

Variable temperature ion trap studies of $\text{CH}_4^+ + \text{H}_2$, HD and D_2 : negative temperature dependence and significant isotope effect

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Received 19 May 2003; accepted 5 November 2003

Abstract

Reactions of methane cations, CH_4^+ , with H_2 , HD and D_2 have been studied in a variable temperature 22-pole ion trap from room temperature down to 15 K. The formation of CH_5^+ in collisions with H_2 is slow at 300 K, but it becomes faster by at least one order of magnitude when the temperature is lowered to 15 K. This behavior is tentatively explained with a longer complex lifetime at low temperatures. However, since tunneling is most probably not responsible for product formation, other dynamical or statistical restrictions must be responsible for the negative temperature dependence. In collisions of CH_4^+ with HD, the CH_5^+ product ion (68% at 15 K) prevails over CH_4D^+ (32%). Reaction of CH_4^+ with D_2 is found to be much slower than with H_2 or HD. The rate coefficient for converting CH_4^+ into CH_3D^+ by H–D exchange has been determined to be smaller than $10^{-12} \text{ cm}^3/\text{s}$, indicating that scrambling in the CH_6^+ complex is very unlikely.

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Keywords: Laboratory astrochemistry; Reactive collisions; Deuteration; ISM: molecules; CH_4^+ ; CH_5^+ ; CH_4D^+

1. Introduction

Collisions at very low relative velocities and with cold reactants are of fundamental interest because they can be used as a very sensitive probe of the potential energy surfaces, especially if weak barriers or small endothermicities are involved or if dynamical constraints hinder the transition from reactants to products. In addition, experimental studies of ion molecule reactions performed at the low temperatures prevailing in dense interstellar clouds are of key importance for understanding the synthesis of molecular species in interstellar space. Rate coefficients are especially needed if they change significantly as a function of temperature, in contrast to the majority of the known reactions.

One of the best understood examples where the reactivity changes remarkably with temperature is the hydrogen abstraction $\text{NH}_3^+ + \text{H}_2 \rightarrow \text{NH}_4^+ + \text{H}$. This reaction has been measured by several groups and using complementary techniques, e.g., in a flowing afterglow

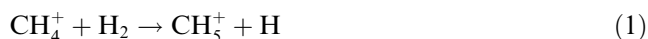
apparatus (FA) between 300 and 800 K [1], in a SIFT apparatus between 80 and 300 K [2], in a Penning trap at very low temperatures (11–20 K) [3], in a SIDT between 20 and 300 K [4], and finally in a 22-pole ion trap at 15 K [5]. In the early measurements starting from room temperature it was observed, that the rate coefficient falls with falling temperature. Later a minimum has been identified at about 150 K and, finally, a significant reincrease was found towards very low temperatures. Furthermore, measurements with isotopic variants of the ammonia ion reaction by Kim et al. [6], Adams and Smith [7] and Dunn and Barlow [8] showed a pronounced isotopic effect, i.e., the rate coefficient of the reaction of NH_3^+ with D_2 is lower than that with H_2 while the reaction of ND_3^+ with H_2 has a larger rate coefficient than $\text{NH}_3^+ + \text{H}_2$. Calculations by Herbst and co-workers [9], using a statistical phase space approach, confirmed the former hypothesis [3,4] that, at low temperatures, the mechanism of $\text{NH}_4^+ + \text{H}$ formation is dominated by the initial formation of a long-lived complex, from which tunneling through a small transition state barrier occurs. For high enough temperatures, on the other side, the reaction rate increases due to the

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increasing probability of classical passage over the transition state barrier.

Some related observations have been made for the isoelectronic reaction, the hydrogen abstraction



however, only at room temperature and above. This interaction of methane cations with hydrogen has been observed several decades ago in a mass spectrometer by Munson et al. [10]. An absolute rate coefficient was first measured by Kim et al. [6] in a 300 K Ion Cyclotron Resonance (ICR) apparatus. This result and also the measurements of Adams and Smith [11] performed in a room temperature Selected Ion Flow Tube (SIFT) showed that reaction (1) is very slow at room temperature despite the fact that the H atom transfer is slightly exothermic. Only every 50th collision leads to a CH_5^+ product indicating some hindrance along the reaction pathway, perhaps a potential barrier. The first dedicated energy-dependent investigations were performed by Federer et al. [12] who measured rate coefficients at energies between 40 and 120 meV, accelerating the ions in a Selected Ion Flow Drift Tube (SIFDT). They found that the rate coefficients decrease with increasing energy. The results presented in this paper, extend the measurements into the opposite direction. In accordance with the trend, the rate coefficients for the title reaction continue to increase with falling temperature. The value at interstellar temperatures is one order of magnitude larger than at room temperature. In contrast, the UMIST database for interstellar chemistry [13] contains a fixed value for reaction (1) which is claimed to be valid for a wide temperature range.

Federer et al. also studied the reverse of reaction (1), $\text{CH}_5^+ + \text{H} \rightarrow \text{CH}_4^+ + \text{H}_2$, by injecting H-atoms into the drift tube. In this case, it was observed that, at room temperature, destruction of CH_5^+ is almost 10 times faster than its formation, although the reaction is endothermic in this direction. The experimental findings have been taken as a hint that reaction (1) must be endothermic, i.e., the free energy $\Delta G = \Delta H - T\Delta S$ must become negative above a certain value of T . This temperature has been estimated to be 150 K [12]. The question whether one is allowed to use simple thermodynamics for describing a bimolecular reaction will be raised in the discussion section. So far, the backward reaction has not been measured below 300 K.

