

Reactions between cold CH_x^+ and slow H and H_2

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Abstract

Using the combination of a linear 22-pole ion trap (22PT) and a coaxial beam of hydrogen atoms, H abstraction from CH_x^+ ($x=1, 4$ and 5) has been studied. The temperature of the trap, $T_{22\text{PT}}$, can be varied between 10 K and 300 K. The velocity distribution of the neutral target beam can be changed by cooling the accommodator ($T_{\text{ACC}}=10$ K - 300 K) and using the focusing features of one or two hexapole magnets. The resulting velocity distributions are characterized by time-of-flight measurements. With the same setup, reactions of mass selected stored ions with a cold effusive beam of H_2 molecules have been measured with the discharge turned off. At temperatures of interstellar space, H-abstraction from CH^+ is efficient. CH_4^+ reacts five times faster with H than with H_2 at 50 K. In contradiction to *ab initio* calculations and to the established proton affinity of methane, CH_5^+ is slowly destroyed in collisions with H in our trap, even at 10 K. Some first results for collisions between CH_x^+ and D atoms are reported. For $x=1$, H-D exchange is quite efficient, even though it is in competition with the exothermic abstraction reaction. For $x=4$, H-abstraction, i.e. formation of HD molecules, dominates. Deuteration of CH_5^+ is measured to be very slow.

Keywords

Astrochemistry, ion-atom reactions, CH_x^+ ions, cold H atoms, low temperature rate coefficient, deuteration

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1 Introduction

Reactions of ions with atomic hydrogen are important in many fields ranging from molecular clouds in interstellar space via planetary and cometary atmospheres to various laboratory plasmas. Despite that, there are only a few experimental studies most of which have been performed in flow systems [1]. There has been one attempt to combine an ion cyclotron resonance cell with an H-atom source [2]. Laboratory studies of the interaction of positive and negative ions with H, N, or O atoms have been summarized in [3], [4], [5] and [6]. First low temperature results for the interaction of cold stored ions with a slow H-atom beam have been reported in [7] and [8]. In the following we summarize the results obtained at selected temperatures for CH_x^+ colliding with H and D. Modeling the temporal changes of the ion composition in the trap, we also have extracted results for collisions of ions with H_2 or D_2 .

Formation and destruction processes of CH_x^+ play an important role in the carbon chemistry in diffuse interstellar molecular clouds. An outstanding cation is methylidyne, CH^+ , the column densities of which are often seen to be orders of magnitude above predictions from standard models (see [9] and references therein). For explaining the formation of this ion, non-thermal conditions are postulated, based on shocks, carbon grain erosion, UV irradiation near young stellar objects, or on other heating mechanism. A recent publication discusses in detail the role of vibrationally excited molecules $\text{H}_2(v>0)$ which have, in collisions with C^+ , a significant influence on the abundances of hydrocarbons, especially the CH^+ [10]. Very recent related activities include the first detection of the ground-state rotational transition in CH^+ ($j=1-0$) with the HIFI instrument onboard the Herschel satellite [11] or the simultaneous monitoring of CH_3^+ with CH^+ [12]. In order to understand such observations and correlations, more laboratory data are needed to describe the non-equilibrium chemistry. The importance of state specific cross sections, e.g. $\text{C}^+ + \text{H}_2(v,j)$, has been mentioned in [13]. First experimental hints to state specific destruction of $\text{CH}^+(v=0,j)$ in collisions with H have been measured recently. These results are presented in a separate publication [14].

For restricting the chemical and physical conditions of the interstellar medium in which CH^+ is so abundant, Indriolo *et al.* [12] have observed the methylidyne cation together with the methyl cation CH_3^+ and, in the same study, investigated various processes linking these two species. As can be seen from Fig. 1, these two ions are coupled by two fast exothermic reactions with H_2 . Another important process, affecting their abundances, is the destruction of the ions via dissociative recombination with electrons. Restricting the chemistry to these processes, the ratio between the abundances of the two ions is governed by a few physical parameters, the temperature T , the fraction of electrons, x_e , and the fraction of molecular hydrogen, f_{H_2} . As discussed below, also the loss of CH^+ in collisions with H or other processes may be important.

Fig. 1 shows schematically the interactions of CH_x^+ ($x=0-5$) ions with hydrogen atoms and molecules. There are two radiative association processes (wavy lines) which have been studied using ion traps (see [15] and references therein). Since they are very slow they are not relevant for the measurements reported in the following. As already mentioned above, the key reaction for forming CH^+ is thought to be the endothermic process

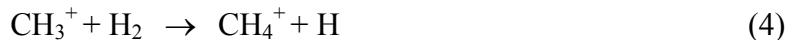


Concerning reaction enthalpies, see Table 1. This reaction, called in the following R_1 and the reverse process R_{-1} , has attracted many theoreticians, also in recent years (see [16], [17], [18]) while most of the experimental studies are several decades old. Since

we report the details of our new low temperature rate coefficients for R_1 in a separate publication [14] we refer to the introduction of that paper for more details. As can be seen from Table 1, hydrogen abstraction from H_2 is exothermic for both CH^+ and CH_2^+ ,



These reactions are fast at room temperature [19] and assumed to be independent of temperature. Since the reaction



is strongly endothermic (see Table 1), CH_3^+ and H_2 can react only via radiative association reaction leading to CH_5^+ [20]. If one disregards the formation of weakly bound cluster ions, e.g. $CH_5^+-H_2$, the end of the reaction chain is protonated methane, CH_5^+ , formed via



This reaction and also collisions of CH_4^+ with HD and D_2 have been studied previously in a variable temperature 22-pole ion trap from room temperature down to 15 K [21].

