

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

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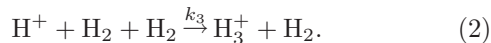
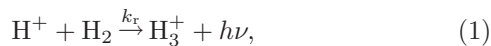
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Abstract. The rate coefficient of the ternary association reaction $H^+ + 2H_2 \rightarrow H_3^+ + H_2$ has been measured at a temperature of 11 K using a 22-pole ion trap. The measurements were made over the density range of $0.5\text{--}10 \times 10^{13} \text{ cm}^{-3}$ using normal hydrogen (with 1/4 $p\text{-}H_2$ and 3/4 $o\text{-}H_2$). 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 $k_3 = (3 \pm 1) \times 10^{-29} \text{ cm}^6 \text{ s}^{-1}$. 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_2^+ (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_r and k_3 , respectively:



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 [5,8]. 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 $\sim 10^{-16} \text{ cm}^3 \text{ s}^{-1}$ 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

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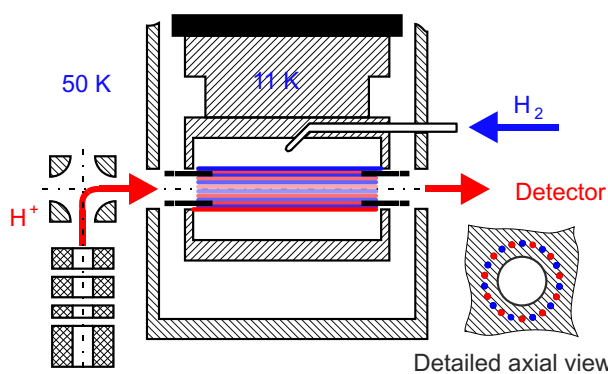


Fig. 1. (Color online) Schematic drawing of the 22-pole trap. From left to right: Produced H^+ ions are mass selected and injected into the trap. The inhomogeneous rf field (22 poles) confines the ions in radial direction, the positive potential on the ring electrodes at both ends of the 22 pole encloses 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, $k^* = k_r + k_3[R]$, 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 $k_3 \sim T^{-(l/2+\delta)}$, where l is the number of rotational degrees of freedom of the separated reactants and δ accounts for the temperature dependence of the stabilization efficiency, see also references [6, 14]. Interesting question is how to account l 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

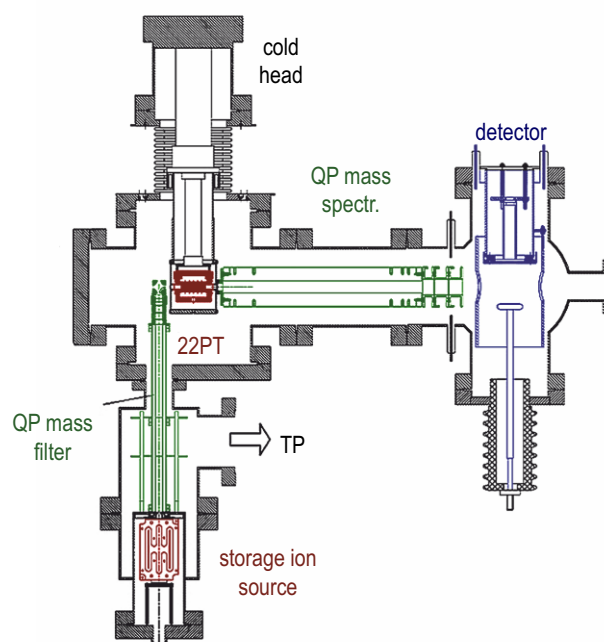


Fig. 2. (Color online) Experimental setup used in the present study. H^+ ions are produced in the ion storage source from hydrogen, selected by the quadrupole mass filter and injected to the 22-pole trap via the electrostatic quadrupole bender. The 22-pole trap is situated in the central chamber (22PT). Extracted ions are analyzed by the second quadrupole mass spectrometer and detected using Daly detector. The background pressure is lower than 10^{-7} Pa.

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:

$$k^* = \frac{-1}{[H_2]t} \ln \frac{[H^+]}{[H^+]_0}, \quad (3)$$

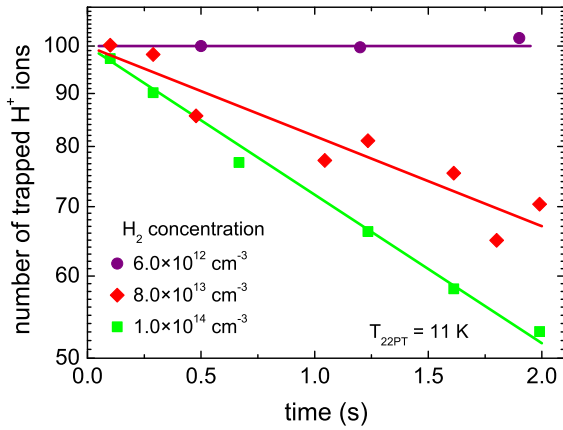


Fig. 3. (Color online) Time evolution of the number of trapped H^+ ions. The initial number of ions in the trap (at $t = 0$) is normalized to 100 which is close to the real number of ions in the trap. The decays were measured at 11 K and a dependency on H_2 concentration is evident.

where t is storage time and $[\text{H}^+]_0$ is initial hydrogen ion density (at $t = 0$). Molecular hydrogen density $[\text{H}_2]$ is homogeneous in the trap. Because k^* is a function of $[\text{H}^+]/[\text{H}^+]_0$, 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:

$$k^* = \frac{1}{[\text{H}_2]t} \ln \frac{[\text{H}^+]_0}{[\text{H}^+]_0 - [\text{H}_3^+]}. \quad (4)$$

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 of the plot a ternary rate coefficient can be evaluated according to the relation $k_3 = (k^* - k_r)/[\text{H}_2]$. The obtained ternary rate coefficient is $k_3 = (3 \pm 1) \times 10^{-29} \text{ cm}^6 \text{ s}^{-1}$. A small dependence of plotted ternary rate coefficients on temperature is interesting. Though the current ternary rate at low temperature is smaller than the previous data at higher temperatures, they agree well within the experimental errors of all experimental methods, probably pointing to a temperature independence (like in the case of $\text{C}^+ + \text{H}_2$).

