

Ion trap studies of H⁻ + H → H₂ + e⁻ between 10 and 135 K

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Abstract

Thermal rate coefficients for forming H₂ via associative detachment in H⁻ + H collisions were determined using the combination of a 22-pole ion trap (22PT) with a skimmed effusive beam of atomic hydrogen penetrating the ion cloud. The temperature of both reactants have been varied independently (ion trap: $T_{22PT} = 10$ K - 150 K, neutral beam accommodator $T_{ACC} = 10, 50, 120$ K). Using various combinations, the temperature range between 10 and 135 K has been accessed for the first time experimentally. The effective number density of H (typically some 10^8 cm⁻³) is determined *in situ* via chemical probing with CO₂⁺ ions. With decreasing temperature, the measured thermal rate coefficients decrease slowly from 5.5×10^{-9} cm³ s⁻¹ at 135 K to 4.1×10^{-9} cm³ s⁻¹ at 10 K. The relative error is 10 %, while the absolute values may deviate systematically by up to 40%, due to uncertainties in the calibration reaction. Significant improvements of the versatile and sensitive experiment are possible, e.g. by using electron transfer from H to D⁺ as calibration standard.

Keywords

H₂ formation, cold H atoms, rf-multipole ion trap, low temperature reactions, early universe chemistry

I. INTRODUCTION

The evolution of matter in the early universe towards the formation of the first stars is determined by atomic and molecular processes involving mainly hydrogen (H, D), helium (^3He , ^4He), electrons, and radiation. Traces of lithium and beryllium are assumed to play only a minor role. Since the elemental composition remains unchanged during this period, one could expect that primordial chemistry is rather simple. However, up to 200 reactions can contribute to the abundance of 23 atomic and molecular species as pointed out by Lepp et al. (2002). Important for star formation is the role of molecules as coolants, i.e. the conversion of translational energy into internal degrees of freedom via inelastic or reactive collisions, followed by radiative transitions.

There has been significant progress in improving the models which predict abundances of molecules and their role as coolants; however, in all these models, most chemical reactions are described just by simple temperature dependent rate coefficients whereas, in principle, one would need state to state cross sections (or elementary rate coefficients) for describing the non-equilibrium chemistry. An example of central importance is the scrambling reaction of H^+ with H_2 and isotopic variants. This collision system is very efficient in converting kinetic energy into internal excitation of the product molecule. Important for the spectrum of the emitted radiation is that not only vibration plays a role but that also rotational states are populated very efficiently to the limit given by the available energy. A recent extensive comparison between theoretical and experimental results for collisions of $\text{H}^+ + \text{D}_2$ and $\text{D}^+ + \text{H}_2$ corroborates this statement (Jambrina et al. 2012).

Several specific uncertainties in the reaction network describing the primordial chemistry have been discussed in recent years. A special problem is the efficiency to form H_2 , the most abundant molecule, and HD , which is important because it has a dipole moment (Glover et al. 2006). But also molecules such as H_3^+ and its isotopic variants or HeH^+ are considered to be important trace molecules and coolants (Glover & Abel 2008; Puy & Sinnore 2007). An interesting case is the HeH^+ ion. This ion (or He_2^+) is the first molecule, ever formed in the primordial universe and, in sequential collisions with H atoms, first H_2^+ and then H_2 is formed. A new ab initio calculation for the proton transfer rate coefficient in $\text{HeH}^+ + \text{H}$ recently lead to the conclusion that the abundance of HeH^+ is more than one order of magnitude higher than predicted before (Bovino et al. 2011).

Formation of a hydrogen molecule from two H-atoms under early universe conditions requires a catalytic gas phase reaction such as $\text{H}^+ + \text{H} \rightarrow \text{H}_2^+ + \text{h}\nu$ followed by $\text{H}_2^+ + \text{H} \rightarrow \text{H}_2 + \text{H}^+$. Besides the proton, an efficient catalyst is the electron, as soon as conditions are such that the life time of H^- gets long enough. The sequence is radiative attachment $\text{e}^- + \text{H} \rightarrow \text{H}^- + \text{h}\nu$ followed by associative detachment (AD)



Due to bound-free, free-bound and free-free transitions, the $(\text{H}-\text{e}^-)$ system plays an important role in the universe, for example for the continuum opacity of late-type stars or in establishing a thermal equilibrium in the photosphere of a star. Despite its abundance, H^- not yet has been observed directly via a specific transition (in the UV, see Ross et al. (2008) and references therein).

