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# Deuterium fractionation in gas-phase reactions measured in the laboratory

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## Abstract

In order to understand quantitatively the enrichment of deuterated molecules observed in non-equilibrium environments such as interstellar clouds, one has to know in detail many state-to-state cross sections. For detailed models, one has to treat both chemical processes such as formation and destruction of the isotopomers and physical processes such as collisional excitation and radiative transitions of the relevant molecular states. This contribution gives a short summary of experimental techniques in the field of low-energy gas-phase collisions such as flow techniques, traps, and beam methods with special emphasis on those methods which can be used to study the dynamics of H–D scrambling. The situation is illustrated with the astrophysically important  $\text{H}^+ + \text{H}_2$  collision system in several isotopic variants. This fundamental system is well understood, and most experimental results are in good accordance with predictions from a dynamically biased statistical model. Less well understood are the different isotopic combinations of  $\text{H}_3^+$  colliding with  $\text{H}_2$ . The  $\text{H}_3^+ + \text{HD}$  variant is discussed in a separate paper in this special issue ( $\text{H}_3^+ + \text{HD} \leftrightarrow \text{H}_2\text{D}^+ + \text{H}_2$ : low-temperature laboratory measurements and interstellar implications, *Planet. Space Sci.*, this volume) while, in this contribution, the situation is illustrated with rate coefficients for isotopic exchange in  $\text{D}_3^+ + \text{H}_2$  collisions. Other examples include the study of deuteration of hydrocarbon ions in a trap at a nominal temperature of 10 K. In particular, the rate coefficients for sequential deuteration of  $\text{C}_2\text{H}_2^+$  in collisions with HD have been measured to be  $7.5 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$  and  $7.0 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ . Another example refers to the reactions that occur when  $\text{CH}_3^+$  is stored in para-hydrogen (*p*- $\text{H}_2$ ) or normal-hydrogen (*n*- $\text{H}_2$ ) containing the natural abundance of HD. At the low densities used, H–D exchange competes only with radiative association. Some hints to the next generation of experiments are given. One of the aims is to study the role of H atoms and D atoms in low-temperature gas-phase chemistry. Another aim is to combine laser and trapping techniques in order to get both state specific rate coefficients and spectroscopic information.

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## 1. Introduction

The chemistry of the interstellar medium is vastly different from other chemical systems since low densities of electrons, atoms and molecules ( $< 10^7 \text{ cm}^{-3}$ ) and low temperatures (10 K in dense molecular clouds) prevail. Therefore, small endothermicities or barriers as well as excitation of the reactants to low-lying fine structure or rotational states can change the outcome of reactions significantly and minor gains in zero-point energies caused by suitable isotopic rearrangement play a key role. In addition the mass dependence of centrifugal barriers and symmetry selection rules

affect the outcome of a chemical reaction when identical atoms are substituted by distinguishable isotopes. The last point is discussed in more detail in another contribution (Gerlich et al., 2002).

Stable isotopes of several elements, D,  $^{13}\text{C}$ ,  $^{15}\text{N}$  and others, have been detected in interstellar molecules. In order to correlate quantitatively XD/XH ratios with parameters such as (i) D / H isotope ratio, (ii) ambient temperatures, and (iii) density of atoms, molecules, and electrons, one has to know in detail the kinetics and dynamics of a variety of processes including chemical reactions, inelastic collisions and radiative transitions. The reactions and parameters used in present gas-phase chemistry models lead to the conclusion that deuterium fractionation is dominated by the molecules HD,  $\text{H}_2\text{D}^+$ ,  $\text{CH}_2\text{D}^+$ ,  $\text{C}_2\text{HD}^+$  the abundance ratio of which, XD/XH, is much larger than the elemental ratio of typically  $\text{D}/\text{H} = 2 \times 10^{-5}$  (Millar et al., 1989). In recent years, the

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activities of interstellar grains in isotope exchange and enrichment have also been accounted for (Millar, 2002).

Molecular rotational emission at far-IR and sub-millimeter wavelengths are very effective probes of interstellar and circumstellar molecules and the next generation instruments such as Herschel will significantly broaden our knowledge. In the case of some symmetric molecules with equivalent hydrogen atoms, a significant dipole moment can result from an H–D substitution. The most obvious example is the HD molecule, which has been observed in emission via a pure rotational transition at 112  $\mu\text{m}$ . Other examples include  $\text{H}_2\text{D}^+$ ,  $\text{C}_2\text{HD}^+$  or cyclic  $\text{C}_3\text{H}_2\text{D}^+$ , other candidates are deuterated PAH's. In order to evaluate the observations, measured intensities have to be correlated to the formation and destruction of these molecules and, possibly, to collisional or other pumping processes. In order to predict this with realistic models, state-to-state cross sections at collision energies of a few meV or low temperature state specific rate coefficients for a variety of inelastic and reactive collision processes are needed.

Isotope exchange has been used often in experiments in order to get detailed information on the microscopic dynamics. Recent examples from this laboratory include deuteration of hydrogen clusters (Paul et al., 1996), isotope exchange in  $\text{H}^- + \text{D}_2$  collisions (Haufler et al., 1997) or near symmetric charge transfer in  $^{36}\text{Ar}^+ + ^{40}\text{Ar}$  collisions (Pullins et al., 2000). Interesting is also the restricted scrambling in  $^{15}\text{N}^+ + ^{14}\text{N}_2$  collisions because the atoms do not have equivalent positions in the linear complex (Glosik et al., 2000). Another point of fundamental interest for isotope exchange is the influence of zero-point energy in the transition region if a reaction is hindered by a small barrier. Such an observation has been reported for the collision system  $\text{C}_3\text{H}^+ + \text{H}_2$  and its isotopic variants, where H–D exchange competes with hydrogen abstraction and radiative association (Sorgenfrei and Gerlich, 1994).

Most of the experimental information for isotope exchange used in current models (Millar et al., 1997; Roberts and Millar, 2000) has been obtained several decades ago. In the 1970s, the detection of more and more interstellar molecular species and the determination of their relative abundances has stimulated the development of various laboratory experiments for studying gas-phase ionic reactions and their extension to appropriately low temperatures. It also should be noted that the laboratory studies have revealed important routes for the synthesis of interstellar molecules and have indicated important new classes of reactions specific to interstellar chemistry. One example is radiative association (Smith, 1993). This contribution briefly summarizes in Section 2 the experimental activities in the field of low-energy gas-phase collisions. A few hints to recent developments using traps and various beam techniques are given. In Section 3, results are reported for  $\text{H}^+$ ,  $\text{H}_3^+\text{C}_2\text{H}_2^+$  and  $\text{CH}_3^+$  ions colliding with well-defined mixtures of *p*- $\text{H}_2$ , *o*- $\text{H}_2$  and HD or  $\text{D}_2$ . Isomerization and deuteration of  $\text{HOC}^+$  in collisions with  $\text{H}_2$  and HD and the

formation of  $\text{DCO}^+$  in collisions with HD, mentioned in the conference contribution, will be discussed in a separate paper.

