Association of H⁺ with H₂ at Low Temperatures

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Abstract. The reaction of association of H⁺ ions with molecular hydrogen was studied for hydrogen number densities in the range 10¹²–10¹⁴ cm⁻³. The radio frequency 22-pole ion trap cooled to the temperature 10–30 K was used in the experiments. The presence of binary and ternary channel of association reaction was observed. Measured rate coefficient of the ternary channel is \( k₃ = (3 ± 1) \times 10⁻²⁹ \text{ cm}^6\text{s}⁻¹ \), the rate coefficient of the binary channel is \( k_r = (2 ± 1) \times 10⁻¹⁶ \text{ cm}^3\text{s}⁻¹ \) at 11 K.

Introduction

The H₃⁺ ions are abundant in many dense and diffuse interstellar clouds [McCall et al., 1998], they are important for formation of complex molecules in the interstellar ionized medium [Oka, 2006]. Studies of the H₃⁺ formation and reactions of the H⁺ at astrophysically relevant conditions are necessary to understand formation and evolution of the first galaxies [Herbst, 2000]. Low concentrations and temperature range 10 – 30 K is inherent to the dense interstellar clouds.

The main reaction of formation of the H₃⁺ ions \( \text{H}_2^+ + \text{H}_2 \rightarrow \text{H}_3^+ + \text{H} \) is fast (rate coefficient is > 10⁻¹⁰ cm³ s⁻¹) and was studied with flowing afterglow technique [Glosik, 1994] and merged beams techniques [Lees and Roï, 1974]. The exothermic association reaction of the H⁺ ions with H₂ has no second particle in product to take out released energy that is why association is very slow. Only a few studies of reaction of H⁺ with H₂ at temperatures the 80–300 K were made [Gerlich et al., 1992a; Johnsen et al., 1976].

We consider two different reactions of H⁺ ions with H₂:

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

\[
\text{H}_3^+ + \text{H}_2 \rightarrow \text{H}_2^+ + \text{H}_2 \quad (2)
\]

These reactions require two steps – formation of excited (H₃⁺)* and its de-excitation to stable H₃⁺ ion prior to eventual dissociation of (H₃⁺)* back to reactants:

\[
\text{H}_2^+ + \text{H}_2 \rightarrow \left( \text{H}_3^+ \right)^* \rightarrow \text{H}_3^+ + \text{H} \quad (3)
\]

\[
\text{H}_3^+ + \text{H}_2 \rightarrow \left( \text{H}_3^+ \right)^* + \text{H}_2 \rightarrow \text{H}_3^+ + \text{H}_2 \quad (4)
\]

The decay of the H⁺ ion density in a hydrogen plasma can be described by the apparent binary rate coefficient: \( k = k_r + k_3 \). To determine the binary \( k_r \) and ternary \( k_3 \) rate coefficients, measurements at wide range of H₂ concentrations are needed.

The rate coefficient \( k_3 \) of the three-body association was measured in high pressure drift tube experiments by Graham et al. [1973] at 300 K and Johnsen et al. [1976] at 135–160 K and 300 K. Both radiative and ternary associations were studied at 80 K by Gerlich et al. [1992a] with the ring electrode trap.

The rate of reactions depends on probability of formation of metastable (H₃⁺)* complexes in collisions of H⁺ with H₂, on the lifetime of (H₃⁺)* and on the probability of deactivation of complexes to stable H₃⁺ ions.

Number of complexes can be estimated from the balance equation (H₃⁺)*:

\[
\frac{dN_{(H_3^+)*}}{dt} = k_{(H_3^+)*}, [H_2] - k_{H_3^+}, N_{(H_3^+)*}, [H_2] - \tau_d^{-1} + \tau_r^{-1} \quad (5)
\]

where \( k_{(H_3^+)*} \) – rate coefficient of formation of (H₃⁺)* in collisions of H⁺ with H₂, \( k_{H_3^+} \) – rate coefficient of de-excitation of (H₃⁺)* in collisions with H₂, \( \tau_d \) – dissociation lifetime (de-dissociation of (H₃⁺)*), \( \tau_r \) – radiative lifetime (de-excitation) of (H₃⁺)*. Re-dissociation of the metastable complexes is explained statistical Rice–Ramsperger–Kassel–Marcus quasiequilibrium theory [Rice and Ramsperger, 1928; Kassel, 1928]. Experimentally dissociation of (H₃⁺)* complexes were measured by Gerlich et al. [1992a].