The central role of H^- in the primordial chemistry and consequences of uncertainties in several rate coefficients have been discussed by Glover et al. (2006) and Glover & Abel

(2008). Theoretical calculations for reaction (1) disagreed among each other in the range of 1 to $5 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ (Sakimoto 1989, Launay et al. 1991, Cizek et al. 1998). A few years ago, the only experimental results have been from flow tubes operated at room temperature and using two different schemes for producing the H-atoms (Schmeltekopf et al. 1967; Fehsenfeld et al. 1973; Martinez et al. 2009).

Meanwhile the situation has changed due to new experimental and theoretical activities. At Columbia University, Savin and coworkers have constructed a dedicated instrument based on the merged beams principle. Using a 10 keV fast H^- beam and converting a fraction of the ions into neutral atoms via photodetachment, reaction (1) could be studied at collision energies between 4 meV and 1 eV (Bruhns et al. 2010). Recently an extension to 4.8 eV has been reported by Miller et al. (2011). Despite the fact that the merged beams technology is rather complex and that the precise detection of the neutral H_2 products from reaction (1) is a challenge, rate coefficients have been determined with rather high accuracy, the total systematic error has been estimated to be only $\pm 24\%$ (Krekel et al. 2010; Bruhns et al. 2010; Miller et al. 2011).

The merged beams results are in very good agreement with calculated cross sections (Cizek et al. 1998) but there is still a discrepancy, not only with the above mentioned old flow tube measurements but also with recent rate coefficients determined at the University of Colorado, Boulder with a tandem flowing afterglow-selected ion flow tube (FA-SIFT) (Martinez et al. 2009). The old and the new flow tube measurements agree with each other; however, they are a factor of 2.2 ± 0.9 smaller than the recently slightly correct merged beams results (Miller et al. 2011). It has been suspected in (Bruhns et al. 2010) that the discrepancy may be due to an error in the AD calibration reaction $\text{Cl}^- + \text{H}$ used for determining the H atom density in the flow tube. Looking at the recent activities related to the specific reaction (1) and realizing that there are certainly more uncertainties in the models simulating the processes in the pregalactic era, it becomes obvious that more dedicated experimental activities are needed.

In the following, we report first results for reaction (1) obtained with an ion trapping instrument, a versatile method which is complementary to the two experimental methods mentioned above and which allows us to extend the temperature range down to 10 K. After a short description of the ion trap and the effusive H-atom beam, new data are presented with emphasis on the accuracy of the absolute values, achieved so far and on planned improvements, especially concerning the determination of the effective number density of the reactants. In the outlook we will mention other primordial reactions which can be studied using temperature variable ion traps and give a short summary to ongoing activities for detecting the electrons produced by reaction (1).

II. EXPERIMENTAL

22PT ion trap

The instrument used in this study was developed at Chemnitz University of Technology and is now operated successfully at the Charles University in Prague. It is based on the combination of a radio-frequency (rf) 22-pole ion trap with an effusive beam source for atomic hydrogen (AB-22PT). The method of using inhomogeneous rf fields for storing ions has been summarized in (Gerlich 1992). Technical details of the present experimental setup can be found in (Borodi 2008) and (Borodi et al. 2009). Previous studies of the interaction of stored CH_n^+ ions with H atoms have been reported in (Gerlich et al. 2011) and (Plasil et al. 2011).

The geometry of the region where the trapped ion cloud and the neutral beam interact is shown in some detail in Figure 1. The importance to determine the effective volume where the reactants overlap is discussed below. Primary H^- ions are produced by electron bombardment of H_2 precursor gas in a storage ion source (Gerlich 1992). After prethermalization in the source, the ions are mass selected using a quadrupole filter, bent by 90° using an electrostatic quadrupole and injected into the 22-pole trap. In radial direction the ions are confined by the rf field created by two sets of 11 poles (*RF1* and *RF2*) precisely mounted on both sides. The potential inside the trap can be corrected locally using the five ring electrodes (*RE*). The entrance and exit electrode (*EN* and *EX*) are used to open and close the trap with electrostatic barriers of some tens of meV. After various storage times the exit electrode is opened, the ions leave the trap, pass through the QP mass spectrometer, and they are converted into a short current pulse using a micro channel plate detector (MCP assembly F4655-12, Hamamatsu). The pulses are accumulated in a 100 MHz counter.

