INTERACTIONS OF IONS WITH HYDROGEN ATOMS

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This progress report presents recent advances in developing a versatile technique for investigation of collisions of ions with open shell neutral intermediates. Combination of a 22-pole ion trap with a beam of H atoms allows accurate determination of rate coefficients at temperatures between 10 K and 300 K. New experimental results on hydrogen abstraction in collisions of CH, CH+, and CH2+ ions with H atoms are reported at temperatures between 10 K and 100 K. In the case of CH and CH+, large rate coefficients of 1.3 × 10^-9 cm^3 s^-1 and 6.0 × 10^-10 cm^3 s^-1 have been obtained at 50 K. CH reacts with D atoms with a total rate coefficient of 2.4 × 10^-9 cm^3 s^-1 the branching ratio being 50 % for hydrogen abstraction and 50 % for atom exchange. For collisions of CH2+ with H atoms rate coefficients of 9 × 10^-12, 1.3 × 10^-11, and 2.3 × 10^-11 cm^3 s^-1 have been determined at trap and nozzle temperatures of 10, 50, and 100 K, respectively. This indicates that this reaction is almost thermoneutral in contrast to thermodynamical data reported in the literature.

1. Introduction

Hydrogen, in the atomic or molecular form, is the most abundant species in interstellar clouds and therefore its interaction with other molecules, molecular ions and particle surfaces has to be carefully taken in account in order to understand chemical evolutions and explain observed abundances. The lack of specific information on its reaction dynamics lets plenty of related questions unanswered. For example it is still not yet known how the hydrogen molecule itself or more complex molecules like methanol are formed in space. Do processes in the gas phase or on particle surfaces play the dominant role? In many cases valuable information can be derived from observed abundances of molecules and structures of deuterated species. For this laboratory experiments are asked for to be performed at conditions relevant for interstellar space.

There are plenty of experimental results on reactions with molecular hydrogen. Unfortunately, radicals such as hydrogen atoms are not as simple to handle and, therefore, only few experiments with H or D atoms have been performed in the gas phase. A general review of ion-atom reactions has been published.1 Except early ICR studies2 most experiments are based on the flow tube tech-
nique. Using the selected ion flow drift tube approach (SIFDT) reactions can be studied at superthermal energies. At temperatures down to 120 K ion – hydrogen atom reactions have been investigated by a variable temperature modification of the selected ion flow tube. However, no general low temperature reaction studies of ions with H atoms have been reported below 100 K.

In this progress report a general methodology is presented which combines a wide field free trapping technique for confining and thermalizing mass selected ions and an atomic hydrogen beam as target. It allows the investigation of reactions of H atoms with ions at temperatures lower than 10 K and can be extended to other radical atoms and condensable neutrals. Results are reported for three benchmark ion-atom reaction systems.

2. Experimental

Fig. 1 shows the novel experimental setup, the Atomic Beam 22-Pole Trap Apparatus (AB-22PT) that has been developed to study H-atom reactions with molecular ions. It is a combination of an effusive source of H / D atoms with a standard trapping apparatus consisting of an ion preparation unit, the central 22PT and an ion detection system. A thorough description of the used rf devices can be found in Refs. 7 and 8.

Primary ions are prepared in a standard storage ion source. CO$_2$ ions are generated directly by electron bombardment from carbon dioxide, both CH$^+$ and CH$_4^+$ from methane, while CH$_3^+$ is produced via the subsequent reaction CH$_4^+$ + CH$_4$ → CH$_5^+$ + CH$_3$. The ions are extracted from the storage ion source, mass filtered in an rf quadrupole, deflected by 90° in an electrostatic quadrupole bender, and injected into the 22PT. There they are stored for time between ms and some seconds. The translational and internal energy distributions of injected
ions accommodate to the cold 22PT environment, $T_{\text{ion}} = 10 \div 300$ K, via radiation and via collisions with buffer gas. In order to accelerate the thermalization process, Helium is introduced in a pulsed mode during injection of the ions. For $\sim 10$ ms, densities of some $10^{15}$ cm$^{-3}$ are achieved. In addition, Helium is let into the 22PT continuously. Typically the He densities, being between $10^{12}$ and $10^{13}$ cm$^{-3}$, are several orders of magnitudes higher than the density of particles from the beam source. After a certain reaction time, the ions are extracted from the 22PT, mass analyzed, and detected using single ion counting technique.

