

DEUTERATION OF CH_n^+ ($n = 3-5$) IN COLLISIONS WITH HD MEASURED IN A LOW-TEMPERATURE ION TRAP

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ABSTRACT

Deuteration of small hydrocarbon ions CH_n^+ via H-D exchange ($n = 3-5$) has been studied in a 22 pole ion trap at a nominal temperature of 15 K. Sequential deuteration from CH_3^+ to CD_3^+ is very fast if one uses pure HD as the target gas. Rate coefficients have been measured to be 1.65×10^{-9} , 1.59×10^{-9} , and $1.50 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$. If, however, CH_3^+ is relaxed in p- H_2 containing traces of HD, the rate coefficient for isotope enrichment is significantly smaller, $(4 \pm 2) \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$. This important result is most probably due to symmetry selection rules influencing this reaction. The ions CH_4^+ and CH_5^+ are not observed, within the experimental uncertainties, to exchange H atoms for D atoms at all. Upper limits for the rate coefficients for forming CH_3D^+ and CH_4D^+ are 1×10^{-12} and $5 \times 10^{-18} \text{ cm}^3 \text{ s}^{-1}$, respectively. Hydrogen or deuterium abstraction in collisions of CH_4^+ with HD occurs with a sum rate coefficient of $4.5 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$. Surprisingly, the more exoenergetic and statistically favored product CH_4D^+ is formed only in 1/3 of the reactive collisions, while CH_5^+ dominates with 2/3. The results are discussed on the basis of the formation of long-lived collision intermediates, open- and closed-shell ions, and barriers along the reaction path. All experimental data clearly indicate that conservation of total nuclear spin plays an important role in these low-temperature chemical reactions involving identical nuclei. Implications of this laboratory work to isotopic fractionation in astrophysical environments are discussed.

Subject headings: astrochemistry — ISM: molecules — methods: laboratory

1. INTRODUCTION

In the last two decades about 20 singly, some doubly, and even triply deuterated molecules have been detected in cold interstellar clouds (Millar 2002). Recent observations include fully deuterated ammonia (Lis et al. 2002), triply deuterated methanol (Parise et al. 2004), and D_2H^+ (Vastel et al. 2004). It is well known and reasonably well understood that the measured abundance ratios of the singly deuterated molecules to their nondeuterated counterparts are significantly larger than the D/H cosmic ratio, sometimes up to a factor of 10^4 . The D/H ratio has been determined to be around 1×10^{-5} , e.g., by measuring the $J = 1 \rightarrow 0$ rotational line of HD. A recent example is the observation by Wright et al. (1999) toward the Orion bar. Deuterium fractionation is strongly related to the physical conditions of the interstellar medium, namely temperatures ranging from 10 to 100 K and densities allowing only bimolecular reactions. The reason is that most deuterium exchange reactions are exothermic because of the difference in the zero-point vibrational energies of the reactants and products. In molecular clouds most of the deuterium is contained in the form of HD. Therefore, it is assumed that deuterium fractionation is first initiated by simple ion-molecule collisions involving HD, followed by D atom or deuteron transfer to more complex molecules, provided that there are no significant barriers on the reaction pathway. Currently, only three initial gas-phase reactions with HD are included in the models: H_3^+ , CH_3^+ , and C_2H_2^+ . For more details see Millar (2002), Millar et al. (1989), Roberts et al. (2002), Maluendes et al. (1992), or Gerlich & Schlemmer (2002).

Deuteration can be used as a very sensitive probe of the physical conditions existing in specific interstellar regions and of the chemistry occurring there. It can give hints to the temperature of the cloud; the densities of atoms and electrons; concentrations of specific molecules; and, as emphasized in this work, the fractional abundance of o- H_2 . These insights into the prevailing conditions depend on our theoretical and experimental knowledge of many elementary processes. Modern model calculations (Roberts et al. 2002; Millar 2002) take into account both gas phase and gas-grain processes; however, rather few reliable input data are available, such as rate coefficients from low-temperature experiments or accurate quantum chemical calculations. Even with the sophisticated methods of quantum chemistry available today, barrier heights and other details of the potential energy surface often cannot be predicted with the required accuracy. Therefore, low-temperature experimental work is necessary to study the related processes. Investigations of ion-molecule reactions have been conducted with various techniques in recent decades, mainly at room temperature or at higher energies and under nonthermal conditions. In a selected ion flow tube (SIFT), Adams & Smith examined many reactions down to 80 K (Adams & Smith 1977; Smith 1992). In the 1980s the first experiments using ion traps were developed, in which chemical processes can be studied at temperatures of a few K and at the low densities prevailing in dense interstellar clouds (Barlow & Dunn 1987; Gerlich & Käfer 1989; Gerlich 1995). The need for low-temperature experiments is especially evident for reactions that show a different behavior at low temperatures in comparison with room temperature. One prominent example is the chain of H-atom abstraction reactions starting with N^+ in a bath of H_2 and leading finally to NH_4^+ , which, via dissociative recombination with an electron, is assumed to be a major source of interstellar NH_3 (Herbst et al. 1991; Gerlich 1993). In addition, for simple systems such as $\text{CH}_4^+ + \text{H}_2$ a negative temperature

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dependence has been observed recently, i.e., the rate coefficient increases with falling temperature ($k \sim T^{-n}$; Asvany et al. 2004).

