On hydrogen negative ion formation and concentration measurements in hollow cathode and positive column glow discharge

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Abstract. The elementary processes with H⁻ participation are studied in a hollow cathode discharge and a positive column glow discharge in order to clarify the main processes for H⁻ formation and destruction. The H⁻ concentration is estimated by modeling these discharges and it is measured by both photodetachment (optogalvanic) method and an emission method developed by us. The H⁻ concentration is investigated as a function of the glow discharge type, gas mixture and discharge conditions. At the chosen discharge conditions the concentration of H⁻ is more than an order of magnitude higher in a hollow cathode glow discharge than in a positive column glow discharge. Besides, the (Ne+H₂) mixture hollow cathode discharge is more favorable for higher H⁻ concentration than the pure H₂ discharge.

1. Introduction

Gases containing negative ions have been of considerable interest for many years in the physics of ionosphere [1,2] and their properties make them very interesting in lasers as working medium [3,4], in new material development and IC technology [5-7], in the fusion for H⁻ and D⁻ beam production [8-10], and in accelerators for increasing the range of particle energy [11]. In electronegative gases the interaction of negative ions with atoms, molecules [12] and light [13] has also been a subject of intensive study. The investigations on negative ions are summarized first in [14,15] and later in [2,5,16-21].

However, the measurement of negative ion concentration in electronegative gases still remains a challenge. The most common methods for measuring negative ion concentration are the probe method [2, 22-27], mass-spectrometry [22,28,29], and the photodetachment method [2,20,21,25]. The theory of negative ion concentration measurement by probes has been proposed by Boyd [30]. The application of the probe method is limited in non-equilibrium or corrosive plasmas though. In the mass-spectrometry method, the pressure range is limited but the largest issue is quantitative measurement. The preliminary negative ion separation by magnetic field before registration appears to
be a favored way for higher efficiency with these two methods [31]. The third, the photodetachment method, is based on the detachment of electrons by negative ions under appropriate energy light illumination. The minimum photon energy necessary for the photodetachment process is several eV [31]. The extra-photodetached electrons change the plasma conductivity, i.e. the optogalvanic effect arises. The optogalvanic measurements increase the method sensitivity and make it one of the most reliable ways for negative ion concentration measurements [2]. The photodetachment process is still under study, for example, in the last years the negative ion bond energy has been determined [32]; a variety of electron negative ion photodetachment types (e.g. H, He, Li, Be) have been studied [33]; some works on photodetachment process modeling have been performed [34], etc.

The hydrogen negative ions are investigated in [2,16-18,22,26-28,64,65,70-73]. They play an important role for negative ion beam production (as H' and D') [8,9], for material development technology [5,6], etc. In many cases mixtures of H2 and other gases are used [35]. The mixtures containing H2 are widely utilized as a working gas in different glow discharges for spectroanalytical sources [29,36-42], laser media [3,4,43], etc. The effect of negative ions especially in a hollow cathode discharge is studied in [2, 44, 45] for H' and in [24,25,44-46] for O'. A part of the results described here for the hollow cathode discharge are published in [47, 48].

The aim of the present work is to clarify the fundamental processes in H' glow discharges (hollow cathode discharge and positive column glow discharge) and the main processes for H' formation and destruction. This is necessary to estimate hydrogen negative ion concentration as a function of glow discharge type, gas mixture and discharge conditions. To reach this aim we investigate the elementary processes with H' participation by modeling of the glow discharges under interest, and as a result the H' concentration is estimated. Besides, H' concentration is measured by both photodetachment method and an emission method proposed by us.

2. Modeling

2.1. Comparison between positive column and hollow cathode glow discharges

Glow discharge with positive column (PCGD) and hollow cathode glow discharge (HCGD) in the (Ne+10%H2) mixture are compared. According to our preliminary experiments [49] for I/V characteristics of HCGD in H2, Ne and different mixtures of (Ne+H2), plasma conductivity has the lowest value in (Ne+10%H2) glow discharge. That is why this mixture was chosen as the working gas in our study.

The theoretical description includes vibrational kinetics for the H2 molecule and more than 30 processes for the following levels and particles: H2 ground electron state, H2 vibrational states H2(v), H atom, H' ion, H' ion, Ne atom, Ne' ion, 1s, 2p, 4d blocks of Ne levels for hollow cathode discharge, and the 2s block of Ne levels for a positive column discharge (all the levels are in Pashen notation). The main processes included in the model and their characteristics for glow discharge with positive column and hollow cathode glow discharge, are presented in Tables 1 and 2, respectively. The cross-sections and transitions probabilities are taken from the references noted in the tables.

| Table. 1. Characteristics of the elementary processes in glow discharge with positive column |
|---------------------------------------------------------------|
| Process | Cross-section (cm²) | Characteristics of the process in glow discharge with positive column |
|---------|---------------------|---------------------------------------------------------------|
| H₂(v)+e → H⁺+H | \( \sigma=6\times10^{-21} \) [15] | \( k_3 \) (see Eq.(7)) |
| H⁺+e → H⁺+hv | \( \sigma=3.7\times10^{-15} \text{cm}^3\text{s}^{-1} \) | |

\[H'\text{ ion formation}\]

\[H'\text{ ion destruction}\]

\( k_3=4.6\times10^7 \text{cm}^3\text{s}^{-1} \) [15,51]

\( k_4=3.9\times10^7 \text{cm}^3\text{s}^{-1} \) [15].
H\(^+\)H\(^-\) \rightarrow H\(^+\)H\(_2\)+e \quad k_5=5x10^{-8}\text{cm}^3\text{s}^{-1} \quad [52]
H\(^+\) \rightarrow H\(_2\)+e \quad k_6=1.8x10^{-7}\text{cm}^3\text{s}^{-1} \quad [15]
H\(^+\)+H\(_2\) \rightarrow H\(^+\)H\(_2\)+e \quad k_7=1.3x10^{-11}\text{cm}^3\text{s}^{-1} \quad [26]
H\(^+\)+e \rightarrow H\(^+\)2e \quad \sigma=1x10^{-16} \quad [52] \quad k_8=5.9x10^{-9}\text{cm}^3\text{s}^{-1}

\(H\) and \(H\(_2\) kinetics\)