For dissociation of molecular hydrogen resp. deuterium a standard rf driven plasma source$^9$ is used. The generated hydrogen atoms pass through an temperature variable accommodator with 1.2 mm inner diameter and 22 mm length resulting in a translational temperature $T_H$. The effusive beam is skimmed and differentially pumped twice. Two hexapole magnets are used for guiding the H / D atoms (weak field seeking). The number density of H and H$_2$ and deuterated analogues in the interaction region has been determined using a calibrated universal detector based on ionization via electron bombardment at the 22PT position. Comparison of the densities measured with and without hexapole magnets reveals that the magnetic guiding field increases the density by more than a factor 10 at beam temperatures between $T_H = 35$ K and $90$ K. The maximal enhancement, a factor of 25, is reached at $60$ K.

Real in situ determination of atomic and molecular densities is achieved via the reaction of CO$_2$$^+$ with H / D and H$_2$ / D$_2$. At 300 K the rate coefficients for these reactions are known from previous studies. At low temperatures they have been measured carefully with the present AB-22PT. Density determination has been performed before and after each set of measurements with primary hydrocarbon ions. Therefore long time drifts of the discharge source can be excluded or corrected for. At $T_H = T_{\text{ion}} = 100$ K, effective H and H$_2$ densities of $10^9$ cm$^{-3}$ have been obtained typically. At temperatures around 22 K the H - H recombination on the accommodator surface is high and atom density is rather low, $10^7$ cm$^{-3}$. At the lowest temperature, $T_H = 12$ K, hydrogen condensate on the surface and the atom density increases to $2 \times 10^8$ cm$^{-3}$. If the 22PT is at lowest temperature of 10 K the H$_2$ background, $5 \times 10^7$ cm$^{-3}$, is rather low due to condensation. Using the described configuration of the AB-22PT, rate coefficients lower than $10^{-13}$ cm$^3$s$^{-1}$ can be determined. In order to further reduce the background of molecules, beam catchers based on effective cryo-pumping can be introduced.
3. Results and Discussion

3.1. \( \text{CH}^+ + \text{H}, \text{CH}^+ + \text{D} \)

From a fundamental point of view, the \( \text{C}^+ + \text{H}_2 \) collision system is one of the model systems for experimental and theoretical studies of the kinetics, dynamics, and energy requirements of endothermic ion-molecular reactions. Consequently, it has been the subject of numerous experimental and theoretical studies, see e.g. Ref. 10 and references therein. The reverse reaction

\[
\text{CH}^+ + \text{H} \rightarrow \text{C}^+ + \text{H}_2 + (0.398 \pm 0.003) \text{ eV}
\]

(1)

represents an important destruction mechanism of \( \text{CH}^+ \) the formation of which is poorly understood in diffuse interstellar molecular clouds. Simple models underestimate the observed abundances and, therefore, it is assumed that shock waves, turbulences or UV radiation must play a role. Until 1984 it was accepted that, at 100 K, the exothermic reaction (1) is slow, \( k = 2 \times 10^{-12} \text{ cm}^3\text{s}^{-1} \) and even slower at lower temperatures whereas phase space theory predicts that the rate coefficient can approach the Langevin limit of \( 2 \times 10^{-9} \text{ cm}^3\text{s}^{-1} \) at low temperatures.\textsuperscript{11} This was confirmed by experimental results obtained with the SIFDT apparatus.\textsuperscript{3, 12} The observed large rate coefficients and a negative temperature dependence indicates that the potential energy surface has no barrier or only a small one.