As mentioned above, there are only the three molecular ions believed to contribute significantly to the transfer of deuterium from HD to more complex species: H_3^+ , CH_3^+ , and C_2H_2^+ . Besides elemental and molecular abundances, the main reason for this limited number is that many exothermic exchange reactions have transition-state barriers inhibiting the reaction from proceeding at low temperatures, one example being the reaction of HCO^+ with HD (Smith et al. 2002). Therefore, a major aim of theoretical treatments of the problem involves the prediction of barrier heights in order to classify the deuterium exchange reactions. The nature of the barriers has been discussed semi-quantitatively by Henchman et al. (1988). According to their model, the ion AH^+ and HD form an entrance channel complex $\text{AH}^+ \cdot \text{HD}$, in which the reactants remain distinct. Via a transition state, H and D can be exchanged, or a strongly bound complex can be formed in which mixing of the chemically equivalent atoms occurs. Because of the exoergicity of the exchange process, the complex prefers to decompose into $\text{AD}^+ + \text{H}_2$, as can be predicted from a simplified phase-space theory by just counting asymptotic states of the products.

A classification of transition-state barriers was proposed by Henchman et al. (1988) based on reactant ions with “filled” and “unfilled” valence shells. In the first case, the entrance channel complex is only weakly bound, and the energy of the transition state is much higher than that of the entrance channel. Therefore, H-D exchange does not occur at low collision energies. In the second case, the unfilled valence shell ion can form a strongly bound complex with a transition state that is way down in the valley of the attractive potential energy surface. In this situation H-D exchange can become a rapid process. Maluendes et al. (1992) replaced the somewhat misleading distinction between “filled” and “unfilled” valence shell ions by the more precise characterization based on a large and small HOMO-LUMO (highest occupied/lowest unoccupied molecular orbital) gap. For example, they report for the $\text{CH}_3^+ + \text{HD}$ collision system, based on detailed *ab initio* calculations, that formation of CH_2D^+ is 3.4 kJ mol^{-1} (405 K) exothermic and that scrambling can occur very efficiently in the strongly bound (-198 kJ mol^{-1}) collision complex, which is characterized by a double well potential with a completely negligible barrier lying 192 kJ mol^{-1} below the reactants’ energy. Based on a simple statistical argument they predict that the overall efficiency for H-D exchange must approach unity at low temperatures. According to these guidelines, ions like H_3^+ or CH_3^+ and its isotopomers, which are known to have strong chemical binding with hydrogen molecules, will undergo deuteration, while ions such as CH_5^+ can form only a weakly bound $\text{CH}_5^+ \cdot \text{HD}$ complex and are therefore not expected to become deuterated in collisions with HD.

It is an open question whether this simple reaction model holds for all astrophysically relevant systems or whether more details of the potential energy surface and dynamical calculations are needed in order to explain dynamical restrictions or to locate reaction paths avoiding barriers. Fundamental questions are related to the role of tunneling or to the dependence of the capture cross section on the rotational state of a molecular reactant. An example is the anisotropy of the ion–molecular hydrogen interaction potential, caused by the quadrupole moment of H_2 . A special dynamical effect of deuteration may concern the $\text{CH}_5^+ + \text{HD}$ system studied here. According to recent theoretical work (e.g., Marx & Parrinello 1999a) the

structure of CH_5^+ sometimes resembles a CH_3^+ and a distinct H_2 entity. Because of this fluctuation one may speculate that it could be possible to exchange the incoming HD molecule for the complete H_2 entity, while the HOMO-LUMO gap rule excludes the exchange of atoms.

Besides the details of the potential energy surfaces, symmetry selection rules closely correlated with the separate conservation of the total nuclear spin play a central role in the process of deuteration, as discussed, for example, for $\text{H}_3^+ + \text{HD}$ by Gerlich et al. (2002). Recently, it was pointed out (Gerlich 2004) that the well-documented basic ideas on symmetry selection rules in chemical reactions (Quack 1977) have not yet been implemented in a consistent way into statistical models describing the influence of the ortho and para forms of the reactants in H-D scrambling. A well-documented example is the process of ternary and radiative association in $\text{CH}_3^+ + \text{H}_2$ collisions. It was attempted by Bates (1987, 1991) to develop a theoretical model that explicitly treats the different nuclear spin configurations for comparing results performed under different experimental conditions (Barlow & Dunn 1987; Gerlich & Käfer 1989) and for making predictions for interstellar environments. The detailed experimental results obtained at 10 K (Gerlich 1994, 1995) did not show the increase of the association rate coefficient as predicted for para-hydrogen by the Bates model, indicating that it does not account properly for the restrictions imposed by the exchange symmetry.

In addition to the above-mentioned studies, the $\text{CH}_3^+ + \text{H}_2$ system has been the focus of many other experimental investigations. Isotope exchange and association reactions of CH_3^+ and its deuterated analogues with H_2 , HD, and D_2 have been studied in a variable-temperature SIFT apparatus by Smith et al. (1982a). From forward and backward reaction rates measured at 295, 205, and 80 K, enthalpy changes have been determined. In particular, the rate coefficients for CH_2D^+ formation in $\text{CH}_3^+ + \text{HD}$ collisions have shown a negative temperature dependence. Extrapolation to interstellar cloud temperatures has indicated that the collisional limiting value should be reached. Since back-deuteration of $\text{CH}_2\text{D}^+ + \text{H}_2$ is rather endothermic and must therefore be slow, it has been concluded that CH_2D^+ plays an important role in the synthesis of deuterated molecules in interstellar space (Smith et al. 1982b).

Low-temperature trap experiments, performed with hydrogen containing traces of HD, always show contributions from isotope enrichment (Gerlich 1995). Unfortunately, competing product channels, interfering masses, and back reactions of deuterated species in collisions with hydrogen (especially o- H_2) complicate the evaluation of such data. Some related results were presented by Gerlich & Schlemmer (2002). Among others, it was reported that the rate coefficient for isotope exchange in $\text{CH}_3^+ + \text{HD}$ is significantly smaller than the collision limit if the ions are relaxed in p- H_2 . Since this is in contrast to the theoretical predictions mentioned above, H-D exchange reactions of CH_n^+ ($n = 3-5$) have been reinvestigated in our laboratory. The experiments were carried out with pure HD in the trap in order to avoid complications with competing forward and backward reactions.