## 2. Experimental

It is obvious that special experimental techniques are needed to study collision processes under interstellar conditions. The three types of experiments which are briefly discussed in the following, are swarm techniques, beam methods, and ion traps. In general, low temperatures are achieved by cryogenic cooling or by supersonic expansions. In several modern laboratories, laser-based methods are combined with these techniques to obtain information on state-specific rate coefficients. Typical criteria for comparing the advantages and disadvantages of specific instruments are based on ion preparation (mass and internal energy), competing reactions (e.g. cluster formation), condensation of the neutral species on the walls, number density range (radiative association), sensitivity (interaction times) and detection efficiency (discrimination).

### 2.1. Swarm techniques

Many ion–molecule reactions have been studied using flowing afterglow (FA) and selected-ion flow tube (SIFT) techniques and a large body of kinetic and thermodynamic data has been obtained. The experimental investigation of reactions relevant to interstellar chemistry owes much to the work of Adams and Smith who used a variable-temperature selected-ion flow tube (VT-SIFT) (Smith and Adams, 1988). Since in the SIFT, a mass analyzed beam of ions is injected into the carrier gas, it became possible to study isotope exchange in ion–neutral reactions. These results, some of which are mentioned below, have been discussed in several reviews (e.g. Adams and Smith, 1983). By construction, the VT-SIFT was limited to liquid nitrogen temperature (80 K). A drift tube apparatus that was cooled with liquid helium has been developed by Böhringer and Arnold (1983) in Heidelberg. In this device, results at temperatures as low as 20 K have been obtained.

Cryogenic cooling has the disadvantage that condensation of the target or buffer gas restricts its range of applicability. One solution to examine reactions at low temperatures which avoids this problem is to use supersonic expansions. The best known example is the CRESU (Cinétique de Reaction en Ecoulements Supersoniques Uniformes) technique (Rowe et al., 1985). In this apparatus ions are injected into the core of a several centimeter thick supersonic flow of He containing a small amount of the neutral molecules as reactants. Kinetic data at temperatures as low as 8 K have been obtained. More details on this technique and a discussion of selected applications to interstellar chemistry can be found in a recent review by Smith and Rowe (2000). An extension to temperatures below 3 K has been made possible by the

development of the free jet flow reactor by Smith (1998). Unfortunately, both methods have not yet been used for laboratory studies of isotope exchange in collisions with HD at the respective low temperatures; however, Hawley and Smith (1992) report rates of isotope exchange of  $C_2H_2^+$  with  $D_2$  and  $C_2D_2^+$  with  $H_2$ .

## 2.2. Beam methods

The only beam method where ion beams with a laboratory kinetic energy of a few meV can be prepared with sufficient intensity is the guided ion beam method (GIB), pioneered by Tely and Gerlich (1974). Different machines, based on this technique, have been constructed in several laboratories as summarized by Gerlich (1992). In most GIB instruments, a room temperature scattering cell is used and the thermal motion of the target gas sets a lower limit to the mean kinetic energy. This problem has been overcome by replacing the scattering cell with a crossed (Tosi et al., 1994) or merged supersonic beam (Glenwinkel-Meyer and Gerlich, 1997). In principle, the idea to merge two beams in order to get low collision energies is already quite old, a first version of a merged beam arrangement has been described by Trujillo et al. (1966).

A more sophisticated merged beam apparatus is the arrangement described by Gerlich (1993). The special feature of this instrument is that the fast neutral beam is replaced by an intense supersonic beam and that, as a consequence, a slow ion beam is needed. This beam is confined by a weak rf field and guided completely within the neutral beam. Primary and product ions are detected via a quadrupole mass spectrometer. The internal temperature of the primary ions and the neutrals can be controlled separately between 10 and 300 K by using a low-temperature ion trapping source and a supersonic beam with a temperature variable nozzle. Collision energies as low as 1 meV have been achieved.

## 2.3. Ion traps

Various ion traps have been used since the 1960s for studying ion–molecule reactions. Using suitable electric or magnetic fields, ions can be confined for long times, and with the use of a buffer gas thermal conditions can be attained. The most common techniques used in chemistry are the ion cyclotron resonance (ICR) apparatus and the Paul trap. Of relevance for interstellar chemistry was the development by Dunn et al. who used a low-pressure Penning ion trap that could be operated down to temperatures below 10 K (Barlow et al., 1986). Another recent approach to construct a dedicated device around a cooled ICR cell is the setup PIRENEA (Piège à Ions pour la Recherche et l'Etude de Nouvelles Espèces Astrochimiques) (Joblin et al., 2000). It has been specifically developed for interstellar chemistry studies including large PAH's and aggregates.

Most data presented and discussed below were obtained using a trapping technique, based on inhomogeneous rf fields. Since this trapping method is well established and sufficiently documented in the literature (Gerlich, 1992, 1993, 1994; Gerlich and Horning, 1992; Schlemmer et al., 1999), only a few comments are made here. For cooling ions in rf ion traps to low temperatures, electrode structures with wide field-free regions are mandatory. Traps consisting of stacks of ring electrodes are used successfully. The workhorse in several laboratories is meanwhile a linear 22-pole, which is also described briefly in Gerlich et al. (2002). The region where the ions are confined is surrounded by walls cooled by a closed cycle refrigeration system. The nominal temperature can be varied between  $T = 10$  and 300 K. The translational and internal degrees of freedom of the ions are coupled to the cold environment by inelastic collisions with helium or hydrogen as buffer gas.

Primary ions are prepared in an external ion source. They are mass selected and formed to a very slow beam. Injection and extraction of ions occurs via pulsed entrance and exit electrodes closing the linear multipole in the axial direction. The storage time can be varied from  $\mu$ s to min or longer. In the absence of target gas the mean-decay time is determined by reactions with background gas, the pressure of which is estimated to be below  $10^{-11}$  mbar at 10 K. For the study of reaction processes, target gas is added at a number density varying from below  $10^9$   $cm^{-3}$  to above  $10^{15}$   $cm^{-3}$ . By choosing a suitable combination of number density and interaction time, the rates of rather fast as well as very slow bimolecular reactions can be measured. This makes this device unique because ternary and radiative association can be distinguished. For studying both forward and reverse reaction rates such as in the case of isotope enrichment and depletion, a special feature of the trapping technique is that one can choose a well-defined gas mixture and evaluate the stationary equilibrium reached after some storage time.