H\(^+\)+e \rightarrow H\(^+\)2e \quad k_9=5.8x10^{-13}\text{cm}^3\text{s}^{-1} \quad [53]
H\(_2\)+e \rightarrow H\(_2\)+2e \quad \sigma=7x10^{-17} \quad [54] \quad k_{10}=2.6x10^{-11}\text{cm}^3\text{s}^{-1}
H\(^+\)+H\(_2\)+e \quad k_{11}=4.8x10^{-12}\text{cm}^3\text{s}^{-1} \quad [55]
H\(^-\)+H\(_2\)+e \quad k_{12}=1.7x10^{-13}\text{cm}^3\text{s}^{-1} \quad [44]
H\(_2\)^++e \rightarrow H\(_2\)+H \quad k_{13}=3.8x10^{-9}\text{cm}^3\text{s}^{-1} \quad [56]

Ne \(_2\) kinetics

Ne\(^+\)+e \rightarrow Ne\(^+\)+e \quad \sigma=7.5x10^{-17} \quad [57] \quad k_{14}=1.3x10^{-13}\text{cm}^3\text{s}^{-1}
Ne\((1s)\)+e \rightarrow Ne\(^+\)+e \quad k_{15}=3.1x10^{-9}\text{cm}^3\text{s}^{-1} \quad [58]
Ne\((2p)\)+e \rightarrow Ne\(^+\)+e \quad k_{16}=2.1x10^{-9}\text{cm}^3\text{s}^{-1} \quad [58]
Ne\((2s)\)+e \rightarrow Ne\(^+\)+e \quad k_{17}=3.2x10^{-9}\text{cm}^3\text{s}^{-1} \quad [55]
Ne\(^+\)+e \rightarrow Ne\((1s)\)+hv \quad A_{23}=9x10^6\text{s}^{-1} \quad [62]
Ne\((2s)\)+e \rightarrow Ne\((2p)\)+hv \quad A_{24}=3.3x10^6\text{s}^{-1} \quad [55]
Ne\(^+\)+e \rightarrow Ne\((2p)\)+hv \quad k_{21}=3.7x10^{-8}\text{cm}^3\text{s}^{-1} \quad [55]
Ne\(^+\)+e \rightarrow Ne\((2s)\)+hv \quad k_{22}=1.5x10^{-6}\text{cm}^3\text{s}^{-1} \quad [55]
Ne\(^+\)+e \rightarrow Ne\((2p)\)+hv \quad A_{25}=9x10^6\text{s}^{-1} \quad [62]
Ne\((1s)\)+e \rightarrow Ne\((2p)\)+e \quad k_{26}=3.7x10^{-9}\text{cm}^3\text{s}^{-1} \quad [55]
Ne\((2p)\)+e \rightarrow Ne\((2s)\)+e \quad k_{27}=1.5x10^{-7}\text{cm}^3\text{s}^{-1} \quad [55]
Ne\((1s)\)+e \rightarrow Ne\((2s)\)+e
Ne\((2s)\)+e \rightarrow Ne\((2p)\)+e
Ne\((2p)\)+e \rightarrow Ne\((2s)\)+e

Diffusion

Ne\(^+\) diffusion \quad \tau_{Ne}=1.3x10^{-6}\text{s} \quad [57]
H\(^+\) diffusion \quad \tau_{H}=1.5x10^{-7}\text{s} \quad [57]
H\(_2\)\(^+\) diffusion \quad \tau_{H_2}=2.1x10^{-7}\text{s} \quad [57]

**Table 2.** Characteristics of the elementary processes in hollow cathode glow discharge at current density \(j=1\text{mA/cm}^2\)

| Process | Cross-section (cm\(^2\)) | Characteristics of the process in hollow cathode glow discharge |
|---------|--------------------------|---------------------------------------------------------------|
| \(H\(_2\)(v)+e \rightarrow H\)+H \quad \sigma=6x10^{-21} \quad [15] | \(K_1\) (see Eq.(7)) |
| \(H\)+H\(_2\)+e \quad \sigma=1x10^{-16} \quad [52] | \(K_0\) (see Eq.(7)) |
| \(H\)+Ne\(^+\)+e \rightarrow Ne\((4d)\)+H \quad k_{14}=1.5x10^{-7}\text{cm}^3\text{s}^{-1} \quad [15] | \(K_1\) (see Eq.(7)) |
| \(H\)+H\(_2\)+e \quad k_{15}=3.9x10^{-7}\text{cm}^3\text{s}^{-1} \quad [15] | \(K_1\) (see Eq.(7)) |
| \(H\)+H\(_2\)+e \quad k_{16}=5x10^{-8}\text{cm}^3\text{s}^{-1} \quad [52] | \(K_1\) (see Eq.(7)) |
| \(H\)+H\(_2\)+e \quad k_{17}=1.8x10^{-8}\text{cm}^3\text{s}^{-1} \quad [15] | \(K_1\) (see Eq.(7)) |
| \(H\)+H\(_2\)+e \quad k_{18}=4.9x10^{-10}\text{cm}^3\text{s}^{-1} \quad [52] | \(K_1\) (see Eq.(7)) |
| \(H\)+H\(_2\)+e \quad k_{19}=7.6x10^{-9}\text{cm}^3\text{s}^{-1} \quad [52] | \(K_1\) (see Eq.(7)) |