2. EXPERIMENTAL

The laboratory measurements have been performed in an ion-trapping apparatus that has been developed for investigating ion-molecule collisions at conditions representative of interstellar clouds. The ion guiding and trapping technique has been thoroughly reviewed by Gerlich (1992), while detailed descriptions of the temperature-variable radio-frequency (RF)

22 pole ion trap have been given by Gerlich & Horning (1992) and Gerlich (1995). The trap consists of 22 stainless steel rods of 1 mm diameter circumscribing a circle of 1 cm diameter and connected alternatively to the two phases of an RF power supply. Typical RF frequencies and amplitudes are $\Omega/2\pi = 17$ MHz and $V_0 = 20$ V, respectively. Radial confinement of the ion cloud is achieved by the very steep effective potential created by the multipole RF field, whereas trapping in the axial direction is achieved by repulsive direct current (DC) voltages applied to the entrance and exit gate electrodes. This arrangement is completely enclosed by copper walls, which are mounted onto a closed-cycle He refrigerator that can be cooled down to a nominal temperature of 10 K. Reactant and buffer gases can be admitted to the 22 pole trap by cooled tubes. The ion cloud injected into the trap adapts to the trap temperature by collisions with the buffer gas leaked in either in a continuous mode or in short (~ 1 ms) intense pulses.

The investigated ions are generated by electron bombardment, mass selected in a quadrupole mass filter, and then injected into the 22 pole ion trap filled with the reactant gas. After a certain trapping time, the trap content is extracted by an electric pulse applied to the exit electrode, analyzed with a second quadrupole mass spectrometer, and detected with near unit efficiency by an ion-counting detector (Daly detector). For determining the changes of the ion composition due to reactions, the sequence (1) ion formation, (2) injection, (3) relaxation and reaction, and (4) analysis is repeated many times for each product mass and typically for 20 different storage times. More details of the method and typical applications in interstellar gas-phase chemistry, in cluster growth, or in state-specific ion-molecule reactions can be found in recent publications (Schlemmer et al. 1999; Gerlich et al. 2002; Smith et al. 2002; Asvany 2004).

For the preparation of ionic hydrocarbons CH_n^+ ($n = 3-5$), methane gas (Messer Griesheim, purity 5.5) was used at a pressure of about 10^{-5} mbar in an external RF storage ion source. The ions CH_4^+ and CH_3^+ are directly generated by electron bombardment, while CH_5^+ is created in the source by the subsequent reaction $\text{CH}_4^+ + \text{CH}_4 \rightarrow \text{CH}_5^+ + \text{CH}_3$. To avoid internal excitation of the ions, the electron energy is kept as low as possible, typically 18 eV. In some cases helium gas has been added to the source. In the electron-bombardment region this also leads to Penning ionization; however, the buffer gas finally causes thermalization of the ions to ~ 350 K because of the labyrinth-type structure of the storage source. In the case of CH_3^+ and CH_5^+ , hydrogen has been used as an additional buffer gas in the source, as hydrogen abstraction reactions of CH_n^+ ($n = 1-5$) with H_2 are known to stop at $n = 3$ or $n = 5$, and association with H_2 is unlikely at the high source temperature. In this way, several ions with interfering masses are removed. For example, D- or ^{13}C -containing hydrocarbon ions with $m = 15$ or 17 amu such as CHD^+ or $^{13}\text{CH}_4^+$ react to CH_3^+ or CH_5^+ equivalents.

After extraction of the primary ions from the source through a pulsed electrode, the ions are selected in a first RF quadrupole operated either at high frequencies and low DC differences, i.e., in the low bandpass mode, or in the standard high mass resolution mode. In the first mode all ions with a mass smaller than a certain cutoff value are injected “smoothly” into the trap. This mode is used if very slow ions with a narrow energy distribution have to be injected into the trap and if the presence of lower mass ions does not disturb the reaction kinetics. The other mode (upper corner of the stability triangle) is used if it is necessary to inject exclusively ions of a particular mass into the

22 pole ion trap, of course at the expense of a wider energy spread. For example, the mass-selective mode was necessary to search for minor traces in determining the upper limit of deuteration of CH_5^+ with HD. After injection of the ions into the trap through the pulsed entrance electrode, they are cooled down to the nominal temperature by using a short He pulse of typically a few ms and of high density ($n_{\text{max}} \sim 10^{15} \text{ cm}^{-3}$).

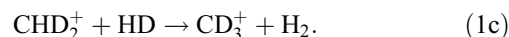
The target gas HD has been purchased from Cambridge Isotope Laboratories, Inc., who specify the purity of the deuterium hydride to be 97%, the rest mainly being H_2 and D_2 . We confirmed this specification by a detailed in situ analysis using the $\text{Ar}^+ + \text{HD}$ reaction in the trap. More details about these tests have been reported by Asvany et al. (2004) and Asvany (2004).

A wide range of storage times (< 1 ms to > 100 s) and densities ($< 10^8$ to 10^{15} cm^{-3}) of the neutral reaction partner can be used in trapping experiments, thus allowing for a large dynamic range in the determination of rate coefficients. The high sensitivity of the 22 pole trapping apparatus is very important for the determination of very small rate coefficients, such as those observed for the reaction between CH_5^+ and HD. This sensitivity is achieved by optimizing the trapping time, the target gas number density, and the number of stored ions (typically 1000). Using the maximum values and accounting for the noise of the detector (typically 1 count s^{-1}), rate coefficients as small as $k = 1 \times 10^{-20} \text{ cm}^3 \text{ s}^{-1}$ can be determined. Depending on the reaction system investigated, this sensitivity is reduced by reaction channels leading to interfering product masses.