The standard sequence (i) filling the trap repetitively with a well-defined number of primary ions, (ii) storing them a for various times and (iii) detecting them is averaged over many iterations, for reducing the statistical errors. For comparison, the number of ions, $N_i(t)$, are normalized to one iteration or normalized to the total number of ions. In general, there is no loss of ions, i.e., the total *number per filling* remains constant. In the present experiment the charged products from the associative detachment reaction are electrons which cannot be detected in the current experimental setup. A method to guide them out from the rf field by superimposing a suitable magnetic field is under development.

The temperature of the ion trap, $T_{22\text{PT}}$, can be varied between 10 K and 300 K. Ions are cooled to the trap temperature by collisions with H_2 buffer gas. For relaxing the kinetic energy of H^- , a few collisions are sufficient. As discussed by Gerlich (1992) and emphasized in (Gerlich 2008a), the influence of the micro motion driven by the oscillating confining field - effects referred to as radio frequency heating - is negligible if high enough frequencies are used. Problems may be caused by potential distortions or parasitic low frequency fields.

Atomic Beam

H atoms are produced by dissociation of H_2 in an rf discharge operating at 0.2 mbar and a gas flow of 5×10^{-3} mbar l s^{-1} . For slowing down the gas emerging from the hot discharge, an accommodator is used the temperature of which can be tuned to $6 \text{ K} < T_{\text{ACC}} < 300 \text{ K}$. It consists of a channel in a copper block (2 mm diameter, length 22 mm) which is coated with a $\sim 50 \mu\text{m}$ thick layer of PTFE for reducing recombination. A mechanical shutter can block the H beam (beam ON or OFF). The geometrical arrangement of apertures and differential pumping ensures that a well collimated beam (divergence $< 1^\circ$) passes through the trap without hitting any surface. The grey shaded areas in Figure 1 indicate the overlap between the ion cloud and the neutral beam. The volume of the ion cloud is $\sim 1.5 \text{ cm}^3$, the interaction volume is about one quarter.

The actual velocity distributions of atoms and molecules emerging from the accommodator has been determined using time of flight measurements. The obtained distributions are in a good agreement with Maxwellians the actual temperatures of which are very close to the accommodator temperature. Deviations are less than 2 K or a few % whatever is larger. In deviation from the description in (Borodi et al. 2009), all measurements of this study have been performed without hexapole magnets for focusing the beam of H atoms. Although this leads to a much lower effective number density in the

trap (about one order of magnitude, see (Borodi et al. 2009)), it has the advantage that one can use flux conservation for absolute calibration, i.e., the total number of H flowing through the accommodator (as atom or in a molecule) remains unchanged if the discharge is switch on or off.

Typical raw data

Figure 2 shows a typical set of raw data. Plotted is the relative number of H^- ions per filling, $N(t)/N(0)$, as a function of trapping time. The repetition period was set to 1 s. The number of initially injected ions, typically 100 H^- per filling, is checked after 20 ms, when most of them already have been thermalized in collisions with ambient hydrogen. Typically H_2 densities have been 10^{12} cm^{-3} , mainly from the ion source gas. Also higher densities have been tested without any effect. Extracting the ions at later times reveals a more or less slow loss, depending on the temperature of the trap and on the presence of the H-atom beam (small symbols and dashed lines: beam OFF, large symbols and solid lines: beam ON). The data have been fitted with exponential functions, resulting in time constants τ longer than 1 min and shorter than 1 s (see numbers on the right side of Figure 2). Without H-atoms the slow loss of primary ions is caused by reactions with ambient background gas. At 11 K, cryopumping inside the trap leads to long storage times. For extending the measurements towards higher temperatures, better vacuum conditions are needed. The rate coefficients for reaction (1) are simply determined from the difference of the rates with the H beam ON and OFF and the effective number density of the H-atoms.

