Spectroscopic Study of Hydrogen Rotational, Vibrational and Translational Temperatures in a Hollow Cathode Glow Discharge

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Abstract. The optical emission spectroscopy is used for determination of hydrogen molecule rotational $T_{\text{rot}}$, vibrational $T_{\text{vib}}$ and translational temperature $T_g$. The experiment was carried out using copper or titanium hollow cathode discharges operated in pure hydrogen. The rotational temperature of excited electron energy levels is determined from Fulcher-$\alpha$ diagonal bands ($d^3\Pi_u \rightarrow a^3\Sigma_g^+$ electronic transition, P, Q and R branches), which were later used to derive rovibronic temperature of the hydrogen molecule ground state, which is assumed equal to $T_g$. The vibrational temperature $T_{\text{vib}}$ is determined for the same electronic transition ($d^3\Pi_u \rightarrow a^3\Sigma_g^+$, with $\nu' = 2, 3, \Delta \nu = 0$). For all temperatures the radial temperature distribution is reported.

1. Introduction
Hydrogen hollow cathode glow discharges (HCGD) have been extensively used for study of fundamental discharge processes as well as for wide variety of applications [1]. For instance, recently, this type of discharge was utilized for producing hydrogen by reforming natural gas [2].

The translational or gas kinetic temperature in gas discharges is a parameter of utmost importance in the field of plasma chemistry while vibrationally excited neutral hydrogen molecules play significant role in the chemistry of weakly ionized hydrogen plasmas [3,4,5]. This is why the modeling of cold, reactive hydrogen plasma includes rotational and vibrational energy of the hydrogen molecule [5].

Several diagnostic techniques are developed to determine gas kinetic temperature $T_g$ like coherent anti-stokes Raman scattering (CARS) [6, 7], laser-induced fluorescence (LIF) [8, 9] and optical emission spectroscopy (OES) [8, 10, 11, and 12]. Here we selected OES. This diagnostic technique provides information about atom, molecule and ion density in excited and ground state, as well as rotational, vibrational, and gas temperature including the excitation temperature of certain group of excited levels [13]. The technique is applied for measurements of the rotational $T_{\text{rot}}$, vibrational $T_{\text{vib}}$ and determines translational temperatures in a hollow cathode glow discharge in hydrogen. The rotational temperature of excited electron energy levels is determined from the Boltzmann plot of intensities of rotational molecular hydrogen lines belonging to Fulcher-$\alpha$ diagonal bands ($d^3\Pi_u \rightarrow a^3\Sigma_g^+$ electronic transition; P, Q and R branches). Following procedure described elsewhere [14, 15] the temperature of ground state rovibronic levels is evaluated. Constrains of rotational temperature are discussed in detail. The vibrational temperature, after certain precautions, is also determined [16, 17, 18, 19], but from the ratio of relative intensities of the H$_2$ Fulcher-$\alpha$ diagonal
bands ($d^3\Pi_u \rightarrow a^3\Sigma_g^+$) electronic transition; Q-branches with $\nu'=2$, 3). The applied method for vibrational temperature determination is based on the assumption that population of rovibrational levels in excited ($n',\nu'$) state is in accordance with the Boltzmann’s distribution.

The dependence of these temperatures and their radial distribution within HC was determined and discussed [20].

2. Experiment

The hollow cathode glow discharge (HCGD) source with two symmetrically positioned kovar anodes and copper (Cu) or titanium (Ti) cathode is used as a discharge source. The HC tube was 50 mm (Cu) or 100 mm (Ti) long with 6 mm internal diameter and 1 mm wall thickness. The construction details of HC discharge source are described elsewhere [21].

All HCGD experiments were carried out with hydrogen (purity of 99.999%). The continuous flow of $H_2$ was sustained between 50 and 450 cm$^3$/min (at room temperature and atmospheric pressure) in the pressure range 2-10 mbar by means of a needle valve and two-stage mechanical vacuum pump.

To operate the discharge in a DC mode, a current stabilized power supply (0–2 kV, 0–100mA) is used. An air-cooled variable 10 kΩ ballast resistor is placed in series with the discharge and power supply. For all measurements, the cathode was grounded.

During the discharge operation, the cathode was either air cooled with a fan (110 mm dia; AC 220V/13W), placed 150 mm from discharge tube, or gradually heated by changing cooling rate of the fan. The temperature of the outer wall of the HC tube is measured by a K-type thermocouple.