3. RESULTS

3.1. Sequential H-D Exchange in CH_3^+

The following sequential reactions have been measured at a nominal temperature of 15 K:



All three reactions are exothermic because of differences in the zero-point vibrational energy. For example, the exoergicity of reaction (1a) has been determined to be 370 (Smith et al. 1982a) or 405 K (Maluendes et al. 1992). A typical measurement of the sequential deuteration of CH_3^+ is presented in Figure 1. On average, about 500 CH_3^+ ions were injected per pulse into the trap filled with HD at a number density of $1.8 \times 10^{10} \text{ cm}^{-3}$. Inspection of Figure 1 reveals a monoexponential decay of the primary ions via reaction (1a) over 4 orders of magnitude. In the nearly pure HD environment, deuteration is so efficient that within 0.3 s, the subsequent reactions (1b) and (1c) convert more than 99% of all ions into fully deuterated CD_3^+ . Additional careful studies at longer reaction times revealed that the remaining number of CHD_2^+ ions is at least a factor of 1000 smaller than the CD_3^+ ions with no indication for an onset of an equilibrium between these two product ions. In addition, no residual CH_3^+ or CH_2D^+ could be detected within the sensitivity of the instrument. This implies that the hydrogenation reactions with HD are at least a factor of 1000 slower than the deuteration reactions.

The lines in Figure 1 are numerical solutions to a system of appropriate rate equations yielding the three rate coefficients for reactions (1a)–(1c), which are summarized in Table 1. Details of the fitting procedure of the data are reported by

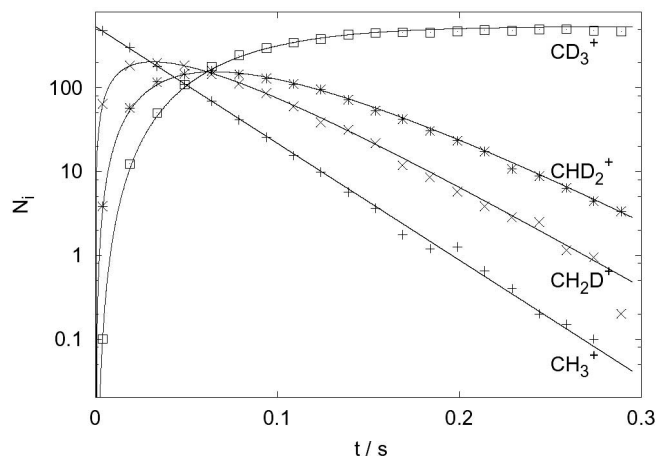


FIG. 1.—Evolution of the number of different ions, $N_i(t)$, extracted from the trap per iteration after a certain storage time t , showing the sequential deuteration of CH_3^+ . The nominal temperature was $T = 15$ K, and pure HD with a number density of $[\text{HD}] = 1.8 \times 10^{10} \text{ cm}^{-3}$ was used as the reactant gas. After 0.3 s, nearly all ions are converted into CD_3^+ . The lines are numerical solutions of a suitable rate equation system fitted to the data. The resulting rate coefficients are listed in Table 1.

Asvany (2004). As can be seen from Table 1, the first deuteration step is 1.04 times faster than the second one, and the second one is 1.06 times faster than the last one. Note that the rate coefficients for reactions (1a)–(1c) are slightly larger than $k_L = 1.32 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$, where k_L is the capture rate coefficient predicted by the Langevin model just using the polarizability of HD. Such a behavior has also been observed for the abstraction reaction $\text{CH}_2^+ + \text{HD}$ (Asvany 2004). The deviation of almost 20% is larger than the estimated experimental uncertainties ($\pm 10\%$), which are mainly due to the calibration of the pressure of the reactant gas and the determination of the actual trap temperature. The reliability of the measured number density has been cross-checked using the calibration reaction $\text{Ar}^+ + \text{HD}$, for which the 300 K literature value is $8.6 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ (Ervin & Armentrout 1985). Other reaction rates measured for different ions with hydrogen and its isotopomers as reactants are also in good accordance with published rate coefficients. As discussed in more detail below, one of the reasons for the measured larger rate coefficients is the long-range attraction with HD.

3.2. Reaction of CH_4^+ with HD

The slightly exothermic reaction of CH_4^+ with hydrogen and especially its temperature dependence are the subject of a

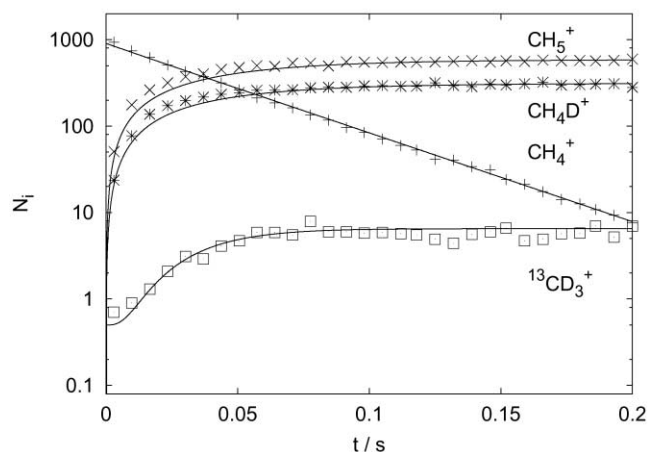
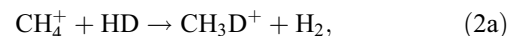


FIG. 2.— CH_4^+ stored at $T = 15$ K and $[\text{HD}] = 5 \times 10^{10} \text{ cm}^{-3}$. As can be seen from the $N_i(t)$ plots, H atom abstraction is, at 68%, the dominant channel leading to the formation of CH_5^+ . Only 32% of the reactive collisions yield the deuterated product CH_4D^+ . The total rate coefficient at this temperature is $4.5 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$. The $^{13}\text{CD}_3^+$ signal comes from sequential deuteration of $^{13}\text{CH}_3^+$ impurities contained in the injected $^{12}\text{CH}_4^+$ beam ($m = 16$ amu).