**H and \(H\(_2\) kinetics\)**

\(H\)+e \rightarrow H\(^+\)+2e \quad k_{20}=1.9x10^{-11}\text{cm}^3\text{s}^{-1} \quad [65]
| Reaction                                      | $\sigma$  | Reference |
|----------------------------------------------|-----------|-----------|
| $\text{H}_2^+ + e \rightarrow \text{H}_2 + 2e$ | $6.4 \times 10^{-17}$ | 66 |
| $\text{H}_2^+ + e \rightarrow \text{H} + \text{H}^+$ | $1 \times 10^{-17}$ cm$^3$s$^{-1}$ | 67 |
| $\text{H}^+ + e \rightarrow \text{H} + \text{hv}$ | $1.7 \times 10^{-13}$ cm$^3$s$^{-1}$ | 44 |
| $\text{H}_2 + e \rightarrow \text{H} + \text{H}$ | $3.8 \times 10^{-9}$ cm$^3$s$^{-1}$ | 56 |
| $\text{H}_2 + e \rightarrow \text{H}^+ + \text{H} + e$ | $1.8 \times 10^{-19}$ | 68 |
| $\text{Ne}^+ + e \rightarrow \text{Ne}^+ + e$ | $7.5 \times 10^{-17}$ | 57 |
| $\text{Ne}(1s) + e \rightarrow \text{Ne}^+ + e$ | $5.2 \times 10^{-16}$ | 58 |
| $\text{Ne}(2p) + e \rightarrow \text{Ne}^+ + e$ | $1.2 \times 10^{-15}$ | 58 |
| $\text{Ne}(4d) + e \rightarrow \text{Ne}^+ + e$ | $5.9 \times 10^{-15}$ | 58 |
| $\text{Ne}^+ + e \rightarrow \text{Ne}(1s) + e$ | $3.5 \times 10^{-18}$ | 59 |
| $\text{Ne}^+ + e \rightarrow \text{Ne}(2p) + e$ | $2.7 \times 10^{-18}$ | 61 |
| $\text{Ne}^+ + e \rightarrow \text{Ne}(4d) + e$ | $6.1 \times 10^{-19}$ | 69 |
| $\text{Ne}(1s) + e \rightarrow \text{Ne}(2p) + e$ | $10^{-16}$ | 61 |
| $\text{Ne}(2p) + e \rightarrow \text{Ne}(4d) + e$ | $5 \times 10^{-20}$ | 69 |
| $\text{Ne}(2p) \rightarrow \text{Ne}(1s) + \text{hv}$ | $10^{-16}$ | 61 |
| $\text{Ne}(2p) \rightarrow \text{Ne}(4d) + \text{hv}$ | $5 \times 10^{-20}$ | 69 |
| $\text{Ne}(1s) \rightarrow \text{Ne}(2p) + \text{e}$ | $9 \times 10^6$s$^{-1}$ | 62 |
| $\text{Ne}(2p) \rightarrow \text{Ne}(4d) + \text{e}$ | $1.1 \times 10^7$s$^{-1}$ | 62 |

**Ne kinetics**

| Reaction                                      | $\sigma$  | Reference |
|----------------------------------------------|-----------|-----------|
| $\text{Ne}^+ + e \rightarrow \text{Ne}^+ + e$ | $7.5 \times 10^{-17}$ | 57 |
| $\text{Ne}(1s) + e \rightarrow \text{Ne}^+ + e$ | $5.2 \times 10^{-16}$ | 58 |
| $\text{Ne}(2p) + e \rightarrow \text{Ne}^+ + e$ | $1.2 \times 10^{-15}$ | 58 |
| $\text{Ne}(4d) + e \rightarrow \text{Ne}^+ + e$ | $5.9 \times 10^{-15}$ | 58 |
| $\text{Ne}^+ + e \rightarrow \text{Ne}(1s) + e$ | $3.5 \times 10^{-18}$ | 59 |
| $\text{Ne}^+ + e \rightarrow \text{Ne}(2p) + e$ | $2.7 \times 10^{-18}$ | 61 |
| $\text{Ne}^+ + e \rightarrow \text{Ne}(4d) + e$ | $6.1 \times 10^{-19}$ | 69 |
| $\text{Ne}(1s) + e \rightarrow \text{Ne}(2p) + e$ | $10^{-16}$ | 61 |
| $\text{Ne}(2p) + e \rightarrow \text{Ne}(4d) + e$ | $5 \times 10^{-20}$ | 69 |
| $\text{Ne}(2p) \rightarrow \text{Ne}(1s) + \text{hv}$ | $9 \times 10^6$s$^{-1}$ | 62 |
| $\text{Ne}(2p) \rightarrow \text{Ne}(4d) + \text{hv}$ | $1.1 \times 10^7$s$^{-1}$ | 62 |

**Diffusion**

| Reaction                                      | $\tau_{\text{free}}$ | Reference |
|----------------------------------------------|--------------------|-----------|
| $\text{Ne}^+$ diffusion                      | $1.1 \times 10^{-5}$s | 57 |
| $\text{H}^+$ diffusion                       | $1.2 \times 10^{-6}$s | 57 |
| $\text{H}_2^+$ diffusion                     | $2.9 \times 10^{-6}$s | 57 |

The electron energy distribution function (EEDF) for positive column glow discharge has Maxwellian shape with electron temperature $T_e=1.2$eV and electron concentration $n_e=7 \times 10^{10}$cm$^{-3}$. EEDF for hollow cathode discharge is considered to contain a Maxwellian part with parameters $T_e=1.7$eV and $n_e=5.3 \times 10^{11}$cm$^{-3}$ and a beam of fast electrons with energy up to cathode potential fall (257eV). To characterize the excitation and ionization by these fast electrons, frequencies were used for direct excitation $\nu_{\text{exc}}=[\sigma_{\text{exc}}(E)/\sigma_{\text{ion}}(E)]\nu_{\text{ion}}$ and ionization $\nu_{\text{ion}}=\sigma_{\text{ion}}(E)j/e$ processes, where $j$ is current density, $e$ is the electron charge and $E$ is the electron energy. The electron temperature $T_e$ and electron concentration $n_e$ in both discharges were measured by the probe method.

The rate constants of the processes with electron participations were calculated by

$$k_{ij} = \frac{2e}{\mu} \frac{\sigma_{ij}(E)f(E)EdE}{\mu},$$

where $\mu$ is electron mass and $2e/\mu = 5.97 \times 10^6$, $E_o$ is threshold energy for the process, $\sigma$ is the cross-section for the process, f(E) is the EEDF.

The free diffusion time is evaluated by $\tau_{\text{free}} = (R/2.4)^2/D_{\text{free}}$, where $D_{\text{free}}$ is the diffusion coefficient, $R$ is the cathode radius. The estimated values of $\tau_{\text{e}}$ of $\text{H}_2(v)$ are $6 \times 10^{-5}$s, $8 \times 10^{-5}$s and $7.5 \times 10^{-5}$s for $\text{H}_2$, (Ne+10%H$_2$) and (Ne+30%H$_2$) hollow cathode discharges, respectively, and $\tau_{\text{e}}=6 \times 10^{-5}$s for (Ne+10%H$_2$) positive column glow discharge.

The ambipolar diffusion coefficient $D$ can be found from

$$D = D_{\text{free}} \left(1 + \frac{T_e}{T_g}\right),$$

where $T_e$ and $T_g$ are the electron and gas temperatures, respectively.