Effective number density

In order to extract absolute rate coefficients from the experiment, one has to account for the spatial distribution of the reactants and for their velocity distributions. Special aspects concerning kinematic averaging in neutral beam - ion trap arrangements can be found in (Gerlich 2008a; Gerlich 2008b; Gerlich & Borodi 2009). For determining the distribution of the relative velocity, it is safe to assume in the present arrangement that we have two ensembles, thermalized to T_{22PT} and T_{ACC} . In such a case the temperature (in the center of mass frame) is the mass weighted average of the temperature. For reaction (1) one gets

$$T = (T_{22PT} + T_{ACC}) / 2 . \quad (2)$$

Note that in our beam-trap arrangement reactions occur only in the nearly field free region, whereas, the target density goes to zero in regions of large amplitude micromotions. As indicated in Figure 1 it is straight forward to account for the spatial overlap, at least under ideal conditions, i.e., a well-skimmed neutral beam with a diameter of 4 mm, an angular divergence of 0.7 degree and a homogeneous density in the region of overlap, and an ion cloud the distribution of which is determined by the effective potential and the temperature of the ions. Some parameters relevant for trapping H^- can be found in Table 1. In axial direction, the electrodes EN and EX are used to close the trap with dc voltages. A few tens of mV are sufficient for confining the ions.

In reality the potential of the ion trap may be influenced by geometrical effects, by perturbations of the surface potential, or by other stray fields. Related experimental tests and strategies to avoid or reduce such effects have been discussed in (Gerlich 1992) and (Gerlich 2008a). An odd situation has been reported by Otto et al. (2009). The spatial distribution of the ion cloud on a 22-pole, imaged by photodetachment, showed 10 intensity maxima close to the rods. The origin of this effect can be explained by the superposition of a dipolar field, caused by a misalignment of the two sets of electrodes against each other. In our trap (see Figure 1) all 22 rods are localized rather precisely on

each end. Nonetheless we observed that, at lower temperatures, the ions spend more time close to the rods than predicted from calculations. Some tests have been performed via photodetachment (PD) with a 660 nm laser beam. Going from 100 to 10 K the PD rate dropped by 20% instead of an increase of 30% expected from the fact that colder ions are confined closer to the axis of the trap. This indicates that there are some forces attracting the ions towards the electrodes. Improvements are possible by cleaning or also by using the ring electrodes (*RE*, see Figure 1), if the perturbations are localized. An alternative solution is to use a reaction for calibrating the effective overlapping volume as described in the following.

Since it cannot be excluded that the ion distribution is affected by perturbations or that some H-atoms were hitting the surface of the entrance or exit electrode in the present experiment, we decided to determine the effective number density via chemical probing with CO_2^+ . This method has the advantage that it accounts automatically for the real overlap integral of the spatial distributions of ions and neutrals. As described by Borodi et al. (2009), collisions of CO_2^+ with molecular hydrogen lead to HCO_2^+ while collisions with H atoms produce HCO^+ . The rate coefficients for the last reaction are independent on the temperature of the CO_2^+ ions and on the velocity of the atoms. Borodi et al. (2009) recommend a value of $k(T) = 4.6 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ for H as target, and $2.2 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ for D. The uncertainty was conservatively estimated to be 40%.

In the present experiment the H-atom density was measured routinely between several runs at an accommodator temperature $T_{\text{ACC}} = 50 \text{ K}$, using the probing reaction. Depending on the conditions of the discharge tube, typical values of some 10^8 cm^{-3} have been obtained. The results have been corrected for the mass dependence of the effective potential which scales with $V_0^2/(m\Omega^2)$. Selected ion trap parameters used for CO_2^+ and H^- are given in Table 1.