Based on the established proton affinity of methane, it can be predicted that reaction R_5 becomes very slow at low temperatures ($k < 10^{-12} \text{ cm}^3\text{s}^{-1}$ below 60 K). This would mean that, in cold interstellar clouds, CH_5^+ is not affected by the abundant H atoms. However, first results [7] already indicated formation of CH_4^+ via reaction R_5 . For evaluating such measurements and for predicting effective rate coefficients under non-equilibrium conditions, the kinematic conditions of the slow neutral beam - ion trap arrangement has been analyzed in detail [22]. The role of the internal excitation of the fluxional CH_5^+ ion and of the translational energy in surmounting the small endothermicity are discussed below.

In addition to hydrogen, there is a small fraction of deuterium which plays a special role in low temperature chemistry. Despite a deuterium abundance of only 10^{-5} , many deuterated molecules have been detected in the interstellar medium including doubly and even triply deuterated species. This phenomenon, called ‘isotope fractionation’ is due to a complex interplay between zero point energies, symmetry selection rules, and barriers. Many details of D-H exchange reactions must be known in order to correlate observed abundances of deuterated molecules with the cosmic D/H isotopic abundance ratio. Isotope enrichment in collisions of ions or neutrals with D-atoms is still an experimentally unexplored class of reactions. In this contribution some first results are reported for the interaction of trapped ions with a beam of D-atoms.

In this paper, we first describe some details of the apparatus. Although the ion trapping technique and its application in low temperature ion chemistry is well established, the combination with an atomic beam is rather new and needs additional explanations, including hints to the kinematics of the beam - ion cloud arrangement. In the results section we restrict ourselves to ions having only one carbon atom; nonetheless, many open questions remain. They are summarized in the conclusion together with a discussion of experimental improvements which will increase the sensitivity and range of application of instruments in which a temperature variable ion trap is combined with a neutral beam.

2 Experimental

2.1 The AB-22PT apparatus

Progress in experimental science is often related to technical innovations. Starting in the 1980s, several groups have developed sophisticated instruments for studying ion-molecule reactions at low temperatures. A thorough overview of various methods can be found in [23]. Our approach is based on inhomogeneous fast oscillating electric fields, usually radio frequency (rf) fields. Special ion guides and an innovative merged beam arrangement have opened up the meV collision energy range with beam methods. A successful, versatile and very sensitive instrument for studying processes with cold ions is based on multi-electrode rf ion traps combined with cryogenic cooling [24]. Concerning the basics of the rf based ion trapping technique and a summary of recent applications we refer to the reviews [25], [15], [26].

In order to overcome the limitations imposed by condensation of neutral species or for using radicals, traps have been combined with skimmed beams of reactants. One of the early realizations was for studying spin-dependent collision processes between stored ions and a beam of polarized atoms [27]. In our group various geometries have been explored [28], [29] including the combination of a neutral carbon beam source to an rf ring electrode trap [30]. Interesting results from a very recent innovative ion trap - molecular beam instrument for astrochemical applications have been reported in [31].

For studying the interaction of cold CH_x^+ ions with atomic hydrogen, the AB-22PT apparatus (atomic beam 22-pole ion trap) has been used. The complete instrument is shown in Fig. 2. The left part is used for preparation of the beam, the right one is a "typical" ion trapping instrument. It is assembled from three modules used for (i) ion preparation (storage ion source and QP mass filter), (ii) ion trapping (22PT) and (iii) mass selection and detection (QP mass spectrometer and scintillation detector). The translational and internal degrees of freedom of the trapped ions are coupled to the cold environment by inelastic collisions with helium or hydrogen buffer gas. Using a pulsed valve, the number density can be raised to such high values that the ions are cooled within a few milliseconds.

2.2 Effusive H-atom beam

The stored ions are exposed to an effusive beam of neutrals originating from a temperature variable tube, termed accommodator in the left part of Fig. 2. For dissociating molecular hydrogen, a standard rf driven plasma source (pressure in the discharge tube 0.2 mbar, gas flow 3×10^{-3} mbar l/s) is used [32]. The effusive beam is skimmed and doubly differentially pumped. For distinguishing between the direct beam and background neutrals, a shutter is placed between the second hexapole and the quadrupole bender. The distances and the diameters of apertures have been chosen such that the neutrals traverse the linear multipole ion trap in the axial direction without hitting any surface. Installing the two hexapole magnets I and II leads to an increase of the flux of atoms. Unfortunately, also the H_2 background is augmented, mainly due to H-H recombination on surfaces.