The main elementary processes for production of $\text{H}^+$ ions in low-pressure plasma are the dissociative attachment $\text{H}_2(v)+e \rightarrow \text{H}+\text{H}^+$ and the electron attachment $\text{H}+e \rightarrow \text{H}^+ + \text{hv}$. The rate-constants of the dissipative attachment process strongly depend on the vibrationally excited $\text{H}_2$ levels since the
cross-section becomes five orders of magnitude higher for vibrational states \( v > 4 \) in comparison with that for \( v = 0 \) [50] (Table 3). This is the reason only \( v = 4 \text{-} 9 \) should be included in the model.

### Table 3. Cross-sections and calculated by us rate-constants of dissociative attachment for vibrationally excited \( \text{H}_2 \) levels in hollow cathode glow discharge and positive column glow discharge

| \( v \) | \( \sigma_{\text{diss}} [\text{cm}^2] \) | \( k_{\text{diss}} [\text{cm}^3/\text{s}] \) in HCGD | \( k_{\text{diss}} [\text{cm}^3/\text{s}] \) in PCGD |
|-------|----------------|-----------------|-----------------|
| 0     | 2.8x10^{-21}  | 2.6x10^{-14}   | 1.5x10^{-14}   |
| 1     | 8.3x10^{-20}  | 9.2x10^{-13}   | 5.9x10^{-13}   |
| 2     | 1.0x10^{-18}  | 1.3x10^{-12}   | 9.3x10^{-12}   |
| 3     | 7.5x10^{-18}  | 1.1x10^{-11}   | 8.8x10^{-11}   |
| 4     | 3.8x10^{-17}  | 6.1x10^{-10}   | 5.4x10^{-10}   |
| 5     | 1.2x10^{-16}  | 2.0x10^{-9}    | 1.9x10^{-9}    |
| 6     | 2.9x10^{-16}  | 5.0x10^{-9}    | 5.3x10^{-9}    |
| 7     | 4.3x10^{-16}  | 7.2x10^{-9}    | 8.2x10^{-9}    |
| 8     | 3.2x10^{-16}  | 5.0x10^{-9}    | 6.0x10^{-9}    |
| 9     | 4.3x10^{-16}  | 5.8x10^{-9}    | 4.6x10^{-9}    |

In the case under consideration the vibrationally excited \( \text{H}_2(v) \) states are populated by impacts of \( \text{H}_2(v=0) \) at the ground vibrational state \( v = 0 \) with slow electrons

\[
\text{H}_2 + e \Rightarrow \text{H}_2(v) + e, \quad (3)
\]

and they are mainly depopulated by

- impacts with electrons \( \text{H}_2(v) + e \Rightarrow \text{H}_2(w>v) + e, \quad (4) \)
- impacts between \( \text{H}_2 \) molecules (5,6)
  - \( v-v \) processes \( \text{H}_2(v) + \text{H}_2(v_1) \Rightarrow \text{H}_2(v_2<v) + \text{H}_2(w_1>v_1), \quad (5) \)
  - \( v-T \) processes \( \text{H}_2(v) + \text{H}_2(v_1) \Rightarrow \text{H}_2(v_2<v) + \text{H}_2(v_1), \quad (6) \)

and diffusion to the cathode walls.

The rate constants for these processes are presented in Table A1 and Table A2 in the Appendix.

Taking into account the noted processes and their rate constants, the balance equations were constructed for vibrational state \( v \) of \( \text{H}_2 \). The calculated populations of the vibrational \( v = 4 \text{-} 9 \) levels of \( \text{H}_2 \) are presented in Table 4.

### Table 4. Populations of \( \text{H}_2 \) vibrational levels in hollow cathode glow discharge and positive column glow discharge

| Vibrational level \( v \) | \( \text{H}_2(v) \) [cm\(^{-3}\)] |
|--------------------------|-------------------------------|
| Hollow cathode glow discharge | Positive column glow discharge |
| 4 | 5.2x10\(^{11}\) | 3.1x10\(^{11}\) |
| 5 | 1.5x10\(^{11}\) | 1.4x10\(^{11}\) |
| 6 | 4.2x10\(^{11}\) | 2.8x10\(^{11}\) |
| 7 | 1.5x10\(^{10}\) | 5.5x10\(^{9}\) |
| 8 | 3.4x10\(^{9}\) | 7.1x10\(^{8}\) |
| 9 | 1.1x10\(^{9}\) | 2.1x10\(^{8}\) |

The rate constants for the dissociative attachment process were evaluated by using Tables 3 and 4:

\[
k_1 = \frac{\sum_{v=4}^{9} \sigma_{\text{diss}}(v) \mathcal{H}_2(v)}{\mathcal{H}_2},
\]

where \( \mathcal{H}_2 \) is the hydrogen molecule concentration at the ground state.

The ion-ion recombination between \( \text{H}^- \) and \( \text{Ne}^+ \) is another important process with \( \text{H}^- \) participation

\[
\text{H}^- + \text{Ne}^+ \rightarrow \text{Ne}^* + \text{H}.
\]
The rate constant for this reaction can be defined by the formula $k_{rec} = 8 \cdot 10^{-7} T_g^{-0.5}$ ($T_g$ is the gas temperature) [51]. It has a value of $4.6 \times 10^{-7}$ cm$^3$/s in our discharge conditions at $T_g = 300$K. We assume that in HCGD the recombination flux distribution is uniform on the three Ne levels 4d, 5d, 6s, and consequently, the ion-ion recombination rate constant is taken $k_{rec} = 1.5 \times 10^{-7}$ cm$^3$/s for each of these levels.

The balance equations are based on the above-mentioned processes. The solution of these balance equations gives the particle concentration and Ne excited levels population: H$^-$ = $4 \times 10^{10}$ cm$^{-3}$, H$^-$ = $1 \times 10^6$ cm$^3$, H$^-$ = $7.3 \times 10^{10}$ cm$^{-3}$, Ne(1s) = $7.6 \times 10^{-3}$ cm$^{-3}$, Ne(2s) = $3 \times 10^6$ cm$^3$, H = $1 \times 10^{15}$ cm$^{-3}$ for glow discharge with positive column; and Ne$^-$ = $1.6 \times 10^{11}$ cm$^{-3}$, H$^-$ = $3.8 \times 10^{10}$ cm$^3$, H$^-$ = $3.5 \times 10^8$ cm$^3$, H$^-$ = $2 \times 10^6$ cm$^3$, Ne(1s) = $3 \times 10^{11}$ cm$^{-3}$, Ne(2p) = $1 \times 10^6$ cm$^{-3}$, Ne(4d) = $1 \times 10^7$ cm$^{-3}$, H = $1.6 \times 10^{15}$ cm$^{-3}$ for hollow cathode glow discharge.