More insight into the energetics of a near-thermo-neutral reaction can be obtained by using isotope substitution due to significant shifts in zero-point energies. In addition the replacement of H by D can modify remarkably the statistical factors, governing the reaction [14]. Up to now only the combination $\text{CH}_4 + \text{D}_2$ has been reported in the literature by Inoue and Wexler [15] as well as Munson [10] who observed very low reaction rates. It must be noted, however, that their low values

may have partly been caused by the non-thermal experimental conditions prevailing in their machines. In the present contribution not only D_2 but also the astrochemically important HD has been used as target.

One interesting additional aspect of this work is that reaction (1) leads to CH_5^+ , a so-called hypercoordinated carbocation (see [16] and references therein). Despite many spectroscopic efforts culminating in the high-resolution infrared spectrum of White et al. [17] the structure of this fluxional molecular ion is an object of an ongoing debate since the spectrum is still awaiting an assignment. One of the basic questions is, whether all five hydrogen atoms are equivalent or whether the three-center-two-electron bond favors a different structure, e.g., a separate H_2 sub-unit bound to a CH_3^+ ion. If there are different bounds, isotope labeling leads to different isomers which may be distinguished via chemical probing. Such an approach has been described in [18] where CH_4 and CD_4 gas has been used to form different isotopomers of CH_xD_y^+ and NH_3 has been used as a probing gas (see also [19]). From these experiments, which have been performed at temperatures above 300 K, rather speculative conclusions have been drawn. Unfortunately, the present work, dealing with cold $(\text{CH}_4 \cdot \text{H}_2)^+$ and $(\text{CH}_5 \cdot \text{H})^+$ collision complexes, does not provide help to solve this puzzle; however, as briefly outlined in the conclusion, more can be expected from a dedicated research of forming CH_5^+ via radiative association of $\text{CH}_3^+ + \text{H}_2$ and isotopic variants or from probing CH_5^+ via scrambling collisions with D or HD, especially at low temperatures.

2. Experimental

2.1. Basics of experiment

The laboratory measurements have been performed in a variable temperature 22-pole ion trap machine. The basics of the trapping technique are summarized in [20], more details can be found in recent publications [21,22]. In brief, ions generated in a storage ion source, are mass selected and injected into a 22-pole ion trap mounted onto a closed cycle He refrigerator. Trapping of the ions in radial direction is achieved by applying two opposite phases of an rf generator (80 V, 17 MHz) to the 2×11 poles of the trap, while confinement in longitudinal direction and control of the ion storage time is done by pulsing the entrance and exit electrodes. The wide field-free region of the 22-pole trap makes experiments at low collision temperatures possible. Reactant and buffer gases are introduced by cooled tubes and are in thermal equilibrium with the cold walls surrounding the trap. The translational and internal degrees of freedom of the ions are coupled to this environment by inelastic collisions with continuously or pulsed introduced buffer gas

or via radiation. In the present configuration, the lowest temperature achieved was about 15 K, higher temperatures are attained with heater wires wound around the trap holder. Temperatures are measured at several points with carbon resistors. Stored ions react with target gas (here hydrogen) the number density of which is determined with an ion gauge which is routinely calibrated with respect to a spinning rotor gauge. After each trapping cycle, primary and product ions are extracted, analyzed by a second quadrupole mass filter and finally detected with high efficiency by a Daly-type detector.

2.2. Ion preparation and mass selection

The CH_4^+ ions are produced by electron bombardment of methane gas (Messer-Griesheim 5.5 purity) in an external rf storage ion source. Trapping the ions in the source makes it possible to operate at pressures below 10^{-5} mbar of methane. For pre-cooling the stored ions to the source temperature of about 350 K, helium gas is added to the source gas. Furthermore, electrons with low kinetic energies (<18 eV) are utilized to reduce internal excitation or fragmentation of the ions. After extracting the ions through a pulsed electrode, they are mass selected by a quadrupole operated either in the low-pass or in the mass-selective mode. The low-pass mode has the advantage of injecting ions with well defined very low kinetic energies into the 22-pole trap; however, at the expense of admitting also some lower mass ions to the trap. The mass-selective mode fully suppresses the unwanted ions but in this case with a broader kinetic energy distribution. As mentioned above, all ions are finally cooled to the desired low temperatures by a short intense He pulse (~ 10 ms) in the trap.

2.3. Target gas

The purity of the deuterium hydride (Cambridge Isotope Laboratories Inc.) is specified to be 97%, the major contamination being H_2 and D_2 . This specification has been confirmed in situ by a detailed analysis based on the $\text{Ar}^+ + \text{HD}$ charge transfer reaction in the trap [23]. Ar^+ is known to react with HD mostly to ArH^+ and ArD^+ , but about 10% of the reaction yields HD^+ by charge transfer. Assuming equal charge transfer probabilities for the various hydrogen isotopes, the H_2 impurity can be derived directly from a comparison of the H_2^+ and the HD^+ product signal. In this way, it was confirmed that the H_2 -content in the bottle was less than 1%. Direct determination of the D_2 impurity is not so simple with this method, because the signal of interest (mass 4) coincides with other products from secondary reactions, for instance with H_2D^+ from a reaction of ArH^+ with HD. Nonetheless, it could be concluded that

D_2 has the same abundance as H_2 , i.e., the total impurity is less than 2%.

