Reactions of Ions with Atomic Hydrogen – Experiment.

P. Jusko, Š. Roučka, R. Plašil, D. Gerlich, J. Glosík
Charles University, Faculty of Mathematics and Physics, Prague, Czech Republic.

Abstract. New experiment is designed and build to study reactions of positive and negative ions with atomic hydrogen at low collisional energies. In the experiment the beam of atomic hydrogen is passing through cloud of ions trapped in RF octopole. Basically the experiment consists from four parts: ion source, atomic beam source, ion trap and ion detector. We use the electron bombardment RF storage ion source with quadrupole mass spectrometer. Ions formed in the source are mass selected and injected to octopole, where they are trapped. In test experiments hydrogen gas is used to form anions $\text{H}^-$. In the atomic beam source $\text{H}$ atoms are created from molecular hydrogen in a RF discharge. The decrease of ion density in the trap due to interaction with $\text{H}$ atoms is monitored by MCP. In the paper details of experimental setup are given and results of test measurements are discussed.

Introduction

The aim of the presented study is design, construction and test of apparatus for measurements of rate coefficient of reaction:

$$\text{H}^- + \text{H} \rightarrow \text{H}_2^- \rightarrow \text{H}_2(v, j) + \text{e}^-(E) + 0.75 \text{ eV}. \quad (1)$$

This reaction (associative detachment) is believed to be one of the possible way to create molecular hydrogen in early universe (see Glover et al. [2006]). The reaction is also of fundamental interest for theoretical physics (e.g. Čížek et al. [1998]). The detailed description of the experiment was written by Roučka et al. [2009]. Here we are describing three major parts of the experiment: $\text{H}$ atom source, source of $\text{H}^-$ anions and ion trap, where $\text{H}^-$ will react with $\text{H}$.

The $\text{H}$ atom source will produce well collimated beam of low energy hydrogen atoms. The source of $\text{H}^-$ has to produce mass selected low energy anions. We will describe details of these two sources and results of their tests.

H atom source

Atomic hydrogen is produced by dissociation of molecular hydrogen in RF discharge in quartz discharge tube. Actually $\text{H}_2$ is flowing through the discharge region where it is dissociated and then the mixture of atomic and molecular hydrogen is flowing through the narrow tube (see Fig. 1 for details).

The temperature along the capillary drops from 300 K down to 10 K. Whole system is named accomodator and it is cooled by a cryogenic cold head. Surface and temperature of capillary inner walls are essential for degree of dissociation of gas flowing from the accomodator. PTFE coated surface is used. After the accomodator the beam of $\text{H}/\text{H}_2$ is formed by a skimmer.

In order to increase ratio between $\text{H}$ and $\text{H}_2$ in the beam a hexapole magnet is used to focus the $\text{H}$ atom beam. For the experiment the source has to be calibrated in order to get a correct number density of $\text{H}$ in the beam and the velocity distribution of $\text{H}$ atoms. Time of flight technique is used to measure $\text{H}$ atom velocity distribution. $\text{H}$ beam is chopped by a wheel and then at the end of a free path $\text{H}$ atoms are ionised and detected. A beam density can be characterised by using a ioniser for converting $\text{H}$ to $\text{H}^+$, or by a calibration reaction (see Borodi et al. [2009]).
Ions in RF field

In this article we are concentrating on ions in one special RF field geometry - two dimensional multipoles. These are usually build from $2n$ rods. In a configuration where we produce fast alternating voltages on a neighbours rods, we are able to create oscillatory field. Provided that the frequency is high enough, slow charged particles are able to see only a effective field created by this configuration. We use $V_0$ as amplitude and $\Omega$ to denominate angular frequency of a oscillatory voltage. $U_0$ stands for the DC potential on one of two rod systems:

$$\phi_0 = U_0 - V_0 \cos \Omega t. \quad (2)$$

Knowing these parameters, we can express the effective potential, which affects charged particles:

$$V^* = \frac{1}{8} qV_0^2 \frac{r^{2n-2}}{\varepsilon} + qU_0 r^n \cos n\varphi, \quad (3)$$

where

$$\hat{r} = \frac{r}{r_0}; \quad \varepsilon = \frac{1}{2n^2 m \Omega^2 r_0^2}. \quad (4)$$

In an actual experiment, we have to be careful when choosing operating parameters, in order to keep ions unaffected by RF field. In this situation parameter $\eta$ called adiabacity parameter is useful:

$$\eta = \frac{n - 1}{n} \frac{qV_0}{\varepsilon} r^{n-2}. \quad (5)$$

Operating conditions which fulfill $\eta < 0.3$ are optimal. More about this topic can be found in Gerlich [1992].

Quadrupole

Best known $2n$ pole is quadrupole with $n = 2$. This device can be fully described by introducing Mathieu’s parameters:

$$q_2 = 4 \frac{qV_0}{m \Omega^2 r_0^2} \quad \text{and} \quad a_2 = 8 \frac{qU_0}{m \Omega^2 r_0^2}. \quad (6)$$
This is the only 2\(n\) pole which has \(x, y\) motion independent, because of underlying differential equations, which becomes coupled for higher multipoles (see Gerlich [1992]). We could follow here to standard description of quadrupole as a mass filter tuned for one particular mass, instead we are going to focus on a less standard use of this instrument. The guiding ability of a quadrupole decreases with mass, thus we can use it as a low mass filter. Equation for a threshold condition can also be found in Gerlich [1992]:

\[
m < \frac{qV_0^2}{\Omega^2 r_0^2 U_0}.
\]  

Advantage of such approach is that quadrupole is operated in safe operating area.