separate paper (Asvany et al. 2004), so we summarize here only the most important results for deuteration. Of importance are the deuteration channel via H-D exchange,



and the two abstraction reaction channels,

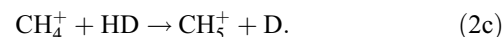


Figure 2 shows the time evolution of N_i , the number of ions of type i , after the initial injection of CH_4^+ in a pure HD environment. The number density was $[\text{HD}] = 5.0 \times 10^{10} \text{ cm}^{-3}$. It is evident that the abstraction reactions (2b) and (2c) prevail, i.e., CH_4^+ ($m = 16$ amu) is converted to CH_5^+ ($m = 17$ amu) and CH_4D^+ ($m = 18$ amu). At the temperature of this measurement, the three reactions (2a)–(2c) proceed with a sum rate coefficient of $k = (4.5 \pm 0.2) \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$. The dominant product is CH_5^+ with a branching fraction of 68%. Both abstraction reactions show the same strong negative temperature dependence as has been reported for the interaction with H_2 (Asvany et al. 2004).

The problem in determining a reliable rate coefficient for reaction (2a) is that the product CH_3D^+ appears at the same mass as the main reaction product, CH_5^+ . Therefore, it was

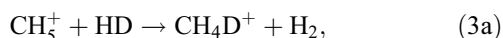
TABLE 1
RATE COEFFICIENTS FOR VARIOUS DEUTERATION REACTIONS AT $T = 15 \pm 5$ K

| Reaction | k ($\text{cm}^3 \text{ s}^{-1}$) | Remarks |
|---|---|--|
| $\text{CH}_3^+ + \text{HD} \rightarrow \text{CH}_2\text{D}^+ + \text{H}_2$ | $(1.65 \pm 0.10) \times 10^{-9}$ | Relaxation of CH_3^+ only in He, pure HD target |
| $n\text{-CH}_3^+ + \text{HD} \rightarrow \text{CH}_2\text{D}^+ + \text{H}_2$ | $(1.5 \pm 0.8) \times 10^{-9}$ | Relaxation of CH_3^+ in n- H_2 |
| $p\text{-CH}_3^+ + \text{HD} \rightarrow \text{CH}_2\text{D}^+ + \text{H}_2$ | $(0.4 \pm 0.2) \times 10^{-9}$ | Relaxation of CH_3^+ in p- H_2 |
| $\text{CH}_2\text{D}^+ + \text{HD} \rightarrow \text{CHD}_2^+ + \text{H}_2$ | $(1.59 \pm 0.10) \times 10^{-9}$ | Pure HD |
| $\text{CHD}_2^+ + \text{HD} \rightarrow \text{CD}_3^+ + \text{H}_2$ | $(1.50 \pm 0.10) \times 10^{-9}$ | Pure HD |
| $\text{CH}_4^+ + \text{HD} \rightarrow \text{CH}_3\text{D}^+ + \text{H}_2$ | $< 1 \times 10^{-12}$ | Deuteration |
| $\text{CH}_4^+ + \text{HD} \rightarrow \text{CH}_4\text{D}^+ + \text{H}$ (32%)..... | | D abstraction |
| $\text{CH}_4^+ + \text{HD} \rightarrow \text{CH}_5^+ + \text{D}$ (68%)..... | $(4.5 \pm 0.2) \times 10^{-10}$ | H abstraction |
| $\text{CH}_5^+ + \text{HD} \rightarrow \text{CH}_4\text{D}^+ + \text{H}_2$ | $< 5 \times 10^{-18}$ | Deuteration |

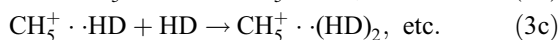
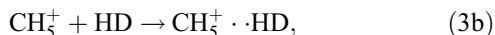
necessary to apply a more complicated analysis based on the careful evaluation of a variety of subsequent reactions. Especially important is that CH_3D^+ product ions formed via reaction (2a) would also abstract an H or a D atom in subsequent collisions with HD, leading to CH_4D^+ ($m = 18$ amu) or CH_3D_2^+ ($m = 19$ amu). As can be seen in Figure 2, ions with $m = 19$ amu are detected indeed; however, this minor product channel is assigned to be $^{13}\text{CD}_3^+$. One test is the time dependence of this channel, which grows very similarly to the main products for $t > 0.05$ s. The slight difference at the beginning is due to the initial $^{13}\text{CH}_3^+ + \text{HD}$ processes. From this and other tests it is concluded that the $m = 19$ amu ions are predominantly produced from $^{13}\text{CH}_3^+$ via fast subsequent deuteration reactions with HD, in analogy to reactions (1a)–(1c). Since these primary ions appear on the same mass as $^{12}\text{CH}_4^+$, they cannot be eliminated by the first mass filter. Using chemical quenching in the ion source, the fraction could be reduced to below 0.5% of the primary ions. Assuming that the secondary abstraction reactions of CH_3D^+ proceed at the same rate as those of the CH_4^+ ion and accounting for other uncertainties, an upper limit of the rate coefficient, $k < 1 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$, has been determined for reaction (2a) (see Table 1).