Another chemical test of the isotopic purity of the HD target gas was based on the observation of products, formed via specific association reactions ([23]). For example, hydrocarbon ions which do not react with HD or which are already at the end of a deuteration sequence only can grow via such a process. For example, association of CD_3^+ with HD yields CHD_4^+ while a collision with H_2 and D_2 impurities produces CH_2D_3^+ and CD_5^+ ions, visible as "side-bands" of the central peak in the mass spectrum. Also this method has led to an upper limit of 2% for the impurities, assuming equal association probabilities.

The H_2 and D_2 gases used in these experiments were purchased from Messer-Griesheim with specified purity of 6.0 and 2.7, respectively.

2.4. Measuring procedure

The measurement of rate coefficients for chemical reactions are performed in the trap in an iterative mode. First, a pulsed bunch of ions is injected with low kinetic energies into the 22-pole trap. The ions are then stored for times varying from microseconds to minutes, the main limitation being the residual gas components which deplete the number of primary ions due to parasitic reactions. In the present case, the unwanted residual gas components are mostly hydrogen and water. At

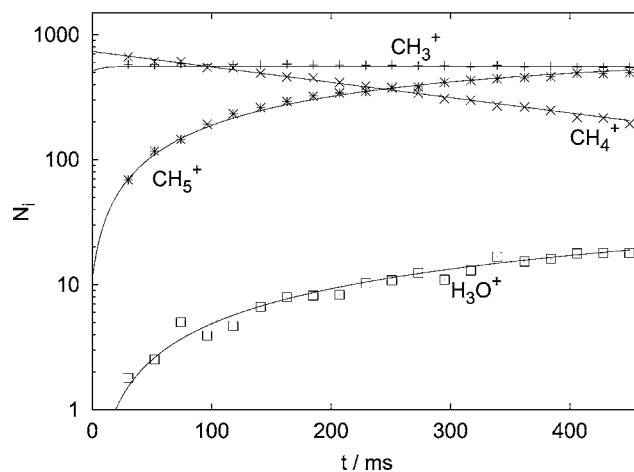


Fig. 1. The number of molecular ions, N_i , trapped and formed for each iteration, is plotted as a function of the storage time t . Twenty different times ranging from 30 to 450 ms were used. Every data point was measured 15 times to obtain better statistics. After injection, primary ions are relaxed to the ambient temperature by using an intense pulse of He buffer gas. In this example, a mixture of both CH_3^+ and CH_4^+ has been used. While the first ion remains almost unchanged, the second one reacts with hydrogen, $[\text{H}_2] = 7.4 \times 10^{10} \text{ cm}^{-3}$, to CH_5^+ . At the temperature of this measurement (300 K), there are minor losses due to reactions with H_2O background gas leading to H_3O^+ products. The solid lines are solutions of an adequate rate equation system leading to a set of rate coefficients (see Table 2).

room temperature, for example, the water number density was in the range of $[\text{H}_2\text{O}] = 1 \times 10^7 \text{ cm}^{-3}$. At cryogenic temperatures, this number is much lower, at least by 2 orders of magnitude.

Typically, only a few hundred parent ions are trapped per pulse in order to avoid saturation of the Daly detector. For improving the statistics and for determining the rates of the investigated reactions with good precision, the procedure *ion formation/trapping* and *reaction/analysis* is repeated often (about 20 times) for typically 20 different storage times and for each of the masses of interest. This is further explained with the example of Fig. 1. In this 300 K experiment, about 700 CH_4^+ ions are injected per pulse into the trap filled with hydrogen at a number density of $[\text{H}_2] = 7.4 \times 10^{10} \text{ cm}^{-3}$. As the first mass filter was operated in the low-pass mode, in addition some 500 CH_3^+ ions were in the primary ion beam coming from the source. Also a few CH_2^+ were initially present; however, they quickly react to CH_3^+ . These ions do not disturb this investigation, as they react extremely slow with H_2 at room temperature. The CH_4^+ ions are transformed via reaction (1) into CH_5^+ . In addition, there are also a few H_3O^+ formed via proton transfer of stored ions to background water molecules.

The solid lines in Fig. 1 represent solutions of a set of coupled rate equations describing the formation and destruction of the corresponding ions. Initial conditions are the number of various ions at short storage times as well as the density of the neutral reactant gas and the background gas. The coupled differential equations are usually solved numerically with a set of assumed rate coefficients which are varied systematically until the agreement with the experimental data is satisfactory. The output of this procedure is a set of rate coefficients.

3. Results

3.1. Temperature dependence

With the methods outlined above and illustrated in Fig. 1, rate coefficients of reaction (1) have been determined for selected temperatures in the range from 15 to 300 K. Hydrogen number densities have been varied between 1×10^{10} and $1 \times 10^{11} \text{ cm}^{-3}$. Typically, repetition periods between 500 ms and 1 s were chosen. The resulting rate coefficients are shown in Fig. 2 as a function of temperature. The errors for the rate coefficients are around 10% and are mainly due to uncertainties in determining the effective H_2 number density. The indicated errors in the measured temperatures are assumed to be 10 K for high temperatures and not more than 5 K in the low temperature range. Inspection of Fig. 2 reveals that the rate coefficient decreases by more than one order of magnitude from $(4.0 \pm 0.2) \times 10^{-10} \text{ cm}^3/\text{s}$ at 15 K to $(3.3 \pm 0.2) \times 10^{-11} \text{ cm}^3/\text{s}$ at room tem-