The number density of H and H_2 is determined *in situ* via chemical probing with CO_2^+ . As discussed thoroughly in [8], this ion reacts exclusively to HCO_2^+ in collisions with H_2 , with H mainly to HCO^+ . Target densities of up to $2 \times 10^9 \text{ cm}^{-3}$ have been reached in the trap; removing the magnets leads to some 10^8 cm^{-3} . For $T_{\text{ACC}} = 12 \text{ K}$ recombination on the accommodator surface reduces the H-atom density to $2 \times 10^8 \text{ cm}^{-3}$. The H_2 background density in the trap is usually slightly higher than that of H. At $T_{22\text{PT}} = 10 \text{ K}$, a

rather low H_2 background of $5 \times 10^7 \text{ cm}^{-3}$ has been reached due to condensation. Note that all number densities are *effective* values, since our calibration method via chemical probing accounts for the spatial overlap of the ion cloud with the beam or background. Note also that we account for the fact that the size of the ion cloud depends on the effective potential. The efficiency of the accommodator to cool translation has been tested by measuring velocity distributions.

Additional information on the beam source and its integration into the trapping apparatus can be found in [22] and [8]. Specific technical aspects such as the preparation of the surface of the accommodator (Teflon or water coating), the importance of the precooler, the long time stability of the dissociation degree and other details can be found in the thesis of G. Borodi [33]. A detailed technical publication is in preparation.

2.3 Kinematics, reaction temperature

In order to understand the capabilities and limitations of the combination of a low temperature ion trap and a cold effusive or velocity selected beam of neutrals, some remarks concerning kinematic averaging have to be made. In the majority of ion trapping experiments performed so far, the stored ions and the neutral reactants are both in thermal equilibrium with the surrounding walls at a common temperature $T_{22\text{PT}}$. and one obtains directly thermal rate coefficients. Adding non-reactive buffer gas for faster or more efficient cooling of the ions does not change the situation as long as the densities are low enough to make ternary processes very seldom. In some applications production of some ions via ternary association can be used as a "thermometer". If the two reactants are thermalized to different temperatures (T_1 and T_2 , m_1 and m_2 are the corresponding masses) one still measures directly *thermal* rate coefficients; however at a mean temperature T which is the mass weighted average of the temperatures of the two reactants, $T = (m_1 T_2 + m_2 T_1)/(m_1 + m_2)$.

In the case of a monoenergetic neutral beam passing through a thermal ion cloud which is equivalent to the beam-target cell arrangement often discussed in the literature, the distribution of the relative velocities is given by a generalized Maxwell-Boltzmann distribution. The special situation of a thermal effusive beam (mass m_1 and temperature T_1) penetrating through a thermalized ion cloud (mass m_2 and temperature T_2) can be treated analytically. One obtains for the distribution of the relative velocity g also a Maxwell-Boltzmann distribution with T given again by $(m_1 T_2 + m_2 T_1)/(m_1 + m_2)$. Due to the isotropy of the ion cloud this result does not depend on the angular distribution of the neutral beam as long as each partial cone, penetrating a representative ensemble of the ion cloud, has the same thermal velocity distribution.

As discussed in [22], the situation becomes more complicated if the H-atom beam is influenced by the hexapole magnets. In this case, measurements are evaluated by calculating *effective rate coefficients* from assumed elementary rate coefficients. This is done by numerical integration of the relevant distribution functions, accounting for the thermal distribution of the ions and the measured velocity distribution of the H-atom beam. This procedure is required for understanding the results measured for $\text{CH}_5^+ + \text{H}$.

An important aspect, related to the distribution of the relative velocity, is that the diameter of the skimmed beam is smaller than that of the ion cloud. As a consequence, collisions are restricted to regions of weak rf fields. It is also worthwhile to mention, that the combination of a linear rf trap with a coaxial beam reduces the impairment of the relative velocity since the micromotion is orthogonal to the beam direction. Such considerations are important if one intends to reach sub-K conditions for ion chemistry, spectroscopy or other applications [22].

3 Results and discussions

The typical measuring procedure of our ion trapping experiment is to fill the trap repetitively with the same amount of primary ions, to store them for various times and to extract all ions for mass analysis. Depending on the cooling efficiency and the conversion rates, the selected time period can be shorter than ms or longer than min. For obtaining stable reproducible conditions, the repetition period is held fixed. The sequence is repeated many times for all ion masses of interest. Several other parameters are changed, including those of the neutral target beam and the temperatures of the ion trap and the accommodator. In order to avoid space charge heating usually less than 10,000 primary ions are filled into the 22PT. There are situations where ions are lost from the trap and also the creation of additional ones has been observed (e.g. from metastables or discharges). Therefore it is routinely checked whether the total *number of ions* remains constant as a function of trapping time, i.e., $\sum N_i(t) = N_0$. For getting small statistical errors, data are averaged over many iterations, especially for the channels with weak signal. Note that, for better comparison, the plotted $N_i(t)$ are normalized to one iteration.

3.1 $\text{CH}^+ + \text{H} / \text{H}_2$

A set of typical experimental results is plotted in Fig. 3. In this measurement, a mass selected cloud of CH^+ ions is exposed to hydrogen molecules and atoms. The competition between reactions with H atoms and H_2 molecules can be seen by a qualitative comparison of the left with the right panel. The data on the left side have been recorded with the discharge switched OFF, on the right side it is ON. The number densities of H and H_2 for the two situations are given in the figure caption. In this example, the trap has been filled each time with 120 ± 11 primary ions. The ion creation and filling procedure has been so stable that the fluctuations are purely statistical.

