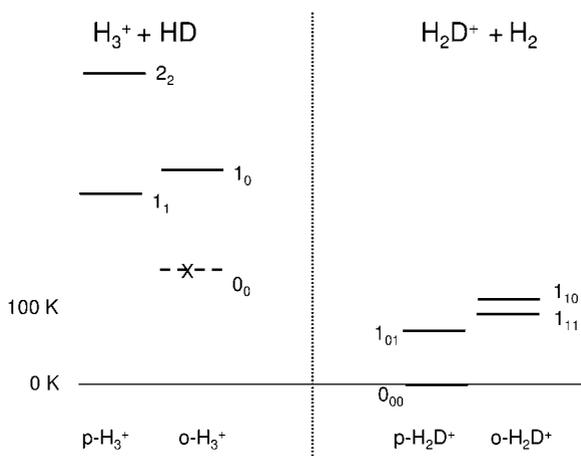
Figure 3. State specific energetics of the $H_3^+ + HD \leftrightarrow H_2D^+ + H_2$ reaction. Only $J = 0$ states of HD and H_2 are considered. For collisions with, $J = 1$, o-H_2, 175 K extra energy has to be added.
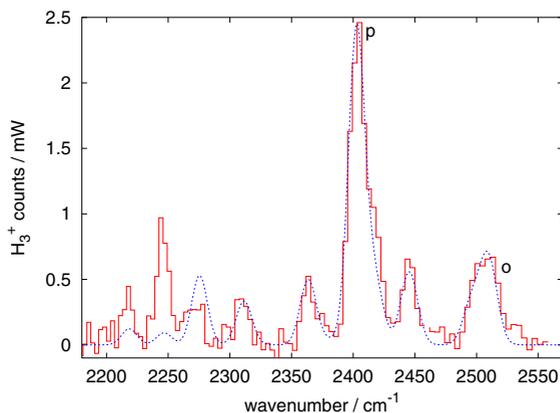
Figure 4. LIR spectrum of H_2D^+ in collisions with n-H_2. The simulation (dotted line) represents contributions from the ν_2 and ν_3 vibrational modes. Transitions of the lowest ortho (o) and para (p) state used for the analysis are marked. Deviations between simulation and spectrum hint at saturation effects which are discussed in the text.

It has been pointed out by Gerlich *et al.* (2002a) that the relative population of the lowest ortho state of H_2D^+ plays a key role for the efficiency of the reverse reaction of deuteration of H_3^+, see Figure 3. In effect the back reaction becomes exoergic in collisions of o-H_2D^+ with o-H_2 since it adds some 175 K of rotational energy. Therefore it is most interesting to determine the rotational distribution of H_2D^+. This has been achieved in the present work by ro-vibrational excitation of H_2D^+ using the free electron laser FELIX, in the range of the fundamental ν_2 and ν_3 vibrational modes. In this way an equivalent of some 3500 K of energy is added, thus enhancing the back reaction with n-H_2 substantially. By detecting the number of H_3^+ products as a function of wavelength, the spectrum of H_2D^+ shown in Figure 4 has been recorded. From the intensities of these lines relative rotational populations of the vibrational ground state H_2D^+ could be derived. For the analysis, recently calculated Einstein A coefficients of the corresponding transitions were used (Ramanlal & Tennyson 2004), from which the corresponding Einstein B coefficients were derived. In addition, it has been assumed that all excited ro-vibrational states undergo hydrogenation with the same efficiency and that the rate of fluorescence, A, is much smaller than the collisional rate at $[H_2] = 7 \times 10^{10} \text{ cm}^{-3}$. The

nominal temperature of the trap was $T = 17$ K. According to the preliminary analysis, the rotational temperature lies between 20 and 30 K, and the population ratio of the lowest ortho and para state of H_2D^+ is about $\sim 3/4$. Preliminary experiments using p-H_2 show much smaller values. These results are in agreement with the general trend that p-H_2 leads to a more efficient relaxation than n-H_2. This is an important result hinting at the crucial role of nuclear spin in low temperature collisions. However, higher populations of the lowest ortho state of H_2D^+ would be expected in both cases based on the previous study of Gerlich *et al.* (2002a).

Before final conclusions can be drawn, several more systematic studies are necessary. The validity of the assumptions made for the analysis have to be checked in future experiments, e.g., by determining the dependence of the signal on the H_2 number density, thus comparing fluorescence, dominating at *low* densities, with collisions, dominating at *high* densities. Moreover, it has to be taken into account that FELIX is a pulsed laser system with micro-pulses of several picosecond duration only. Therefore saturation effects influence the experimental outcome. In order to overcome such a limitation, experiments with continuous laser excitation are underway. Also a narrower bandwidth excitation allows for the determination of the kinetic temperature of the ion cloud.

4. Conclusions

Deuteration of CH_4^+ in collisions with HD shows that the simple classification of "unfilled" and "filled valence shells" even in the more sophisticated version of Maluendes *et al.* (1992) cannot be used as a general guidance to distinguish reactants, which do or do not undergo H-D exchange. In contrast, this example demonstrates that not even the knowledge of particular points along the minimum energy path is sufficient. Due to the dynamical restrictions occurring along the reaction path dynamical calculations are necessary to predict the fate of the reactants.