It is seen from the above shown results that the obtained H$^-$ ion concentration in a hollow cathode discharge is $2 \times 10^8$ cm$^{-3}$ what is one order of magnitude higher than in a positive column glow discharge. The main reason for this result is the higher vibrational level population and higher electron concentration in the HCGD than in the PCGD. In both discharges the main elementary process for H$^-$ ion production is dissociative attachment of an electron to a vibrationally excited H$_2$. The H$^-$ loss in hollow cathode discharge is mainly due to the ion-molecule collisions between H$^-$ and H$_2$ while in glow discharge with positive column, except above-mentioned ion-molecule collisions, the H$^-$ ion diffusion has a significant contribution to H$^-$ losses, as well. Thus, higher H$^-$ concentration in hollow cathode discharge was obtained and for this reason the following estimation continued only in this discharge.

2.2 Hollow cathode discharge with H$_2$ and (Ne+H$_2$) mixtures

In the previous paragraph the mixture (Ne+10%H$_2$) was modeled. In the same way, the hollow cathode discharge has been modeled in pure H$_2$ and (Ne+30%H$_2$) mixture. In these cases, the measured electron temperature and electron concentration using the probe method are $T_e$ = 3.0 eV, $n_e$ = $2.0 \times 10^{11}$ cm$^{-3}$ for pure H$_2$ hollow cathode discharge and $T_e$ = 2.3 eV, $n_e$ = $2.9 \times 10^{11}$ cm$^{-3}$ for (Ne+30%H$_2$) hollow cathode discharge. The main elementary processes and their characteristics for H$_2$ and (H$_2$+30%Ne) hollow cathode discharges are listed in Tables 5 and 6.

| Table 5. Cross-sections and calculated rate-constants of dissociative attachment for vibrationally excited H$_2$ levels in H$_2$ and (Ne+30%H$_2$) hollow cathode glow discharges |
|---|---|---|
| $v$ | $k_{diss}$ [cm$^3$/s] in H$_2$ HCGD | $k_{diss}$ [cm$^3$/s] in (Ne+30%H$_2$) HCGD |
| 0 | $3.5 \times 10^{-14}$ | $3.3 \times 10^{-14}$ |
| 1 | $1.1 \times 10^{-12}$ | $1.1 \times 10^{-12}$ |
| 2 | $1.1 \times 10^{-11}$ | $1.4 \times 10^{-11}$ |
| 3 | $1.0 \times 10^{-10}$ | $1.1 \times 10^{-10}$ |
| 4 | $5.2 \times 10^{-10}$ | $5.8 \times 10^{-10}$ |
| 5 | $1.6 \times 10^{-9}$ | $1.8 \times 10^{-9}$ |
| 6 | $3.6 \times 10^{-9}$ | $4.3 \times 10^{-9}$ |
| 7 | $4.9 \times 10^{-9}$ | $6.0 \times 10^{-9}$ |
| 8 | $3.2 \times 10^{-9}$ | $4.0 \times 10^{-9}$ |
| 9 | $3.5 \times 10^{-9}$ | $4.6 \times 10^{-9}$ |
Table 6. Elementary processes and their characteristics for H$_2$ and (Ne+30%H$_2$) hollow cathode glow discharges at current density $j=1$ mA/cm$^2$

| Process | Characteristics of the process in H$_2$ | Characteristics of the process in (Ne+30%H$_2$) |
|---------|----------------------------------------|-----------------------------------------------|
| H$_2$(v)+e $\rightarrow$ H$^+$H | $K'_1$ (see Eq(7)) | $K''_1$ (see Eq(7)) |
| H$^+$e $\rightarrow$ H$^+$hv | $K''_2=5.7\times10^{-15}$ cm$^3$s$^{-1}$ | $K''_2=5.3\times10^{-15}$ cm$^3$s$^{-1}$ |

### H$^-$ ion formation

- $H^+$Ne$^+$ $\rightarrow$ Ne(4d)+H $-\quad K'''_6=1.5\times10^{-7}$ cm$^3$s$^{-1}$
- $H^+$H$^+$ $\rightarrow$ H+H $-\quad K''_4=3.9\times10^{-7}$ cm$^3$s$^{-1}$
- $H^+$H$_2$ $\rightarrow$ H$^+$H$_2$+e $-\quad K''_5=5\times10^{-8}$ cm$^3$s$^{-1}$
- $H^-$H $\rightarrow$ H$^2$+e $-\quad K''_6=1.8\times10^{-9}$ cm$^3$s$^{-1}$
- $H^-$+e $\rightarrow$ H$+$2e $-\quad K''_8=9.3\times10^{-9}$ cm$^3$s$^{-1}$

### H$^-$ ion destruction

- $H^-$Ne$^+$ $\rightarrow$ Ne(4d)+H $-\quad K''_3=3.9\times10^{-9}$ cm$^3$s$^{-1}$
- $H^-$+H$^+$ $\rightarrow$ H+H $-\quad K''_4=3.9\times10^{-7}$ cm$^3$s$^{-1}$
- $H^-$+H$_2$ $\rightarrow$ H$^+$H$_2$+e $-\quad K''_5=5\times10^{-8}$ cm$^3$s$^{-1}$
- $H^-$+H $\rightarrow$ H$^2$+e $-\quad K''_6=1.8\times10^{-9}$ cm$^3$s$^{-1}$
- $H^+$e $\rightarrow$ H$^+$+2e $-\quad K''_9=1.9\times10^{-11}$ cm$^3$s$^{-1}$

### H$^-$ and H$_2$ kinetics

- $H^-$+H$_2$ $\rightarrow$ H$+$H+hv $-\quad K''_{13}=3.8\times10^{-9}$ cm$^3$s$^{-1}$
- $H^+$+e $\rightarrow$ H$^+$+H+hv $-\quad K''_9=1.9\times10^{-11}$ cm$^3$s$^{-1}$
- $H^+$+e $\rightarrow$ H$^+$+H$^+$+e $-\quad K''_{14}=1\times10^{-10}$ cm$^3$s$^{-1}$