## 3. Results and discussions

The variety of methods described has been used to study a large number of ion–molecule reactions over a wide range of densities and temperatures, mostly under thermal conditions. Concerning isotope fractionation under interstellar conditions, these activities slowed down about 20 years ago, and there are almost no recent experiments performed with merged beams or flow techniques on this subject. Excluding the present work, it seems to be correct to assume that the review by Millar et al. (1989) contains most of the experimental information on deuteration. In the following the situation will be illustrated for three collision systems. Several new rate coefficients are reported.

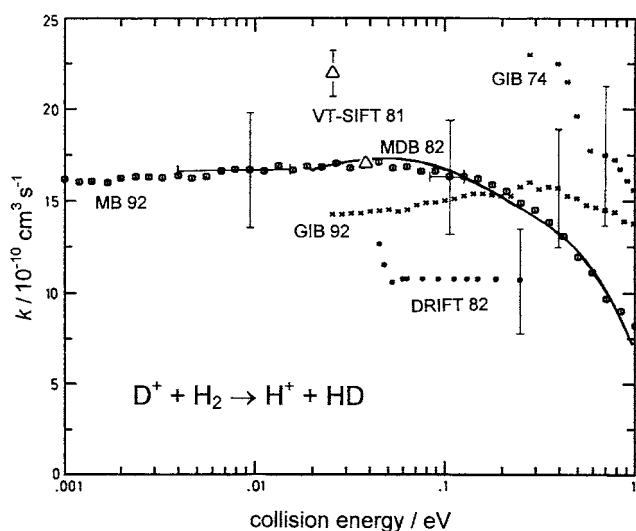


Fig. 1. Energy dependence of the rate coefficients for the exothermic proton–deuteron exchange  $D^+ + H_2 \rightarrow H^+ + HD$  measured with different instruments (guided ion beam: GIB 74: Ochs and Telyo (1974), VT-SIFT 81: Henchman et al. (1981), DRIFT 82: Villinger et al. (1982), GIB 92 and MB 92: Gerlich (1992)). The heavy line shows a rate coefficient, calculated with the MDB (most dynamically biased) statistical theory by Gerlich (1982). Errors of the various experiments are indicated schematically as bars or crosses.

### 3.1. $D^+ + H_2$

The understanding of H–D scrambling in isotopic variants of the  $(H + H_2)^+$  system is both of fundamental and astrophysical importance, especially for the chemistry of the early universe. An important role in the gas-phase deuterium fractionation is played by the elementary reaction



which is exothermic by 39.5 meV (458 K) from left-to-right as a result of the difference in the zero-point energies of  $H_2$  and HD (35.8 meV) and the difference in the ionization potentials of H and D (3.7 meV). This simplest of the chemical reactions has been studied extensively both experimentally and theoretically. As a result the dynamics of H–D exchange processes at low energies is well understood, also for other isotopic modifications (Henchman et al., 1981; Gerlich, 1982). A selection of experimental results obtained until 1990 have been summarized in a review by Gerlich (1992), see for example Figs. 64–66, 75, 76, 85 and 87 therein.

As a typical example, Fig. 1 shows a selection of data measured with different techniques. Note that the cross sections, measured with beam experiments, have been converted into effective rate coefficients in the usual way. Thermal rate coefficients, measured at a given temperature  $T$ , are included in the figure at a collision energy,  $E_T = 3/2 k_B T$ , where  $k_B$  is the Boltzman constant. The first results from a guided ion beam apparatus (GIB 74), published by Ochs and Telyo (1974) increase too steeply with falling energy. This

is most probably due to the uncertainty in the collision energy in this early experiment. The repetition of the measurement in an improved GIB instrument used energy calibration by time-of-flight (Gerlich, 1992). The values (GIB 92) have a weak maximum at 300 meV and fall slowly below  $1.5 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$  at the lowest nominal collision energy achieved, 25 meV. The two VT-SIFT results measured by Henchman et al. (1981) are shown as solid triangles. They appear to indicate another temperature trend. Finally there are the DRIFT data from Villinger et al. (1982) which are rather small, but still within the limits of the combined errors of the experiments which are indicated schematically as bars or crosses. The merged beam results (Gerlich, 1992) cover an energy range of three orders of magnitude. Above 0.3 eV they show a slightly different energy dependence but it is obvious that this does not concern the low-energy behavior. The fact that the statistical theory (MDB 82) follows in all details the merged beam results must be regarded as fortuitous. More details on this theory are discussed below.

Comparison of many detailed experiments, especially state-to-state cross sections (Gerlich, 1977) and several statistical calculations led to the conclusion that the interaction in the intermediate  $H_3^+$  collision complex is strong enough to randomize (i) the decay angle of the collision complex, (ii) the product states and (iii) the branching into the various product channels. This means that a suitable statistical theory can be applied. One approach is the most dynamically biased (MDB) statistical theory. In this theory, classical trajectory calculations were utilized to define a criterion for forming a strongly coupled complex. An early version of the theory has been mentioned in (Gerlich, 1977). More details can be found in Gerlich et al. (1980). A rather general formulation which uses an analytical approximation for complex formation,  $P_{ic}$ , and which can be applied to all isotope variants of the  $H^+ + H_2$  collision system, has been published in (Gerlich, 1982). It is important to note, that this analytical function depends only on the total energy  $E$ , the translational energy  $E_T$ , the reduced mass  $\mu$  and the orbital angular momentum of the relative motion. For illustration, Fig. 2 shows the complex formation probability in  $H^+ + H_2(j)$  collisions as a function of the orbital angular momentum  $l$  and the rotational state  $j$  at a total energy of 1 eV. Inspection shows that the step function,  $P = 1$  or 0, which is often used in statistical calculations (Light, 1967) is not in accord with the MDB model.