Experimental

Experiments with ion traps are highly convenient for study of association reactions. In the experimental apparatus ions are confined in the radio frequency field of the 22-pole trap without collisions with the walls of...
Figure 1. Schematic diagram of the experiment. Produced H⁺ ions are guided to the ion trap and confined in the RF field for a defined time (the 22-pole ion trap can be cooled down to 10 K). Reactant gas (H₂) is flowing into the 22-pole trap and it is cooled to the temperature of the trap. After a defined reaction time the trap is opened and the primary and product ions are detected by a detector system.

Figure 2. The basic scheme of the apparatus used to study the ion–neutral reactions. The 22-pole ion trap (22PT) is mounted on the cold head of the cryogenic system. Ions are produced in the storage ion source, mass selected with quadrupole mass filter and guided into the trap. After extraction from the trap ions are analyzed with the mass filter and counted with the MCP ion detector.

the trap [Gerlich, 1992b]. The trapped ions interact with neutral gas (normal hydrogen in the present experiments) that is flowing into the trap (for details see Figure 1).

The trap is cooled down to 10.4 K with a closed cycle helium cryogenic refrigeration system, which consist of a water-cooled compressor and a cold head inserted to vacuum chamber. The temperature of the trap is measured by calibrated silicon diodes (Lakeshore DT-471-C4). To set the temperature the trap is heated up by a resistive wire placed on the top of the cold head. Normal hydrogen (with ¼ para-H₂ and ¾ ortho-H₂) can be either leaked into the trap directly or via the storage ion source chamber. Ions are produced in the ion source by an electron impact (Figure 2), then stored and at the beginning of the measurement guided by the mass-selective quadrupole into the 22-pole trap, where they are cooled down to the temperature of the neutral gas.

After defined time (trapping time) ions are released and guided through the second quadrupole mass filter to the ion detector (in the experiment the Daly type [Daly, 1960] and the microchannel plate (MCP) [Wiza, 1979] detectors were used). The apparatus is pumped to the UHV (background concentration of the gas in the 22-pole trap is < 10⁶ cm⁻³ at 11 K) with turbomolecular pumps mounted on chambers of the storage ion source, 22-pole trap and detector chambers. The concentration of H₂ gas inside the trap varies from 10¹¹ to 10¹⁴ cm⁻³. Hydrogen pressure in the ion trap is measured by an ionization gauge, which is calibrated by a spinning rotor gauge.

Measurement

In the experiment the apparent binary rate coefficient of the reaction \( k' \) was measured from the decrease of number of the H⁺ ions in the trap and from the increase of number of the H₃⁺ ions. The first method is applicable for high concentration of H₂ gas (see examples plotted in Figure 3). At low H₂ concentrations it requires a long reaction time; this makes it sensitive to eventual impurities in the reactant gas. Measuring of the decrease of the
H+ signal depends on the relative amount of H+ and it is insensitive to mass discrimination of detection system [Wood, 1978][Sreekumar, 2010]:

\[
k^* = \frac{1}{t[H_2]} \ln \frac{N_{H^+}(0)}{N_{H^+}(t)},
\]

(6)

\(t\)—trapping time, \(N_{H^+}(0)\)—number of H+ ions extracted from the trap after very short trapping time (immediately after their injection into the trap), \(N_{H^+}(t)\)—number of H+ ions extracted from the trap after a trapping time.