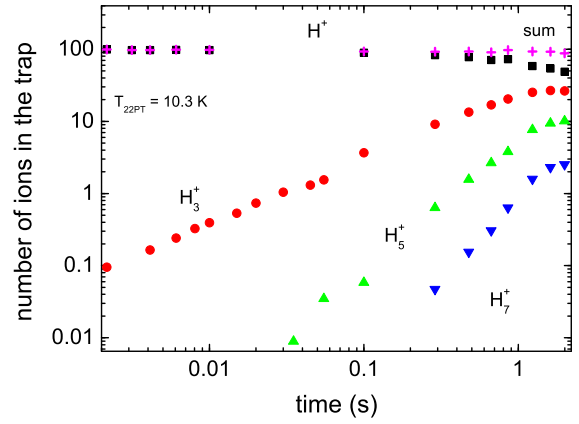


Fig. 4. (Color online) The measured evolution of the ion composition in 22-pole trap at 10.3 K and $[\text{H}_2] = 1.4 \times 10^{14} \text{ cm}^{-3}$. A mass discrimination is already considered. H_3^+ , H_5^+ and H_7^+ ions are produced in secondary reactions. The displayed ions are the only ones observed in the range 1–7 amu, i.e., we can exclude eventual influence of HD on measured decay of H^+ density.

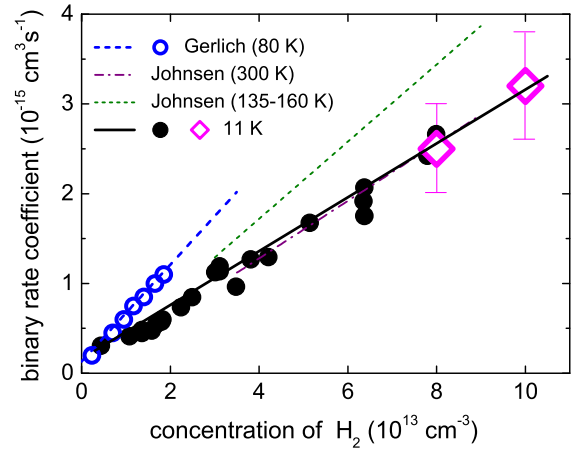


Fig. 5. (Color online) Apparent binary rate coefficient as a function of the number density of H_2 . From the linear slope a ternary rate coefficient can be evaluated. Open diamonds indicate values derived from the decay of the number of primary ions. Closed circles represent values evaluated from H_3^+ 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 -H₂ and 3/4 o -H₂) 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 -H₂ and o -H₂ 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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References

1. M. Larsson, A.E. Orel, *Dissociative Recombination of Molecular Ions* (Cambridge University Press, Cambridge, 2008)
2. C.P. Morong, J.L. Gottfried, T. Oka, *J. Mol. Spectrosc.* **255**, 13 (2009)
3. R. Plasil, J. Glosik, V. Poterya, P. Kudrna, J. Ruzs, M. Tichy, A. Pysanenko, *Int. J. Mass Spectrom.* **218**, 105 (2002)
4. J. Glosik, *Int. J. Mass Spectrom.* **139**, 15 (1994)
5. D. Gerlich, S. Horning, *Chem. Rev.* **92**, 1509 (1992)
6. J. Glosik, G. Bánó, E.E. Ferguson, W. Lindinger, *Int. J. Mass Spectrom. Ion Proc.* **176**, 177 (1998)
7. N.G. Adams, D. Smith, *Chem. Phys. Lett.* **79**, 563 (1981)
8. D. Gerlich, *J. Chem. Soc. Faraday Trans.* **89**, 2199 (1993)
9. Š. Roučka, P. Jusko, I. Zymak, R. Plašil, D. Gerlich, J. Glosik, in *18th Symposium on Application of Plasma Processes, Book of Contributed Papers*, edited by J. Orságh, P. Papp, Š. Matejčík (FMFI UK, Bratislava, 2011), p. 204
10. E. Graham, D.R. James, W.C. Keever, I.R. Gatland, D.L. Albritton, E.W. McDaniel, *J. Chem. Phys.* **59**, 4648 (1973)
11. R. Johnsen, C. Huang, M.A. Biondi, *J. Chem. Phys.* **65**, 1539 (1976)
12. D.R. Bates, *J. Phys.* **B12**, 4135 (1979)
13. E. Herbst, *J. Chem. Phys.* **70**, 2201 (1979)
14. N.G. Adams, D. Smith, *Int. J. Mass Spectrom. Ion Proc.* **81**, 273 (1987)
15. D. Gerlich, in *Molecules and Grains in Space*, edited by I. Nenner, 1st edn. (AIP Press, New York, 1994), pp. 489–500
16. D. Gerlich, in *Low Temperatures and Cold Molecules*, edited by I.W.M. Smith, 1st edn. (World Scientific Publishing, New York, 2008), pp. 121–174
17. W. Paul, B. Lücke, S. Schlemmer, D. Gerlich, *Int. J. Mass Spectrom. Ion Proc.* **149–150**, 373 (1995)