An example of a low mass filter can be seen at Fig. 2(a). The data has been measured in the apparatus shown at Fig. 3. Same effect can be seen also in higher order multipoles. Example of low mass filtering in a storage ion source (see next section) can be seen at Fig. 2(b). In this case the quadrupole is set for mass one, and \(U_0\) in a storage ion source is changed.

![Graph](image)

(a) Quadrupole as a low mass filter for positive ions. Formed in storage ion source from \(\text{H}_2^+\). Operating conditions are \(V_0 = 35.5\) V and \(\Omega/2\pi = 7.6\) MHz. Values for threshold \(U_0\) voltages (see Eq. 7) are marked by dashed lines.

(b) Low mass filtering in a storage ion source (SIS). The output of the SIS is further mass selected to allow only mass one. Operating conditions of the SIS are \(V_0 = 14.5\) V and \(\Omega/2\pi = 19.2\) MHz

**Figure 2.** Effect of DC difference applied in multipoles. Due to complicated configuration in storage ion source we are unable to calculate threshold voltages.

**Experimental setup**

Experimental setup for a rate constant measurement (without the H atom source) is shown on Fig. 3. This setup consists from 3 RF devices (left to right on Fig. 3): Storage ion source (SIS), quadrupole (QP) for mass selection and octopole (OP) for anion confinement.

Anions are created by electron impact with a target gas in the SIS where they are stored using RF and stationary fields. Anions can be injected to the QP section for mass selection, from where correct mass can follow to the OP section. Here anions can again be confined using electrostatic ring electrodes. H atom from the source can be chopped by a simple mechanical shutter. Detection of anions is done by MCP.

This setup allows us to do these simple measurements:

- Fill and store \(\text{H}^-\) in a trap for specified time
- Fill and store \(\text{H}^-\) in trap with H beam on, for the same period.

Provided we know the concentration of the H atom beam, calculation of the rate constant is straightforward.
**Figure 3.** Experimental setup. Anions are created in the SIS at the left, mass selected in the quadrupole (center) and stored in the octopole. H atom beam is coming from the H atom source not shown on this picture.

**H⁻ production**

The cleanest way of creating H⁻ is for sure the way using only molecular hydrogen. However the creation of H⁻ is not so effective in pure H₂ as can be seen in Table 1. We consider only H⁻ creation evoked by electron impact. H₂ is affected by two major precesses:

- Dissociative attachment \( AB + e^- \rightarrow A^- + B \)
- Polar attachment \( AB + e^- \rightarrow A^- + B^+ + e^- \)

Dissociative attachment is dominant at electron energies up to 17 V at higher electron energies the Polar attachment is becoming favoured (see Massey [1976]). We were able to test only H₂ as a source gas up until now, water vapor seems also as an option. However H₂ has a advantage that it does not react with H⁻, the same is not true for H₂O.

**Table 1.** Cross section for formation of anions by electron impact at indicated electron energies.

<table>
<thead>
<tr>
<th>Source</th>
<th>Product</th>
<th>( \sigma ) [cm²]</th>
<th>( e^- ) energy [eV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂</td>
<td>H⁻</td>
<td>3.5 ( \cdot 10^{-20} )</td>
<td>14.4</td>
</tr>
<tr>
<td>O₂</td>
<td>O⁻</td>
<td>1.5 ( \cdot 10^{-18} )</td>
<td>6.0</td>
</tr>
<tr>
<td>H₂O</td>
<td>H⁻</td>
<td>7.1 ( \cdot 10^{-18} )</td>
<td>6.5</td>
</tr>
<tr>
<td>H₂O</td>
<td>O⁻</td>
<td>3.5 ( \cdot 10^{-18} )</td>
<td>6.5</td>
</tr>
<tr>
<td>NH₃</td>
<td>H⁻,NH₂⁻</td>
<td>1.5 ( \cdot 10^{-18} )</td>
<td>6.2</td>
</tr>
</tbody>
</table>

**H⁻ experimental results**

For test experiments the experimental setup consist only from SIS, quadrupole and detector. In the experiment H⁻ are formed from H₂ . Evidence of presence of anions of mass one at the detector is shown at Fig. 4. Time of flight spectra obtained for different accelerating voltage of these anions are shown at Fig. 5.

We were able to detect approx. \( 6 \cdot 10^3 \) s⁻¹ anions. We do not know our conversion efficiency on the MCP, but we expect it to be around 0.5 (see Stephen and Peko [2000]). Also gas pressure in the SIS chamber is limited in current experimental setup to \( 2.5 \cdot 10^{-6} \) mbar, the presented data here were measured at \( 1.2 \cdot 10^{-6} \) mbar.
Figure 4. Low mass filter for negative anions. Dashed line indicates calculated value of a threshold voltage (for mass = 1 amu) according to Eq. 7. Operating conditions of the QP are $V_0 = 21.0 \, \text{V}$ and $\Omega/2\pi = 7.6 \, \text{MHz}$.

Figure 5. Time of flight for anions exiting from SIS. Operating conditions of the SIS are $V_0 = 14.5 \, \text{V}$ and $\Omega/2\pi = 19.2 \, \text{MHz}$. Voltage on End plates = Voltage on B-1 = $-0.6 \, \text{V}$ . SIS was opened for 1 $\mu\text{s}$ with pulse 2.5 V high. $U_{\text{QP}}$ acts as accelerating voltage.

Conclusion

In this paper we shown that we are able to produce anions $\text{H}^-$ in SIS from $\text{H}_2$ and that we are able to guide and detect these anions. We also outlined our further steps to get to the setup where measurement of rate constants for anions reacting with atomic hydrogen will be measured.

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References


