Probing the structure of CH$_5^+$ ions and deuterated variants via collisions†

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Numerous recent calculations have provided a rather detailed picture how the protonated methane, CH$_5^+$, really may look like at very low temperatures; however, there is not yet any experiment, providing information on the correlation of a structure of this fluxional ion with a state to state transition induced by a photon or a collision. Various efforts in spectroscopy and mass spectrometry have contributed important pieces to the puzzle but there are no real final conclusions, e.g. infrared spectra in the region of the C–H stretching vibration are waiting for assignment since several years. This contribution reviews and discusses the potential and the limitations of a correlation of a structure of this fluxional ion with a state to state transition induced by a photon or a collision.

Introduction

Protonated methane, CH$_5^+$, has been subject of many experimental and theoretical investigations since its first mass spectrometric detection in 1952. Numerous calculations (see, for example, the recent publications 1–5, and references therein) lead to the conclusion that the global minimum of the potential energy surface is the C(d) isomer which may be pictured as a CH$_3$ tripod and a three-center two-electron bond associating two hydrogens; however, there are two more nearly isenergetic structures. Detailed studies of the nuclear motion, e.g. the very recent diffusion Monte Carlo (DMC) studies carried out on a high quality full dimensional potential energy surface 5, corroborated the conclusion 1 that CH$_5^+$ is an extremely floppy molecule. Even in the ground state, the zero-point energy allows the molecular system to explore all $S_l = 120$ equivalent minima of the potential energy surface.

In spite of this scrambling motion, the evaluation of the intermolecular dynamics provides evidence of the structure. For example, the distributions of the C–H or the H–H distances of the ground state wave function show clear preferences of certain regions of the phase space. Very interesting, especially also for the present experimental work, are the results calculated for several deuterated variants. The replacement of the proton, a fermion, by a deuteron, a boson, reduces the exchange symmetry; in addition it changes the zero point energy. At low temperatures, D–H exchange reactions lead to isotope enrichment, an important process in astrochemistry. The recently reported DMC zero point energies for CH$_5^+$ and CD$_5^+$ are 10 975 cm$^{-1}$ and 8080 cm$^{-1}$, respectively. 5 Because of the C(d) structure described above, the CD$_3$H$_2$ isotope is of specific interest. DMC calculations lead to a zero point energies of 9148 cm$^{-1}$ and indicate that this isotopomer becomes more localized in the CD$_3$H$_2$-H$_2$ minimum. 3 This can be understood on the basis of the harmonic values of the zero point energies which differ by some 100 cm$^{-1}$ depending on the location of the D atoms. For the C(d) state, the lowest energy is obtained for an arrangement where the three deuterons are placed in the tripod in accordance with the calculations of McCoy et al. 3

All these very interesting results do not provide so far any quantitative prediction how protonated methane really behaves in various experiments. The computation of vibrational transitions requires first a method to calculate the eigenvalues of the excited states with spectroscopic accuracy. Since this is...
not easy, the rich and complicated high-resolution infrared spectrum recorded in the region of C–H stretches near 3000 cm$^{-1}$ has to wait to become assigned.\textsuperscript{7} Also, the interesting predissociation infrared spectra of (CH$_{5}$)$^+$ (H)$_n$ clusters ($n = 1–6$) are far from being understood in detail.\textsuperscript{7,8} Although the additional $n$ hydrogen molecules are only weakly interacting, the spectra do not give direct hints to the structure of the unperturbed CH$_5$$^+$. Nonetheless, such experiments or also low energy scattering experiments provide important information on the interaction of the CH$_5^+$ core with the ligands or suitable collision partners, respectively. An important result from the (CH$_{5}$)$^+$ (H)$_n$ spectra is that the scrambling motion of the CH$_5^+$ core is slowed down by adding H$_2$. Most probably, it becomes frozen for $n = 3$ despite the very low binding energies.\textsuperscript{7}

It has been recently pointed out by Bunker et al.\textsuperscript{10} that it is probably best to start with a pure rotational spectrum of CH$_5^+$ if one really wants to compare high level theoretical results obtained for the ground state with experimental observations. A simple estimate of the spectral location can be obtained assuming that the large amplitude motions average out to a spherical top. The DMC value of such a mean rotational constant of CH$_5^+$ is 3.91 cm$^{-1}$.\textsuperscript{5} In a more sophisticated analysis the zero point oscillations lead to a fine structure in the rotational spectrum, as shown in a detailed theoretical study of the millimeter-wave spectrum.\textsuperscript{10} The $J = 1 \leftarrow 0$ transition is predicted to be centered in the 220–235 GHz region. Two interesting absorption spectra have been simulated by Bunker et al.\textsuperscript{10} assuming ensembles of ions thermalized at 300 and at 77 K. It will be outlined in the conclusions that there are realistic chances to record such a spectrum combining ion trapping, sub-K$_B$ buffer gas cooling, millimeter waves, and finally collisional probing.

