Probing the low-temperature rotational population of H$_2$D$^+$

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Abstract. The gas phase exchange reactions of isotopologues of H$_3^+$ with isotopologues of H$_2$ are responsible for the observed deuteration in low-temperature interstellar clouds. At the prevailing cryogenic temperatures many quantum effects, as zero-point vibrational energies, large rotational level spacings and nuclear spin effects become important. In order to understand the processes on a level-to-level basis, experiments in a 22-pole ion trap are carried out accompanied by microcanonical simulations. In particular, the method of laser induced reaction (LIR) is applied to probe the four lowest rotational levels of H$_2$D$^+$.

1. Introduction
Before an interstellar cloud collapses into a proto-star, possibly surrounded by a planetary disc, it is characterized by strong depletion of heavier molecules, leaving predominantly molecular hydrogen isotopologues and helium in the gas phase, and of course electrons and ice-covered dust grains. The dominant ionic species besides H$^+$ and H$_2^+$ in such an environment is cold H$_3^+$ and its isotopic counterparts produced by the chain of exothermic reactions [1, 2, 3, 4]:

\[
\begin{align*}
H_3^+ + HD &\iff H_2D^+ + H_2 \\
H_2D^+ + HD &\iff D_2H^+ + H_2 \\
D_2H^+ + HD &\iff D_3^+ + H_2
\end{align*}
\]

H$_2$D$^+$ and D$_2$H$^+$ have been detected in cold clouds [5, 2] by their low rotational transitions, and there is a wealth of singly and even multiply deuterated molecules detected up to date (see for example [6, 7, 8, 9, 10] and references therein) which are formed by secondary reactions. In order to have a sensitive spectroscopic probe for the properties prevailing in cold interstellar clouds, it is of uttermost importance to understand the physical processes responsible for the formation and destruction of the basic ionic molecules. For H$_3^+$ and its isotopologues, these processes are mainly the above given ion-molecule reactions, the depletion reactions with heavier molecules (mainly CO), and the encounters with electrons. While many of the contributions to the DR2007 conference proceedings deal with the destruction of H$_3^+$ isotopologues by dissociative recombination with electrons, this paper gives an excerpt of the efforts to understand the exchange reactions (1-3) on a state-specific basis.

At the low-temperatures of interstellar clouds (10-100 K), many quantum mechanical effects such as zero-point vibrational energies (ZPVE), large rotational level spacings and different nuclear
Figure 1. Schematic PES of the $\text{H}_4\text{D}^+$ collision system. The numbers are based on the most recent calculations on $\text{H}_5^+$ [12]. Internal rotation of the $\text{H}_2$ moiety and the hop of the central proton have a relatively low barrier, while a higher barrier has to be overcome for the in-plane rotation of the $\text{H}_3^+$ triangle. That this motion indeed occurs in the complex has been demonstrated by isotopic measurements [13, 14]. In the case of the $\text{H}_4\text{D}^+$ complex, the $\text{H}_2\text{D}^+$ + $\text{H}_2$ exit channel is lower by about 160 cm$^{-1}$ (232 K) due to zero-point vibrational energies. Spin species determine the outcome of the deuteration reactions (1-3). For example, around 20 K, only the four lowest rotational states are substantially occupied for $\text{H}_2\text{D}^+$. Furthermore, it is currently discussed [11] that small amounts of o-$\text{H}_2$ can drive the backward direction of reaction (1), resulting in reaction rates differing from simple thermal equilibrium considerations. The influence of the ZPVE is illustrated in the schematic potential energy surface (PES) in Figure 1, where the exit channel leading to the right side of reaction (1), $\text{H}_2\text{D}^+$ + $\text{H}_2$, is exothermic by about 232 K. The details of the PES are based on the most recent ab initio calculations of Xie et al. [12]. As shown, the forming $\text{H}_4\text{D}^+$ complex can perform three types of internal motion, of which the so-called proton hop and triangle in-plane rotation lead to isotopic exchange.

To understand the underlying processes, our research group explores the exchange reactions by (i) measuring the rate coefficients as a function of temperature and different ortho/para-composition of $\text{H}_2$, (ii) using laser induced reactions (LIR) to probe the lowest rotational levels of the involved species and investigating their kinetics, and furthermore the measurements are complemented by (iii) microcanonical calculations to understand the results. This contribution gives some examples of our experimental and theoretical efforts.

2. Experimental Section

The experimental procedures are described in detail elsewhere [15, 16, 17, 18, 19, 20, 21]. In brief, a cryogenic 22-pole ion trap [22, 23] is used to investigate mass-selected ions produced in an external ion source. Several hundred ions are initially cooled by collision with He gas and kept in the trap to study their reactions with an admitted neutral reaction partner (usually isotopologues of $\text{H}_2$), and also a laser beam can be used to excite the cold ions and initiate reactions in the trap (LIR).

