Radiative association of H$^+$ and H$_2$ – experimental study

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Abstract. The radiative and ternary association reaction of H$^+$ ions with H$_2$ was studied using a 22-pole RF trap. An overall effective binary rate coefficient ($k_{\text{eff}}$) was measured over a broad range of hydrogen densities to determine contributions from the binary and ternary process. The binary rate coefficient of the radiative association was measured for temperature 11–28 K at hydrogen density where ternary process can be neglected. The obtained binary rate coefficient of the radiative association at 11 K is $k_r(11 \text{ K}) = (1.7 \pm 0.5) \times 10^{-16} \text{ cm}^3 \text{s}^{-1}$.

1. Introduction
The presented studies were motivated by the fundamental character of processes, in which H$_3^+$ ions are formed, or where they excite or recombine [1,2,3,4,5], and by importance of H$_3^+$ ions in astrophysics [6,7,8] and plasma physics in general. The most elementary and fundamental interaction between ion-molecule processes is the interaction of proton with H$_2$ molecule. This process was studied many times theoretically, particularly because of large probability of conversion of ortho-H$_2$ to para-H$_2$ and vice versa in their interaction with proton (see e.g. refs. [9,10]). The number of previous studies of association of H$^+$ with H$_2$ and formation of H$_3^+$ ions is nevertheless very small. This is very surprising, if we realize the fundamental character of this association process and the importance of H$_3^+$ ions in plasmas, where ion can transfer proton to other atoms or molecules because of low proton affinity of H$_2$ molecule H$_3^+$ [11].

Association reactions stabilized by radiation or by collision with a third particle are important processes in low temperature plasmas. It is now also generally accepted that binary radiative association is an important process in formation of complex molecules in interstellar clouds [12,13,14,15]. There are also many studies of clustering ternary association reactions and reverse collision induced dissociation processes carried out in order to obtain enthalpies of formations and information on structure of complex ions [16,17]. Hydrogen containing plasmas are environment where these processes play important role, e.g. reactions forming H$_3^+(H_2)_n$ cluster ions [18]. For more detail and some experimental results see review by D. Gerlich and S. Horning in ref. [19], where the results of several studies of binary and ternary association reactions are presented and discussed.

The association of H$^+$ with H$_2$ can have two channels in hydrogen containing plasma:

\[ \text{H}^+ + \text{H}_2 \rightarrow \text{H}_3^+ + h\nu \quad (1) \]

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where $k_r$ and $k_3$ are the binary and ternary association rate coefficients, respectively. At higher hydrogen densities, where both channels can play an important role we can expect dependence of the overall effective binary rate coefficient ($k_{\text{eff}}$) on $H_2$ number density: $k_{\text{eff}} = k_r + k_3[H_2]$. The ternary process (2) was studied at 80 K by Gerlich (ring electrode trap experiment [19]). The ternary rate coefficient at 300 K was also measured by Graham, et al. [20] and by Johnsen, et al. [21] using hydrogen buffered drift tube experiments. Only very recently we studied ternary association at 11 K using 22-pole ion trap [22]. To our knowledge the radiative association of $H^+$ with $H_2$ was not systematically studied up to now. There are only some indications from the studies of ternary process at 80 K [19] leading to the rate coefficient $k_r(80 \text{ K}) \sim 1.3 \times 10^{-16} \text{ cm}^3\text{s}^{-1}$. Temperature dependence of both processes, as well as their dependence on para/ortho form of $H_2$ was not measured up to now. In the present paper we describe study of radiative association of $H^+$ with $H_2$ using the 22-pole ion trap at temperatures 11–28 K.

2. Experiment

The radiative association of $H^+$ with $H_2$ is a very slow process. As we will show later on, at temperatures ~11 K the binary rate coefficient is of the order of $k_r \sim 10^{-16} \text{ cm}^3\text{s}^{-1}$. The measurement of a rate coefficient of such slow process requires a special experimental arrangement. The level of reactive impurities in a gas in a reaction volume has to be below 0.1 ppm. Fortunately, the reaction with He is apparently very slow and other impurities with the exception of HD and $D_2$ are mostly frozen out at 11 K.

To study the mentioned process of radiative association and to measure the reaction rate coefficient we used 22-pole RF ion trap. The details and the principle of ion traps were described elsewhere (see e.g. refs. [23]). Here we will only give a short description of the actual trap and of the apparatus. In the present experiment, the 22-pole is immersed to a massive copper chamber, which is connected to a cold head of a thermostat (the closed-cycle helium refrigerator). The trap can be filled with hydrogen or helium, which is in thermal equilibrium with the walls. The trapped ions are cooled by collisions with cold buffer gas. Gerlich described the principle of the experiment, the details of the used 22-pole trap and the constructions of apparatus in several comprehensive reviews [24,25]. The arrangement of the trap used in the present experiment is shown in figure 1.