If only H_2 is present (left side), the fast hydrogen abstraction reaction R_2 is followed by R_3 . Under the conditions of our experiment the final product is CH_3^+ . Further hydrogenation of this ion can only occur via radiative association of CH_3^+ with H_2 [20]. For this process the time constant is several hours as can be calculated from the hydrogen number density in the trap and the very low rate coefficient ($5 \times 10^{-14} \text{ cm}^3 \text{ s}^{-1}$ at $T_{22\text{PT}} = 50 \text{ K}$). If the discharge is switched ON (right panel), a significant fraction of the hydrogen molecules dissociate to H atoms. It is obvious that they convert primary CH^+ ions into C^+ products via the exothermic reaction R_{-1} .

Comparison of the two sets of data reveals that the decay rate of the number of CH^+ ions increases by more than a factor of 3 if the discharge is switched ON. Exponential fits to the CH^+ data lead to decay time constants of $\tau_{\text{OFF}} = 1.38 \text{ s}$ and $\tau_{\text{ON}} = 0.39 \text{ s}$. This is not so much due to the reaction of CH^+ with H atoms but more due to an increase in the overall hydrogen density in the trap. As can be seen from the production rate of CH_2^+ products, there are also more H_2 molecules if the discharge is running. The reason is the efficient guiding of atoms in the hexapole magnets and the formation of an additional H_2 background molecules via H - H recombination on surfaces. Especially problematic are H atoms deflected from the magnets which hit the electrodes inside the trap and recombine. Due to the low pumping speed in the trap region, they contribute to the H_2 background more than the molecules formed inside the hexapole guides. For critical measurements, requiring low molecular background, it is better to remove the magnets. An additional advantage to working without magnets, is that one can rely on conservation of hydrogen flux, i.e. each molecule forms two H atoms [8].

For extracting rate coefficients from such experimental data, the temporal evolution of the number of stored ions, $N_i(t)$, is modeled by solving numerically a system of differential equations simulating the chemistry occurring in the trap. Sometimes the situation is very simple and only two channels are of importance (see left side of Fig. 3). In other situations (e.g. deuteration with D and D₂), many competing reactions play a role and various products may appear at the same apparent mass. In such situations additional independent measurements are needed for extracting rate coefficients. Often the trapped ion cloud is not only modified by the reactions of interest. Relaxation processes (affecting trapping or detection efficiency) or reactions with background gas can play a role. Routinely, tests are performed to ensure that the trapping field is sufficient to lead to a time independent number of ions in the trap. Apparent ion loss or gain also can be caused by reactions leading to non-detected masses or by mass dependent discrimination effects. This, however, is not a problem for the CH_x⁺ reactions reported in this paper. In all cases excellent fits have been obtained as illustrated in Fig. 3. All resulting rate coefficients are included in Table 2 and 3. The errors of the absolute values for reactions with molecular target are estimated to be 20%, while those with atomic reactants are 40%, mainly due to the uncertainty of the calibration reaction [8].

The situation of our present knowledge on reaction R₁ is plotted in Fig. 4. The rate coefficients at temperatures above 300 K are experimental results from a SIFDT experiment [34]. The two data points, labeled AB-22PT, at T_{22PT} 50 K and 80 K have been reported in [7]. Additional measurements performed under various conditions have confirmed that the reaction is fast in this temperature range. It is recommended to use in astrochemical models $10^{-9} \text{ cm}^3 \text{ s}^{-1}$ between 50 and 100 K. The lines are results from various theoretical treatments discussed in [17]. Inspection reveals that phase space theory (PST) or quasi classical trajectories (QCT) are in accordance with the trend of the experimental results while quantum mechanical calculations, using the RIOSA-NIP method, significantly underestimate hydrogen abstraction [16]. The extension of measurements for reaction R₁ towards lower temperatures has been successful recently. Surprisingly, the results do not follow the trend predicted by statistical models! A detailed discussion of the new data including the extraction of rate coefficients for specific rotational states is beyond the scope of this paper and is reported in [14].

3.2 CH₂⁺ + H / H₂ and CH₃⁺ + H / H₂

The reactions R₂ and R₃ are both fast as predicted from the simple Langevin model. Our derived rate coefficients (e.g. extracted from Fig. 3, see Table 2 and 3) are in good agreement with previous results measured at room temperature. A systematic study of any weak temperature dependence has not yet been performed. It also would require a mass selected injection of CH₂⁺.

These observations are in accordance with the exothermicities for the two reactions given in Table 1. Some new values of ΔH_0 presented in this table are based on recent measurements which are mentioned in the caption of Table 1. The new value for R₁ is discussed in [14]. An interesting aspect of the new data is that the exothermicity of reaction R₂ may be smaller than 0.4 eV which could allow some back-conversion of CH₂⁺ in collisions with fast H atoms. The energetics of R₅ are very uncertain as discussed below.