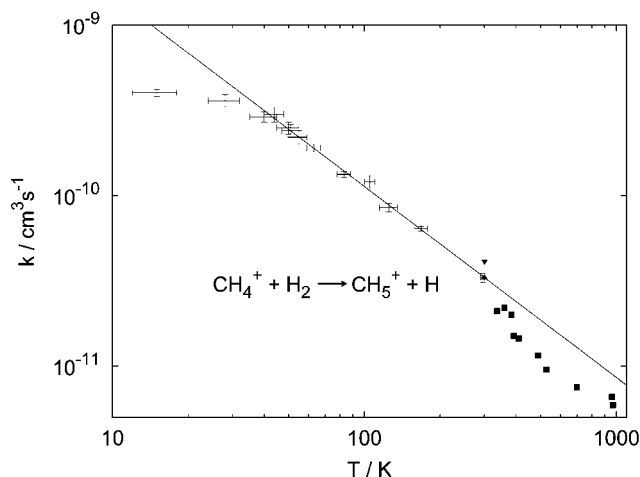


Fig. 2. Temperature-dependent rate coefficients for reaction (1). The results from this work (including error bars) cover the range from 15 to 300 K. These data have been fitted with $k(T) = \alpha(T/300)^\beta$ for $T > 50$ K, see also Table 1. The two additional points at 300 K are from [11] (▲) and [6] (▼). At higher energies results from a SIFDT experiment [12] are included (■). For details see text.

perature. The data have been fitted using the function $k = \alpha(T/300)^\beta \exp(-\gamma/T)$. This parameterization is commonly used for including experimental or theoretical results in reaction networks describing interstellar chemistry [13]. For the high temperature range, the parameter γ was set to zero while α and β were fitted (straight line in Fig. 2). For including the low temperature behavior, also γ was varied. The resulting best fit parameters are listed in Table 1.

At 300 K two earlier measured values are included as filled triangles in Fig. 2. The result of Adams and Smith [11] (upright triangle), $k = 3.3 \times 10^{-11} \text{ cm}^3/\text{s}$, is in excellent agreement with the present work. Kim et al. [6] have reported $k = 4.1 \times 10^{-11} \text{ cm}^3/\text{s}$. In addition, values from the SIFDT-measurements of Federer et al. [12] are shown in Fig. 2 as filled squares. For comparing these non-thermal results with the other ones, the mean kinetic energy of the drifting ions has been converted into an effective temperature T by using simply the relation $\langle E_{\text{trans}} \rangle = 3/2kT$. According to their data, the rate coefficient reaches a value of around $6.5 \times 10^{-12} \text{ cm}^3/\text{s}$ at an energy of 120 meV (corresponding to 960 K, see Fig. 2). Due to the well-known difficulties of comparing thermal rate coefficients with results from SIFDT ex-

Table 1
Temperature dependence of the rate coefficient, $k = \alpha(T/300)^\beta \exp(-\gamma/T)$

Reaction	α ($10^{-11} \text{ cm}^3/\text{s}$)	β	γ (K)	Temperature range (K)
$\text{CH}_4^+ + \text{H}_2 \rightarrow \text{CH}_5^+ + \text{H}$	3.3	-1.12	0	50-300
	3.4	-1.35	23	15-300

The indicated temperature ranges were fitted.

periments, the deviation of the high temperature data from the low temperature fit should not be over-interpreted. In any case, however, these data demonstrate that the rate coefficient is still decreasing with increasing kinetic and internal energies, which are equivalent to temperatures of about 1000 K.

3.2. Formation of CH_4D^+ in collisions with HD

Rate coefficients with a negative temperature dependence have also been measured for reactions of CH_4^+ with HD and D_2 at temperatures between 300 and 15 K. Table 2 compiles the results for collisions with H_2 , HD and D_2 . Also for the deuterated reactants the rate coefficients drop by at least one order of magnitude between 15 and 300 K. To get a deeper insight into the underlying reaction dynamics, the two separated product channels for collisions with HD,



Table 2

Rate coefficients (in units of $10^{-11} \text{ cm}^3/\text{s}$) and branching fraction for reactions with H_2 , HD and D_2

T (K)	H_2	HD		D_2
	k	k	CH_5^+ fraction (%)	K
15	40 ± 2	45 ± 2	(68 ± 2)	12 ± 2
300	3.3 ± 0.2	2.2 ± 0.1	(58 ± 2)	1.1 ± 0.2
k_L	157	132	–	117

k_L denotes the Langevin rate coefficient for the corresponding target molecule.

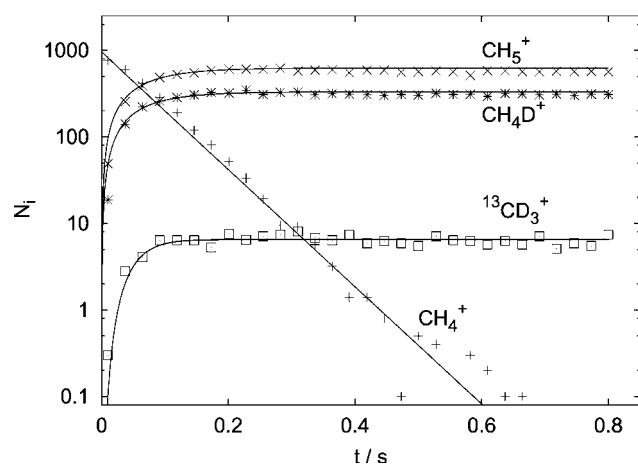
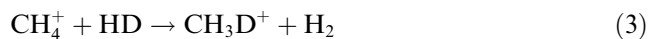