3.3. Collisions of CH_5^+ with HD

Finally, we present experimental results for collisions of protonated methane, CH_5^+ , with HD. In extensive measurements no hint has been obtained that the exchange reaction,



takes place at low temperatures. As can be seen in Figure 3, initially injected CH_5^+ ions disappear slowly because of radiative and ternary association adding one or more HD molecules,



A rather high HD number density of $[\text{HD}] = 1.7 \times 10^{13} \text{ cm}^{-3}$ has been used in the example shown in Figure 3. In addition, the storage time was extended up to 4 s for further increasing the sensitivity. In order to concentrate on the dominant association processes and to find a limit for the deuteration reaction (3a), some less important trace ions such as $m = 19$, 21, and 24 amu have been omitted in the plot but not in the evaluation. Inspection shows that CH_5^+ is growing in the HD bath according to reactions (3b) and (3c). At the high number density used in this experiment, association is dominated by three-body processes. The effective rate coefficients for reactions (3b) and (3c), i.e., the products $k^* = k_3[\text{HD}]$, are both determined from comparisons with numerical simulations to be $k^* = 5.8 \times 10^{-15} \text{ cm}^3 \text{ s}^{-1}$ (see fit in Fig. 3). Measurements at different HD number densities yield for the association (3b) both the radiative and the ternary rate coefficients, $k_r = 2 \times 10^{-16} \text{ cm}^3 \text{ s}^{-1}$ and $k_3 = 2.9 \times 10^{-28} \text{ cm}^{-6} \text{ s}^{-1}$, respectively. Further details about the association processes of $\text{CH}_n^+ + \text{HD}$ and H_2 ($n = 3, 5$) have been discussed by Asvany (2004).

To determine the upper experimental limit of the rate coefficient for reaction (3a), dedicated measurements with a long trapping time, high HD number density, and a rather large number of CH_5^+ ions have been conducted. As can be seen in Figure 3, there is a minor amount of CH_4D^+ ions present in the trap. This fraction most probably originates from CH_3D^+ or $^{13}\text{CH}_4^+$ injected with the primary beam ($m = 17$ amu). These

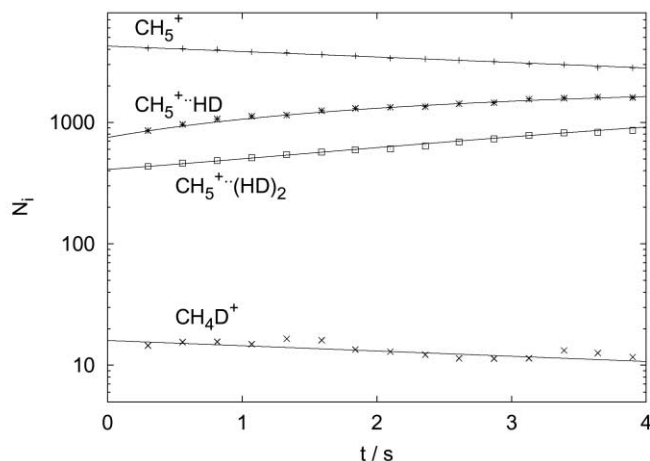


FIG. 3.— CH_5^+ stored at $T = 15$ K and $[\text{HD}] = 1.72 \times 10^{13} \text{ cm}^{-3}$. Two subsequent association steps to $\text{CH}_5^+ \cdot (\text{HD})$ and $\text{CH}_5^+ \cdot (\text{HD})_2$ can be observed. The CH_4D^+ (or also $^{13}\text{CH}_5^+$) signal stems merely from injected CH_3D^+ impurities (or $^{13}\text{CH}_4^+$). A detailed analysis of the ions with $m = 18$ amu leads to the conclusion that the rate coefficient for deuteration of CH_5^+ (reaction [3a]) is less than $5 \times 10^{-18} \text{ cm}^3 \text{ s}^{-1}$. Some other minor impurities stored in the trap have been omitted in this figure for simplicity.

ions react very fast to CH_4D^+ or $^{13}\text{CH}_5^+$ in a step similar to reaction (2c). The CH_3D^+ ions in the primary beam are generated in the ion source because of some back-streaming of HD from the trap. In Figure 3, there is no increase of the CH_4D^+ signal that could be attributed to the deuteration step (reaction [3a]). In total, the CH_4D^+ ions rather disappear because of secondary reactions, namely association similar to reaction (3b). Assuming equal association rates for CH_4D^+ and CH_5^+ leads to the simulation (bottom solid line) for the CH_4D^+ contribution shown in Figure 3. Taking the experimentally determined standard deviation of the decay rate of CH_4D^+ into account, one obtains an upper limit for the rate coefficient for deuteration of CH_5^+ , reaction (3a), of $k < 5 \times 10^{-18} \text{ cm}^3 \text{ s}^{-1}$. This value is included in Table 1 as upper limit for this reaction.

4. DISCUSSION

The systematic experimental study on the deuteration of CH_n^+ ($n = 3-5$) ions in collisions with HD reveals fast (CH_3^+) and slow (CH_4^+ and CH_5^+) deuteration processes, which, at first glance, can be predicted using the simple rule given by Henschman et al. (1988). In particular, the slow reactions (2a) and (3a) are in agreement with the expectations from the model, as they give a yes or no answer when the rate coefficient is as small as found. This is not so for the fast reaction. Especially the differences between the results obtained with pure HD and the previous measurements summarized by Gerlich & Schlemmer (2002) need some consideration beyond the level of this model.

4.1. $\text{CH}_3^+ + \text{HD}$

The effective sequential deuteration of CH_3^+ in HD found in this study can be described by assuming that a strongly bound collision complex is formed (e.g., 198 kJ mol^{-1} without zero-point energy, as reported by Maluendes et al. 1992). This complex is a hypercoordinated carbocation, a molecule that has been the subject of many experimental and theoretical investigations (see, e.g., Sefcik et al. 1974; Komornicki & Dixon 1987; Müller et al. 1997; Marx & Parrinello 1999b; White et al. 1999) since its first mass spectrometric detection in 1952. Most of these investigations show that there are only negligibly small barriers

to the scrambling movements of H or D atoms. Recent theoretical calculations confirm the near equivalence of the H atoms, obtaining a barrier height of only ~ 3.4 kJ mol⁻¹ (Müller et al. 1997) for the C_{2v} transition between two minima of C_s symmetry. Since this molecule is already very floppy in its ground state, it is not easy to envision that dynamical effects restrict the H-D scrambling. One exception may be collision complexes that are formed with a large total orbital angular momentum.