With the AB-22PT technique the rate coefficient for reaction (1) has been determined at 50 K and 100 K. For \( T_H = T_{\text{ion}} = 50 \text{ K} \) a rate coefficient of \( 1.3 \times 10^{-9} \text{ cm}^3\text{s}^{-1} \) has been obtained. At an accommodator temperature of 100 K and a trap temperature of 80 K, a value of \( 8.7 \times 10^{-10} \text{ cm}^3\text{s}^{-1} \) has been measured. Note that in this case the internal temperature of the \( \text{CH}^+ \) ion was somewhat smaller than the collisional temperature. The experimental and theoretical results are summarized in Fig. 2. The non-thermal results of SIFDT technique have been converted using the approximation \( KE_{\text{cm}} = \frac{3}{2} kT \), the validity of which has been shown for atomic ions in drift fields. However, the contribution of rotational energy of \( \text{CH}^+ \) can differ from translational energy and this may lead to differences in the “temperature” dependences. Our low temperature data which are close to Langevin limit show that there is no barrier that would significantly hinder the reaction. The theoretical values of phase space theory describe well the behavior of the reaction.\textsuperscript{11} Recent RIOSA-NIP calculations\textsuperscript{13} which account for all reactive channels including hydrogen atom exchange, show the correct temperature trend; however, they underestimate the measured
value by almost a factor 10. This indicates that more work needs to be done in order to understand low temperature processes from first principles.

Figure 2: Experimental and theoretical rate coefficients for the indicated hydrogen abstraction reaction.

The H - H exchange in CH⁺ + H collisions is thermoneutral and it can be expected, e.g. from phase space theory, that the rate coefficient is much smaller than C⁺ production which is exothermic. Using the isotopically labeled system CH⁺ + D both channels, hydrogen abstraction and atom exchange

\[
\begin{align*}
\text{CH}^+ + D &\rightarrow \text{C}^+ + \text{HD} + 0.434 \text{ eV} \\
&\rightarrow \text{CD}^+ + \text{H} + 0.046 \text{ eV}
\end{align*}
\]

can be distinguished. Also this system has been investigated in the trap at \( T_{\text{coll}} = 80 \text{ K} \). Surprisingly the same rate coefficient \((1.2 \pm 0.2) \times 10^{-9} \text{ cm}^3\text{s}^{-1}\), has been obtained for both channels indicating the importance of the atom exchange channel. It is obvious that more detailed theoretical studies are needed in order to understand the dynamics of this basic reaction system.

3.2. CH₄⁺ + H

An interesting reaction system which proceeds via the intermediate collision complex CH₅⁺ is

\[
\text{CH}_4^+ + \text{H} \rightarrow \text{CH}_3^+ + \text{H}_2.
\]
With the ICR technique,\(^2\) no hydrogen abstraction reaction has been observed with H and D atoms although this process is exothermic by 2.7 eV and formation of CH\(_5^+\) collision complex is as well exothermic by 4.6 eV. Note that the detection limit of the ICR experiment was 10\(^{-11}\) cm\(^3\)s\(^{-1}\).

Our investigations show that reaction (2) is highly reactive at low temperatures. The values 6.0 \times 10\(^{-10}\) cm\(^3\)s\(^{-1}\) and 5.1 \times 10\(^{-10}\) cm\(^3\)s\(^{-1}\) have been obtained at \(T_H = T_{ion} = 50\) K and at \(T_H = 100\) K and \(T_{ion} = 80\) K, respectively. Based on the Langevin limit, 2 \times 10\(^{-9}\) cm\(^3\)s\(^{-1}\), this means that every forth collision leads to reaction. Assuming that the rate coefficient obtained at 300 K by the ICR technique is correct, the reaction has very strong negative temperature dependence. This may be explained by the formation of a long lived CH\(_5^+\)\(^*\) complex in combination with a bottle neck hindering the transition towards the product channel. In order to make final conclusions on energetic and dynamics, additional measurements over the full accessible temperature range are planned.

\[ \text{Figure 3. Temperature dependent rate coefficients for forward (squares) and backward (circles) reaction } \text{CH}_4^+ + \text{H}_2 \leftrightarrow \text{CH}_5^+ + \text{H}. \]

### 3.3. \text{CH}_5^+ + \text{H}

An interesting reaction system including two fluxional CH\(_4^+\) and CH\(_5^+\) ions is

\[ \text{CH}_4^+ + \text{H}_2 \leftrightarrow \text{CH}_5^+ + \text{H} \quad (3) \]