III. RESULTS AND DISCUSSION

Rate coefficients for reaction (1) have been measured in several iterations and under various conditions as described above. Usually data were collected by holding the accommodator temperature fixed and by varying the 22-pole temperature between 10 and 150 K. Higher trap temperatures could not be used because of ion loss due to reactions with gas impurities. Figure 3 shows a collection of typical sets of data as a function of translational temperature, each of them covering a range of 70 K. As indicated, the different symbols correspond to $T_{\text{ACC}} = 10, 50, \text{ and } 120 \text{ K}$. The 50 K values are absolute based on the calibration reaction while the two other sets of measurements have been matched to them using the region where the data overlap. Higher temperatures T_{ACC} are possible; however, the dissociation degree of the H-atom source decreases (Borodi 2008). The overall trend is well reproduced accounting for the statistical uncertainties of each data point. All individual data were reduced by binning leading to the result plotted in Figure 4. The error bars represent the standard deviation of each data point. Not shown is the fact that there is a systematic uncertainty of 40%. As discussed above it is caused by the calibration reactions. Below 20 K the actual ion temperature may be higher by up to 5 degrees, at higher temperatures the error is less than 2%.

In the overlapping regime our results are in good accordance with the results from (Bruhns et al. 2010). For better comparison, their experimental results which have a total systematic uncertainty of 24%, are represented just by the solid curve taken from Figure 10 of (Bruhns et al. 2010). Note that this curve, showing the derived thermal rate coefficients, should be shifted up by 8.6 % according to a recent new evaluation (Miller

et al. 2011). For solving the discrepancy with the flow measurements, it is mandatory to extend the ion trap experiments to higher temperatures. This is possible by improving the vacuum conditions, e.g. by mounting the trap on a different support such that it can be baked. Alternatively, there is the possibility to create a fast beam of H atoms.

Inspection of Figure 4 reveals the good agreement of our data with the low temperature prediction of the two theories (Sakimoto 1989; Cizek et al. 1998). They are both based on the same interaction potential from (Senekowitsch et al. 1984) which is significantly more attractive than the polarization potential. A recent new calculation of the potential curve (Pichl 2005) agrees well and it is stated that further improvements have to account for correlation effects in the electron and proton motion. Sakimoto (1989) discusses convincingly the fact, that at energies below 0.1 eV, the rate coefficient for reaction (1) is determined just by a simple capture condition at large distances. During the succeeding approach of the two atoms, the probability to detach the electron is close to unity. From this point of view, our data may indicate that the potential is even more attractive at distances which are probed by 1 meV collisions (partial waves up to $l = 10$, turning point at distances larger than $10 a_0$).

For such conclusions, we have to reduce the uncertainties in the determination of absolute rate coefficients and in our temperature scale. This is possible by better characterizing the flux of the H-atom beam (see discussion by Borodi et al. (2009)) and by characterizing the ion cloud using photodetachment. The ions can be influenced by varying the effective potential and shifted with the correction electrodes. Cleaning the electrodes (stainless steel) always has some effect on potential distortions. Since a calibration reaction has a lot of advantages, it is also planned to establish the exothermic electron transfer from H to D^+ as one. Since this one-electron system is much better understood from first principles than the 3-electron reaction (1), it is ideal for determining the effective H density. Also the reverse process, the 3.70 meV endothermic electron transfer from D to H^+ is well characterized by theory (Esry et al. 2000). The threshold onset is a critical test of the instrument.

A final remark has to be made to reaction (1). Measured absolute integral cross sections (or rate coefficients) are in general a critical test for theory; however, in the present case the outcome of the $H^- + H$ collision is rather insensitive to the actual photo-detachment process occurring at distances of a few a_0 . A more sensitive experiment is to observe the competition between electron transfer and photodetachment in $H^- + D$ and $D^- + H$ collisions. Corresponding work is in progress. Most information on the details of the dynamics can be obtained by determining how the exothermicity of 3.724 eV is distributed among the degrees of freedom of the products, i.e., the kinetic energy of the electron and the rovibrational population of H_2 . The population of the rotational states is mainly determined by conservation of total angular momentum since only p-electrons are ejected. From this it can be concluded that, for example at a collision energy of a few meV (corresponding to $J_{MAX} \sim 20$), more than 1 eV goes into rotation of H_2 . The actual population of the vibrational states depends on the coupling in the collision complex. Interesting predictions already have been made by Cizek et al. (1998) (see Figure 5). Such information is certainly also of importance for cooling early universe matter.