The determination of rate coefficients is exemplified for the reaction $\text{H}_4^+$ + HD. A pulse of several hundred $\text{H}_4^+$ ions is injected into the trap containing pure HD gas (> 98%) with known number
density. After a certain reaction period, the ionic trap content is extracted, mass analyzed and counted by a detector. The sequence of trapping, reaction and detection is sequentially repeated many times for different product masses and trapping times. By fitting numerical solutions of a suitable rate equation system to the data and knowing the HD number density, the rate coefficients of the involved reactions can be determined. Usually, the measurements are repeated at different nominal temperatures of the trap, from room temperature down to a nominal minimum of 13 K, to obtain the temperature dependence of the reaction.

With LIR, an extension of this trapping technique, a laser beam is shone into the trap to excite the stored ions. Thereby an endothermic reaction, as for example all backward directions of reactions (1-3) can be substantially promoted if the corresponding ion (H$_2$D$^+$, D$_2$H$^+$ or D$_3^+$) is excited. Thus ion spectroscopy can be performed by counting the product ions, those on the left side of reactions (1-3), as a function of the laser frequency, and also measurements on the reaction kinetics are possible. While this work focuses mainly on the spectroscopy and dynamics of H$_2$D$^+$ and D$_2$H$^+$ in reaction with H$_2$, as illustrated in Figure 2, the reaction with Ar atoms have been shown to be useful in probing the lowest rotational levels of H$_3^+$ isotopologues [24, 25, 26, 27].

![Figure 2](https://example.com/figure2.png)

**Figure 2.** Explanation of LIR: H$_2$D$^+$, being in one of the four lowest rotational states at low temperature, is excited by a IR laser. Thus its reaction with H$_2$, no longer being endothermic by 232 K, is enhanced. Spectroscopy can be performed by measuring the number of H$_3^+$ reaction products as a function of the laser frequency. Furthermore, the populations of the lowest levels can be probed due to their proportionality to the H$_3^+$ signal. The given percental populations are explained in section 4.3.

### 3. Microcanonical model

A microcanonical model is developed with the aim to determine state-to-state reactive and inelastic rate coefficients consistent with experimental results. These rate coefficients are urgently needed to understand the H$_3^+$ isotopic fractionation phenomenon and to perform radiative transfer codes for H$_2$D$^+$ and D$_2$H$^+$.

The model describes all state-to-state thermal rate coefficients for the H$_3^+$ + H$_2$ collision system in all isotopic variants. The formation of the H$_3^+$ collision complex is described by the Langevin model. Assuming both reactants to be kinetically thermalised, the state-to-state rate coefficients are calculated by averaging the state-to-state cross sections on a Maxwellian collision energy distribution. The complex is described by three strictly conserved quantities which are (i) the total energy (ii) the total nuclear spin symmetry and (iii) the total angular momentum. The total energy is conserved and all degrees of freedom (rotational and kinetic) are assumed to mix completely their energies through a long-lived strongly bound complex. Furthermore, it
ions per trap filling

Figure 3. Measurement of the sequence of forward reactions (1-3) leading to full deuteration of H$_3^+$ in a bath of 13 K cold HD with a density [HD]=6.3 × 10$^{10}$ cm$^{-3}$. The equilibrium reached after a storage time of 150 ms is given by endothermic hydrogenation reactions with HD. From the measured HD number density and the simulated decay rate (solid red line) for H$_3^+$, the rate coefficient $k_1$=1.3 × 10$^{-9}$ cm$^3$s$^{-1}$ is determined for reaction (1) at a nominal temperature of 13 K.

is assumed that the long lifetime of the complex leads to a full scrambling of the nuclei by the motions depicted in Figure 1. This full scrambling hypothesis enables us to derive nuclear spin statistics using the permutation group as described by Quack [28]. The rotational angular momenta statistics are derived with regular angular momentum algebra using the $K$ (spatial) rotation group.

The mathematical details of the statistical method are described elsewhere [29]. They are quite similar to that from Park & Light [30] but it was generalised to isotopic variants. Our results are in good agreement with their results for the H$_3^+$ + H$_2$ system despite the fact that we did not account for tunnelling nor above-barrier reflection effects nor charge-quadrupole interaction terms.