### Ne kinetics

- Ne+e $\rightarrow$ Ne$^+$+e $-\quad K''_1=356\times j$ s$^{-1}$
- Ne(1s)+e $\rightarrow$ Ne(2p)+e $-\quad K''_{16}=9.5\times10^{-9}$ cm$^3$s$^{-1}$
- Ne(2p)+e $\rightarrow$ Ne(4d)+e $-\quad K''_{17}=4.8\times10^{-8}$ cm$^3$s$^{-1}$
- Ne$^+$e $\rightarrow$ Ne(1s)+e $-\quad K''_2=2\times10^{-9}$ cm$^3$s$^{-1}$
- Ne$^+$+Ne$^+$e $\rightarrow$ Ne(2p)+e $-\quad K''_{18}=3.5\times10^{-7}$ cm$^3$s$^{-1}$
- Ne(1s)+e $\rightarrow$ Ne(2p)+e $-\quad K''_{19}=2.6\times10^{-12}$ cm$^3$s$^{-1}$
- Ne(2p)+e $\rightarrow$ Ne(4d)+e $-\quad K''_3=9\times10^{-10}$ cm$^3$s$^{-1}$
- Ne(4d)+e $\rightarrow$ Ne(2p)+e $-\quad K''_{20}=1.1\times10^{-12}$ cm$^3$s$^{-1}$

### Diffusion

- Ne$^+$ $\rightarrow$ Ne$^+$ t$''_{Ne}$=6.7x10$^{-6}$s
- H$^+$ $\rightarrow$ H$^+$ t$''_{H^+}=1.6x10^{-6}$s
- H$_2^+$ $\rightarrow$ H$_2^+$ t$''_{H_2^+}=2.0x10^{-6}$s

The solution of the balance equations gives the following results: H$^+$ =2x10$^{10}$ cm$^{-3}$, H$_2^+$ =2x10$^{10}$ cm$^{-3}$, H$^-$ =7x10$^{15}$ cm$^{-3}$, for H$_2$ HCGD discharge; and Ne$^+$ =1.3x10$^{10}$ cm$^{-3}$, H$^+$ =1x10$^{10}$ cm$^{-3}$, H$_2^+$ =7x10$^{15}$ cm$^{-3}$, H$^-$ =4x10$^{10}$ cm$^{-3}$, Ne(1s) =3x10$^{11}$ cm$^{-3}$, Ne(2p) =7x10$^{10}$ cm$^{-3}$, Ne(4d) =8x10$^{10}$ cm$^{-3}$, H = 1x10$^{15}$ cm$^{-3}$ for (H$_2$+30%Ne) HCGD discharge.

Hydrogen negative ion concentration is an order of magnitude higher in the (H$_2$+30%Ne) mixture than in the pure hydrogen discharge. Our estimations show that in both the H$_2$ and (H$_2$+Ne) discharges the main elementary process for H$^-$ creation is dissociative attachment. The collisions of H$^-$ with H$_2$ and H are the most important processes for H$^-$ destruction in both discharges. Obviously, H$_2$ and H concentration decreases by an order of magnitude in the mixture compared with the pure H$_2$ discharge. This leads to a reduction of the contribution of H$^-$ destruction processes.
3. Experimental results

3.1. H⁻ ion measurements by optogalvanic method

The H⁻ concentration was measured by the optogalvanic method based on the photodetachment process. This process represents a detachment of an electron from a negative ion by absorbing a photon with an appropriate energy:

\[ \text{H}^- + h\nu \rightarrow \text{H} + e. \]  

(9)

The additional electrons as a result of this process lead to a plasma conductivity change, which is registered as a current change via the Langmuir’s probe inserted into the hollow cathode plasma. The probe current change \( \Delta i \) due to laser illumination, at the probe potential equals to the plasma potential, may be expressed as [2]

\[ \Delta i = s \left( \frac{eP}{\pi r^2 \nu} \right) H^- \sigma_{ph}, \]  

(10)

where \( P \) is the laser power, \( r \) is the laser radius, \( H^- \) is the hydrogen negative ion concentration, \( \sigma_{ph}=3 \times 10^{-17} \text{ cm}^2 \) is the photodetachment cross-section for H⁻ [68] and \( s \) is the sensitivity factor of the probe.

In our experiment an Ar⁺ laser generating a wavelength of \( \lambda=488.0 \text{nm} \) was used. The laser power is 0.1W and the laser beam radius is 0.1cm. The chosen laser wavelength is non-resonant towards Ne and H₂ optical transitions. The sensitivity factor \( s \) of the probe characterizes the number of electrons registered by the probe, which are produced by one photodetached electron from the negative ion. This factor must be taken into account since the laser beam diameter (corresponding to the region where the photoelectrons arise) is larger than the electron mean free path, which is a prerequisite for creating additional electrons. For this reason, the determination of \( s \) is necessary in every particular case. As the \( s \) calculation is difficult it can be obtained by an alternative method, proposed by us, namely by measuring under the same conditions the photoionization signal produced by photoionization from highly excited Ne levels. The sensitivity factor was evaluated by using equation (9), where H⁻ concentration is substituted with the concentration of highly excited Ne states and \( \sigma_{ph} \) - with the Ne photoionization cross-section (\( \sigma_{\text{ion}}=2 \times 10^{-17}\text{ cm}^2 \)).

The evaluated probe sensitive factors are \( s=28 \) for the hollow cathode and \( s=80 \) for the positive column glow discharges. These calculations have used the measured optogalvanic photoionization signals \( \Delta i=8 \text{nA} \) and \( 6 \text{nA} \); and the concentrations of highly excited Ne levels \((10^{7}\text{cm}^{-3} \) and \( 3 \times 10^{6}\text{cm}^{-3} \)) (see Part 2. Modeling) for hollow cathode glow discharges (HCGD) and for glow discharge with positive column (GDPC), respectively. Taking the optogalvanic photodetachment signals \( \Delta i \) of 20nA, 225nA and 70nA for H₂, (Ne+10%H₂) and (Ne+30%H₂) HCGD, the H⁻ ion concentration was determined to be \( 2 \times 10^7, 2 \times 10^8 \) and \( 5 \times 10^7 \), respectively. For PCGD the measured optogalvanic photodetachment signal \( \Delta i \) was 15nA and consequently the hydrogen negative ion value is \( H^- \) \( =5 \times 10^6\text{cm}^{-3} \).