One of the stimuli for this paper was the critical comment by Kramer\textsuperscript{11} who disputes the theoretical results of Marx and Parrinello\textsuperscript{12} based on earlier experimental results from a Fourier transform ion cyclotron resonance (FTICR) study.\textsuperscript{12} They indicate that there are stable isomers while the $ab$ \textit{initio} path integral simulations indicated scrambling of all five atoms, also in the case of partial deuteration.\textsuperscript{5} The basic question is whether CH$_5^+$ can be synthesized in different structures separated by high enough barriers to be of importance for a “near-thermal” IC experiment or whether there is just an arrangement of five equivalent H-atoms, even at a few K. Chemical reactions for probing structures are well established. A recent example is the excited HOC$^+$ isomer which is well separated from the ground state HCO$^+$. Using chemical probing with CH$_4$ or NO the isomers can be easily distinguished and one can, for example, determine the HOC$^+$ + H$_2$ isomerization rate.\textsuperscript{13}

In the ICR experiment\textsuperscript{14} isotopically labeled CH$_5^+$ ions have been produced in an external ion source containing a mixture of CH$_4$ and CD$_4$ gases. It has been reported that only deutertated methane, CH$_4D+$ and protonated per-deuternate-methane CD$_4H^+$ was formed at low pressure. In addition, it was claimed, based on other experiments, that these ions are formed via migration of a proton (or deuteron) from hydrogen into the 3c–2e bond leading to an HD-molecule well separated from the CH$_4$ (CD$_4$) triplet. The next assumption in the chain of arguments is that only this HD group of the so synthesized isomer participates in the chemical probing via proton or deuteron transfer to NH$_3$. Ignoring possible isotope effects, one obtains finally NH$_4^+$ and NH$_2$D$^+$ with a ratio of 1 : 1. It is not the aim of this work to analyze in detail all the difficulties occurring in the various ICR experiments\textsuperscript{12,14,15} which, by the way, came to different conclusions concerning the structure of CH$_5^+$. A basic problem is certainly that both the formation and the chemical probing reactions occurred at temperatures above 300 K and, in addition, the solvation energy gained upon formation of the reaction complexes is almost 1 eV. Even if there would be a barrier much higher than the theoretical predictions there are several possibilities for intra- or intermolecular H–D scrambling. Most problematic in the experiment of Heck et al.\textsuperscript{7,12} is the well-described fact that the results were extremely sensitive to the average number of collisions in the ion source. The reported information that already 0.2 collisions destroyed the selectivity in isomer production, is an obvious hint to experimental problems.

In this contribution we illustrate the potential and the limitations of detailed collision experiments in finding correlations between structure and reactivity. All examples presented are related to protonated methane and deuterated variants. In order to learn more about the fundamental CH$_5^+$ + CH$_4$ reaction and to search for practicable methods to synthesize CH$_5^+$ ions in specific states, detailed studies have been performed in the universal guided ion beam instrument.\textsuperscript{15,17} Integral and differential cross sections have been measured for the first time from collision energies of several eV down to thermal energies. Formation of CH$_5^+$ $\rightarrow$ radiative association of CH$_4^+$ + H$_2$ has been thoroughly studied in several ion trapping machines. This process is of significance for the synthesis of this ion in dense interstellar clouds but also for more detailed studies on this molecule. Very surprising are recent results for the process CH$_5^+$ + H$_2$ $\leftrightarrow$ CH$_5^+$ + H studied in both directions. The rate coefficients measured for H–D scrambling prove that isotope enrichment at low temperatures is not only very important for astrochemistry but it is also a unique chemical probe providing deep insight into molecular structures and reaction dynamics. So far, none of these studies provide clear evidence for the structure of CH$_5^+$. However, it will be outlined in the conclusion that, in principle, the experimental methods are available today to make a significant step forwards understanding of protonated methane.

Experimental

For many years, studies of ion–molecule reactions at room temperature or down to the temperature of liquid nitrogen were dominated by flow and swarm techniques yielding more or less reliable thermal reaction rate coefficients and by ICR traps operating usually under hyperthermal conditions. Methods providing detailed information on reaction dynamics were restricted to higher energies, typically above 1 eV. As can be seen from a comprehensive summary of the experimental methods available today,\textsuperscript{18} many sophisticated instruments have been developed meanwhile. A special role in this development plays the use of inhomogeneous, time dependent electric fields in addition to electro- or magnetostatic fields. Within the last three decades, since the construction of the first guided ion beam (GIB) apparatus (see ref. 19, and references therein), many devices have been developed, using rf multipole ion guides, traps and other electrode structures operated with ac or rf fields.\textsuperscript{20} The success of the method in many fields and specific applications is due to its versatility and unique sensitivity.

All results presented in this contribution have been obtained with rf ion guides and ion traps. The integral and differential cross sections for CH$_4^+$ + CD$_4$ reactive collisions have been measured with the GIB-TOF arrangement in which the GIB technique is combined with time-of-flight (TOF) determination of velocities. Radiative association, isotope exchange reactions and hydrogen or proton abstraction reactions have been studied in several temperature variable ion trapping machines. The most recent innovation is the combination of an atomic hydrogen beam with a 22-pole trap. Since all instruments are described in detail in the literature only a short summary of the most important features is given here.

The guided ion beam technique is best known for routinely measuring integral cross sections at low kinetic energies. The step-by-step improvement of this technique includes the extension of the laboratory energy below 10 meV, the detection of
photon from chemiluminescent reactions, and the inclusion of lasers and molecular beams. The first molecular ion spectrometer in which a long octopole ion guide became the central element, has been developed in the group of Y. T. Lee (see ref. 7, and references therein). A very important discovery was that the guided ion beam technique is capable of providing information on product velocity distributions. Today it is possible to determine absolute doubly differential cross sections with very high sensitivity and in a range of energies and scattering angles inaccessible to standard crossed ion beam methods. As described in detail by Mark and Gerlich,\textsuperscript{17} the product velocity vector \( \mathbf{v} \) is measured by a procedure that combines time of flight analysis with variation of the guiding field. Since the system is rotationally symmetric, it is sufficient to determine two velocity components, \( v_{\text{r}t} \), parallel to the axis of the octopole and \( v_{\text{r}t}' \), the transverse component.