3.3 CH₄⁺ + H / H₂

Fig. 5 shows a typical result for reactions of cold CH₄⁺ ions if they are exposed to a mixture of hydrogen atoms ($[H] = 9 \times 10^8 \text{ cm}^{-3}$) and molecules ($[H_2] = 1.4 \times 10^9 \text{ cm}^{-3}$). The primary ions (~1200 per filling) have been thermalized to the trap temperature of 80 K via buffer gas collisions ($[He] = 3.7 \times 10^{12} \text{ cm}^{-3}$). The temperature of the H atom

source has been set to $T_{ACC} = 100$ K. For the evaluation of this measurement it is important to note that the number of CH_4^+ ions decays mono-exponentially, i.e. back-reactions or other processes do not play a role in this time window. After 1 s about 50 % have been converted into products, most of them being CH_3^+ .

In contrast to the rate coefficient from the UMIST data base [19] which is based on an early ICR experiment [2], the dominant product is CH_3^+ which is formed via the exothermic reaction R_4 . A factor 5 slower is the formation of CH_5^+ via reaction R_5 . The constant sum of all ions indicates that other products or reactions are negligible. Fitting the data points leads to the rate coefficients given in Table 2 and 3.

The rate coefficient determined for R_5 agrees well with previous studies performed in a 22PT from 300 K down to 15 K [21]. For completeness, these results are included in Fig. 6. The values increase with decreasing temperature proportional to $T^{-1.1}$ and level off below 30 K where a maximum of $4 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ is reached.

3.4 $\text{CH}_5^+ + \text{H}$

Despite many experimental and theoretical efforts in the last years, the molecule CH_5^+ is still far from being fully understood. This is due to the complexity of the potential energy surface which is very flat near the various minima and which leads to large-amplitude motions, even at low temperatures. Various schemes to probe the structure of this ion via collisions have been summarized in [35]. An impressive variety of spectral information has been collected in recent years and compared with state of the art predictions (see [36] and references therein); however, all this is not yet sufficient to understand this fluxional molecule in detail or to predict rotational transitions with the accuracy required for searching for this astrochemically important ion in space. One solution of this problem will be the direct experimental observation of the $J = 1 \leftarrow 0$ spectrum which is predicted to be centered in the region 220–235 GHz [37].

As summarized in a recent Faraday Discussion (142: Cold and Ultracold Molecules), trapping and cooling molecules opens up many exciting prospects. One of the applications of the combination of our trapping technique with a cold effusive H atom beam which has been discussed in [22], is to cool all degrees of freedom of the floppy CH_5^+ ion to a few K or even to the "sub-K" range. In an optimistic outlook of this contribution it has been proposed that one may be able to observe millimeter-wave induced excitation of CH_5^+ from the rotational ground state by using chemical probing with H atoms or alternatively, proton or deuteron transfer to CH_4 .

Fig. 6 presents a collection of rate coefficients measured so far at room temperature and below for the collision system CH_6^+ . The error bars include only the statistical errors and the uncertainty in the determination of the translational temperatures. It can be seen that both the forward and reverse reaction are rather slow at 300 K. Some tentative explanations have been given in [21]. First results for hydrogen abstraction from CH_5^+ have been presented in [7]. A detailed discussion of the kinematics, of the internal cooling of the trapped ion, and the kinetic energy distribution of the H-atom beam has been given in [22]. As mentioned there, the energetics of reaction R_5 which are based on potential energy surfaces calculated with high level *ab initio* methods [38], are rather uncertain. One of the conclusions of these calculations was that reaction R_5 should be endothermic by more than 100 meV. From this value one can conclude immediately that CH_4^+ production should become very slow at temperatures below 100 K. This is in contradiction to all experimental data obtained up to date at various temperatures of the ion trap, T_{22PT} and for two temperatures of the accommodator, $T_{ACC} = 92$ K and 12 K. Possible experimental problems, e.g. insufficient cooling of the internal degrees of freedom

of the ion, is very unlikely as discussed in [22] and recently for CH^+ in [14]. It also has been confirmed with time-of-flight measurements that the H-atoms are really thermalized to T_{ACC} .

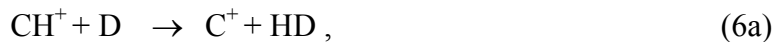
In order to evaluate the unexpected experimental data quantitatively, an analytical function has been used for describing the dependence of the elementary rate coefficients for reaction R_5 both on the kinetic energy of the H-atoms and on the internal excitation of CH_5^+ . The details of this calculation which accounts for the thermal energy content of the ions and the measured velocity distributions of the atoms, has been described in [22]. The results obtained are the solid lines following the two sets of data points in Fig. 6. One of the obvious conclusions of this evaluation is that we need a colder H-atom beam. This is illustrated with the dashed line in the lower right corner. It shows an effective rate coefficient, calculated with our analytical rate coefficient under the assumption that the H-atoms have a kinetic energy of 1 meV. First velocity distributions of a thermal 8 K H-atom beam have been obtained recently; however, the flux is rather low and it has not yet been used for studying collisions with CH_5^+ .

In order to fit the data as shown in Fig. 6, it was necessary to set the threshold to 3.5 meV. In addition we had to presuppose that internal energy of the ion is much less efficient in promoting the reaction than the kinetic energy of the H-atom. This information can be extracted qualitatively directly from the data since $T_{22\text{PT}}$ determines primarily the internal excitation of the ions while variation of the accommodator temperature determines the translational energy. Concerning the reaction mechanism, these observations allow us to conclude that the available energy is not scrambled in the collision complex, on the contrary, the impinging H-atom abstracts the H from CH_5^+ via a direct process.

