Ternary association of $H^+$ ion with $H_2$ at 11 K, experimental study

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Abstract. The rate coefficient of the ternary association reaction $H^+ + 2H_2 \rightarrow H_3^+ + H_2$ has been measured at a temperature of 11 K using a 22-foil ion trap. The measurements were made over the density range of $0.5 - 10 \times 10^{13} \text{ cm}^{-3}$ using normal hydrogen (with 1/4 p-H$_2$ and 3/4 o-H$_2$). We measured an apparent binary reaction rate coefficient and from the obtained linear dependence on the hydrogen density we calculated the ternary reaction rate coefficient $k_3 = (3 \pm 1) \times 10^{-29} \text{ cm}^3 \text{ s}^{-1}$. From the measured data we can deduce that there exists very slow radiative association with the rate coefficient of the order of $k_r \lesssim 3 \times 10^{-16} \text{ cm}^3 \text{ s}^{-1}$ at 11 K.

1 Introduction

Cations $H_3^+$ are important ions in many types of hydrogen containing plasmas including astrophysically relevant plasmas [1], hydrogen discharges, etc. As the simplest polyatomic molecule it serves as a benchmark for rigorous theoretical studies [2]. In plasmas containing molecular $H_2$ and molecular ions $H_3^+$ (but also ions HeH$^+$, ArH$^+$, etc.) the $H_3^+$ is formed predominantly via a fast proton transfer from $H_2^+$ to $H_2$ [3,4]. In addition, $H_3^+$ ions can be also formed via association of $H^+$ ions with $H_2$. The question is how probable it is in a certain plasmatic environment. We consider the following binary and ternary association processes with the rate coefficients $k_2$ and $k_3$, respectively:

$$H^+ + H_2 \xrightarrow{k_2} H_3^+ + h\nu, \quad (1)$$

$$H^+ + H_2 + H_2 \xrightarrow{k_3} H_3^+ + H_2, \quad (2)$$

If the collision complex is stabilized via emission of a photon we talk about radiative association, if the collision complex is stabilized via collision with a third body we talk about ternary association. As described in detail in [5], the ternary association is usually viewed as a process composed from two consecutive steps. In the first step a collisional intermediate complex is formed in a two-body collision of $H^+$ with $H_2$ and in the second step the complex is stabilized in a collision with neutral $H_2$. In this interaction, a part of the internal energy of the complex is removed and reverse dissociation toward reactants is closed (for a more general discussion and some examples see, e.g., Refs. [6,7]). If we realize the importance of $H_3^+$ ions it is surprising that there are only a few studies of a $H_3^+$ formation by the association of $H^+$ with $H_2$. In the case of radiative association it is partly because of experimental difficulty to measure rate coefficients ($k_r$) of the order of $10^{-16} \text{ cm}^3 \text{ s}^{-1}$ or lower [3,8]. To our knowledge this radiative association reaction was not studied systematically up to now, there are only some indications from studies of ternary rate coefficients [5]. These studies suggest that the radiative association has rate coefficient of the order of $\sim 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ at 80 K. We also have some preliminary data indicating that at 11 K the binary rate coefficient is of the order of $k_r \sim 2 \times 10^{-16} \text{ cm}^3 \text{ s}^{-1}$ [9]. Using available low temperature ion traps it is in principle possible to study the association reaction and measure the rate coefficients down to 10 K. The question is how radiative association will compete with ternary association at particular experimental conditions, bearing in mind that $H_2$ is used in ion source and it is difficult to reduce the partial pressure in the trap. Because up to now the radiative association was observed in a low pressure limit of more general association process [5,8], it is obvious to start with a study of the ternary $H_2$ assisted association process.

For over 35 years there were several studies of ternary association of $H^+$ with $H_2$. The ternary reaction rate coefficient at 300 K was measured by Graham et al. [10] and by Johnsen et al. [11] using hydrogen buffered drift tube experiments; the high pressure enables them to measure very small rate coefficients. Gerlich used the ring electrode trap experiment to measure the ternary rate coefficient at 80 K. This study and studies of several other
H$_2^+$ H$^+$

**Fig. 1.** (Color online) Schematic drawing of the 22-pole trap. From left to right: Produced H$^+$ ions are mass selected and injected into the trap. The inhomogeneous rf field (22 poles) confines the ions in radial direction, the positive potential on the ring electrodes at both ends of the 22 pole encloses the ions in axial direction. The ions are extracted and analyzed by the detector. The trapping volume and H$_2$ gas are cooled down to 11 K.

Associative ion-molecule reactions by using ion trap technique were described in the review by Gerlich and Horning [5]. They also gave a classical description leading to the conclusion that the overall association reaction can be described by an effective (apparent) binary rate coefficient, $k^* = k_1 + k_3[R]$, where [R] is the density of the stabilizing neutral reactant.