Fig. 3. CH_4^+ stored at $T = 15 \text{ K}$ in pure HD ($[\text{HD}] = 3.5 \times 10^{10} \text{ cm}^{-3}$). The rate coefficient derived from the decay of CH_4^+ is $k = (4.5 \pm 0.2) \times 10^{-10} \text{ cm}^3/\text{s}$, the branching fraction to form CH_5^+ is 68%. Also visible as a product is $^{13}\text{CD}_3^+$, originating from $^{13}\text{CH}_3^+$ parent ions overlapping with the primary injected beam of CH_4^+ (both mass 16). $^{13}\text{CH}_3^+$ is completely deuterated in three fast reactions with HD.

have been investigated at 15 and 300 K. One typical measurement performed at 15 K and at a number density of $[\text{HD}] = 3.5 \times 10^{10} \text{ cm}^{-3}$ is shown in Fig. 3. In this experiment around 1000 primary CH_4^+ -ions were injected into the trap and every storage step was repeated ten times. It can be seen that the number of CH_4^+ ions decays exponentially while CH_5^+ ions (mass 17) and CH_4D^+ ions (mass 18) are formed. The origin of the minor product $^{13}\text{CD}_3^+$ (mass 19) will be discussed below.

It is obvious that reaction (2b), i.e., formation of CH_5^+ dominates over reaction (2a) leading to the deuterated CH_4D^+ . Interestingly the branching fraction of the formation of CH_5^+ increases from 0.58 at 300 K to 0.68 at 15 K. Special care has been taken for the branching measurements not to be influenced by small CH_2D^+ -impurities injected with the CH_4^+ primary beam. These species are completely deuterated in two fast consecutive steps to CD_3^+ (mass 18) which are then indistinguishable from the CH_4D^+ products under investigation. These two species can be separated since association of CD_3^+ in collisions with HD is much faster than any further reaction of the $\text{CH}_4\text{D}^+/\text{CH}_5^+$ products of reaction (2). Radiative and ternary association of these CH_5^+ -analogues are at least three orders of magnitude slower than those of CD_3^+ , see [23] for details. The results for the branching fractions are included in Table 2.

An important experimental test for understanding the reaction mechanism is whether HD scrambling occurs in a collision with HD, i.e.,



The CH_3D^+ product has the mass 17 and it is therefore indistinguishable from CH_5^+ from reaction (2b). One clear hint that reaction (3) is only a minor channel compared to reaction (2) is that the rate coefficients determined from the exponential decay of CH_4^+ are quite similar for collisions with H_2 and HD at 15 K (see Table 2). Since this attenuation rate coefficient also includes reaction (3) it can be deduced that the reactivity is not much enhanced by taking HD instead of H_2 . Moreover, at 300 K the reaction rate with HD is even smaller than with H_2 . Thus the presence of the additional reaction channel (3) does not seem to play a role.

Due to the mentioned mass overlap problem it is hard to determine an accurate value for the rate coefficient of reaction (3). However, a simulation of the subsequent reaction steps has been used to derive an upper limit. CH_3D^+ is a deuterated version of CH_4^+ and will therefore most likely be subject of hydrogen (deuterium) abstraction, similar to reaction (2). For this consecutive reaction the same rate coefficients have been assumed as for reaction (2) and the products are CH_4D^+ on mass 18 and CH_3D_2^+ on mass 19. CH_4D^+ from these subsequent reactions and from reaction (2)

Table 3

There is no experimental evidence for H–D scrambling in $\text{CH}_4^+ + \text{HD}/\text{D}_2$ collisions

Reaction	k (15 K)
$\text{CH}_4^+ + \text{HD} \rightarrow \text{CH}_3\text{D}^+ + \text{H}_2$	$< 1 \times 10^{-12} \text{ cm}^3/\text{s}$
$\text{CH}_4^+ + \text{D}_2 \rightarrow \text{CH}_3\text{D}^+ + \text{HD}$	$< 1 \times 10^{-13} \text{ cm}^3/\text{s}$

The given values for the rate coefficients are upper limits for k from the numerical solutions of the sets of coupled rate equations.

cannot be distinguished. A certain fraction of the mass 19 signal corresponds to $^{13}\text{CD}_3^+$ which stems from $^{13}\text{CH}_3^+$ (mass 16) entering the trap together with the CH_4^+ parent ions. Its contribution has been determined in independent measurements to be $(0.7 \pm 0.1)\%$ as can be seen in Fig. 3. In the simulation, the number of mass 19 products would increase significantly above this level when the rate coefficient of reaction (3) is assumed to exceed $1 \times 10^{-12} \text{ cm}^3/\text{s}$. Therefore one can take this value as an upper limit. Kim and co-workers give a similar upper limit for the exchange reaction of $\text{CD}_4^+ + \text{H}_2 \rightarrow \text{CD}_3\text{H}^+ + \text{HD}$ ([6]). For the H-atom exchange in the reaction of CH_4^+ with D_2 an even lower limit of $1 \times 10^{-13} \text{ cm}^3/\text{s}$ has been derived in the present study, see Table 3. In the latter case, the experimental sensitivity to derive an upper limit is somewhat higher due to the smaller total reaction rate, as detailed in the following section.