Based on the function  $P_{ic}$  and using a general formulation of a statistical theory as given by Miller (1970) or by Quack (1977), a complete statistical theory has been formulated. The MDB theory, which is based on parameterizing the scattering matrix, obeys automatically microreversibility and includes the restrictions imposed by conservation of nuclear spin and parity. Applications to the reactions of  $N^+$  with  $H_2$  and  $D_2$  and to the special case of ortho–para transitions in  $H^+ + H_2$  collisions have been discussed in (Gerlich,



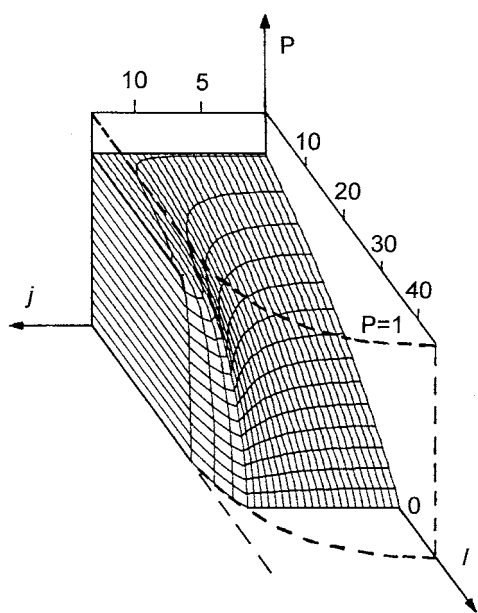


Fig. 2. Complex formation probability  $P$  at a total energy of 1 eV for the system  $\text{H}^+ + \text{H}_2(j)$  as a function of the orbital angular momentum  $l$  and the rotational state  $j$ . Note that the  $P$  does not reach 1 as assumed in many phase space theories. Large orbital angular momenta hinder formation of a statistical complex.

1989, 1990), respectively. It should be emphasized that this theory allows one to predict state-to-state cross sections as a function of the collision energy for all isotope combinations of the  $\text{H}_3^+$  collision system. From these results, averaged quantities can be derived, such as equilibrium constants, thermal rate coefficients, state-specific rate coefficients as well as effective rate coefficients, usually needed for non-equilibrium situations. As a typical application, Fig. 3 shows thermal rate coefficients calculated for the indicated exchange reactions. Close inspection of the plotted lines reveals that they are curved, a consequence of the fact that only a few reactant and product states compete with each other. The Arrhenius-type parameters presented in Table 1 are the results from a fit to the numerical results derived between 30 and 130 K. The deviation of the derived enthalpy change,  $B = 504$  K, from the above-mentioned endothermicity of reaction (1a), 458 K, is due to the contribution of the first rotational state of HD. A careful analysis of such detailed results leads to the conclusion that one should avoid to predict low-temperature kinetics with relationships, e.g. equilibrium constants, derived from simple thermodynamics. This point has been discussed in detail by Gerlich (1989), Giles et al. (1992) and in Gerlich et al. (2002). It is obvious that in the case of minor deviations from the thermodynamic equilibrium, state-specific cross sections are mandatory for reliable estimates.

Comparison of experiment and theory reveals that the overall trend is in accordance with the often applied rule of thumb that exothermic ion–molecule reactions occur at a rate close to the capture (or Langevin) limit and

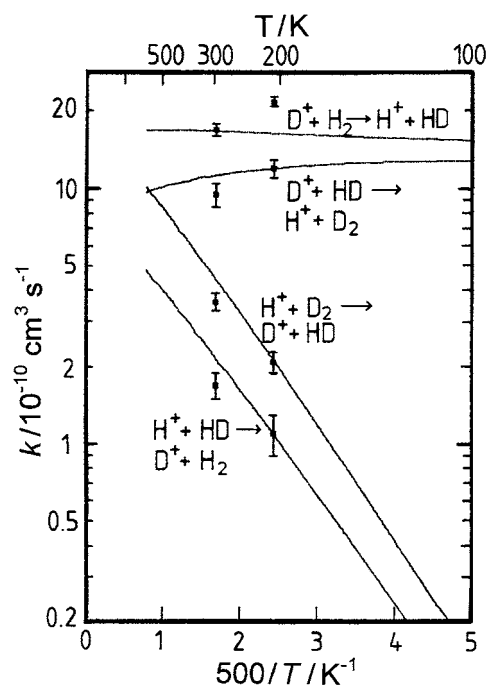


Fig. 3. Thermal rate coefficients for the indicated proton deuteron exchange reactions. The experimental points have been measured by Henchman et al. (1981), the lines are the results of a statistical calculation by Gerlich (1982). Complete thermalization of the kinetic energy of the protons and deuterons and of the ortho–para ratios has been assumed.

Table 1  
Temperature dependence of rate coefficients,  $k = A \exp(-B/T)$

Reaction	$A/\text{cm}^3 \text{ s}^{-1}$	$B/\text{K}$	Ref./remarks
$\text{D}^+ + \text{H}_2 \rightarrow \text{H}^+ + \text{HD}$	$1.66(-09)$	5.6	Statistical theory (fit 30–130 K)
$\text{H}^+ + \text{HD} \rightarrow \text{D}^+ + \text{H}_2$	$2.1(-09)$	0	MBH 1989
$\text{H}^+ + \text{HD} \rightarrow \text{D}^+ + \text{H}_2$	$1.34(-09)$	504	Statistical theory (fit 30–130 K)
	$1.0(-09)$	464	MBH 1989
$\text{D}_3^+ + \text{H}_2 \rightarrow \text{H}_2\text{D}^+ + \text{D}_2$	$1.5(-09)$	192	fit Fig. 4, high temp.

that the endothermic direction can be approximated with an Arrhenius-type function. For reaction (1a), however,  $k_L = 2.1 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$  is never reached since the collision complex decays also back to the reactant channel. Comparison of  $k_L$  with the measured values reveals that the probability for the  $\text{H}_2\text{D}^+$  complex decaying towards products reaches a value close to 0.8 at low energies and about 0.6 at energies above 0.2 eV, in accordance with simple statistics based on counting distinguishable atoms. At first sight, the comparison of the VT-SIFT results in Fig. 3 where the theory is also rather good; however, one should be aware that erroneous conclusions can be made if one extrapolates the temperature trends of a few points towards lower temperatures. This can be seen from a comparison of the numerical values given in Table 2 and also