Concerning temperature dependence of rate coefficient of the ternary association process, in the first approximation we can refer to the treatment developed by Bates [12] and Herbst [13]. This treatment predicts that the rate coefficient of ternary association varies as

$$k_3 \sim T^{-l/(2+l)}$$

where $l$ is the number of rotational degrees of freedom of the separated reactants and $\delta$ accounts for the temperature dependence of the stabilization efficiency, see also references [6, 14]. Interesting question is how to account for reaction of atomic ion with molecule H$_2$ at low temperatures, e.g., at 10 K. A more realistic discussion should be based on the number density of the states of the formed intermediate complex, see discussion in reference [5]. The rate coefficient of association of C$^+$ with H$_2$ is nearly constant at temperatures below 40 K [5, 15]. Temperature dependence for the ternary association of H$^+$ with H$_2$ has to be measured. In the present paper we describe measurements of hydrogen assisted ternary association of H$^+$ with H$_2$ using the 22-pole ion trap at 11 K.

**2 Experiment**

In the present study, H$^+$ ions are produced in a storage ion source via an electron bombardment of hydrogen. The ions are mass filtered and injected into the 22-pole trap via electrostatic quadrupole bender (see Fig. 1). In the trap ions are confined in the nearly field-free effective potential created by the inhomogeneous rf field (for details see recent review [16]). The trap is surrounded by a copper box, mounted onto the cold head of a closed-cycle helium refrigerator (lowest temperature 10 K). Hydrogen gas is flowing to the trap through a pipe connected to the copper block. The translational energy (temperature) of the stored ions is coupled to the cold environment by inelastic collisions with hydrogen molecular gas. Figure 2 shows schematically the 22-Pole Trap Apparatus instrument used in the present study. For analysis, both primary and product ions are extracted, mass analyzed in the quadrupole mass spectrometer (QPMS) and counted. The pressure in the ion trap is measured by an ionization gauge which is calibrated by a spinning rotor gauge.

**3 Results and conclusions**

In the experiment the trap is periodically filled with H$^+$ ions and after certain reaction time the reactant and product ions are extracted from the trap, mass selected and detected. The relative number of ions in the trap is measured as a function of the storage time. It is relative because of mass discrimination of the extraction and detection system. There are two possibilities to obtain apparent binary reaction rate coefficient ($k^*$) from these data. The first possibility is to measure the decrease of the H$^+$ signal (decay curve); from this decrease the rate coefficient $k^*$ can be calculated:

$$k^* = \frac{-1}{[H_2]^l} \ln \frac{[H^+]_t}{[H^+]_0},$$

(3)
where \( t \) is storage time and \([H^+]_0\) is initial hydrogen ion density (at \( t = 0 \)). Molecular hydrogen density \([H_2]\) is homogeneous in the trap. Because \( k^* \) is a function of \([H^+]_0/[H^+]\), it is sufficient to measure relative density of \( H^+ \). The relative density of ions can be obtained by counting ions stored in the trap for the reason that the volume of the ion cloud is constant. The examples of measured decay curves are plotted in Figure 3. From the slope of the decay curves and corresponding hydrogen density the rate coefficient \( k^* \) has been obtained using formula (3).

This procedure is used in studies of fast reactions. The disadvantage is that decay can be influenced by eventual impurities in the reactant gas. For slow reactions it is more convenient to obtain the reaction rate coefficient by measuring initial density of reactant ions and increase of product ions densities. The rate coefficient is then given by the formula:

\[
k^* = \frac{1}{[H_2]_0 t} \ln \frac{[H^+]_0}{[H^+]_0 - [H_3^+]}.
\] (4)

The examples of the measured time evolutions of relative densities of primary ion (\( H^+ \)), product ion (\( H_3^+ \)) and secondary product ions (\( H_5^+ \) and \( H_7^+ \)) in the trap are plotted in Figure 4.

Obtained apparent binary rate coefficients measured at different hydrogen densities are plotted in Figure 5 together with previous data obtained in a drift experiment at 135–300 K [11] and data measured with a ring electrode trap at 80 K [5]. From the linear slope a ternary rate coefficient can be evaluated. Open diamonds indicate values derived from the decay of the number of primary ions. Closed circles represent values evaluated from \( H_3^+ \) relative density increase after the correction for mass discrimination. Previous results from Johnsen et al. [11] and Gerlich and Horning [5] at different temperatures are also included.

Further temperature variable measurements in our group are in progress.

From the plotted data we can conclude, that radiative association is rather slow, also at 11 K. A detailed analysis of the data allows the conclusion that the rate coefficient is of the order of \( k_r \lesssim 3 \times 10^{-16} \text{ cm}^3 \text{ s}^{-1} \). As was already mentioned we have some preliminary studies (see [9]) made at very low hydrogen densities and these are in agreement with this value. This is comparable with earlier value obtained at 80 K [5].

In this contribution we report the first results for the ternary association of \( H^+ \) in a pure hydrogen environment measured in a 22-pole ion trap at 11 K. Normal hydrogen
(with 1/4 \(p\)-H\(_2\) and 3/4 \(o\)-H\(_2\)) was used in the present experiment; such hydrogen is not in thermal equilibrium at 10 K. It is very probable that the studied reaction is sensitive to the relative population of \(p\)-H\(_2\) and \(o\)-H\(_2\) states at low temperatures (see, e.g., [17]). Further studies covering extended range of hydrogen densities and temperatures are in progress. State sensitive studies using para enriched hydrogen are in preparation.

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