The guided ion beam arrangement used in the present study has been described in detail previously.\textsuperscript{16} It consists of a double octopole system in which primary ions are injected with a defined kinetic energy. The CH\(_4\)\(^+\) and CD\(_4\)\(^+\) ions have been produced in a storage ion source by electron bombardment of methane at a very low pressure to avoid reactions to CH\(_2\)\(^+\). By tuning the electron energy close to the ionization potential, internal excitation has been kept rather low but could not be avoided. The mass selected ions are injected into a first rather short octopole (length 13.6 cm, rod diameter 0.2 cm), which guides the primary ions into and through the scattering cell (effective length 4.6 cm). RF amplitudes are typically below 150 V, and frequencies are usually set between 12 and 20 MHz. The gas used in the ion source and in the scattering cell was methane (Messer-Griesheim 5.5 purity). The second octopole (length: 46.8 cm) is used for determining the velocity of reaction products. Both ion guides are coupled to the same rf generator but they can be operated with a different amplitude and dc bias. Typical tests and the routine measuring procedures are explained in ref. 16 and in some more recent applications.\textsuperscript{21–23}

Originally, the development of multi-electrode rf traps was motivated by the goal to construct an ion source with \textit{in situ} phase space compression \textit{via} inelastic buffer gas collisions or to synthesize specific ions which cannot be produced otherwise. Dedicated constructions for studying collision processes at very low temperatures followed later. Various low temperature studies relevant for the formation, modification, or destruction of CH\(_4\)\(^+\) have been performed in the last 15 years using temperature variable ion traps. The first results relevant for this summary, association of CH\(_4\)\(^+\) and CD\(_4\)\(^+\) in collisions with \( \text{n-H}_2, \text{p-H}_2, \) or D\(_2\) at 80 K, have been obtained with a liquid nitrogen cooled ring electrode trap using hydrogen or helium buffer gas.\textsuperscript{24} More recent work has been performed in variable radio-frequency 22-pole ion trap machines a detailed descriptions of which has been given in ref. 25. This trap consists of 22 rods with 1 mm diameter, arranged equally spaced around a 10 mm diameter circle. Several technical details have been summarized in a recent review.\textsuperscript{20} Typical applications of this technique in interstellar gas phase chemistry, cluster growth, or state specific ion–molecule reactions can be found in current publications.\textsuperscript{13,26,27} An innovative development of actual interest from this laboratory is the combination of such an ion trap with a temperature variable atomic hydrogen beam.

The basic procedure used in all ion trap measurements reported in this work, is the generation of ions in an external storage ion source, mass selection and injection into the ion trap cooled either by liquid nitrogen or a closed cycle He refrigerator. With a suitable cold head, wall temperatures of 5 K have been achieved. The trapping of the ions in radial direction is achieved by applying two opposite phases of an rf generator (less than 100 V, typically 15 MHz for the mass range of interest for this work) to the two sets of rods, while confinement in longitudinal direction and control of the ion storage time is done by pulsing the entrance and exit electrodes. An important feature of rf traps is the possibility to relax or modify ions by inelastic or reactive collisions with buffer or reactant gases introduced by cooled tubes. Reactant gas number densities can be varied between \( 10^{10} \text{ to } 10^{15} \text{ cm}^{-3} \). Using a fast piezo valve, short and very intense pulses of He or H\(_2\) can be injected into the trap. In general, thermal equilibrium with the cold walls surrounding the trap is achieved. In order to determine absolute rate coefficients, typically with a relative error of less than 20\%, the number density of the reactant neutrals is continuously monitored 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 detected with high efficiency by a Daly-type detector.

### Results and discussion

#### Reactions leading to CH\(_5\)\(^+\)

Since its first study reported more than 50 years ago, many details of the reaction

\[
\text{CH}_4^+ + \text{CD}_4 \rightarrow \text{CH}_3D^+ + \text{CH}_5
\]

(1)

have been investigated. In addition to the ICR study\textsuperscript{12} mentioned in the introduction, many methods such as tandem mass spectrometry, crossed beams and selected ion flow tubes (SIFT) have been used to collect information on the collision mechanisms leading to protonated methane. For summaries, see Henchman et al.,\textsuperscript{28} Herman et al.,\textsuperscript{29} and references therein. The temperature or energy range extended from 80 to 300 K or from 0.6 to several eV, respectively. Based on angular dependent measurements, the obtained distributions have been interpreted in terms of mechanisms such as proton stripping, H-atom abstraction or decomposition of an intermediate collision complex.\textsuperscript{29} Isotopic labeling allows to distinguish between a variety of channels, \textit{e.g.}:

\[
\begin{align*}
\text{CH}_4^+ + \text{CD}_4 &\rightarrow \text{CH}_3D^+ + \text{CH}_5, \\
&\rightarrow \text{CH}_4D^+ + \text{CH}_4, \\
&\rightarrow \text{CD}_3H^+ + \text{CH}_2D, \\
&\rightarrow \text{CD}_2H^+ + \text{CD}_3.
\end{align*}
\]

The guided ion beam results, presented in this contribution, clearly show that a detailed comparison between these channels and the above mentioned reaction mechanisms is not straightforward. For example, there is no direct correlation between proton transfer contribution to channel (2a) and backward scattering, as will be shown below. Fig. 1 presents the effective integral cross sections \( \sigma_{\text{eff}} \) measured with the guided ion beam apparatus, as effective rate coefficients \( k_{\text{eff}} \). The conversion of \( \sigma_{\text{eff}} \) into \( k_{\text{eff}} \) has been discussed in detail by Gerlich.\textsuperscript{16} It can be seen that the absolute values for reaction (1) and the sum over all channels for reaction (2a)–(2d) differ significantly. In addition, the difference depends on the collision energy. Comparison with the SIFT values\textsuperscript{29} reveals an overall reasonable agreement; however, there are some significant differences in the absolute values. A detailed analysis of this discrepancy which may be partly due to internal excitation of the primary ions, is out of the aim of the present paper.