Scrambling of H and D is an important way for efficient H-D exchange as seen for CH_3^+ + HD because atoms can swap places without the need of breaking and forming the very strong bonds of the reactants. This process is linked to the chemical equivalence of the atoms involved. Conservation of total nuclear spin in collisions with identical nuclei has to be considered. Therefore state-to-state rate coefficients are needed. One experimental route towards this aim is the determination of rotational state populations. Only several hundred H_2D^+ are needed to detect a ro-vibrational LIR-spectrum. It is possible to determine the rotational population from such spectra based on several assumptions. A first example spectrum has been analyzed. However, more systematic LIR studies are necessary. Once reliable rotational state populations have been derived at low temperatures, more extensive modelling of the H_3^+ and CH_3^+ systems can be used to derive state-to-state rate coefficients for inelastic and reactive collisions. With the advent of SOFIA and the Herschel satellite several observations detecting transitions between the lowest rotational states of H_2D^+ and D_2H^+ are planned. It will be interesting to see how experiment, astrophysical modelling and observation compare.

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References

Asvany, O., Schlemmer, S., & Gerlich. D. 2004a, *Ap. J.* 617, 685

Asvany, O., Savic, I., Schlemmer, S., & Gerlich., D. 2004b, *Chem. Phys.* 298, 97

Asvany, O., Giesen, T., Redlich, B., & Schlemmer, S. 2005a, *Phys. Rev. Lett.* 94, id.073001

Asvany, O., Kumar, P., Redlich, B., Hegemann, I., Schlemmer, S., & Marx, D. 2005b, *Science* 309, 1219

Bates, D.R. 1991, *Ap. J.* 375, 833

Black, J.H., & Dalgarno, A. 1977, *Ap. J. Suppl.* 34, 405

Federer, W., Villinger, H., Tosi, P., Bassi, D., Fergusson, E., & Lindinger, W. 1985, in *Molecular Astrophysics-State of the art and future directions*, eds. G.H.F. Diercksen *et al.* (Reidel, Boston), p. 649

Flower, D.R., Pineau des Forêts, G., & Walmsley., C.M. 2004, *A&A* 427, 887

Gerlich D. & Horning, S. 1992, in *Ion-Molecule Reactions*, ed. Z. Herman, *Chemical Reviews* 92, 1509

Gerlich, D., Herbst, E., & Roueff, E. 2002a, *Planetary and Space Science* 50, 1275

Gerlich, D. & Schlemmer, S. 2002b, *Planetary and Space Science* 50, 1287

Gerlich, D. 2004, in *XIV Symposium in Atomic, Cluster and Surface Physics*, ed. P. Casavechia (La Thuile, Italy), 1

Henchman, M., Paulson, J.F., Smith, D., Adams, N.G., & Lindinger, W. 1988, in *Rate coefficients in astrochemistry*, eds. T.J. Millar and D.A. Williams, p. 201

Jacox, M.E. 1994, *J. Phys. Chem. Ref. Data* 3

Lis, D.C., Roueff, E., Guerin, M., Phillips, T.G., Coudert, L.H., van der Tak, F.F.S., & Schilke, P. 2002, *Ap. J.* 571, L55

Maluendes, S.A., McLean, A.D., & Herbst, E. 1992, *Ap. J.* 397, 477

Mikosch, J., Kreckel, H., Wester, R., Plašil, R., Glosík, J., Gerlich, D., Schwalm, D., & Wolf, A. 2004, *J. Chem. Phys.* 121, 11030

Millar, T.J. 2003, *Space Science Reviews* 106, 73

Quack, M. 1977, *Mol. Phys.* 34, 477

Parise, S., Castets, A., Herbst, E., Caux, E., Ceccarelli, C., Mukhopadhyay, I., & Tielens, A.G.G.M. 2004, *A&A* 416, 159

Ramanlal, J. & Tennyson, J. 2004, *MNRAS* 354, 161

Savic, I. & Gerlich, D. 2005, *Phys. Chem. Chem. Phys.* 7, 1026

Savic, I., Schlemmer, S., & Gerlich, D. 2005, *Ap. J.* 621, 1163

Schlemmer, S., Kuhn, T., Lescop, E., & Gerlich, D. 1999, *Int. J. Mass Spectrom.* 185, 589

Schlemmer, S., Lescop, E., v. Richthofen, J., & Gerlich, D. 2002, *J. Chem. Phys.* 117, 2068

Schlemmer, S., Asvany, O., & Giesen, T. 2005, *Phys. Chem. Chem. Phys.* 7, 1592

Vastel, C., Phillips, T.G., & Yoshida, H. 2004, *Ap. J.* 606, L127

Walmsley, C.M., Flower, D.R., & Pineau des Forêts. G. 2004, *A&A* 418, 1035

Discussion

Kroes: CH_4^++HD produces mostly CH_5^+ through a dynamic mechanism (H farther away from centre of mass of HD). For which other systems do you expect this mechanism to be important as well?

Schlemmer: The effect of producing more hydrogenated than deuterated species has been predicted by David Clary's group for the collision of O^++HD. However, no experiments have been carried out so far. Based on the arguments given in their publication one could expect this effect in many systems exhibiting hydrogen abstraction.