The measured H⁻ concentrations are in good agreement with the theoretical values. The H⁻ concentration is an order of magnitude higher in the \( \text{(Ne+10\%H₂)} \) mixture than that in the H₂ hollow cathode discharge. It can be concluded that at the chosen discharge conditions the concentration of H⁻ is more than an order of magnitude higher in HCGD than in PCGD. At the same time the \( \text{(Ne+H₂)} \) mixture hollow cathode discharge is more favorable for the higher H⁻ concentration than the pure H₂ discharge.
Figure 1. Optogalvanic photoionization signal (*) from Ne (multiplied by a factor of ten) and optogalvanic photodetachment signal (o) from (Ne+10%H₂) hollow cathode discharges (left scale). The probe characteristics of Ne and (Ne+10%H₂) hollow cathode discharges refer to the right scale.

3.2 H⁻ ion measurements by emission method for the (Ne+H₂) mixture

In the hollow cathode glow discharge some excited Ne levels are effectively populated also through the ion-ion recombination [45]

\[
\text{H}^- + \text{Ne}^+ \rightarrow \text{Ne}(4d, 5d, 6s') + \text{H}.
\]

(11)

The 4d, 5d, 6s'Ne levels have energy in energetic resonance with the above reaction, i.e. they are away from the Ne ionization potential at a distance equal to the electron binding energy in H⁻ ions (Figure 2). According to [45] the ion-ion recombination process could considerably contribute to the population of the above-mentioned Ne levels because of the relative high value of its cross-section (σ =10⁻¹³cm²). Higher intensity increase of spectral lines originating from the levels populated by ion-ion recombination was observed.

Figure 2. Neon energetic levels under consideration.

The principle in our work is to derive the H⁻ ion concentration by quantitative estimation of the contribution of the main processes related to 4d, 5d, 6s'Ne levels population, and by measuring the intensity change of the spectral lines connected with above-mentioned Ne levels. Consequently, the question is, which processes do populate these levels and what are their contributions? From the modeling of the discharge, described in part 2.1, it can be concluded that:

- The Ne⁺ concentration is higher by one and two orders of magnitude than the concentration of H⁺ and H₂⁺, respectively. Taking into account that the rate constants of the recombination between H⁺ and
both neon positive ions and hydrogen positive ions have the same order of magnitude [52] the results from modeling allow us to neglect H⁻ losses through recombination by impact with H₂⁺ and H⁺.

The Ne 4d levels are populated predominantly by direct excitation and ion-ion recombination since the calculated direct excitation, recombination and stepwise excitation are 1x10¹⁴, 5x10¹² and 2x10¹⁰ cm⁻³ s⁻¹, respectively. They are depopulated by spontaneous emission.

Taking into account that the excited neon 4d levels are populated by direct excitation and ion-ion recombination and they are depopulated by spontaneous emission, the ratio of the intensities I of an appropriate spectral line, emitted from Ne 4d level in the (Ne+H₂) mixture and in the Ne hollow cathode discharge, can be written as

$$\frac{I_{Ne+H_2}}{I_{Ne}} = \frac{\text{excitation by electron impact in } (H_2 + Ne) + k_{rec} Ne^+ H^-}{\text{excitation by electron impact in } Ne}$$

(12)

Since the direct excitation by beam electrons with energy ε up to the potential fall in the hollow cathode glow discharge can be expressed as υ_ex Ne, the formula becomes

$$\frac{I_{Ne+H_2}}{I_{Ne}} = \frac{\nu_{exc}^N(Ne+H_2) N_o(Ne+H_2) + k_{rec} Ne^+ H^-}{\nu_{exc}^N Ne N_o}$$

(13)

where υ_ex is the excitation frequency (see Table 2), N_o(Ne+H₂) and N_o Ne are the concentrations of Ne ground state atoms in (Ne+10%H₂) and Ne hollow cathode discharges, respectively.

The necessary Ne⁺ ion concentration can be found by assuming that direct ionization from the ground states is the basic process for Ne⁺ ion formation and the diffusion to the cathode walls is the main elementary process for their loss

$$Ne^+ = (\sigma_{ion} j / e)N = v_{ion} N_0 \tau,$$

(14)

where σ_{ion} is the cross-section for ionization, υ_ex is the excitation frequency and τ is the time for ambipolar diffusion. Using the values, listed in Table 2, namely υ_{ion}=468 js⁻¹, j_{ion}=1.1x10⁻⁷ s⁻¹, N_0=2.9x10¹⁶ cm⁻³, it was calculated that the Ne⁺ concentration in (Ne+10%H₂) HCGD was Ne⁺ =1.5x10¹¹ cm⁻³.

The validity of the proposed method for H⁻ concentration measurements is proved by using NeI 533.0nm or NeI 534.1nm spectral lines, beginning from Ne 4d levels. To show the influence of the hydrogen addition to the direct excitation process by electron impact, we also registered a proper spectral line (NeI 540.0nm) not optically connected with Ne 4d levels and consequently not influenced by ion-ion recombination flux.

The relative intensities of NeI 533.0nm and NeI 534.1nm spectral lines, emitted from (Ne+H₂) and Ne hollow cathode discharges, were photoelectrically registered by spectrograph DFS-13. The intensities were measured in an open-ended Al hollow cathode (radius 6mm, length 40mm, total gas pressure 1Torr and a discharge current of 14mA). Figure 3 shows intensity decreases for NeI 533.0nm, NeI 534.1nm and a relatively higher intensity decrease for NeI 540.0nm. The decrease in intensity is due to the decrease of direct excitation caused by the change in electron energy distribution function when hydrogen is added. The decreased direct excitation for the population of 4d levels is partly compensated by the ion-ion recombination process.
Figure 3. Relative intensities (I) of NeI 533.0nm, NeI 534.1nm and NeI 540.0nm spectral lines registered in Ne (a) and (Ne+10%H2) (b) hollow cathode glow discharges.

Substituting in the equation (13) with the measured intensity ratio of relative intensities for NeI 533.0nm or NeI 534.1nm spectral lines $I_{Ne+H2}/I_{Ne}=0.96$, neon atom concentration in Ne discharge $N_o=3.2x10^{16}cm^{-3}$, neon ion concentration $Ne^+=1.5x10^{11}cm^{-3}$, ion-ion recombination rate constant $k_{rec}=1.5x10^{-7}cm^{3}s^{-1}$ we then obtain the $H^-$ ion concentration as $H^=\left(3.0 \pm 0.5\right) \times 10^8cm^{-3}$. The error is estimated taking into account the relative error (MSD) of spectral line intensity registration.