3.5 Deuteration with D

H-D isotope scrambling at low temperatures is not only a very sensitive technique to probe reaction dynamics and molecular structures but it is also of central importance for forming deuterated molecules under interstellar conditions. With D atoms, any exchange reaction is exothermic because it always leads to a lowering of zero point energy. Studying deuteration in an ion trap is straight forward; however the extraction of rate coefficients is more complicated since additional product channels play a role and since there is some ambiguity in the assignment of certain masses. In order to account for sequential processes and for reactions with D_2 background, measurements have been performed at short and long storage times and also with the discharge turned off. In the following we discuss only a few selected rate coefficients which are given in Table 2 and 3. More details may be found in the thesis of G. Borodi [33].

Fig. 7 shows an important and unexpected result for the competition between H-abstraction and H-D exchange,

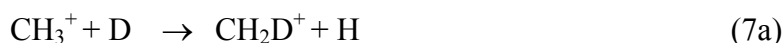


In this measurement the trapped CH^+ ions are exposed to a mixture of D and D_2 . Concerning the effective densities and the temperatures see the figure caption. Similar to the processes discussed in combination with Fig. 3, also reactions with the molecular D_2 background leads to products with increasing masses. All this has been taken into account for simulating the data. Inspection of the rate coefficients given in Table 2 and 3 reveals that the dominant products are formed via reactions R_{6a} and R_{6b} while, for ex-

ample the formation of CD^+ in collisions of CH^+ with D_2 is more than one order of magnitude slower.

The result that more CD^+ products are formed via H-D exchange than C^+ products via hydrogen abstraction is very surprising if one looks at the potential energy surface [16]. Since it is attractive for most approaches of the reactants one expects the formation of the strongly bound CHD^+ collision complex, followed by a decay to the energetically favored $C^+ + HD$ channel. There are certainly some CD^+ products formed via a near linear $HC^+ - D$ approach; however this cannot explain at all the very large rate coefficient. This surprising result together with the unexpected low temperature behavior of $R_{.1}$ reported in [14] may lead to some new insight of this fundamental reaction.

Rate coefficients for H-D exchange in collisions of CH_2^+ with D could not yet be extracted due to competition with reactions occurring with the molecular background in the beam and overlapping masses. It will require the preparation and injection of mass selected ions in the future. Much less problematic is the reaction



since it is fast enough for being observed directly despite competing reactions with D_2 . The results are presented in Table 2 as well as the results for the two channels



Considering that both the CH_4^+ primary ion and the CDH_4^+ collision complex are fluxional ions, it is surprising that scrambling is rather inefficient and that hydrogen abstraction dominates. For the reaction



both channels have been detected but the rate coefficients are very small (see Table 2). Despite the additional gain of zero point energy in reaction R_{9a} , formation of CH_4^+ is much slower than in reaction $R_{.5}$. Also in the CDH_5^+ collision complex scrambling is very inefficient. Apparently, the large-amplitude motion of the five protons around the carbon nucleus does not allow us to conclude, that an exchange with an external D-atom is simple. In this context it is important to mention that a detailed analysis of the deuteration process in collisions of CH_5^+ with HD [39] has revealed that an H-D exchange is slower than $5 \times 10^{-18} \text{ cm}^3/\text{s}$.

4 Conclusions and outlook

The combination of a temperature variable ion trap with an effusive beam of slow H atoms has been used to study a selected class of reactions responsible for adding hydrogen to, or for removing it from simple hydrocarbon ions. Some of the new results are in accordance with expectations or predictions from simple models. In other cases it is recommended to replace the rate coefficients in chemical networks (e.g. [19]) with those reported in this paper, including deuteration of some ions in collisions with D.

None of our results helps directly to get a better understanding of CH^+ abundances observed in space. On the contrary, the 50 K rate coefficient for $R_{.1}$ is almost a factor 2 larger than used in the UMIST data base. However, the new results including the recent extension of measurements towards lower temperatures [14] will hopefully contribute to better understand the reactions occurring in dense interstellar clouds. It is obvious that

one should use a complete subset of reactions for critical evaluation of observed correlations of molecular abundances. In the case of CH^+ and CH_3^+ [12], one certainly has to account at least for reaction R_1 .

There are a variety of experimental improvements which will increase the selectivity and sensitivity of the instrument. Using cryo-pumping, especially inside the trap, will significantly reduce the molecular background. This will allow for example to study the threshold onset for reaction R_2 as a function of the kinetic energy of the atoms. Also the atomic beam can be improved, including its flux, velocity spread and dissociation degree at low accommodator temperatures. The dynamic range and the high sensitivity of the rf ion trapping technique allows us to determine very small rate coefficients, also for ion - H-atom reactions. Estimates show that it is within the reach of the instrument to get first experimental information on the radiative association reaction



There are some considerations that the low temperature rate coefficient may be much larger than predicted with theoretical methods [14].