The radial distribution spectra recordings were performed in equidistant steps perpendicular to the discharge axis, with an estimated spatial resolution of 0.30 mm. For radial intensity measurements the discharge was run between HC and rear anode, located at 20 mm from the cathode. All spectroscopic measurements of the gas discharge in HC are performed end-on and, in this way, the Abel inversion procedure required to convert integral radial intensity measurement into radial intensity distribution, see e.g. [22] is avoided. The light from the discharge was focused with an achromat lens (focal length 75.8 mm) onto the entrance slit of spectrometer (2 m focal length with 651 g/mm reflection grating; the reciprocal dispersion of 0.74 nm/mm in first diffraction order). Spectral line recordings were performed with an instrumental profile very close to Gaussian with the measured full half-width of 0.018 nm. Signals from CCD detector (29.1mm, 3648 pixels) are A/D converted, collected and processed by PC.

3. Basics of hydrogen molecular temperature measurement

In previous studies Fulcher-α band spectroscopy was used because of its strong visible emission intensity and few perturbations. Namely, the most of the excited electronic states of hydrogen are considerably perturbed and simple adiabatic models like Franck – Condon approximation and Hön-London formulae are not valid for calculation of transition probabilities in this case. The choice of the Fulcher-α, rather then $g\Sigma_u^+ \rightarrow \Sigma^+$ molecular system was encouraged by this fact. Mainly Q-branches of the Fulcher-α band system are considered to be free from perturbations. Due to A-type doubling, $d^3\Pi_u$ state degenerates into the $d^3\Pi_u^-$ and $d^3\Pi_u^+$ states. The $d^3\Pi_u^-$ can only have a Q-branch, whereas the $d^3\Pi_u^+$ has P and R branches, in the spontaneous rovibronic emissions to $a^3\Sigma_g^+$. Since the degenerated $d^3\Pi_u^-$ state interacts strongly with the $d^3\Sigma_u^+$ state, the P and R branches of Fulcher-α are perturbed and relative transition probabilities for these lines differ from Hön-London factors [15]. Therefore, we used Q-branches from $d^3\Pi_u^-$ state. In order to prove that the observed electronic transition have resolved rotational structure with almost fully separated lines, Fortrat parabola of all three branches, see figure 1a, versus line wave numbers (m is an integer, which numbers successive lines) are drawn in figure 1b.
3.1. Rotational temperature

Detailed description of the rotational temperature determination is given in [20] and, therefore, minimum details will be given here for completeness. If the populations of rotational levels in excited vibronic state \((n',\nu')\) are close to the Boltzmann’s distribution, the logarithm intensity of a spectral line of rovibronic transition \((N''\nu''\rightarrow N''\nu'')\) is a linear function of the upper level energy. By plotting \(\ln \left( \frac{I_{n',\nu',N''}}{v^4 g_{a.s.} H_{N''}} \right)\); \(v\) is a wave number, \(g_{a.s.}\) - the statistical weight of the \(n',\nu',N'\) rovibronic level, caused by nuclear spin and the symmetry with respect to the permutation of the nuclei ('a' or 's'), \(H_{N''}\) - Hönl-London (HL) factors against term values for upper level a straight line is obtained, whose slope \(\frac{hc}{k T_{rot}(n',\nu')}\) may be used for determination of the rotational temperature \(T_{rot}(n',\nu')\) of excited state. In the case of the \(\Sigma \rightarrow \Pi\) electronic transition \(H_{N''}\) may be written as: \((N''-1)\) for P branch, \((2N''+1)\) for Q branch and \((N''+2)\) for R branch [23].

Within the framework of the model discussed in [15] the logarithm of the scaled rovibrational population density should be a linear function of the rotational energy in ground \(X^1\Sigma_g^+, \nu = 0\) vibronic state:

\[
\ln N_{\nu''}^{\nu'} = \ln \left( \frac{N_{\nu''}}{g_{a.s.}(2N'+1)\tau_{\nu'}^{\nu''}} \right) = -\frac{hc E_{X0N}^{\nu'}}{k T_0(n',\nu')} + \text{const.}
\]  

(1)

where is: \(N_{\nu''}^{\nu'}\) - scaled rovibronic population density, \(\tau_{\nu'}^{\nu''}\) - radiative lifetime of \(n',\nu',N'\) level and \(E_{X0N}^{\nu'}\) - rovibronic term value of ground vibronic state. Than \(T_0(n',\nu')\) is the rotational temperature of the ground vibronic state determined from the rotational population density distribution of an excited \((n',\nu')\) vibronic state. Further, according to [15], the temperature \(T_0(n',\nu')\) can be considered as a valid estimation of the ground state rovibronic temperature i.e. H\(_2\) translational temperature \(T_t\).