More robust should be the comparison of the branching ratios, measured for the reaction channels (2a)–(2d). As can be seen from Fig. 2, the CD\(_3\)H\(^+\) product ("proton transfer") dominates at low collision energies, while the CH\(_3\)D\(^+\) product ("D-abstraction") becomes dominant above 1 eV. Since the lowest collision energy which is accessible with the GIB apparatus (here, \( E_C = 30 \text{ meV} \)) is close to thermal, the measured branching ratio should be comparable to the 300 K...
SIFT results. Unfortunately, the present percentages for reaction (2a): 50%, (2b): 25%, (2c): 16%, (2d): 9% deviate significantly from the SIFT results, (2a): 25%, (2b): 10%, (2c): 43%, (2d): 22%. The most probable explanation is again that the primary ions coming from the storage source are internally excited since it had to be operated at low densities.

In order to learn more about the reaction mechanisms at low collision energies, differential cross sections for reaction (1) have been measured with the GIB apparatus. The method, as well as the evaluation and presentation of the data, has been described in detail by Mark and Gerlich. 17 A typical result obtained at a rather weak guiding potential is plotted in the upper part of Fig. 3, while the lower part shows a result from a crossed beam study (Fig. 1 taken from Herman et al.29). Note that the standard differential scattering method records the product flux \( \frac{d^3N}{dv_1 dv_0} \) by moving the detector with acceptance \( dv_0 \) to different angles. The geometry defined by the ion beam guide is different. The product flux \( \frac{d^2N}{dv_1 dv_0} \) is recorded without any movable parts just by time of flight and by variation of the guiding field. Advantages include safe guidance of slow primary and product ions and integration over the azimuthal angle \( \phi \).

The one-dimensional distribution \( \frac{dN}{dv_1} \) presented in Fig. 3 can be compared directly with the product flux displayed as contour plot in velocity space (Newton diagram). Inspection reveals that the overall agreement between the two results is very good. The dominant features are three peaks and the fact that there is almost no sideward scattering, as can be seen from the structure in the 2-D plot and from the fact that in the GIB experiment very low rf amplitudes are sufficient to collect most products. It is obvious that backward scattering (left of the center-of-mass velocity CM, P ss) prevails. In addition to a lower peak in forward direction (H ss), both measurements show product ions grouping around CM. The absolute heights of the two experimental distributions (see contour lines: P ss: 10, CM: 5, H ss: 6) are also in good overall agreement; however, for a more quantitative comparison, one has to take into account that the ion guide integrates automatically over the azimuthal angle while the differential detector in a crossed beam arrangement sees a much smaller fraction of the angular distribution. Of course, the angular resolution of the GIB method is rather crude as can be estimated from the separation of the three product groups. Most important for the present work is, however, the understanding of the formation of protonated methane, e.g. in a typical ion source as used in ref. 12. For this, angular distributions at near thermal energies as provided only by the GIB method, have to be used.
It can be seen from Fig. 4 that CH$_4$ + CD$_4$ collisions do not lead simply to CD$_4$H$^+$ by a specific reaction mechanism as assumed by Heck et al.$^{12}$ The left side shows results for reaction (2a), the most important channel. It is obvious that at 1.25 eV backward scattering prevails. The dominant reaction mechanism is in accordance with the simple picture that the CD$_4$ molecules, coming from the right, just strip a proton from the CH$_4^+$ ion (in Fig. 3 the “spectator stripping” location is marked with $P_{\text{cm}}$); however, there are evidently also product ions which are scattered into the forward direction or which appear in the vicinity of the CM motion (dashed line). A corresponding observation can be made for reaction channel (2b) (right side of Fig. 4). At high energies, more products appear in forward direction. They may be described as simply being formed via a D-atom pick-up of the CH$_4^+$ ion coming from the left. Note, however, that CH$_4$D$^+$ production requires in reality more interaction (e.g. electron transfer followed by deuteron transfer). This obviously leads to a lower cross section (see Fig. 2) and to a less pronounced stripping peak. At low energies, the three groups are getting less and less distinguishable. This is, in part, due to the limited angular resolution, however, it is certainly also due to a change in reaction mechanisms towards preferential formation of a long-lived complex, as can be supposed from the measured energy dependence.

In summary, it can be said for reactions (1) and (2) that there is no simple selective mechanism which transfers, for example as assumed by Heck et al.$^{12}$ The GIB measurements provide clear evidence that there is always significant isotope, angular and energy scrambling in CH$_4^+$ + CH$_3$CD$_2$ collisions. In addition, there are significant isotopic effects some of which already have been discussed in detail by Henchman et al.$^{28}$ Nonetheless, the present results indicate that there may be ways to synthesize specific CH$_5^+$ isotopomers if they would exist at all. If one produces these ions in a GIB apparatus and makes use of velocity and mass selection, one could pick out a well-defined group of ions which have been formed by a specific stripping process. In such an approach, also the internal energy of the primary ions and the product ions could be chosen. However, with the present theoretical understanding of the CH$_5^+$ ion it is rather certain that an energy resolution limited by 300 K thermal conditions is not sufficient. All these conditions have not been fulfilled in the ICR experiment.$^{12}$ In addition, taking into account the fact that the FTICR results were so critically dependent on the ion source conditions that already, on average, 0.2 collisions destroyed the selectivity, it is safe to conclude that the mechanism described by Heck et al.$^{12}$ could not produce stable CD$_4$H$^+$ or CH$_4$D$^+$ isomers. Therefore, also the comment by Kramer$^{11}$ that the calculations reported by Marx and Parrinello$^1$ are in conflict with mass spectral studies, has no sound experimental basis.