Table 2  
Rate coefficients for deuteration reactions at 10 K

Reaction	$k/\text{cm}^3 \text{ s}^{-1}$	Ref.	Remarks
$\text{D}^+ + \text{H}_2(j=0) \rightarrow \text{H}^+ + \text{HD}$	2.3(-09)		Statistical theory
$\text{D}^+ + \text{H}_2(j=1) \rightarrow \text{H}^+ + \text{HD}$	1.6(-09)		Statistical theory
$\text{D}_3^+ + \text{H}_2 \rightarrow \text{H}_2\text{D}^+ + \text{D}_2$ collision energy 2 meV	4(-10) 9.5(-11)		Nozzle 300 K, ions 300 K Nozzle 300 K, ions 20 K
$\text{D}_3^+ + \text{H}_2 \rightarrow \text{D}_2\text{H}^+ + \text{HD}$ collision energy 2 meV	2.6(-11) 1.8(-10) 9.5(-11)		Nozzle 40 K, ions 20 K Nozzle 300 K, ions 20 K Nozzle 40 K, ions 20 K
$\text{H}_3^+ + \text{HD} \rightarrow \text{H}_2\text{D}^+ + \text{H}_2$	3.5(-10) 1.7(-09)	GHR02 MBH89	22PT, pure HD
$\text{H}_2\text{D}^+ + \text{H}_2 \rightarrow \text{H}_3^+ + \text{HD}$	4.9(-11) 7.3(-13) 3.6(-18)	GHR02 GHR02 MBH89	22PT $n\text{-H}_2$ 22PT $p\text{-H}_2$ , 1% $\text{H}_2(j=1)$
$\text{C}_2\text{H}_2^+ + \text{HD} \rightarrow \text{C}_2\text{HD}^+ + \text{H}_2$	7.5(-10) 1(-09)		22PT, pure HD
$\text{C}_2\text{HD}^+ + \text{H}_2 \rightarrow \text{C}_2\text{H}_2^+ + \text{HD}$	< 8(-16) < 1(-33)	MBH89 MBH89	22PT $p\text{-H}_2$
$\text{C}_2\text{HD}^+ + \text{HD} \rightarrow \text{C}_2\text{D}_2^+ + \text{H}_2$	7.0(-10)		22PT, pure HD
$\text{C}_2\text{H}_2^+ + \text{HD} \rightarrow \text{C}_2\text{H}_3^+\text{D}$	1.8(-11)		rad. ass.
$\text{CH}_3^+ + \text{HD} \rightarrow \text{CH}_2\text{D}^+ + \text{H}_2$	2.6(-10) 1.3(-09)		22PT $p\text{-H}_2$
$\text{CH}_2\text{D}^+ + \text{H}_2 \rightarrow \text{CH}_3^+ + \text{HD}$	2.2(-14) < 1(-26)	MBH89 MBH89	22PT $p\text{-H}_2$

Only reference to MBH89 (Millar et al., 1989) is given which is a compilation of the relevant data with further references. GHR02 refers to Gerlich et al. (2002) in this volume.

from the results for  $\text{H}_2\text{D}^+$  destruction discussed in Gerlich et al. (2002). In summary, it is recommended to use the MDB results if one needs state-to-state cross sections at low total energies or if one intends to derive low temperature effective rate coefficients for non-equilibrium conditions.

Another system which is closely related to reaction (1a) and which may play a certain role in deuterium fractionation is the charge transfer channel



Today, there is no experimental information on the outcome of this elementary reaction. Especially challenging are experiments with rotationally selected  $\text{HD}^+(j)$  at very low kinetic energies. Note that this exothermic reaction starts on the first electronically excited potential energy surface and ends on the ground potential energy surface. Therefore non-adiabatic coupling determines in a complicated manner the magnitude of the cross section and the branching ratio.

### 3.2. $\text{D}_3^+ + \text{H}_2$

Reactions of  $\text{H}_3^+$  with  $\text{H}_2$  have been studied extensively in various deuterated combinations. For example, the energy dependence of the integral cross section for the exothermic proton transfer reaction,  $\text{H}_3^+ + \text{D}_2 \rightarrow \text{D}_2\text{H}^+ + \text{H}_2$ , has been measured at very low collision energies by means of the tra-

ditional merged beam technique by Douglass et al. (1982) and in the first version of the slow merged beam apparatus (Gerlich, 1989). Both sets of results show that the reaction occurs with a cross section close to the Langevin limit. A VT-SIFT study of all possible deuterated  $\text{H}_3^+ + \text{H}_2$  combinations has been published by Giles et al. (1992).

One deuterated molecule of special importance is the  $\text{H}_2\text{D}^+$  ion. Its role in interstellar ion chemistry, especially for deuterating other molecules, has been discussed thoroughly in the literature (Millar et al., 1989; Millar, 2002). It is formed via the classic proton transfer reaction



Low-temperature experiments which are discussed in this special issue (Gerlich et al., 2002) have shown that the  $\text{H}_3^+/\text{DH}_2^+$  ratio is a sensitive function of the  $o\text{-H}_2/p\text{-H}_2$  ratio. Another interesting related experiment, ortho-para transitions in  $\text{H}_3^+ + \text{H}_2$  collisions, has been performed by Cordonnier et al. (2000). This process is also based on scrambling of protons in the  $\text{H}_5^+$  collision complex. Unfortunately, the dynamics of proton deuteron exchange in this intermediate molecule are not at all understood with the required reliability. The reason for this is most probably the fact that the  $\text{H}_3^+ + \text{H}_2$  potential energy surface does not allow the use of an unrestricted statistical theory as used in reaction (1).

Another interesting isotopic analogue of reaction (2a), where the scrambling dynamics in the endothermic direction

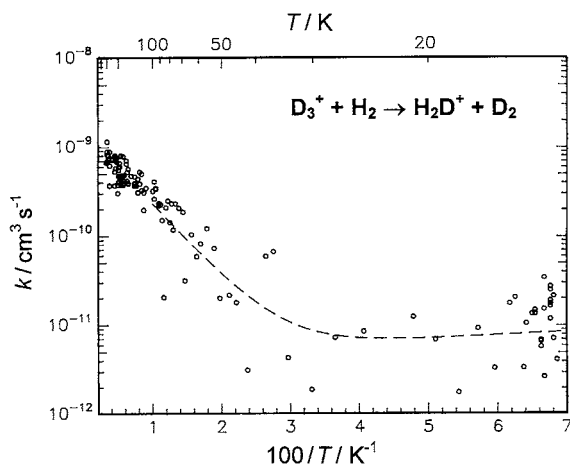


Fig. 4. Thermal rate coefficients for the deuteron transfer reaction in  $D_3^+ + p\text{-H}_2$  collisions. The experimental points have been measured using the temperature variable 22-pole trap. The dashed line is a fit to the data using two functions  $k_i = A_i \exp(-B_i/T)$ . The parameters obtained for  $i = 1, 2$  are presented in Table 2.

can be studied is



The first channel is 29 meV endothermic, the second 20 meV. It has been discussed in Gerlich (1993), see Fig. 10 that a simple statistical model based on counting identical atoms, fails completely. At low energies the difference in endothermicity favors reaction (2c). But as soon as the total energy gets larger than 50 meV, the branching ratio is determined by the fact, that reaction (2b) can proceed via a direct deuteron jump while (2c) requires more complicated rearrangements.

Reaction (2b) has been studied in the 22-pole ion trap as a function of temperature with  $p\text{-H}_2$  as target gas. In order to record the temperature dependence, data are taken during the cooling procedure. Therefore, the results plotted in Fig. 4 are not equidistant and the statistical errors of the individual rate coefficients are rather large. In order to fit the data with an Arrhenius-type function  $k = A \exp(-B/T)$ , two sets of parameters were necessary. The data obtained in the temperature range 300–50 K are included in Table 1. The low-temperature behavior is most probably due to some remaining  $o\text{-H}_2$  although direct heating of  $D_3^+$  by inelastic collisions with  $H_2(J = 1)$  is spin forbidden.