Another indication that the four hydrogen atoms bound to the carbon do not exchange with the atoms from the target molecule comes from the $\text{CH}_4^+ + \text{D}_2$ collision system. If scrambling would play a role in the course of hydrogen addition, one would also expect CH_3D_2^+ products where the colliding D_2 is incorporated while a hydrogen atom from the CH_4^+ parent is removed. From a point of view of simple statistics this case should occur in 4 out of 6 cases. However, the signal on the corresponding mass is measured to be smaller than 1% (see [23]). Therefore it can be concluded that reaction (1) proceeds via addition of one hydrogen atom which is abstracted from the incident target molecule.

3.3. Differences in collisions with H_2 , HD and D_2

As has been mentioned above and can be seen from Table 2, the rate coefficients for D-atom abstraction in collisions of CH_4^+ are strongly dependent on temperature between 15 and 300 K. The rate coefficient at room temperature has been determined before by Inoue and Wexler [15] to be $0.9 \times 10^{-11} \text{ cm}^3/\text{s}$. Note that their value might be somewhat low due to the higher kinetic energy of ions in ICR-experiments leading to non-thermal conditions. Utilizing the technique of resonance-heating, they also observed a falling rate coefficient with increasing energy.

As can be seen from the summary in Table 2, the total rate coefficients at $T = 300 \text{ K}$ decrease substantially with the level of deuteration of the neutral reactant. It drops by a factor of three when using D_2 instead of H_2 . A similar drop is present at $T = 15 \text{ K}$. However, at low temperatures the total rate coefficient with HD as a target is significantly larger than that for H_2 . In contrast to these findings the Langevin rate coefficients for the three neutral reactants are not much different. Using simply the averaged polarizability, one obtains $k_L = 1.57 \times 10^{-9} \text{ cm}^3/\text{s}$ for collisions of methane cations with H_2 , $k_L = 1.32 \times 10^{-9} \text{ cm}^3/\text{s}$ with HD, and $k_L = 1.17 \times 10^{-9} \text{ cm}^3/\text{s}$ with D_2 , the small changes being due to the increasing reduced mass. The contribution of the quadrupole term of hydrogen as well as the ion-dipole interaction for HD as target has been neglected in this calculation. Nonetheless the dipole moment of HD, which is 8.51×10^{-4} debye [24] most probably plays a role in favoring reaction (2a) over (2b) (see below). In summary, other dynamical constraints have to be considered in order to explain the rather large differences in the total rate coefficients for H_2 , HD and D_2 .

4. Discussion

Several pieces of information concerning the hydrogen abstraction reaction of CH_4^+ have been collected in this work. First, at low temperatures reaction (1) is proceeding at a substantial fraction of the collision rate. Second, this reaction follows a strong negative temperature dependence up to at least 1000 K. Third, reaction (3), H–D exchange of CH_4^+ in collisions with HD, is very slow. Therefore it can be assumed that H–H scrambling is also very unlikely to occur. Fourth, the branching ratio of reaction (2) is in favor of the hydrogenated CH_5^+ product over the deuterated CH_4D^+ product. Fifth, hydrogen abstraction is slowed down when using HD or D_2 instead of H_2 . In the following a qualitative picture of the potential energy surface (PES) is discussed and some remarks concerning reaction dynamics are made which may explain the experimental facts.

Reaction (1) is near thermoneutral. From the heats of formation of reactants and products at 0 K [13] an exothermicity of 19 kJ/mol is derived. In Federer et al. [12] a value of 5 kJ/mol has been used in their discussion. This is the first information the PES shown in Fig. 4 is based on. Since at 300 K, 98% of the $\text{CH}_4^+ + \text{H}_2$ decay back to the input channel, the transfer to the product channel must be significantly hindered, e.g., by a potential barrier, a dynamical bottle neck or by an extremely small phase space (endoentropic). It is surprising that, at 15 K, the path towards products is found in every fourth collision. As common in low-temperature collision processes the discussion is simpli-

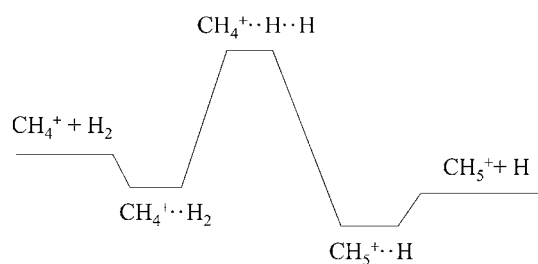


Fig. 4. Schematic illustration of the stationary points of the potential energy surface for the $\text{CH}_4^+ + \text{H}_2$ collision system. The absolute values which are not known, have been adopted from [9] for the isoelectronic $\text{NH}_3^+ + \text{H}_2$ system. Note that there is probably no barrier in the transition region. This is used here only symbolically for indicating the fact, that the transfer from the left to the right is hindered by some dynamical constraints.

fied if one makes the assumption that the abstraction reaction (1) proceeds in two well separated steps. First, an intermediate collision complex is formed which, at low enough temperatures, may be long-lived even if the H_2 molecule is only loosely attached to the CH_4^+ ion,