A better defined way to synthesize this interesting ion with the three-center, two-electron bonding arrangement is the radiative association process

$$\text{CH}_3^+ + \text{H}_2 \rightarrow \text{CH}_5^+ + h\nu$$

(3) which plays an important role in interstellar hydrocarbon chemistry. This reaction was first studied in the pioneering low temperature and low density experiment by Barlow and Dunn$^{30}$ using a 10 K Penning ion trap. In a series of subsequent studies, starting with the 80 K ring electrode trap$^{34}$ and the development of more and more sophisticated rf ion traps, very detailed information became available.$^{25,31}$ Fig. 5 shows a typical result obtained with a 10 K 22-pole trap using $p$-H$_2$ gas as a target.$^{32}$ It can be seen that the number of injected CH$_3^+$ ions decays slowly while several products, N(t), are slowly growing with different rates. The dominant product is protonated methane formed almost exclusively via reaction (3) at the low hydrogen number density used in this measurement ($[\text{H}_2] = 8.7 \times 10^{10}$ cm$^{-3}$). After 1 min, half of the number of CH$_3^+$ ions have been converted into CH$_5^+$ via radiative stabilization of the collision complex. The second dominant product is CH$_2$D$^+$ (open circles) which is formed in collisions with traces of HD via the reaction

$$\text{CH}_3^+ + \text{HD} \rightarrow \text{CH}_2\text{D}^+ + \text{H}_2.$$  

(4)
This process is discussed in more detail below. Also, the CH₂D⁺ ion reacts with hydrogen via the analogue of reaction (3) to CH₃D⁺ (crosses in Fig. 5). Interesting for the understanding of the structure of the CH₃⁺ ion are also the subsequent collisions with hydrogen leading to thermalization and also to the formation of CH₄⁺ (stars) and CH₂⁺ (for clarity only the simulation is shown).

A significant role in all these low temperature collisions is played by those hydrogen molecules which are in the ortho state. They contribute at least 14.4 meV to the total energy and \( I = 1 \) to the total nuclear spin. It was attempted by Bates \(^{23,34}\) to develop a theoretical model which explicitly treats the different nuclear spin modifications not only in reaction (3) but also in the inelastic CH₃⁺ + p-H₂ or CH₃⁺ + o-H₂ collisions which lead to cooling or heating of the trapped ions. The detailed experimental results obtained at 10 K did not show the predicted significant increase of the rate coefficient for a pure para hydrogen environment \(^{23,35}\). As discussed in more detail below, this is most probably due to the fact that the model did not account properly for the restrictions imposed by the exchange symmetry.

Some experimental results are summarized in Fig. 6 showing rate coefficients \( k^* \) as a function of the number density of the ambient hydrogen, both for p-H₂ (filled dots) and n-H₂ (open circles).\(^{23}\) As discussed in detail in ref. 31, the formation of association products via radiative and ternary collisions can be described, at low number densities \( M \), by an effective rate coefficient

\[
k^* = k_3 M + k_1
\]

where \( k_3 \) is the termolecular rate coefficient and \( k_1 \) describes the bimolecular process (3). In the first case this intermediate complex is stabilized via an additional collision with a third body \( M \) (ambient hydrogen or additional He buffer gas). The solid and the dashed lines in Fig. 6 are fits to the experimental points using eqn. (5). Some of the resulting parameters which have been reported in detail\(^{25}\) are repeated in the figure caption. Inspection shows that for \([H₂] < 10^{12} \text{ cm}^{-3}\) the ions are mainly formed via the bimolecular process with emission of a photon while for \([H₂] > 10^{13} \text{ cm}^{-3}\) the effective rate coefficient \( k^* \) increases proportionally to the hydrogen number density.

For the synthesis of protonated methane via association it is important to note that one can easily reach rate coefficients \( k^* > 10^{12} \text{ cm}^{-3} \text{ s}^{-1} \). This high efficiency of the association process is primarily due to the very long mean lifetime of the CH₃⁻+H₂ collision complex at 10 K which is about 0.1 and 0.4 \( \mu s \) for n-H₂ and for p-H₂, respectively. It is also important to realize that one can produce other well-defined isotopomers of CH₅⁺ via reactions (3), (4) or in CD₂⁺ + H₂ collisions. It is expected that the long time conservation of the total nuclear spin will also make it possible to produce CD₃⁺+o-H₂. In this case, it is an interesting question whether the rotation of H₂ is conserved as internal rotation of the molecule bound to the CD₃⁺ tripod.