IV. CONCLUSION AND OUTLOOK

Using the rf ion trapping technique and by exposing an H^- ion cloud to a cold effusive beam of hydrogen atoms, thermal rate coefficients for reaction (1) have been measured in a temperature range so far unexplored. The temperature dependence is in accordance

with simple theoretical predictions based on capture via the long range attraction. In the overlapping energy range, there is good agreement with the merged beams results reported by Krekel et al. (2010), Bruhns et al. (2010) and Miller et al. (2011). Due to our rather large systematic uncertainty, caused by the calibration reaction, our present results cannot solve the discrepancy between merged beams and flow tube results at 300 K (Martinez et al. 2009). Improving the accuracy of our instrument and going to higher temperatures will solve this problem. Work is in progress to use the electron transfer in $D^+ + H$ collisions as calibration standard.

The versatile instrument opens up new possibilities to study reactions which are of interest for early universe chemistry, or which are of central importance for testing fundamental theories. The need to determine state specific rate coefficients for $\text{HeH}^+(v=0,j) + H$ already has been mentioned in the introduction. Radiative association of two atoms, especially with H, is an experimental challenge. With today's technologies, it should be possible to detect HeH^+ from $H^+ + \text{He}$. Storing H^- and operating the beam source with deuterium will allow us to study the competition between electron transfer and associative detachment in $H^- + D$. Also mutual neutralization of H^- and H^+ can be studied in a trap since the effective potential is proportional to the square of the charge, i.e., the rf field confines simultaneously positive and negative ions.

A challenge for theoretical predictions for reaction (1) is an experiment which can determine the kinetic energy of the detached electrons and which provides information on the rovibrational population of the H_2 product. Simulations show that one can superimpose an rf field and a suitable magnetic field such that electrons are guided out of the trap and that one can detect them. Moreover the integration of an electron spectrometer using magnetic adiabatic collimation should be possible. Corresponding work is in progress.

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Figure captions

Figure 1: Detailed drawing of the central part of the 22-pole ion trap apparatus. H^- ions are injected into the trap via the electrostatic quadrupole bender. To the right, ions move via the quadrupole mass spectrometer towards the detector. The cold effusive H-atom beam comes from the left. The grey shaded areas indicate the overlap between the ion cloud and the neutral beam. For photo detachment studies, a laser beam is injected from the right.

Figure 2: Relative number of H^- ions per filling as a function of storage time (ion trap temperature: $T_{22\text{PT}} = 11$ and 103 K, hydrogen beam temperature $T_{\text{ACC}} = 50$ K, small and large symbols correspond to H atom beam OFF and ON, respectively). The statistical errors are in the order of or smaller than the size of the symbols. Fitting the data with $\exp(-t/\tau)$ (solid and dashed lines) leads to the time constants τ shown on the right.

Figure 3: Measured rate coefficients, shown as a function of the translational temperature. The data shown as squares, diamonds, and triangles have been measured at $T_{\text{ACC}} = 10, 50,$ and 120 K, respectively. Variation to $T_{22\text{PT}}$ between 10 and 150 K covers each time a range of 70 K (in the center of mass system).

Figure 4: Comparison of our ion trap results (squares, bars indicate the statistical errors, the systematic uncertainty is larger, see text) with previous measurements and results from theory. The solid line indicates the thermal rate coefficient $k(T)$, derived from the merged beams data published by Bruhns et al. (2010). The theoretical results of Sakimoto (1989) and Cizek (1998) are in good overall accord agreement while the Langevin limit and the 300 K flow tube measurements are significantly smaller (from left to right: Schmeltekopf et al. 1967, Fehsenfeld et al. 1973, Martinez et al. 2009, shifted for better readability,).

Tables

Table 1: Diameter of the ion cloud (d_1 for H^- and d_2 for CO_2^+ for different kinetic energies E of the ions calculated from the effective potential (Gerlich 1992). The 22-pole has been operated with $\Omega/2\pi = 18$ MHz and $V_0 = 50$ V and 25 V for mass 44 and 1, respectively. Note that the inner free diameter of the 22-pole is 10 mm. Assuming that the kinetic energy distributions of CO_2^+ and H^- are the same, the volume of the CO_2^+ cloud is about 1.27 times the volume of the H^- ions as can be seen from $(d_1/d_2)^2$, the ratio of the areas.

E / meV	d_1 / mm	d_2 / mm	$(d_1/d_2)^2$
100	9.21	8.17	1.271
10	8.21	7.28	1.272
1	7.32	6.49	1.272