Figure 1. The principal scheme of the 22-pole RF ion trap. $H^+$ ions produced in the ion source are injected via the quadrupole bender into the 22-pole RF trap [19,23,24]. The positive potential on the ring electrodes at both ends of the 22-pole is used to trap ions in the axial direction. By lowering the potential on the output electrode, the trapped ions leave the trap towards the mass spectrometer and the detector. The trapping volume and $H_2$ gas can be cooled down to 11 K.

Figure 2 shows schematically the 22-pole trap apparatus used in the present study. $H^+$ ions are produced in the storage ion source via electron bombardment of hydrogen. The ions are mass filtered and injected into the 22-pole trap via the electrostatic quadrupole bender. After the defined reaction time, both primary and product ions are extracted, mass analysed in the quadrupole mass spectrometer (QPMS) and counted. Hydrogen pressure in the ion trap is measured by an ionization gauge, which is
calibrated by a spinning rotor gauge. Normal hydrogen (with ¼ of para-H\textsubscript{2} and ¾ of ortho-H\textsubscript{2}) was used in the present experiments. The background pressure is lower than 10\textsuperscript{−7} Pa.

Figure 2. The experimental setup used in the present study. The ions are produced in the ion storage source from hydrogen [23]. After passing through the quadrupole mass filter, selected H\textsuperscript{+} ions are injected into the 22-pole trap via the electrostatic quadrupole bender. The 22-pole trap is situated in the central chamber (22PT). After defined reaction time, the ions are extracted from the trap, analysed by the second quadrupole mass spectrometer and detected by MCP.

The injected H\textsuperscript{+} ions can be stored in the trap up to several seconds and during this time they react with the present hydrogen gas. The product ions are also stored in the trap. The relative number of primary ions (H\textsuperscript{+}) and product ions (H\textsubscript{3}\textsuperscript{+}) can be measured after the opening of the trap. The product ions can further react with H\textsubscript{2} and the secondary product ions are formed. The example of the obtained mass spectra is shown in figure 3. High sensitivity and high resolution of mass spectrometer and detection system is obvious. We observed H\textsuperscript{+} and H\textsubscript{3}\textsuperscript{+} ions and the secondary products H\textsubscript{5}\textsuperscript{+}, H\textsubscript{7}\textsuperscript{+} and H\textsubscript{9}\textsuperscript{+}.

Figure 3. Typical mass spectrum of the ions trapped in the 22-pole ion trap measured at 950 ms after the injection of H\textsuperscript{+} ions. The spectrum was measured at 11 K and at H\textsubscript{2} density [H\textsubscript{2}] = 1\times10\textsuperscript{14} cm\textsuperscript{−3}. Spectrum confirms trapping and detection of ions of mass 1–9 amu. Note that the ions of mass 2 and 4 were not present in the trap; this indicates that deuteration is not playing significant role at used conditions.

3. Results and discussion
We measured the effective binary rate coefficient \(k_{\text{eff}}\) of the reaction of H\textsuperscript{+} ions with H\textsubscript{2} as a function of H\textsubscript{2} density. In the actual experiment \(k_{\text{eff}}\) was measured from the decay of number of the H\textsuperscript{+} ions in the trap or from the increase of the number of H\textsubscript{3}\textsuperscript{+} ions produced in the trap. Assuming linearity of the detection system at low ion densities, it is sufficient to measure “ion counts” detected by the detection system, because only relative number of ions in the trap is required to determine the effective rate coefficient.

\[
k_{\text{eff}} = \frac{1}{t[H_2]} \ln \frac{N_{H^+}(0)}{N_{H^+}(t)}
\]

(3)
where we use: \( t \) – trapping time, \( N_{\text{H}^+}(0) \) – number of \( \text{H}^+ \) ions injected into the trap, \( N_{\text{H}^+}(t) \) – number of \( \text{H}^+ \) ions extracted from the trap after a trapping time \( t \). Note that in formula (3) only the ratio of the initial and final number of ions is required. Examples of a decrease of the number of \( \text{H}^+ \) ions in the trap measured at three different \( \text{H}_2 \) densities are shown in figure 4.

![Figure 4](image_url)

**Figure 4.** The typical decrease of the number of ions \( \text{H}^+ \) in the trap due to the reaction with \( \text{H}_2 \). The initial number of ions is normalized to 100 as it is a typical initial number of ions attained in our experiment. The rates of the decays depend on the actual \( \text{H}_2 \) number density in the trap.

We used also similar method, where rate coefficient is obtained by monitoring the number of produced \( \text{H}_3^+ \) ion and decay of number of \( \text{H}^+ \). This requires determination of the mass discrimination of the mass spectrometer and the detection system. The mass discrimination was determined by the measurements at high hydrogen densities. The measured dependence of \( k_{\text{eff}} \) on hydrogen density in the trap volume (at 11 K) is plotted in figure 5. The value of \( k_{\text{eff}} \) is increasing with increasing hydrogen density; this indicates substantial contribution from ternary \( \text{H}_2 \) assisted association process. At hydrogen number densities \( [\text{H}_2] < 10^{12} \text{ cm}^{-3} \), the dependence is levelling to \( k_{\text{eff}} \sim 1.7 \times 10^{-16} \text{ cm}^3 \text{ s}^{-1} \). This clearly indicates domination of radiative association at low hydrogen densities. The obtained dependence is fitted with function \( k_{\text{eff}} = k_r + k_3[H_2] \).