Here, it should be emphasized that the model predicts Boltzmann distribution in excited electronic-vibrational states. If one makes an additional assumption, that the rotational energy term \(F_\nu \propto B_{\nu'} N(N + 1)\) (according to the rigid rotator expression [14] then the following relation between rotational temperatures in the ground and electronically excited state may be obtained:

\[
\frac{T_0(n',\nu')}{B_{X0}} = \frac{T_{rot}(n',\nu')}{B_{\nu'}}
\]  

(2)

where \(B_{\nu'}\) and \(B_{X0}\) are rotational constants of excited and ground vibronic states.
3.1.1. Constrains of rotational temperature. The rotational temperature $T_{rot}(n', \nu')$ of excited state may have a physical meaning, when the characteristic time of rotation-translation relaxation $\tau_{RT}$ for the $n', \nu'$ vibronic state under the study is much shorter than the characteristic time of population and deactivation processes. In this case the rotational population distribution in the state $n', \nu'$ is close to Boltzmann’s distribution law with rotational temperature equal to translational temperature, i.e. gas temperature [14]. In an opposite extreme case, when the radiative lifetime is much smaller than $\tau_{RT}$, rotational collisional mixing of neutral species during the lifetime of the state $n', \nu'$ is not sufficiently efficient to ensure equilibrium of rotational distribution with the gas temperature. The degree of relation between the rotational population density distribution in $n', \nu'$ state and the population of ground electronic state should be proven within the framework of excitation-deactivation balance equations, see e.g. [13].

3.2. Vibrational temperature

The procedure described in [14, 23] for vibrational temperature $T_{vib}$ determination is used. If population density $N_{\nu'}$ of the vibrational levels is close to Boltzmann distribution law with $T \approx T_{vib}$, the intensity ratio of the two consecutive vibration bands of the same sequence is given as in [24]. If one introduces measured band intensities in two bands arising from different initial vibrational levels, it is possible to determine the vibrational temperature $T_{vib}$ of an excited molecule:

$$\frac{1}{T_{vib}} = \frac{k}{\hbar c G(\nu'') - G(\nu')} \ln \left( \frac{V_{\nu'\nu'2}}{V_{\nu'\nu'1}} \right) + \ln \left( \frac{I_{\nu'2}^{em}}{I_{\nu'1}^{em2}} \right) \qquad (3)$$

Where is: $G(\nu')$ - vibrational term value for upper vibrational level; $\nu'_{\nu'\nu''}$ - corresponding transition frequency, which, to the first order approximation, can be the frequency of the band origin, $A_{\nu'\nu''}$ - the transition probability for spontaneous emission between vibrational states and $I_{\nu'\nu''}^{em}$ – band integral intensity. For transition probabilities and term values, see e.g. [25].

4. Results and discussion

The electronic transition $d^3\Pi_u \rightarrow a^3\Sigma_g^+$ is in the visible part of electromagnetic spectra (595-645nm) [26], see an example of recorded spectra in figure 2.

Relative intensities of spectral lines of P, Q and R branches of various bands of: $d^3\Pi_u^+ \rightarrow a^3\Sigma_g^+$; $d^3\Pi_u^0 \rightarrow a^3\Sigma_g^+$ electronic transitions have been measured in above mentioned pressure range, see Experimental. Then, the relative population densities of rovibronic levels were calculated from (2) using data presented in Table 2 of [15]. Here, it should be mentioned that, in general case, the difference between semiempirical $N$-dependencies of the transition probabilities and those predicted by the Hönl-London formulae are significant and may even attain orders of magnitude. This may lead to systematic errors in rovibronic population densities calculated from (2). On other hand, there are certain cases when the difference between semiempirical $N$-dependencies of the transition probabilities and those predicted by the Hönl-London formulae vanish. Two examples of the population at the HC axis of the $d^3\Pi_u^+, 0, N$ and $d^3\Pi_u^0, 0, N$ levels evaluated from the intensities of R, P and Q branches of corresponding diagonal bands are presented in figures 3 and 4. In cases 3a and 4a, the Hönl-London factors were used for all branches as well as for Q branch in figures 3b and 4b. For this branch semiempirical data are identical with Hönl-London factors [15]. For P and R branches in figures 3b and 4b, semiempirical transition probabilities are used from Table 2 in [15]. Here, one should notice that in figures 3b and 4b, data points for all three branches evaluated with semiempirical transition probabilities represent a single data set for the Boltzmann plot. In the same figures solid
lines correspond to best fits, while dashed lines determine upper and down limit slopes and they are used for estimation of the temperature measurement uncertainty.