There is a wide range of applications of instruments like the AB-22PT apparatus now operated in Prague or the Tucson CoMB-RET instrument [31]. Extension of the reported measurements, i.e. collisions with H or D, towards larger hydrocarbon cations or also anions are obvious and urgently needed in astrochemistry. Another very useful experimental extension is to use a high temperature accommodator, e.g. for producing fast H-atoms or hot H_2 molecules. The importance of vibrationally excited H_2 for forming CH^+ has been mentioned above and it seems to be straightforward to extend the temperature range reported in [40] to 2000 K.

Present activities concentrate on the formation of H_2 via associative electron detachment in $\text{H}^- + \text{H}$ collisions. A critical test case for the apparatus and its kinematic limits is the 3.6 meV endothermic electron transfer from D to H^+ .

Finally there is the huge field of combining multielectrode ion traps with lasers or other light sources [36]. How long will it take before we get the first rotational spectra from a micro- or millimeter-wave induced reaction? CH^+ is a test candidate, CH_5^+ a challenge.

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Figure captions

Fig. 1. Addition and abstraction of hydrogen atoms or molecules from CH_x^+ . Thick solid lines symbolize fast bimolecular reactions, thin lines endothermic processes or processes with barriers. The wavy lines indicate radiative association. In the center of this contribution are the processes from the right to the left, i.e. dehydrogenation in collision with H atoms.

Fig. 2. Detailed view of the AB-22PT apparatus, the combination of an atomic beam source with a temperature variable 22-pole ion trap. In order to get an impression of the overall size, the vacuum system and the modules are plotted at scale (most of the flanges are CF 100 and CF 160). The central element of the instrument is the rf trap which is mounted onto a cold head of a closed-cycle He refrigerator (Leybold RGD 210). Primary ions are produced in a storage ion source, mass selected, and injected into the trap via an electrostatic quadrupole bender. Helium buffer gas is used to cool the stored ions to the temperature of the surrounding walls ($T_{22\text{PT}}$). Primary and product ions are extracted, mass analyzed in a QPMS and counted using a Daly type detector. The left part of the apparatus is dominated by the H-atom source. Hydrogen molecules are dissociated in a water cooled rf discharge tube. The atom flow passes through a glass tube which is water cooled at the entrance and connected to the precooler (100 K) at the exit. The accommodator (copper) cools the atoms to the final temperature which can be set at any value between $T_{\text{ACC}}=7$ K and 300 K. The atom beam is doubly skimmed and can be shut off by a shutter in front of the quadrupole bender. The two focusing hexapole magnets serve as guiding elements for H/D atoms and consequently enhance the atom density inside the 22PT.

Fig. 3. Reactions of CH^+ ions with H_2 and H at $T_{22\text{PT}} = T_{\text{ACC}} = 50$ K. Plotted is the number of primary and product ions per filling, N_i , as a function of the storage time t . The lines are solutions of a set of differential equations accounting for the competing reactions. The sum of all ions (Σ) is constant. With discharge OFF (left panel, $[\text{H}_2] = 6 \times 10^8 \text{ cm}^{-3}$) hydrogen abstraction leads in a first step to CH_2^+ and in a second one to CH_3^+ . Switching the discharge ON (right panel) leads to atomic hydrogen with $[\text{H}] = 4 \times 10^8 \text{ cm}^{-3}$ and to additional products, especially to C^+ . The faster decay of CH^+ is partly due to this additional channel but also due to an increase of the number density of molecular ($[\text{H}_2] = 1.7 \times 10^9 \text{ cm}^{-3}$) due to H-H recombination (see text).

Fig. 4. Temperature dependence of the rate coefficient for the hydrogen abstraction reaction R_1 . The two data points at $T_{22\text{PT}} 50$ K and 80 K are from [7]. Additional measurements have reconfirmed these results [33] and lead to the recommended value given in Table 2. At higher energies experimental results from a SIFDT experiment [34] are included. A detailed discussion of theoretical aspects of the system can be found in [17], including results from phase space theory (PST) and quasi classical trajectories (QCT). Quantum mechanical calculations, using the RIOSA-NIP method, significantly underestimate hydrogen abstraction [16].

Fig. 5. Reactions of CH_4^+ ions with hydrogen atoms ($[\text{H}] = 9 \times 10^8 \text{ cm}^{-3}$, $T_{\text{ACC}} = 100$ K) and hydrogen molecules ($1.4 \times 10^9 \text{ cm}^{-3}$). The primary ions are thermalized via collisions with He ($3.7 \times 10^{12} \text{ cm}^{-3}$) to $T_{22\text{PT}} = 80$ K. The reaction with molecular hydrogen leading to CH_5^+ is rather slow in accordance with recently published 22PT results [21]. The derived rate coefficients are given in Table 2 and 3.

Fig. 6. Temperature dependence of rate coefficients for the CH_6^+ collision system. The steep temperature dependence of the exothermic reaction $\text{CH}_4^+ + \text{H}_2 \rightarrow \text{CH}_5^+ + \text{H}$ has

been discussed in [21]. For the $\text{CH}_5^+ + \text{H}$ collision system, two sets of data ($T_{\text{ACC}} = 12$ and 92 K) are shown as a function of $T_{22\text{PT}}$. The lines are the result of a detailed analysis of the data, using an analytical *ansatz* for the cross section and accounting for the experimental boundary conditions. The dashed line is the prediction from the model for a monoenergetic H atom beam with a kinetic energy of 1 meV.