As mentioned above, low temperature trap experiments, performed with hydrogen containing traces of HD, always show contributions from isotope enrichment.\(^{25,36}\) The D-H exchange reaction (4) has been the subject of many experimental and theoretical studies (see ref. 37, and references therein). Detailed \( \textit{ab initio} \) calculations\(^{38}\) show that formation of CH₅D⁺ is 3.4 KJ mol⁻¹ (405 K) exothermic and that scrambling can occur very efficiently in the strongly bound \(( \sim 198 \text{ KJ mol}^{-1} )\) CH₅⁺ collision complex. Based on simple statistical arguments it has been concluded that the overall efficiency for H-D exchange should approach unity at low temperatures. This has been confirmed recently in an ion trapping experiment.\(^{37}\) Using pure HD as target gas, sequential deuteration from CH₃⁺ to CD₃⁺ was observed to be very fast. The rate coefficients, measured for the replacement of the first, the second and finally the last H atom, are \( 1.65 \times 10^{-8} \text{ cm}^{-3} \text{ s}^{-1} \), \( 1.59 \times 10^{-8} \text{ cm}^{-3} \text{ s}^{-1} \), and \( 1.50 \times 10^{-9} \text{ cm}^{-3} \text{ s}^{-1} \), respectively.

These results seem to be in excellent accordance with the concept of efficient scrambling in a strongly bound collision complex the structure of which is known to be very floppy already in its ground state. Most surprising, however, is the result that relaxation of CH₃⁺ in p-H₂ reduces the H-D exchange efficiency by a factor of 4 while the corresponding experiment with n-H₂ leads to a result in agreement with the rate coefficient measured with pure HD. This important result is most probably due to symmetry selection rules imposed by the conservation of the total nuclear spin; however, it is not yet understood in detail. It is unlikely that the additional energy which is provided in the \textit{ortho}-environment by \( H₂(\text{for} \, J = 1) \) accelerates the reaction because of the large gain in zero-point energy by the H-D exchange. One explanation for the reduced efficiency is that the mobility of H, D or also HD may be restricted in the collision complex, \textit{e.g.}, there exists a nuclear-spin protected substructure in the p-CH₃⁺-HD intermediate. Another possibility is that the decay of the collision complex towards the CH₃D⁺ + H₂ products is hindered by some constraints. Inspection of the low lying rotational states reveals that the rotational ground state of p-CH₃⁺ is forbidden by symmetry and that there are, for pure p-CH₃⁺, at maximum two states accessible at 15 K. In contrast, collisions of CH₃⁺ with n-H₂ can lead to higher rotational states of n-CH₃⁺, especially if the not yet fully understood process of energy pooling in subsequent collisions with \( H(\text{for} \, J = 1) \) plays a role.

Another rather selective way to produce CH₅⁺ is the hydrogen abstraction reaction

\[
\text{CH}_4^+ + H_2 \rightarrow \text{CH}_5^+ + H
\]

since it is almost thermoneutral and, therefore, leads directly to cold products if one starts with ground state reactants. This process and the reverse one (see below) have been investigated at energies between 40 and 120 meV in a SIFDT apparatus.\(^{39}\) Formation of CH₅⁺ has been found to be surprisingly slow at 300 K and to become even slower with increasing energy provided by the drift field. Recently, additional measurements have been performed using the variable temperature 22-pole ion trap.\(^{40}\) In accordance with the trend found in the drift tube, the rate coefficients for reaction (6) increase with falling.
temperature. The measured data rise from the room temperature value, \( k = 3.3 \times 10^{-11} \text{ cm}^2 \text{ s}^{-1} \), down to 15 K by more than one order of magnitude to \( k = 4.0 \times 10^{-10} \text{ cm}^2 \text{ s}^{-1} \), with an initial temperature dependence \( k \sim T^{-1.1} \). Since at 300 K, 98% of the \( \text{CH}_5^+ - \text{H}_2 \) collision complexes decay back to the input channel, the transfer to the product channel must be significantly hindered, e.g. by a dynamical bottleneck or by an extremely small phase space. Tunneling is most probably not responsible for this behavior.

As mentioned in the Introduction, isotope scrambling at low temperature is a very sensitive probe for reaction dynamics and molecular structures. However, a careful interpretation has to account for the differences in zero point energies not only in the initial and final molecules but also in the transition states. In addition, one has to be aware of the restrictions imposed by symmetry selections rules. Low temperature results for \( \text{CH}_5^+ \) \((n = 3-5) + \text{HD} \) have been reported recently.\(^1\) For the analogue of reaction (6), three different product channels are possible

\[
\text{CH}_4^+ + \text{HD} \rightarrow \text{CH}_3\text{D}^+ + \text{H}_2, \quad (7a)
\]
\[
\rightarrow \text{CH}_5^+ + \text{D}, \quad \text{and} \quad (7b)
\]
\[
\rightarrow \text{CH}_4\text{D}^+ + \text{H}. \quad (7c)
\]

The rate coefficient for converting \( \text{CH}_4^+ \) into \( \text{CH}_3\text{D}^+ \) by \( \text{H} - \text{D} \) exchange has been determined to be smaller than \( 10^{-12} \text{ cm}^2 \text{ s}^{-1} \), indicating that scrambling in the \( \text{CH}_3\text{D}^+ \) complex is very unlikely. Hydrogen or deuterium abstraction in reactions (7b) and (7c) occurs with a sum rate coefficient of \( 4.5 \times 10^{-10} \text{ cm}^2 \text{ s}^{-1} \). Surprisingly, the more exoenergetic and statistically favored product \( \text{CH}_4\text{D}^+ \) is formed only in 1/3 of the reactive collisions, while \( \text{CH}_5^+ \) dominates with 2/3. Also, this result indicates that conservation of total nuclear spin plays an important role in these low temperature chemical reactions involving identical nuclei. Reaction of \( \text{CH}_5^+ \) with \( \text{D}_2 \) is found to be much slower than with \( \text{H}_2 \) or \( \text{HD} \). Collisional probing of \( \text{CH}_5^+ \)