At low concentrations of \([H_2]\) the ternary channel is negligible and the slow radiative channel of reaction is dominant. The rate coefficient of the slow radiative association reactions can be measured by monitoring the increase of the number of the produced \(H_3^+\) ions. This method is more sensitive but mass discrimination needs to be taken into account:

\[
k^* = \frac{1}{t[H_2]} \ln \frac{N_{H^+}(0)}{N_{H^+}(0) - N_{H^+}(t)}.
\]

(7)

\(N_{H^+}(t)\) — number of H+ ions extracted from the trap after the trapping time \(t\). Processes of the decay and growth of the number of ions in the trap are compared in Figure 4.

Precision of the obtained \(k^*\) depends on the accuracy of the measurements of hydrogen concentration. For the same pressure in the 22-pole trap chamber the concentration of the \(H_2\) in the trap changes with the temperature. It also depends on used gas inlet and on pumping speed of turbomolecular pumps. The pressure was measured with the calibrated spinning rotor gas friction vacuum gauge connected directly to the 22-pole trap.

Accurate adjustment of the mass analyzing system is important for the detection of ions with the mass 1 amu (atomic mass unit). The resolution of the mass spectrometer is configured for light masses of ions (Figure 5). To reduce mass discrimination (lower sensitivity of the detection system for light masses) number of ions is counted at the maxima of the peaks.

**Figure 3.** Decay of the number of H+ ions inside the trap. Number of ions injected into the trap is normalized to 100 (typical initial number of ions). Data were measured with the 22-pole trap cooled down to 11 K at indicated \(H_2\) densities. The rate coefficient is calculated from the slope of the fitted straight line. The dependence of the decay rate on the concentration of hydrogen is obvious.

**Figure 4.** Measured decay of the number of H+ ions and growth of the \(H_3^+\) in the 22-pole trap at 11 K and \([H_2] = 1.0 \times 10^{14} \text{ cm}^{-3}\). The mass discrimination is already accounted. The initial number of the H+ ions is normalized to 100.
Figure 5. Mass spectra of ions extracted from the trap 950 ms after the injection of H\(^+\) ions into the trap (concentration of the H\(_2\) is 1.0 \times 10^{14} \text{ cm}^{-3} \). The mass filter is configured to recognize separate peaks of light masses of H\(^+\), H\(_3^+\), H\(_5^+\) and H\(_7^+\) ions. The distribution of the number of cluster ions H\(_{2n+1}^+\) is indicating that cloud of ions is approaching to the equilibrium.

Figure 6. Dependence of the apparent binary association rate coefficient on the concentration of H\(_2\). The open squares indicate the values measured from the decays of the relative densities of the H\(^+\) ions. The small full circles indicate the values measured from the growth of the H\(_3^+\) ions (the mass discrimination is accounted), the blue curve is the plot of the \(k^* = k_b + k_3[H_2]\) function.

The effective binary rate coefficients measured at hydrogen densities within the range of concentration 6 \times 10^{12} – 1 \times 10^{14} \text{ cm}^{-3} are plotted in Figure 6. Contribution from the radiative association is visible at low hydrogen concentrations. The ternary rate coefficient is obtained from the linear slope of the plot at high hydrogen concentrations; \(k_3 = (3 \pm 1) \times 10^{-29} \text{ cm}^3 \text{s}^{-1}\). The binary rate coefficients of the radiative association reaction determined from the fit of the data measured at 11 K is \(k_b = (2 \pm 1) \times 10^{-16} \text{ cm}^3 \text{s}^{-1}\).

Conclusion

The apparent binary reaction rate coefficients of the association reaction of H\(^+\) ions with H\(_2\) at 11 K has been measured for the wide range of hydrogen concentrations. The dependence of the apparent binary reaction rate coefficient on the hydrogen concentration has been measured. The linear increase shows that the ternary channel of the reaction predominates over the binary in the range of concentrations 2 \times 10^{13} – 10^{14} \text{ cm}^{-3}. From the measured dependence the rate coefficients of the binary and ternary channels were obtained.

Additional experiments covering broad range of temperatures and hydrogen pressures are in progress.

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