Fig. 7. Collisions of CH^+ ions with D-atoms ($[\text{D}] = 8 \times 10^8 \text{ cm}^{-3}$, $[\text{D}_2] = 3 \times 10^9 \text{ cm}^{-3}$, $T_{\text{ACC}} = 36 \text{ K}$, $T_{22\text{PT}} = 80 \text{ K}$). The rate coefficients for both product channels are rather large (see Table 2). The unexpected observation that H-D exchange is faster than the exothermic hydrogen abstraction reaction, is discussed in the text.

Tables

Table 1. Reaction enthalpies involving ground state reactants and products. The energies are based on the measured dissociation energy of CH^+ [41], bond dissociation energies derived in [42] and [43]. The thermochemistry of reaction R_2 remains rather uncertain. For completeness, the exergic radiative association processes are included with energies taken from [41], [44] and [45].

	Reaction	ΔH_0 / eV	Ref. [19]
1	$\text{C}^+ + \text{H}_2 \rightarrow \text{CH}^+ + \text{H}$	+0.393	+0.40
2	$\text{CH}^+ + \text{H}_2 \rightarrow \text{CH}_2^+ + \text{H}$	-0.5 ± 0.1	-0.61
3	$\text{CH}_2^+ + \text{H}_2 \rightarrow \text{CH}_3^+ + \text{H}$	-0.803	-0.91
4	$\text{CH}_3^+ + \text{H}_2 \rightarrow \text{CH}_4^+ + \text{H}$	+2.771	
5	$\text{CH}_4^+ + \text{H}_2 \rightarrow \text{CH}_5^+ + \text{H}$	-0.010	
	$\text{C}^+ + \text{H} \rightarrow \text{CH}^+ + h\nu$	-4.085	
	$\text{C}^+ + \text{H}_2 \rightarrow \text{CH}_2^+ + h\nu$	-4.51	
	$\text{CH}_3^+ + \text{H}_2 \rightarrow \text{CH}_5^+ + h\nu$	-1.775	

Table 2. Rate coefficients for reactions with H or D

Reactions				$k^a/\text{cm}^3\text{s}^{-1}$	T^b/K	T_{ACC}/K	references
CH ⁺	+ H	→ C ⁺	+ H ₂	1.0 (- 9)	50-100		average value
				1.3 (- 9)	50	50	[7]
				8.7 (-10)	80	100	[7]
				7.5 (-10)	300		[1]
CH ₄ ⁺	+ H	→ CH ₃ ⁺	+ H ₂	6.0 (-10)	50	50	
				5.1 (-10)	80	100	
				<1 (-11)	>300		[2], non thermal
CH ₅ ⁺	+ H	→ CH ₄ ⁺	+ H ₂	8.7 (-12)	10	12	[22]
				2.3 (-11)	10	92	
				2.1 (-11)	300	12	
				2.8 (-11)	300	92	
				1.5 (-10)	300		[34]
CH ⁺	+ D	→ C ⁺	+ HD	1.2 (- 9)	80	36	
		→ CD ⁺	+ H	1.3 (- 9)	80	36	
CH ₃ ⁺	+ D	→ CH ₂ D ⁺	+ H	1.0 (- 9)	50	50	
CH ₄ ⁺	+ D	→ CH ₃ ⁺	+ HD	1.0 (-10)	50	50	
		→ CH ₃ D ⁺	+ H	2.5 (-11)	50	50	
CH ₅ ⁺	+ D	→ CH ₄ ⁺	+ HD	5.5 (-13)	50	50	
		→ CH ₄ D ⁺	+ H	1.0 (-12)	50	50	

Table 3. Rate coefficients for reactions with H₂ or D₂

Reactions				$k^a/\text{cm}^3\text{s}^{-1}$	T^b/K	T_{ACC}/K	references
CH ⁺	+ H ₂	→ CH ₂ ⁺	+ H	1.2 (- 9)	50	50	
CH ₂ ⁺	+ H ₂	→ CH ₃ ⁺	+ H	1.6 (- 9)	50	50	
CH ₄ ⁺	+ H ₂	→ CH ₅ ⁺	+ H	1.1 (-10)	80	100	
				1.2 (-10)	80		[21]
CH ⁺	+ D ₂	→ CD ⁺	+ HD	1.0 (-10)	80	36	
		→ CHD ⁺	+ D	3.5 (-10)	80	36	
		→ CD ₂ ⁺	+ H	2.4 (-10)	80	36	
CH ₃ ⁺	+ D ₂	→ products		8.0 (-10)	50	50	
CH ₄ ⁺	+ D ₂	→ CH ₄ D ⁺	+ D	2.5 (-11)	50	50	
CH ₅ ⁺	+ D ₂	→ CH ₄ D ⁺	+ HD	1.1 (-12)	50	50	
		→ CH ₃ D ₂ ⁺	+ H ₂	2.5 (-11)	50	50	

^a The errors of the absolute values for reactions with molecular reactants are estimated to be 20%, those with atomic reactants are 40%, mainly due to the uncertainty of the calibration reaction [8].

^b Temperature of the ion trap ($T_{22\text{PT}}$) or translational temperature