An upper limit for the rate coefficient for this process, K_{1a} , is the Langevin rate coefficient k_L . No substantial barrier has to be overcome to reach this complex since the measured low temperature rate coefficient amounts to a considerable fraction of the collision limit, k_L . This complex is weakly bound since there does not exist a bound CH_6^+ molecule. Due to its fragile nature the complex usually redissociates quickly into the educts



but there must be a way to proceed towards products,



Within this simple model, the dynamics of the $\text{CH}_4^+ + \text{H}_2$ reaction system (1) is determined predominantly by the two decay rates for process (1b) and (1c), K_{1b} and K_{1c} . As a consequence the rate coefficient for reaction (1) can be approximated by

$$k = k_L K_{1c} / (K_{1b} + K_{1c}). \quad (4)$$

According to the Langevin model the rate coefficient k_L at which the reactants can overcome the centrifugal barrier in the entrance channel to form the complex is temperature independent. Therefore the complex formation is thought to be of minor importance for the temperature dependence of reaction (1). The second important parameter in expression (4) is K_{1b} . The order of magnitude of the life time of the CH_6^+ complex, $\tau_{\text{dis}} = 1/K_{1b}$, may be about 1 ns at 15 K assuming that it is similar to that of the CH_6D^+ complex formed in $\text{CH}_5^+ + \text{HD}$ collisions. The latter complex is also bound only by van der Waals forces and its lifetime has been estimated from the rate of ternary association (see [23]).

Since it is rather safe to assume, within this simple model, that the lifetime of the complex increases monotonically with decreasing temperatures, K_{1b} drops accordingly. Statistical models usually predict a T^n dependence. The third and presently most uncertain parameter is the rate K_{1c} . If tunneling would be the determining process, this value would drop also significantly with decreasing temperature. This would lead to an obvious contradiction to the experimental observations. From the experimental results it can be concluded that $K_{1c} \sim 1/3K_{1b}$ at 15 K and $K_{1c} \sim 0.02K_{1b}$ at room temperature. This indicates that K_{1c} may be only weakly temperature-dependent.

As discussed above the lifetime of the complex is rather long compared to the time scale of any internal motion (vibration, rotation). This can be taken as an argument that the collision complex has enough time to redistribute the energy statistically among all states which are in accordance with its good quantum numbers. If this is really fulfilled, the rates K_{1b} and K_{1c} can be calculated from the relevant phase space volumina. In this context it becomes evident, that the question, whether a bimolecular reaction can be treated with simple thermodynamic quantities as presented in [12] and mentioned in Section 1, and whether it is allowed to say that reaction (1) is an endoentropic reaction must be obviously denied. The complete mixing of the phase space is a necessary condition, but a statistical theory which correctly describes the collision of two molecules, must account properly for all constants of the motion!

In the present case, especially with the unknown structure of the CH_5^+ product, it is not easy to get a reasonable estimate for the competing phase space volumina. However, it is presumed that also an exact statistical calculation will lead to a result deviating from the experimental observations. Most probably reaction (1) is influenced by additional dynamical constraints, hindering the access to some regions of the phase space. There may be degrees of freedom which are only weakly coupled, or there are additional hidden constants of the motion, restricting the reaction steps (1b) and (1c). One candidate is the total nuclear spin which plays an important role if identical atoms are involved as in the title reaction.

Despite the fact that the $\text{NH}_3^+ + \text{H}_2$ system and the $\text{CH}_4^+ + \text{H}_2$ are isoelectronic and that, at first side, the negative temperature dependence of the rate coefficients for both reaction systems may have a similar explanation, the dynamical reasons must be quite different. For the ammonia system, rate coefficients have been calculated as a function of temperature and compared to a variety of experimental results [1-4,6]. The theoretical treatments were based on the minimum energy pathway of Herbst et al. [9], which also has been used as illustration in Fig. 4. In these calculations good qualitative

agreement has been obtained and it has been found that tunneling is the dominant pathway at low temperatures.

With increasing temperatures the complex lifetime becomes shorter thus leading to a negative temperature dependence. In the $\text{NH}_3^+ + \text{H}_2$ case a minimum value for the rate coefficients has been found at a temperature of about 150 K followed by a positive temperature dependence at higher temperatures. In this temperature range, Fehsenfeld et al. have derived an effective barrier height of 0.09 eV (9 kJ/mol) from an Arrhenius plot. Taking tunneling into account, Herbst et al. [9] derived a larger value of (20 ± 2) kJ/mol. In view of these considerations one could argue that also $\text{CH}_4^+ + \text{H}_2$ may have a minimum in the rate coefficient at higher temperatures. However, it is apparent from Fig. 2 that this minimum must occur at temperatures exceeding 1000 K implying a barrier height much larger than for the ammonia system and subsequently even smaller reaction rate coefficients. In reality the rate coefficients are more than a factor of 100 larger thus ruling out tunneling in the present case.

A more subtle question to address is why significant isotope effects are observed when using deuterated hydrogen instead of H_2 . When comparing the absolute values of the rate coefficients for H_2 , HD and D_2 one has to take into account the branching ratios and the fact that, for example in reaction (2), the unbiased probability to pick an H atom from HD is only half the one for H_2 as a target in reaction (1). Accounting for this the rate coefficient for the formation of CH_5^+ is almost the same for HD and H_2 at 300 K. However, at 15 K this channel is faster by a factor of 1.5 when using HD instead of H_2 . In a similar comparison the CH_4D^+ product channel is favored at both temperatures for HD as compared to D_2 as a target by a factor of about two. In general HD is reacting faster with respect to H_2 and D_2 . Therefore, the heteronuclear nature of HD might be a root to understand the isotope effect.