Using a simple statistical counting model, one expects from a decay of the CH₄D⁺ collision complex a 40% chance to get CH₃⁺ + HD products and a 60% chance to get a deuterated ion, CH₂D⁺ + H₂. In the experiment deuteration is even more efficient than this simple counting of outcomes suggests. Maluendes et al. (1992) have proposed another simple model for deuteration reactions with HD by treating separately the entrance and the exit channel, which can be reached via a transition state. Starting from the transition state, such a system can either deuterate (probability: $x < 1$) or fall back into the entrance complex (probability: $1 - x$). However, in the latter case, because of the low collision energy and the large phase space available for the entrance complex, the system has only a small chance to decompose back into reactants. Therefore, it reaches the transition state over and over again until finally the deuterated ion is formed. In fact, the presently measured rate coefficients for pure HD turn out to be 10%–20% larger than the Langevin limiting value. HD possesses a dipole moment, an anisotropic polarizability, and, most importantly, a permanent quadrupole moment all contributing in addition to the long-range ion-induced dipole interaction. Quantitatively, the dipole moment of HD (8.51×10^{-4} D; see Thorson et al. 1985) is too small to be of importance, while the quadrupole moment is known to influence the capture cross section, especially if hydrogen is in its rotational ground state. Of importance for the long-range interaction and for orienting the HD is also the fact that the center of mass and center of charge is separated in HD. A detailed statistical calculation is necessary to account for all this.

As already indicated above, rate coefficients for reaction (1a) have also been determined by analyzing data from trapping experiments performed with H₂ and containing only traces of HD in its natural abundance, $[HD]/[H_2] = 3 \times 10^{-4}$ (Gerlich & Schlemmer 2002; Gerlich 1995). These experimental data, which have been obtained with the same apparatus as the new results, have been critically reevaluated and are included in Table 1. Most surprising is the result that relaxation of CH₃⁺ in p-H₂ reduces the H-D exchange efficiency by a factor 4, while the corresponding experiment with n-H₂ leads to a result in agreement with the rate coefficient measured with pure HD. The rather large errors are a consequence of the complicated reaction scheme, which involves p-H₂, o-H₂, and HD as reaction partners and a variety of competing reactions and inelastic collisions. In the reevaluation, deuteration of CH₅⁺ has been completely switched off in accordance with the results of the present study. It also was shown that a faster backward process (reverse of reaction [1a]) could not lead to the necessary increase of the rate coefficient for the forward reaction. In addition, a variety of possible experimental artifacts have been discussed and excluded as potential causes for the observed differences, such as depletion of HD by condensation in the para-hydrogen generator or any type of segregation of H₂ and HD in the trap itself.

The difference between the present and the previous rate coefficients for reaction (1a) given in Table 1 must be a consequence of the relaxation of the stored CH₃⁺ ions in the ambient

p-H₂. For example, a well-understood result from 10 K trapping experiments (Gerlich 1995) is the dependence of the lifetime of CH₃⁺ · H₂ collision complexes on the ratio of the ortho- to para-hydrogen prevailing in the trap. In the case of nearly pure p-H₂, the mean complex lifetime is 386 ns, much longer than in the case of n-H₂, 123 ns. In analogy, one would also expect that the CH₃⁺ · HD complexes live longer in the para-hydrogen environment, which would lead, in contrast to the experiment, to more scrambling. In addition, from a point of view of energetics there are no obvious reasons for restricting the H-D exchange. Reaction (1a) is so exothermic (370 K) that many product states can be excited. The main distinction between the two experiments, which must be responsible for changes in reactivity, is based on different populations of the para and ortho states of CH₃⁺. Inspection of the low-lying rotational states (Crofton et al. 1988) reveals that there are, for pure p-CH₃⁺, a maximum of two states accessible at 15 K. Note that the rotational ground state of p-CH₃⁺ is forbidden by symmetry. In contrast, relaxation of CH₃⁺ in n-H₂ can lead to higher rotational states of n-CH₃⁺. If there is no He buffer gas present, the process of energy pooling explained by Gerlich et al. (2002) for H₃⁺ may also play a role. Nonetheless, it is very unlikely that these small changes in internal energy of the reactant ions are the reason for the difference in reactivity.

In summary, it is speculated that the restrictions imposed by the exchange symmetry and the conservation of total nuclear spin reduce the H-D exchange efficiency in the para environment. It is unlikely that the additional energy that is provided in the ortho environment by H₂ ($J = 1$) accelerates the reaction, because of the large gain in zero-point energy by the H-D exchange. As emphasized recently by Gerlich (2004), all these questions may be answered by a complete statistical calculation that accounts properly for all symmetry selection rules. In order to stimulate such theoretical activities, more systematic experimental tests are planned based on a systematic variation of well-defined amounts of HD and o-H₂ added to the p-H₂ target gas or on separating relaxation and reaction by using a pulsed HD gas inlet. In addition, laser-induced reactions (Schlemmer et al. 1999, 2002) shall be used to probe the stationary population of the ortho and para forms of CH₃⁺ in the trap and, potentially, to determine state-specific rate coefficients.

4.2. CH₄⁺ and CH₅⁺ + HD

The results for the other two systems studied in this work seem to be easier to understand. Obviously, the CH₄⁺ · HD collision complex decays rather quickly into the exothermic channels (2b) and (2c), leaving no chances for H-D exchange. It is surprising, however, that channel (2c) dominates. This also may be caused by symmetry selection rules, especially if the nuclear spins of the hydrogen atoms sum up to $I = 5/2$ in the collision complex. More information on this system can be found in Asvany et al. (2004).