The outcome of the model is a complete set of state-to-state thermal rate coefficients in the temperature range 5–50 K [29]. We did not extend the calculations to higher temperatures because (i) only low temperatures are relevant for the H$_3^+$-driven deuterium fractionation in interstellar clouds, (ii) breakdown of the full scrambling hypothesis is expected toward higher temperatures as more direct reactions will occur, and (iii) the calculation time increases quickly with energy because of the increasing number of accessible rotational states. The set of state-to-state rate coefficients are consistent with the detailed balance principle and the thermodynamical equilibrium constants.

4. Selected Results
4.1. Temperature dependence of rate coefficients
Already much insight can be gained into exchange processes by investigating reactions of the type (1-3), both in forward and backward direction, as a function of temperature and, if applicable, also varying the ortho/para-composition of the H$_2$ neutral reaction partner. As a simple example, the fundamental deuteration reaction (1), H$_3^+$ + HD, has been reinvestigated. Figure 3 shows an example measurement performed at the currently lowest nominal temperature of the 22-pole ion trap, $T$=13 K. A monoexponential decrease of the H$_3^+$ ions can be seen in the deuteration reaction with HD, from which the rate coefficient for reaction (1) has been deduced, $k_1$=1.3 × 10$^{-9}$ cm$^3$s$^{-1}$. The rate coefficients of the following deuteration reactions leading to D$_3^+$ and endothermic backreactions can also be deduced from such measurements, but are not discussed here for brevity. A series of such measurements at different nominal
which show an asymptotic increase towards the Langevin limit of measured rate coefficients agree well with those of Adams and Smith [1] at higher temperature, trap temperatures is summarized in Fig. 4 together with available literature data [11, 1]. The backward rate of about $10^{-10}$ cm$^3$ s$^{-1}$ for n-H$_2$ and around $10^{-9}$ cm$^3$ s$^{-1}$ for p-H$_2$. As this work finds both forward and backward rates of the process $(1)$ increased by a factor of four compared to the previous measurement [11], it is an interesting question to what extent it will influence current astrochemical deuteration models [4, 3, 31].

Fig. 4. Temperature dependence of reaction (1). Besides the measurements of this work, with error bars in the range of 15%, also the data of Gerlich et al. [11] and Adams and Smith [1, 13] are shown, as well as the limiting Langevin rate coefficient $k_L = 1.7 \times 10^{-9}$ cm$^3$ s$^{-1}$. Furthermore, the results of the microcanonical model for the two lowest ortho and para rotational states of H$_3^+$ are shown (see text).
4.2. Overtone spectroscopy of H$_2$D$^+$ and D$_2$H$^+$

By applying the LIR detection scheme outlined in the experimental section, several rovibrational transitions originating from the four lowest levels of H$_2$D$^+$ and D$_2$H$^+$ have been measured. The detections serve not only spectroscopic purposes, but also provide a tool for further exploring low-temperature collision dynamics and non-thermal rotational populations. Similar experiments for probing the low rotational levels of H$_3^+$ are described in this proceedings [26]. In a first stage of the experiments, the free-electron laser FELIX [32] has been used to prove the feasibility of the detection scheme [33] shown in Fig. 2 by exciting the known fundamental vibrational bands of H$_2$D$^+$ and D$_2$H$^+$ [34, 35, 36]. Later, commercial diode laser systems operating in the range 6200-7200 cm$^{-1}$ have been applied due to their reliability and easy handling. As the overtone and combination band spectroscopy performed with the diode lasers has been published [21], only a brief overview is given here.

Guided by high-accuracy ab initio calculations [37, 38, 39], 20 H$_2$D$^+$ transitions from the overtone and combination bands (0,3,0), (0,2,1) and (1,2,0) have been found, and also 7 transitions for D$_2$H$^+$ [21]. The narrow width of the lines, corresponding to a Doppler temperature in the range 24-27 K, allowed to determine the line positions with an accuracy of about 0.002 cm$^{-1}$. The comparison of the measured and ab initio predicted line positions shows differences which depend systematically on the vibrational band. In general, the differences are lower than 0.15 cm$^{-1}$ for H$_2$D$^+$, and less than 0.05 cm$^{-1}$ for D$_2$H$^+$, even at these high excitation energies. Furthermore, the ab initio predicted Einstein B coefficients have been tested for pairs of transitions starting from the same lower rotational level. No deviation between experiment and prediction could be seen within an experimental accuracy of about 10% [21]. The reliability of Einstein coefficients is not only of uttermost importance for astronomical applications, but also when is comes to the determination of level populations as shown in the next section.