As has been discussed in detail in state selected low temperature experiments on $\text{CO}^+ + \text{CO}$ [25] the rate of redissociation of a loosely bound complex depends strongly on the rotational state of the reactants. It is significantly slower for low lying rotational states than it is for high energy states. Therefore one could interpret the differences in collisions with H_2 and HD as the result of reactions with two species at different energies. In fact, at 15 K only the lowest rotational state, $j = 0$, is occupied in HD while the $n\text{-H}_2$ used in the experiment consists of 75% $o\text{-H}_2$ ($j = 1$) and 25% $p\text{-H}_2$ ($j = 0$). Thus using $n\text{-H}_2$ leads to a population of higher energy states in the complex. However, as described before, the H_2 , HD and D_2 entities remain as intact molecules in the complex. Therefore it is supposed that orthopara conversion within the complex is

an unlikely process since it would require a nuclear spin flip. Another way of converting H_2 rotation into internal energy of the whole complex would be proton or H-atom scrambling between the ion and the neutral molecule. The exchange reaction (3) has been shown to be a very unlikely process. Also from the absence of CH_3D_2^+ products in $\text{CH}_4^+ + \text{D}_2$ collisions it may be concluded that reorganization of hydrogen atoms or molecules is not very probable, also at long complex life times. In summary there is no obvious route for $o\text{-H}_2$ to release its internal energy to the complex in order to decrease the lifetime. Dedicated experiments with $p\text{-H}_2$ should be performed to see whether the results are more consistent with those for HD or for $n\text{-H}_2$. From such experiments it might be possible to judge whether the physical picture of an increased temperature is correct.

A final question to discuss is the fact that CH_4^+ prefers to abstract the H atom from the HD target molecule instead of the D atom. As discussed in detail in [14], e.g., for $\text{D}_3^+ + \text{H}_2$ scrambling collisions, the simple statistical weight of the competing product channels determines often the outcome at elevated temperatures while, at low temperatures, the difference in zero-point energies restricts the formation of certain product channels. Based on such results, the energetically lower lying product channel $\text{CH}_4\text{D}^+ + \text{H}$ would dominate. If, however, scrambling is not occurring like for the title reaction, the branching ratio is determined by other mechanisms, may be just by the orientation of the HD during the approach of the ion. An example illustrating this is the isotopic branching ratio which has been calculated for the $\text{O}^+ + \text{HD}$ reaction using the rotationally adiabatic capture theory [26]. The authors find the branching ratio $[\text{OH}^+]/[\text{OD}^+]$ larger than unity, especially for non rotating HD. An explanation based on a simple classical picture is that the isotopic substitution separates the center of charge from the center of mass leading to an enlarged orientation probability of the H-atom facing the ion prior to reaction. At the moment this is the most likely explanation of the isotope effect observed in reaction (2), however, it also may be taken as a hint to other dynamic restrictions controlling reaction (1).

5. Conclusions

Our investigations with a 22-pole ion trap show that temperature dependent reaction rate measurements using different isotopic configurations give detailed insight into the dynamics of ion-molecule reactions. In the case of $\text{CH}_4^+ + \text{H}_2$, a picture different from common tunneling mechanism, had to be drawn to explain the negative temperature dependence of the rate coefficient. Detailed calculations are needed to explain the dynamical re-

strictions within the collision complex. The similarity of the isotope effect of the hydrogen abstraction for $\text{CH}_4^+ + \text{HD}$ and $\text{O}^+ + \text{HD}$ suggests that long-range HD orientation via the dipole may play a role. Thus the isotope effect may be partly related to the entrance channel while the negative temperature dependence is most probably affected by properties of the exit channel of this reaction.

It is hoped that these studies encourage ab initio calculations of the PES of the $\text{CH}_4^+ + \text{H}_2$ system and quantum chemical investigations, especially at low temperatures. Dedicated experiments to measure the energy dependence at higher collision energies may indicate a minimum in the rate coefficient like in the case of $\text{NH}_3^+ + \text{H}_2$. The most important next experimental step is, however, to study the reverse of reaction (1), especially in the threshold region which should be somewhere between 15 and 300 K. The combination of a temperature variable 22-pole ion trap with a beam of slow hydrogen atoms is close to completion and first results for $\text{CH}_5^+ + \text{H}$ and $\text{CH}_5^+ + \text{D}$ are expected soon.

Besides the efficiency of the various reaction paths leading to final product states in $\text{CH}_4^+ + \text{H}_2$ collisions, the question remains, whether all hydrogen atoms are equivalent in the formed protonated methane. It is rather sure that the dynamics of the reaction system discussed in this paper are too complicated to draw some related conclusions. An important experimental observation providing information on the structure of CH_5^+ is that this ion survives millions of collisions with HD without deuteration. Another way to better define synthesis of CH_5^+ ions can be achieved via radiative or ternary association. In any case it is very challenging if not impossible to develop chemical probing methods for distinguishing different isomers of this floppy molecule. A more realistic approach with a 22-pole trap is probably to utilize the method of IR laser induced reactions [27] and to record infrared and far-infrared spectra of very cold CH_5^+ relaxed in *p*- H_2 or alternatively in *n*- H_2 . Partial substitution of hydrogen with deuterium, may be also tritium can be used to break the exchange symmetry. Of course this also may lead to structural modifications due to changes in zero point energies.

Acknowledgements

Financial support by the Deutsche Forschungsgemeinschaft (DFG) is gratefully acknowledged, especially via the Forschergruppe FOR 388 "Laboratory Astrophysics".

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