In order to study the dynamics of reaction (2b) and (2c) in more detail and for directly measuring the cross section at the threshold, additional experiments have been performed using the merged beam apparatus as described in Gerlich (1993). For separating the influence of internal excitation and translational energy, the two reactants have been prepared in various ways. Before the  $D_3^+$  ions enter the interaction region they have been relaxed in a 22-pole trap via collisions with  $n\text{-D}_2$  at 20 K or, alternatively, at room

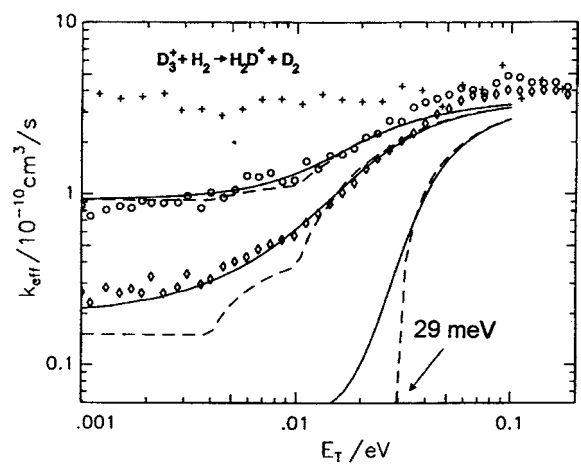


Fig. 5. Effective rate coefficient for deuteron transfer in  $D_3^+ + n\text{-H}_2$  collisions measured with a merged beam apparatus as a function of the translational energy  $E_T$ . For ground state reactants the onset of the reaction would be at  $E_T = 29$  meV, as indicated by the dashed line. Comparison with the solid line indicates the kinetic energy resolution. The three data sets correspond to three combinations of preparation of the reactants: (i) nozzle and ion trap at 300 K (crosses), (ii) nozzle at 300 K, ions cooled to 20 K (circles), (iii) nozzle at 40 K, ions cooled to 20 K. The dashed lines are rate coefficients for assumed populations. Accounting for the experimental resolution, one obtains the solid lines which match more or less the data points. Obviously full thermalization of the reactants was not achieved.

temperature. The target beam was a supersonic beam of  $n\text{-H}_2$  with a temperature variable nozzle. Some tests were performed using  $p\text{-H}_2$ .

Fig. 5 shows a selection of different results for channel (2b) as a function of the mean collision energy  $E_T$ . For better comparison, the measured effective cross sections have been multiplied with the mean relative velocity and plotted on a logarithmic scale. This conversion procedure which leads to effective rate coefficients, has been discussed in detail in Gerlich (1992), see also Tosi et al. (1994). For ground state reactants the onset of the reaction would be at  $E_T = 29$  meV. A line-of-centers model has been used to simulate the cross section in the threshold region and to get some quantitative information on kinetic energy resolution. The solid line indicates that in this merged beam apparatus the onset is shifted by about 10 meV, but the rate coefficient should drop to zero at collision energies below 10 meV.

As explained above, different data sets have been recorded with reactants having different internal energy. When both reactant sources are operated at room temperature, the effective rate coefficients (crosses) have a value of about  $4 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ , independent on collision energy. Operating the nozzle at 300 K and cooling the ions to 20 K leads to a decrease by a factor of five (circles). In this case the reactivity at low collision energies is due to the rotational energy of the hydrogen, the relaxation of which is known to be rather inefficient in an expansion. This can be seen from the third set of data (rhombs) where the nozzle was operated at 40 K. The solid lines which match more or less the

data points have been calculated by assuming state-specific cross sections (dashed lines) and accounting for instrumental averaging. Obviously, full thermalization of the reactants was not achieved or another problem with the complicated merged beam apparatus caused the low signal remaining at low collision energies. The lowest rate coefficient measured was  $2 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ . The assumed population of internal states indicates an internal excitation of about 60 K.

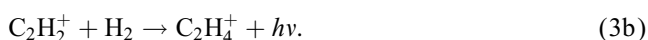
Analogous results have been obtained for reaction (2c). A few selected results for the lowest collision energy are given in Table 2. The experimentally determined ratio  $\text{H}_2\text{D}^+/\text{HD}_2^+$  could possibly be taken as an indicator for the energy range where a statistical theory is applicable. At the lowest total energy this ratio was  $\text{H}_2\text{D}^+/\text{HD}_2^+ = 0.25$ . This is in qualitative accordance with the fact that the  $\text{HD}_2^+ + \text{HD}$  products are favored by a simple statistical factor 2 and by the difference in the two thresholds. It may be that a complete statistical theory may explain the observed rate coefficients. With increasing collision energy the  $\text{H}_2\text{D}^+/\text{HD}_2^+$  ratio grows very fast and it reaches already a value of 10 at 0.1 eV. This is a clear indication that direct processes dominate at this energy and for this special system, where three D-atoms are initially in the ion.

### 3.3. $\text{C}_2\text{H}_2^+ + \text{HD}$

Reactions of acetylene ions with hydrogen molecules have attracted a lot of attention within the last years. For example the possibility that  $\text{C}_2\text{H}_3^+$  may be abundant at low temperatures is of importance for preparing astrophysical observations, because it has a strong microwave emission spectrum due to its dipole moment. But, as discussed in detail by Gerlich (1993), the hydrogen abstraction reaction

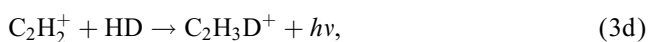
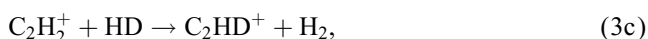


is endothermic by about 50 meV. Therefore, at low temperatures, the dominant loss of  $\text{C}_2\text{H}_2^+$  is radiative association



This reaction has a rate coefficient of  $k_r = 4.6 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$  at the trap temperature of 10 K and for *p*- $\text{H}_2$  (Gerlich, 1993). Recently, Schlemmer et al. (2002) studied reaction (3a) in great detail by exciting the ions with an infrared laser to various  $\text{C}_2\text{H}_2^+(v_3 = 1, J)$  states. Rotationally, resolved spectra have been obtained by monitoring  $\text{C}_2\text{H}_3^+$  produced by the laser induced H-atom transfer. The dependence of the product signal on specific transitions and on several parameters (storage time, laser fluence, target gas density) has provided detailed information on state specific rate coefficients.