![Figure 5](image_url)

**Figure 5.** The dependence of the effective binary association rate coefficient \( k_{\text{eff}} \) on hydrogen density measured at 11 K. The dashed line indicates the fit of the data by function \( k_{\text{eff}} = k_r + k_3[H_2] \). The straight lines indicate contributions from the radiative \( (k_r) \) and ternary channel \( (k_3[H_2]) \). Note that at the hydrogen densities below \( 1 \times 10^{12} \text{ cm}^{-3} \) the influence of the ternary channel is very small and we can measure the rate coefficient of the radiative association directly. The obtained value is \( k_r(11 \text{ K}) = (1.7 \pm 0.5) \times 10^{-16} \text{ cm}^3 \text{ s}^{-1} \).

To obtain temperature dependence of the rate coefficient of the radiative association we measure \( k_{\text{eff}} \) at \( [\text{H}_2] = 1 \times 10^{12} \text{ cm}^{-3} \) for several temperatures in the range 11–28 K. At fixed temperature 11 K and otherwise identical experimental conditions we also measured \( k_{\text{eff}} \) at several \( \text{H}_2 \) densities from 1 up to \( 3 \times 10^{12} \text{ cm}^{-3} \). The obtained data are plotted in figure 6.
The effective binary association rate coefficient \( k_{\text{eff}} \) measured at low hydrogen densities. Three sets of data are plotted. The first set (filled circles) was measured at 11 K over broad range of hydrogen densities (see also figure 5). The second set (open circles) was measured at \([\text{H}_2] = 1\times10^{12}\ \text{cm}^{-3}\) and several temperatures. The third set (crosses) was measured for several hydrogen densities at 11 K with otherwise identical experimental conditions. The dashed line indicates fit through the data from the first set (see data in figure 5).

![Figure 6](image生动和清晰描述了有效二元关联速率系数的测量。三组数据被绘制。第一组（实心圆圈）在11 K下测量了广范围的氢密度（见图5）。第二组（空心圆圈）在 \([\text{H}_2] = 1\times10^{12}\ \text{cm}^{-3}\)和几种温度下测量。第三组（交叉符号）测量了几种氢密度的11 K实验条件。虚线显示了第一组数据的拟合结果（见图5中数据）。

The temperature dependence of \( k_{\text{eff}} \) measured at low hydrogen densities is plotted in a log-log scale in figure 7. The measured \( k_{\text{eff}} \) is in a good approximation and equal to the rate coefficient of radiative association because the ternary association is negligible at such low hydrogen densities (see data in figures 5 and 6). The obtained data were fitted with power function – giving a straight line in a log-log scale. From the measured \( k_{\text{eff}} \) the rate coefficient \( k_2 \) can be obtained by correcting it for the contribution from the ternary process, i.e. by subtracting the value of \( k_3 [\text{H}_2] \) from the measured \( k_{\text{eff}} \). In the first approximation at \( T > 11\ \text{K} \), we can use the \( k_3 \) measured at 11 K. In this way we obtain the lower limit for \( k_c \), because we can expect that \( k_3 \) is constant or it is decreasing with increasing temperature. For the correction, \( k_3 = (3\pm1)\times10^{-29}\ \text{cm}^6\ \text{s}^{-1} \) was used. The dash dotted line in figure 7 represents the lower limit for \( k_c \).

We suppose that an influence of the ternary process will not increase with temperature. The dash dotted line in figure 7 represents the lower limit of \( k_c \).

![Figure 7](image展示了11 K下不同氢密度的温度依赖性。实心圆圈表示 \( k_{\text{eff}} \) 测量值。封闭圆圈表示从整个 \( k_{\text{eff}} \) 的依赖关系中获得的 \( k_c \) 值。虚线是最佳拟合的直线，对应于温度的 \( T^{-1} \) 依赖性。虚线点线代表 \( k_c \) 的下限（见正文讨论）。

4. Conclusion

We used the 22-pole RF ion trap to measure the temperature dependence of the radiative association reaction of H\(^+\) ions with normal \( \text{H}_2 \) at temperatures 11–28 K. Value obtained at 11 K is \( k_c (11\ \text{K}) = (1.7\pm0.5)\times10^{-16}\ \text{cm}^3\ \text{s}^{-1} \). To our knowledge it is the first time that the rate coefficient of the radiative association of H\(^+\) with \( \text{H}_2 \) was measured in this temperature range. The experiments covering broader range of temperatures and \( \text{H}_2 \) densities are in progress.
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