4.3. Probing low rotational levels with LIR

Besides doing spectroscopy by counting the number of product ions as a function of the laser frequency, LIR can also yield additional information on the collision system. To give an example, the population of the lowest rotational states of H$_2$D$^+$ can be measured by exciting the corresponding transitions and counting the H$_2$D$^+$ ions formed by the backward direction of reaction (1). The relative population of H$_2$D$^+$ in the probed rotational state ($J_{K_a,K_c}$) is then given by

$$[\text{H}_2\text{D}^+] / [\text{H}_2\text{D}^+]_{J_{K_a,K_c}} \sim \frac{[\text{H}_2^+]_{BP}}{BP}$$

where $[\text{H}_2^+]$ is the (background corrected) number of signal counts, $B$ is the Einstein coefficient for absorption, and $P$ the measured laser power. The absolute percental population of the four lowest rotational levels (see Fig. 2) can then be calculated by neglecting the population of higher-lying rotational levels with $J \geq 2$, which have an estimated population of less than 1 % at the low temperatures. First tests of this probing scheme have already been performed by exciting fundamental transitions of H$_2$D$^+$ in the 2300-3000 cm$^{-1}$ range with the free electron laser FELIX [33], and a similar scheme using collisions with Ar atoms is used to determine the ortho/para ratio of H$_3^+$ ions which are used for dissociative recombination measurements at the TSR storage ring in Heidelberg [26].

Due to nuclear spin selection rules [28, 40, 29] in collisions with o/p-H$_2$, the low-temperature rotational population of H$_2$D$^+$ will deviate from a thermal Boltzmann distribution. As pointed out by Gerlich [11], for example, even small traces of o-H$_2$ can enhance the rotational population of ortho-H$_2$D$^+$, leading to an increased destruction of H$_2$D$^+$ to form H$_3^+$ by the backward direction of reaction (1). To probe the rotational population of H$_2$D$^+$ in a bath of n-H$_2$ (consisting of 75 % o-H$_2$ and 25 % p-H$_2$) at the lowest nominal temperature of 13 K, the
diode laser system has been used in an automated measurement procedure, and the obtained percental population is included in Fig. 2 for the corresponding levels. As mentioned in the preceding section, the kinetic ion temperature is measured to be about 27 K. The discrepancy to the nominal temperature has been investigated [41], and is most probably caused by small heating effects in the trap and insufficient thermalization of some parts of the trap, in particular the trapping electrodes. The measured populations yield a rotational temperature of about 27 K if one considers populations within the para and ortho species separately. On the other hand, the ortho/para ratio is enhanced. Taking into account the rotational level energies and the nuclear and rotational degeneracies, one expects only a total population of 31 % for the ortho-states at 27 K. In contrast, the measured population in Fig. 2 gives a total population of (43±4) % for the ortho-states. In summary, it is observed that the ortho-states of H$_2$D$^+$ in low-temperature collisions with n-H$_2$ are enhanced, and it can be speculated that this enhancement would be even more pronounced in the absence of backreactions which destroy ortho-H$_2$D$^+$ preferentially [11].

5. Future potential of low-temperature trapping and LIR

This contribution gives a brief overview of the activities to understand the exchange reactions (1-3) which are responsible for the gas-phase deuteration processes in low temperature interstellar clouds. Fig. 4 shows the temperature dependence of reaction (1), and the temperature dependence of the other isotopic exchange reactions and in particular equilibrium situations are currently under investigation as a function of reaction temperature and also for the possible different neutral collision partners: n-H$_2$, p-H$_2$, HD and n-D$_2$. For the production of p-H$_2$ a catalytic generator has been built and is now successfully used. In-situ test reactions with N$^+$ [14] show that a p-H$_2$ purity better than 99% can be obtained in the experiments. The presented LIR-investigations applying commercial diode laser systems comprise spectroscopic determination of line positions, transition strengths and rotational populations in collision with n-H$_2$. Future work will extend the population measurements for different o/p-composition of the H$_2$ collision partner and compare the results to the microcanonical model. Furthermore, the lifetimes of highly excited states and rotationally inelastic rate coefficients of H$_2$D$^+$ ions colliding with H$_2$ will be measured. Such information can be obtained by considering the competition between depletion of an occupied rotational level by laser excitation and refilling by inelastic collisions with H$_2$. It is hoped that, together with microcanonical simulations, an insight into the state-to-state rotationally inelastic collisions can be gained. Further interesting ions to be investigated by LIR are CH$_3^+$, C$_2$H$_2^+$ and their isotopologues. These molecules are held responsible for deuteration in high-temperature clouds due to the higher exothermicity of their exchange reactions [31, 16]. As the IR-spectroscopy of the fundamentals of these species has been well established by Oka, it is straightforward to transfer the methods presented here for H$_3^+$ to the carbon containing species. Unfortunately, overtone transitions for the CH$_3^+$ and C$_2$H$_2^+$ species have not yet been predicted and thus must be searched for.

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