It has been investigated in both directions by SIFDT technique\(^{12}\) in the regime from thermal (300 K) to 0.12 eV center of mass kinetic energy, \(KE_{cm}\). An exothermicity, \(\Delta H = 5\) kJ/mol, and an entropy change, \(\Delta S^0_{298} = 31\) Jmol\(^{-1}\)K\(^{-1}\) has been
derived for forward direction. From these results it has been concluded that reaction (3) is exoergic but endoentropic. Therefore the rate coefficient in backward direction, \( k_b \), should decrease steeply from \( 10^{-10} \text{ cm}^3\text{s}^{-1} \) at 20 meV (150 K) to \( 10^{-12} \text{ cm}^3\text{s}^{-1} \) at 8 meV (60 K) as indicated by the dotted line in Fig. 3. The rate coefficient in forward direction, \( k_f \), has been recently measured from 300 K down to 15 K using a 22PT, see full squares in Fig. 3.

In the present work, reaction (3) has been investigated in backward direction at 10, 50, and 100 K. The temperature of the accommodator has been set at the 22PT value except for the lowest temperature where only 12 K have been achieved. The rate coefficient, \( k_b \), increases slightly from \( 9 \times 10^{-12} \text{ cm}^3\text{s}^{-1} \) at 10 K to \( 2.3 \times 10^{-11} \text{ cm}^3\text{s}^{-1} \) at 100 K, see solid circles in Fig. 3. Approaching 300 K, \( k_b \) should increase significantly according SIFDT results. Our result at \( T_H = 100 \text{ K} \) and \( T_{\text{ion}} = 300 \text{ K} \), see open circles in Fig. 3, shows that \( k_b \) does not reach SIFDT value and therefore the internal temperature (\( T_{\text{ion}} \)) of CH\(_5^+\) does not influence reactivity significantly. The small variation of \( k_b \) with internal temperature of CH\(_5^+\) ions can be taken as an argument that a direct process is involved and the H atom impact determines predominantly the reactivity. It should be noted that this statement is based on both our and SIFDT results the difference between which may be also caused by experimental uncertainties. Our result at \( T_H = T_{\text{ion}} = 100 \text{ K} \) agrees with prediction done in Ref. 12 within the error of measurement whereas \( k_b \) does not drop significantly at lower temperatures as predicted. This indicates that the reaction is almost thermoneutral.

4. Conclusion

The presented results demonstrate that the combination of an rf ion trap with a neutral beam is a versatile tool for revealing information on reactions between ions and radical atoms at low temperatures. Using H or D atoms, the fundamental collision systems C\(^+\) + H\(_2\) or HD, CH\(_3^+\) + H\(_2\) and CH\(_4^+\) + H\(_2\) have been studied in detail in the reverse direction. A comparison of the experimental findings with theoretical results or expectations indicate that our understanding of these systems is still quite limited. Some of the observations can be explained with statistical models; however it is obvious that one has to account for nuclear spin restrictions which are known to be important in H and D atoms containing systems at low temperatures. For the simple tri-atomic CH\(_2^+\) and CHD\(^+\) collision system the measurements indicate that a statistical theory is not satisfactory. In order to account correctly for direct collisions, quantum mechanical calculations beyond the so far used approximations\(^ {13} \) are needed. Reactions which proceed via the CH\(_5^+\) intermediate may be described by statistical methods since already
the ground state of protonated methane is very fluxional and all H atoms are equivalent. This, however, does not explain the observed increase of reactivity by more than a factor 50 going from room temperature to 50 K. Predictions for the reactions occurring on the CH₆⁺ potential energy surface are handicapped by the fact, that already the asymptotic energies are uncertain. Besides that it is desirable to calculate correctly the actual phase spaces of the two competing channels CH₅⁺ + H and CH₄⁺ + H₂ at the temperatures of the present work. In contrast to the conclusions made in Ref. 12, it is expected that a low temperatures the formation of CH₅⁺ should be “exoentropic”.

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References