As briefly discussed in the Introduction, the experimental method of chemical probing can be very sensitive. In combination with ion trapping it has been used successfully to separate different isomers and to distinguish ground state ions from excited ones. A rather general method for spectroscopic studies of cold ions is isotope exchange in the endothermic direction which may be stimulated by absorption of a photon with sufficient energy. This was one of the motivations to study the scrambling reaction

\[
\text{CH}_5^+ + \text{HD} \rightarrow \text{CH}_4\text{D}^+ + \text{H}_2 \quad (8)
\]

in a low temperature ion trap, first in this endothermic direction. However, the rate coefficient has been found to be smaller than \( 5 \times 10^{-18} \text{ cm}^2 \text{ s}^{-1} \). This value indicates that the approaching HD cannot penetrate into the “closed shell” of the \( \text{CH}_5^+ \) sphere. It is also in accordance with the barrier predicted by \textit{ab initio} calculations. For more details, see ref. 37, and references therein.

As mentioned above, reaction (6) is thought to be slightly exothermic.\(^3\) It is therefore surprising that the rate coefficients for the reverse reaction,

\[
\text{CH}_5^+ + \text{H} \rightarrow \text{CH}_4^+ + \text{H}_2 \quad (9)
\]

which has been studied also in a drift tube by injecting mass selected ions and H-atoms, are so large that, at room temperature, destruction of \( \text{CH}_5^+ \) via reaction (9) is almost ten times faster than formation via reaction (6). The experimental findings, especially the energy dependence, have been explained by Federer et al.\(^5\) with the argument that reaction (6) is exothermic but endoentropic. Meanwhile, reaction (9) and also \( \text{CH}_5^+ + \text{D} \) have been studied in a newly developed apparatus combining a temperature variable hydrogen atom beam with a 22-keV ion trap.\(^4\) Rate coefficients of \( 10^{-11} \text{ cm}^2 \text{ s}^{-1} \) have been measured for reaction (9) at 10 K, which indicates an endo-ergicity much smaller than 5 \( \text{kJ} \text{ mol}^{-1} \) as derived in ref. 39. Problematic in the low temperature trapping experiment may be the fact that the \( \text{CH}_5^+ \) ions which are formed in an external storage source, have been relaxed so far only in collisions with He. There are certainly enough collisions that the translational degrees of freedom and soft vibrations are thermalized to the 10 K environment; however, the resulting population of the internal states of the ions is correlated with the total nuclear spins \( I = 1/2, 3/2 \) and 5/2 which are most probably populated with their 300 K statistical weights. A detailed analysis accounting properly for all states involved should be possible today with the detailed information which is available for \( \text{CH}_5^+ \). It is also hoped that the exact thermochemical data for reaction (9) are soon known well enough that one can decide whether hydrogen atoms destroy \( \text{CH}_5^+ \) in interstellar clouds. This information is also of interest for deciding whether H atoms are a suitable chemical sensor for laser probing of ultracold \( \text{CH}_5^+ \).

Another method to probe the structure or internal energy of \( \text{CH}_5^+ \) ions is the energy dependence of the radiative association reaction

\[
\text{CH}_5^+ + \text{H}_2 \rightarrow \text{CH}_5^+ + \text{hv} \quad (10)
\]

as well as ternary and deuterated equivalents. The rate coefficient for reaction (10) has been measured to be \( k_1 = 4.4 \times 10^{-14} \text{ cm}^3 \text{ s}^{-1} \) and \( k_2 = 9.0 \times 10^{-15} \text{ cm}^3 \text{ s}^{-1} \) for \( \text{p-H}_2 \) and \( \text{n-H}_2 \), respectively. Comparison of these results with ternary rate coefficients allows the conclusion that collision complexes are formed with lifetimes of several ns corresponding to thousands of vibrational periods. Since there is no scrambling at all, as discussed above (reaction (8)) the collision complex must be considered as a cluster ion where the additional \( \text{H}_2 \) or \( \text{HD} \) molecule is bound only by a rather weak van der Waals forces to the central \( \text{CH}_5^+ \) ion core. In this case, it is obvious that the inner and outer binding sites for hydrogen are not equivalent at all. It may be that the presence of the outer molecule in the collision complex leads to such a structural rearrangement of the \( \text{CH}_5^+ \) that exchange becomes even more restricted. This idea is corroborated by the infrared spectra and calculations of \( \text{CH}_5^+ - (\text{H}_2)_n \) which indicate that the presence of solvating \( \text{H}_2 \) leads to a more rigid structure of the \( \text{CH}_5^+ \) core.\(^3\) This leads finally to the interesting question whether there is any chance that a stable stored \( \text{CH}_5^+ - \text{HD} \) cluster ion isomerizes spontaneously to the energetically favored \( \text{CH}_4\text{D}^+ - \text{H}_2 \) structure. The simple process of collision induced braking of the van der Waals bound could reveal such exchange processes and help to find reaction pathways which may need seconds or even minutes instead of ns.