Concerning deuteration via the reactions



some qualitative analysis already has been made by Gerlich and Horning (1992) for distinguishing between  $\text{C}_2\text{H}_3^+$  and

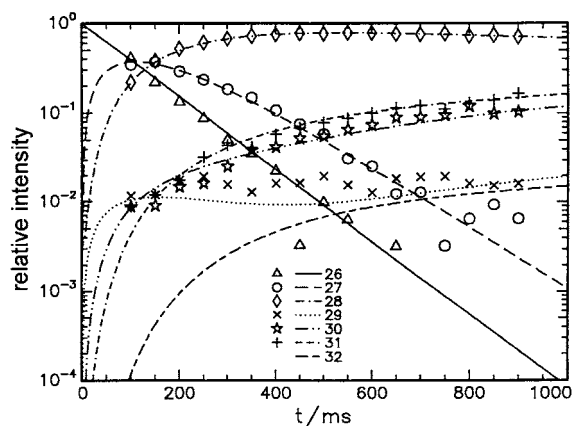
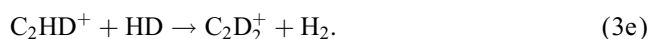


Fig. 6. Time evolution of  $\text{C}_2\text{H}_2^+$  ions stored in the 10 K—22-pole ion trap filled with pure HD target gas ( $[\text{HD}] = 1.2 \times 10^{10} \text{ cm}^{-3}$ ). The dominant reactive changes occurring up to 1 s, are the sequential formation of  $\text{C}_2\text{HD}^+$  (mass 27) and  $\text{C}_2\text{D}_2^+$  (mass 28). In addition various isotopomers of  $\text{C}_2\text{H}_4^+$  are formed by radiative association and by H–D exchange. The number of ions with mass 32, i.e.  $\text{C}_2\text{D}_4^+$  was below the sensitivity limit. The lines are the solutions of a model calculation, resulting in a set of rate coefficients (see Table 2).

$\text{C}_2\text{HD}^+$  ions. These experiments were performed with hydrogen containing HD in the global terrestrial abundance of  $[\text{HD}]/[\text{H}_2] = 3 \times 10^{-4}$  and with hydrogen, purified from HD (Gerlich, 1994). In order to measure the exchange reaction (3c) with higher accuracy, experiments with pure HD have been performed. One typical result is shown in Fig. 6. The low number density of  $1.2 \times 10^{10} \text{ cm}^{-3}$  makes sure that a negligible amount of association products (3d) is due to ternary association. The initially injected  $\text{C}_2\text{H}_2^+$  ions are mainly converted by reaction (3c), followed by the second deuteration step



After long enough storage time most acetylene ions are converted into doubly deuterated ones. As can be seen from a comparison of the rate coefficients collected in Table 2, the actually measured 10 K value,  $k = 7.5 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ , is only slightly smaller than the value used in model calculations of interstellar clouds,  $k = 1 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ . The backward rate coefficient of reaction (3c),  $k = 8.3 \times 10^{-16} \text{ cm}^3 \text{ s}^{-1}$ , has been deduced from a measurement, where *p*- $\text{H}_2$  was used.

In addition to the acetylene ions, isotopomers of  $\text{C}_2\text{H}_4^+$  are formed via association and H–D exchange. In order to extract the relevant rates from the measurements, the time dependence of the data has been approximated with solutions of adequate kinetic equations. It is obvious that this procedure provides rather reliable results for the dominant reactions (3c) and (3e). The lines, shown in Fig. 6, follow nicely the exponential decay of the initial ions, the up and down of the monodeuterated intermediate ion and the final product  $\text{C}_2\text{D}_2^+$ . Less unique is the solution for the complicated interplay of the ions with four H or D atoms. There-



fore, the set of data resulting in the solutions plotted in Fig. 6, is not presented here. It only must be mentioned that the reaction (3d) seems to be 3–4 times faster than radiative association with  $n$ -H<sub>2</sub>. This may be due to the additional dipole moment of the complex or due to the fact that HD as buffer gas is a more efficient cooler than H<sub>2</sub> with possible traces of  $o$ -H<sub>2</sub>.

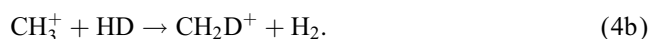
### 3.4. CH<sub>3</sub><sup>+</sup>/CH<sub>5</sub><sup>+</sup> + H<sub>2</sub>/HD

In the reaction chain of hydrocarbons, the radiative association process



plays an important role because of the CH<sub>4</sub><sup>+</sup> + H channel is meanwhile known to be endothermic. The rate coefficient  $k_r$  has been under debate for some time as summarized by Gerlich and Horning (1992); however, additional trap experiments at various temperatures and for different  $n$ -H<sub>2</sub> and  $p$ -H<sub>2</sub> number densities have established reliable values for  $k_r$  and the ternary association rate coefficient  $k_3$  (Gerlich, 1995).

The CH<sub>3</sub><sup>+</sup> ion also plays an important role in the fractionation reactions involving HD via the exchange



Due to the large exothermicity of 370 K, it is generally assumed that the reverse reaction can easily be computed from a simple Arrhenius function. As in the above discussed reactions (1)–(3), the magnitude of the rate coefficient for reaction (4b) is determined by the mobility of H and D in the CH<sub>3</sub><sup>+</sup>–HD complex. Theoretical calculations of the potential energy surface indicate that binding to the central C-atom seems to make all five hydrogen atoms fully equivalent and that there are no barriers hindering an efficient exchange (Maluendes et al., 1992; Marx and Pironello, 1999). Protonated methane serves as a prototype of a strongly bound but very floppy molecule due to its three center two electron (3c–2e) bonding of the proton to methane. Nonetheless, the structure of this ion, and the internal mobility of a D atom is, still under debate (Kramer et al., 1999).

Reactions (4a) and (4b) have been studied in the 22-pole ion trap at 10 K. The target gas was para-hydrogen at a number density  $[\text{H}_2] = 8.7 \times 10^{10} \text{ cm}^{-3}$  and containing HD in its natural abundance  $[\text{HD}]/[\text{H}_2] = 3 \times 10^{-4}$ . Fig. 7 shows a typical change of ion compositions if CH<sub>3</sub><sup>+</sup> ions are injected and stored for up to 60 s. The dominant product is CH<sub>5</sub><sup>+</sup>, formed via radiative association (4a) with a rate coefficient of  $k = 1.1 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$ . In addition, reaction (4b) also plays a significant role. Although the HD density in the trap was only  $[\text{HD}] = 2.6 \times 10^7 \text{ cm}^{-3}$ , almost 10% of all ions are converted into mass 16 due to the H–D exchange (4b). The derived rate coefficient for reaction (4b),  $k = 2.6 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ , is significantly smaller than the currently accepted value. Inspection of the results presented in Table 2 reveals that also the reverse reaction