The upper limit of the H-D exchange rate coefficient determined for low-temperature collisions of CH₅⁺ with HD indicates that the approaching HD cannot penetrate into the “closed shell” of the CH₅⁺ sphere. A maximum of 1 out of 10⁸ collisions may lead to deuteration, although collision complexes are formed with lifetimes of a few ns, corresponding to thousands of vibrational periods, as derived from ternary association (Asvany 2004). This complex must be considered as a cluster ion, where the HD molecule is bound only by rather weak van der Waals forces to the central CH₅⁺ ion core. Apparently, the inner and outer H atoms in this system are not at all equivalent, and scrambling probably would require the

breaking of the outer HD bond. The barrier for this process is apparently too high for it to occur. The other possible reaction mechanism mentioned briefly in the introduction would involve the replacement of a H_2 unit by HD, which was suspected to be possible because of the fluxional nature of CH_5^+ . This can be ruled out by the present experiment. It may even be that the presence of the HD in the entrance channel complex leads to a slight structural rearrangement of the CH_5^+ , such that exchange becomes even more restricted. Infrared spectroscopy of $\text{CH}_5^+ \cdot (\text{H}_2)_n$ by Boo et al. (1995) and calculations have indicated that the presence of solvating H_2 leads to a more rigid structure of the CH_5^+ core. This leads to the interesting question of whether there is any chance that the stable $\text{CH}_5^+ \cdot \text{HD}$ cluster ion isomerizes spontaneously to the energetically favored $\text{CH}_4\text{D}^+ \cdot \text{H}_2$ structure. Spectroscopy on stored ions or chemical probing could reveal such processes and help to find reaction paths that would need minutes instead of nanoseconds.

5. INTERSTELLAR IMPLICATIONS

Fractionation of deuterium in interstellar clouds is a complex affair. There are a variety of secondary exchange reactions, all of which compete with many other thermal and nonthermal processes, such as radiative association, grain-surface reactions, mantle evaporation, and dissociative recombination (Millar et al. 1989; Roberts & Millar 2000a, 2000b; Millar 2002). It was mentioned in the introduction that a crucial point is the use of the proper temperature dependence of the rate coefficients. A recent example is the hydrogen abstraction reaction $\text{CH}_4^+ + \text{H}_2$. Formation of CH_5^+ in collisions with H_2 is exothermic but nonetheless very slow at 300 K, but it becomes faster by at least 1 order of magnitude when the temperature is lowered to 15 K (Asvany et al. 2004). In addition, the results from the present study clearly show that it is a must to study the influence of the ortho and para forms of the involved molecules both on inelastic collisions (energy pooling) and on H-D or D-H scrambling processes. Finally, it can be foreseen that state-specific rate coefficients are required for understanding in detail the interactions of hydrogen- and deuterium-containing molecules with HD. The central role of conserving the total nuclear spin is best illustrated by the inefficiency of ortho-para transitions in scrambling $\text{H}^+ + \text{H}_2$ collisions (Gerlich 1990); however, we are still not yet able to fully understand the more complex reactions presented here.

A variety of important conclusions can be drawn from the present results. There are currently no consequences concerning the role of CH_5^+ , since this ion has been known by chemists and modelers to be inert toward D atom exchange in collisions with HD at room temperature. In accordance with theoretical considerations (Maluendes et al. 1992), the present work confirms that this also holds at the low temperatures prevailing in the interstellar medium. If deuterated CH_5^+ is observed at all, it

may have been formed via radiative association of deuterated CH_3^+ or H_2 . In addition, formation of $\text{CH}_5^+ \cdot \text{HD}$ via radiative association (Asvany 2004) is possible, although probably too slow ($k_r = 2 \times 10^{-16} \text{ cm}^3 \text{ s}^{-1}$), since CH_5^+ is efficiently destroyed via dissociative recombination with electrons leading to CH_4 and CH_3 , as described by Smith (1992). An interesting related project that is ongoing in this laboratory is the low-temperature outcome of $\text{CH}_5^+ + \text{H}$ or D collisions. There is experimental evidence that at 10 K scrambling or CH_4^+ formation is rather slow.

Important for interstellar and circumstellar chemistry are the experimental findings for the methane cation, CH_4^+ , for which only data measured by Adams & Smith (1977) at room temperature have been available until now. Our measurements (Asvany et al. 2004) show that the reaction of CH_4^+ with HD and H_2 has a strong negative temperature dependence with rate coefficients at least 1 order of magnitude higher at 10 K than at room temperature. Inclusion of this new data in astrochemical networks (Le Teuff et al. 2000) will certainly have an impact on future model calculations of interstellar gas-phase chemistry.

Deuteration of CH_3^+ has been found to be rather fast, and CH_2D^+ , together with H_2D^+ and C_2HD^+ , will probably keep its central role in passing the interstellar deuterium, available as HD, to more complex molecules via gas-phase reactions (Millar 2002; Gerlich & Schlemmer 2002). Because of their higher exothermicity, the deuterated hydrocarbon ions are of special importance for higher temperature interstellar clouds (e.g., Orion, $T = 70 \text{ K}$; Millar et al. 1989). In order to make the models more realistic, the experimentally determined rate coefficients have to be included, of course in addition to the gas-grain interaction. For the recently measured reaction rate coefficients for forming and destroying H_2D^+ (Gerlich et al. 2002), this already has been done by Roberts et al. (2002). For reaction (1a) Table 1 offers three different rate coefficients, and it is not obvious which value one should take in models. The result obtained with pure HD is a factor of 1.3 higher than that used by Millar et al. (1989). Nonetheless, it is not recommended to use this new value, since it is rather certain that the rotational population of the CH_3^+ ions in interstellar space is different from the present 15 K experiment using He as a cooling gas. It is also questionable whether thermalization in pure p- H_2 really leads to an ion ensemble that is representative for dense interstellar clouds. If one assumes that cold p- CH_3^+ ions dominate in dense interstellar clouds, the much smaller rate coefficient given in Table 1 should be used in chemical model calculations.

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