**Conclusion**

This contribution clearly reveals that there are many experimental techniques available today for getting detailed insight into collision dynamics involving the protonated methane; however, it also is rather certain that \( \text{CH}_5^+ \) is too complicated for extracting directly detailed information on its structure from quantities such as rate coefficients, integral cross sections or even a complete scattering diagram. Evidence has been provided that the comments of Kramer\(^11\) made in connection with the ICR experiment of Heck et al.\(^12\) are not corroborated by any of the recent experiments. Nonetheless, there are many interesting new experimental results which contribute to our understanding of the properties and behavior of this fundamental ion. An astonishing result is that, despite the fact that it is very fluxional and that the five protons can scramble in a wide phase space, this ion survives millions of collisions with...
HD without exchanging an H for a D. Other results presented show that isotope exchange observed at low temperatures is a very sensitive chemical sensor due to zero point energies; however one has to be aware that the outcome of a scrambling reaction is not necessarily determined by the asymptotic energies. Often the dynamics are influenced by the shifts of zero point energies in transition states.\(^\text{27}\) In addition, one has to account in detail for the fact that partial substitution of hydrogen with deuterium atoms or tritium breaks the exchange symmetry and the restrictions imposed by the conservation of the nuclear spin.

The results presented in this paper indicate that some of the new experiments raise more questions than they answer; however it is hoped that they will also stimulate new experimental initiatives. For example, more work needs to be done in order to understand the formation, decay, isomerization, and deuteration of the (CH\(_4\)–H\(^+\))\(^+\) and (CH\(_2\)–H\(_2\))\(^+\) collision complexes formed at total energies of a few meV.\(^\text{41}\) Interesting new information can be expected from a dedicated research program devoted to synthesize CH\(_3^+\) via radiative or ternary association of CH\(_3^+\) + H\(_2\) and isotopic variants. It is rather certain that, although starting with a scattering state (energy continuum), very specific CD\(_2^+\)\(_\text{H}\) ions can be synthesized via radiative association, e.g. starting with ground state CD\(_3^+\) ions and O–H\(_2^+\)(J = 1). Looking at the details of the potential surface\(^\text{3}\) it can be presupposed that the rotational quantum number of the hydrogen molecule is conserved in an adiabatic transition into the essentially unhindered internal rotation of the diatom attached to the CD\(_3^+\) tripod via the 3c–2e bond. Note that internal relaxation of the molecule in collisions with He cannot change the total nuclear spin of the fermions, \(I = 1\).

What should be done in future experiments in order to learn more about the structure of the protonated methane ion or to solve similar questions in molecular physics? It is rather sure that methods such as Coulomb explosion or spectroscopy in He droplets always introduce perturbations and that, in general, one has to work with free unperturbed free ions. Considering the sensitivity of the methods available today, this restricts experiments to ion trapping combined with analytical methods such as collisional probing, the central subject of this paper. The sophisticated spectroscopic methods\(^\text{5}\) which are usually based on absorption of light are at their sensitivity limits, e.g. such as CH\(_3^+\).\(^\text{42}\) In contrast, it has been demonstrated in several recent experiments\(^\text{43–45}\) that the method of laser induced reactions needs only a few hundred ions for getting spectral and dynamical information. Choosing low temperatures and a suitable reaction one can record a spectrum almost without background by counting the light induced products as a function of wavelength. Overtone excitation followed by a suitable reaction may be a rather general solution for characterizing low lying states of really cold ions. The power of such an approach has been proven by probing trapped H\(_3^+\) ions stored in Ar.\(^\text{46}\) Very recently, in this field has been demonstrated by recording the first IR overview spectrum for free CH\(_3^+\)\(^+\) using proton transfer to CO\(_2\) in a 22-pole arrangement at 110 K.\(^\text{47}\) Although this information can be expected from a dedicated research program on the large amplitude motion in CH\(_5^+\) experiment is a big step forward, the results seem to corroborate Bunkers remark (ref. 10) that first millimeter-wave spectra should be recorded. They may then provide detailed information on the large amplitude motion in CH\(_3^+\) required for assigning finally internal motions described as C–H stretch or H–C–H bending vibrations.

This raises the question whether it is possible to detect a pure rotational spectrum of CH\(_3^+\) by inducing a reaction with a frequency in the region 220–235 GHz where the calculations predict the J = 1 ← 0 transitions. The answer is that it is a very challenging but realistic goal to develop a chemical probing method for distinguishing different rotational states of this floppy molecule. Based on the simple consideration that the photon energy \(h\nu\) and the ion temperature \(T\) should fulfill the condition \(h\nu > kT\), one has to produce very cold ensembles of ions. Temperatures of about 5 K have been reached today in rf ion traps applying He buffer gas cooling. It is planned to achieve sub-K conditions using a pulsed effusive beam of 4 K He or 10 K p-H\(_2\). Cutting off the fast part of the velocity distribution with a shutter—its time resolution is sufficient—the trapped ions can be cooled further down but interacting only with the very slow buffer gas. Another challenge is to find a collision process for chemical probing. Also for this purpose it is planned to use a suitable atomic (e.g. H-atoms) or super-sonic molecular beam and make use of well-defined reaction dynamics (velocity dependence, s-wave scattering, angular distributions). Suitable reactions (isotope exchange or radiative association) have been mentioned, another idea is to probe CH\(_3^+\) via resonant (or near resonant by using \(^{13}\)C) proton transfer to a supersonic beam of cold CH\(_4\) molecules.

It is rather certain that such detailed experiments, probing CH\(_3^+\) via collisions, will provide more information on this fundamental ion than obtained in the last 50 years. They may finally also provide spectral lines which can be compared with \(ab\) \(\text{initio}\) methods and which will tell us how the protons or deuterons are really swarming around the central carbon. Of course, such a research program would also contribute significantly to our understanding of ultracold collisions, of excitation processes under interstellar conditions and would help to identify interstellar molecules in the submillimeter range.

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