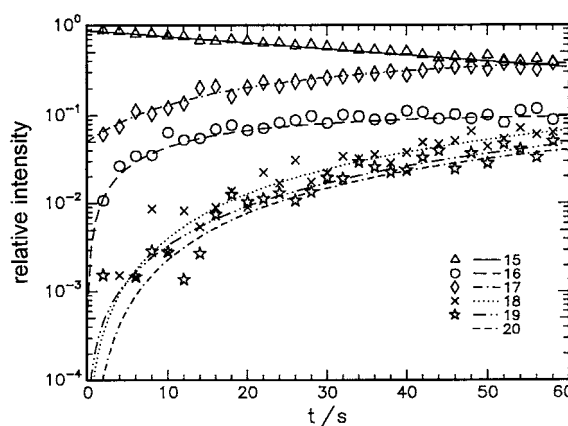


Fig. 7. Time evolution of CH<sub>3</sub><sup>+</sup> ions stored in the 10 K–22-pole ion trap filled with para-hydrogen ( $[\text{H}_2] = 8.7 \times 10^{10} \text{ cm}^{-3}$ ). During the storage time which extends here to 60 s, mainly CH<sub>5</sub><sup>+</sup> (mass 17) is formed via radiative association. The rate coefficient is  $k = 1.1 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$ . A significant fraction of the ions (10%) is converted into mass 16. This is due to H–D exchange with HD being present with its natural abundance,  $[\text{HD}]/[\text{H}_2] = 3 \times 10^{-4}$ . The lines are solutions of coupled rate equations which include the 16 reactions shown schematically in Fig. 8.

is not negligible. As discussed in more detail in Gerlich et al. (2002) this is probably caused by minor traces of ortho-hydrogen. Nonetheless, in the experiment shown in Fig. 7, almost 30% of the CH<sub>3</sub><sup>+</sup> are deuterated after a storage time of 1 min. This provides strong evidence that in this case (and under the conditions of the trapping experiment) the large endothermicity plays the dominant role in isotopic fractionation.

The various lines shown in Fig. 7 are solutions of a rather complex system of coupled rate equations which include the sixteen reactions illustrated schematically in Fig. 8. As can be seen from this figure, there are two different ions for masses above 17 introducing some arbitrariness in the evaluation. Therefore, no rate coefficients are reported for the formation of multiply deuterated CH<sub>3</sub><sup>+</sup> or of the various isotopomers of CH<sub>5</sub><sup>+</sup>, especially also since more detailed experiments are planned, including infrared laser induced reconversion of CH<sub>2</sub>D<sup>+</sup> and CH<sub>4</sub>D<sup>+</sup> stored in very cold hydrogen gas. The spectra of these molecules, which should be recorded over a wide range in the IR and FIR, certainly will provide interesting information on internal scrambling motions and on the dynamics of H–D exchanging reactions.

## 4. Conclusions

Recent and future advances in sub-millimeter and infrared instrumentation require not only more activities in laboratory spectroscopy but also many more details of the relevant collision processes are needed for understanding the astronomical observations of interstellar matter at different evolutionary stages. This paper shows that there is an increasing

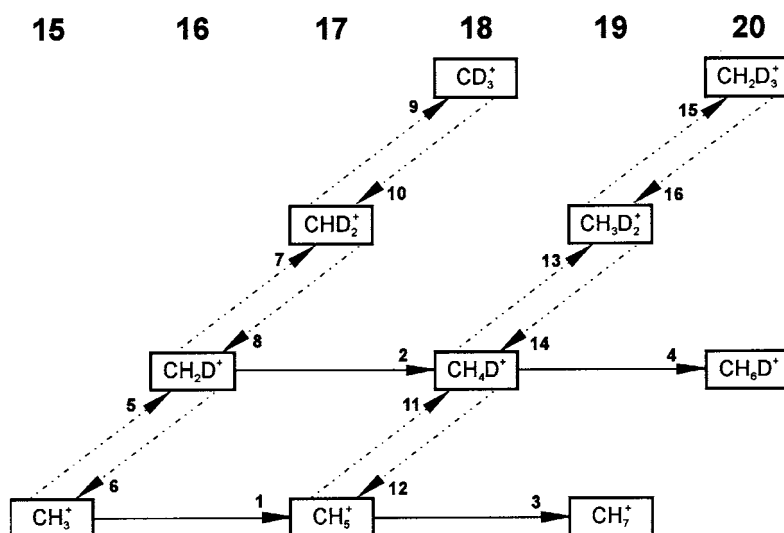


Fig. 8. The scheme shows reactions of  $\text{CH}_3^+$  in para hydrogen at 10 K. The arrows indicate the sequence which have been used to simulate the experimental results plotted in Fig. 7. Formation of  $\text{CH}_5^+$  and  $\text{CH}_7^+$  is dominated by radiative association ( $> 90\%$ ), while deuteration occurs via collisions with traces of HD (natural abundance  $[\text{HD}]/[\text{H}_2] = 3 \times 10^{-4}$ ).

need in state specific rate coefficients to satisfy the demands of the increasingly sophisticated chemical models.

Today, there is a variety of experimental methods available which are able to operate at low temperatures and it is expected that more data will become available on deuteration of molecules in the future. Meanwhile, multipole ion traps are more and more established in various laboratories due to their unique high sensitivity and versatility. Future experimental work in these devices can readily acquire data at the required low temperatures, such as the  $\text{C}_3\text{H}^+/\text{C}_3\text{D}^+$  branching ratio resulting from the reaction  $\text{C}_3^+ + \text{HD}$ , the various reaction paths to produce  $\text{DCO}^+$ , the formation of deuterated water  $\text{H}_2\text{DO}^+$ , or the question how doubly deuterated ammonia can be produced in dense molecular clouds.

In this laboratory, the combination of an ion trap with an atomic hydrogen beam is close to completion, significantly extending the flexibility of this device. In this combination, the basic reactions  $\text{H}_3^+ + \text{D} \rightarrow \text{H}_2\text{D}^+ + \text{H}$  may be studied to address doubts, as to whether this reaction really proceeds with a rate coefficient of  $1 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$  as generally assumed (Millar et al., 1989). Also, for the endothermic reverse reaction or for the above-mentioned reactions (1b) and (1c), experimental rate coefficients can be measured at temperatures relevant for isotope fractionation.

Further experimental progress relevant to interstellar chemistry is to be expected by combining existing techniques with laser methods for preparation of the reactants, for analysis of the products, for spectroscopy and for particle detection. The already mentioned modification of the low-temperature equilibrium of stored ions by exposing them to a continuous infrared laser field will provide unprecedented spectroscopic and dynamic information, especially for deuterated ions and for H–D exchange.

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