Similarly for (Ne+30%H2) we measured $I_{Ne+H2}/I_{Ne}=0.71$ for NeI 533.0nm. Substituting in (13) with $N_o=2.24x10^{16}cm^{-3}$, neon ion concentration $Ne^+=0.7x10^{11}cm^{-3}$ [from (14)], ion-ion recombination rate constant $k_{rec}=1.5x10^{-7}cm^{3}s^{-1}$ we obtain the $H^-$ ion concentration as $H^=\left(8.0 \pm 1.3\right) \times 10^7cm^{-3}$.

The $H^-$ ion concentrations, calculated using this model, measured and estimated by optogalvanic and emission methods, are summarized in Table 7.

Table 7. Values of $H^-$ concentration obtained by modeling, optogalvanic and emission methods.

| Hollow cathode discharge | Positive column discharge |
|--------------------------|--------------------------|
| $H_2$                    | $Ne+10\%H_2$             | $Ne+30\%H_2$             | $Ne+10\%H_2$             |
| modeling                 | $7x10^6cm^{-3}$          | $2x10^8cm^{-3}$          | $4x10^7cm^{-3}$          |
| Optogalvanic method      | $2x10^7cm^{-3}$          | $2x10^8cm^{-3}$          | $5x10^7cm^{-3}$          |
| Emission method          | -                        | $3x10^8cm^{-3}$          | $8x10^7cm^{-3}$          |
|                          |                          |                          | $1x10^7cm^{-3}$          |
|                          |                          |                          | $5x10^6cm^{-3}$          |
4. Conclusion

Our results show that the obtained H⁻ ion concentration in a hollow cathode discharge is one order of magnitude higher than in a positive column glow discharge. Both modeling and experiments show H⁻ production enhancement when H₂ is mixed with Ne. The optimum mixture for our discharge conditions, (Ne+10%H₂), leads to an order of magnitude increase of H⁻ ion concentration in comparison with pure H₂ hollow cathode glow discharge. For (Ne+H₂) hollow cathode glow discharge we propose an emission method for measurement of hydrogen negative ion concentration and the results obtained by this method are favourably compared with those for the optogalvanic method. The advantages of the emission method are its contactlessness and simplicity.

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Appendix 1

Table A1. Rate constants for the processes (2-3) connected with the vibrational states of H₂ for hollow cathode glow discharge (HCGD) and positive column glow discharge (PCGD)

| Process | HCGD discharge | PCGD discharge |
|---------|----------------|----------------|
| k(0,1)  | 3.7 x 10^-9    | 2.9 x 10^-9    |
| k(0,5)  | 9.0 x 10^-13   | 7.0 x 10^-13   |
| k(0,6)  | 3.5 x 10^-13   | 8.8 x 10^-14   |
| k(0,7)  | 1.1 x 10^-14   | 1.4 x 10^-14   |
| k(0,8)  | 1.3 x 10^-15   | 1.4 x 10^-15   |
| k(0,9)  | 2.1 x 10^-16   | 1.7 x 10^-16   |
| Process |               |                |
| k(4,5)  | 7.4 x 10^-9    | 5.8 x 10^-9    |
| k(4,6)  | 9.3 x 10^-10   | 7.3 x 10^-10   |
| k(4,7)  | 1.1 x 10^-10   | 9.1 x 10^-11   |
| k(4,8)  | 1.4 x 10^-11   | 1.1 x 10^-11   |
| k(4,9)  |               |                |

k(4,5)=k(5,6)=k(6,7)=k(7,8)=k(8,9); k(4,6)=k(5,7)=k(7,9); k(4,7)=k(5,8)=k(6,9); k(4,8)=k(5,9)

Table A2. Rate constants for the processes (4) and (5) connected with the vibrational states of H₂ for hollow cathode glow discharge and positive column glow discharges

| Process | Process (4) | Process (5) |
|---------|-------------|-------------|
| K(v,v2|v1,w1) (cm^3 s^-1) | K(v,v2) (cm^3 s^-1) |
| K(4,3 | 0,1)=1.5 x 10^-12 | K(4,3)=4 x 10^-12 |
| K(5,4 | 0,1)=1.5 x 10^-12 | K(5,4)=9 x 10^-13 |
| K(6,5 | 0,1)=1.5 x 10^-12 | K(6,5)=4 x 10^-14 |
| K(7,6 | 0,1)=1.3 x 10^-12 | K(7,6)=1 x 10^-12 |
| K(8,7 | 0,1)=1.2 x 10^-12 | K(8,7)=4 x 10^-14 |
| K(9,8 | 0,1)=1.1 x 10^-12 | K(9,8)=7 x 10^-13 |
Appendix B

**Table B1** The populations of H$_2$ vibrational levels in H$_2$ and (Ne+30%H$_2$) hollow cathode glow discharges

| Vibrational level v | H$_2$(v) (cm$^{-3}$) | (Ne+30%H$_2$) HCGD |
|---------------------|----------------------|----------------------|
| 4                   | 8x10$^{11}$          | 7.2x10$^{11}$        |
| 5                   | 1.2x10$^{11}$        | 1.4x10$^{11}$        |
| 6                   | 1.7x10$^{10}$        | 2.8x10$^{10}$        |
| 7                   | 2.7x10$^{9}$         | 5.5x10$^{9}$         |
| 8                   | 3.2x10$^{8}$         | 7.1x10$^{8}$         |
| 9                   | 4.5x10$^{7}$         | 2.1x10$^{7}$         |

**Table B2**

| v  | $k_{\text{diss}}$[cm$^3$/s] in H$_2$ HCGD | $k_{\text{diss}}$[cm$^3$/s] in (Ne+30%H$_2$) HCGD |
|----|------------------------------------------|-----------------------------------------------|
| 0  | 3.5x10$^{-14}$                           | 3.3x10$^{-14}$                               |
| 1  | 1.1x10$^{-12}$                           | 1.1x10$^{-12}$                               |
| 2  | 1.4x10$^{-11}$                           | 1.4x10$^{-11}$                               |
| 3  | 1.0x10$^{-10}$                           | 1.1x10$^{-10}$                               |
| 4  | 5.2x10$^{-10}$                           | 5.8x10$^{-10}$                               |
| 5  | 1.6x10$^{-9}$                            | 1.8x10$^{-9}$                                |
| 6  | 3.6x10$^{-9}$                            | 4.3x10$^{-9}$                                |
| 7  | 4.9x10$^{-9}$                            | 6.0x10$^{-9}$                                |
| 8  | 3.2x10$^{-9}$                            | 4.0x10$^{-9}$                                |
| 9  | 3.6x10$^{-9}$                            | 4.6x10$^{-9}$                                |