Figure 2: Emission spectra of rotational lines for Fulcher-α system diagonal band; R, Q, P branches with $\Delta \nu = 0, \nu' = 0$. Experimental conditions: titanium HC discharge in pure H$_2$ at $p=2.5$mbar; $I=90$ mA; $U=400$V.

Figure 3: Semilogarithmic plot of population densities for $d^3\Pi_u, 0, N'$ rovibronic levels of H$_2$ calculated from measured intensities with: (a) Hönl-London factors and (b) semiempirical transition probabilities [15]. Discharge conditions: copper HC discharge in H$_2$ at $p=3$mbar; $I=45$mA; $U=455$V.

One can notice from figure 3a that populations for the same rovibronic level evaluated from spectral line intensities of different branches using Hönl-London factors leads to the large spread of temperature values when Cu HC is used see figure 3a. With Ti HC, see figure 4a, the spread is well within an estimated experimental uncertainty of line intensity measurement.
Figure 4: Semilogarithmic plot of population densities for $d^3\Pi_u, 0, N'$ rovibronic levels of H$_2$ calculated from measured intensities with: (a) Hönl-London factors and (b) semiempirical transition probabilities [15]. Discharge conditions: titanium HC discharge in H$_2$ at $p=3$ mbar; $I=90$ mA; $U=400$ V.

In the case, when semiempirical data [15] are used for temperature evaluation, see figures 3b and 4b, large spread of temperature data occurs, but the average values are in agreement with those in figures 3a and 4a. It is interesting to note that, in contrast to Hönl-London factors approach, semiempirical results from the P branch in both experiments with Cu and Ti HC, see figure 3b and 4b, can’t be correctly fitted with one straight line. This may be indication that semiempirical values for the first several lines of this transition should be reconsidered.

Here, it should be outlined that the Q-branch of the Fulcher-α band system ($d^3\Pi_u \rightarrow a^3\Sigma_g^+$ electronic transition) is considered as being most reliable for temperature determination. There are two reasons: (i) temperature derived from the Boltzmann plots set by using HL or semiempirical transition probabilities agree well within experimental uncertainty, see figures 3 and 4; and (ii) the spectral lines of the P and R branches are difficult to investigate experimentaly since they come from levels of the $d^3\Pi_u$ state, which is perturbed by the $e^3\Sigma_u^+$ state [26].

The rotational temperature of the ground vibronic state is evaluated from the results for the Q-branch ($\nu'=\nu''=0$) of the Fulcher-α band system ($d^3\Pi_u \rightarrow a^3\Sigma_g^+$ electronic transition) using the calculated term values this state. The results for both HCGD are presented in figure 6. The temperature at the axis of Cu and Ti HCGD are $T_0(0,0) = (800 \pm 100)$K and $T_0(0,0) = (980 \pm 100)$K, respectively. Although the current density is same for both hollow cathodes ($j=4.8$ mA/cm$^2$), different temperatures at the discharge axis are most likely caused by different power inputs, see Experimental.

Further, an attempt was made to investigate in which way the population of excited vibrational states of Q branch influence estimated values of $T_0$. Using the Hönl-London factors approach the rotational temperature of excited states is determined from the Q branch for different excited vibrational levels $\nu'$. The results for different radial positions along HC diameter are given in the lower part of figure 6. Here, it should be mentioned that radial temperature profiles, given in figure 6, are symmetrical within the experimental scatter and, therefore, the results are mirrored at the $r=0$. 
Figure 5: Semilogarithmic plot of rotational population densities of $d^3\Pi_{\nu}, 0$ versus rotational energy of the molecular hydrogen ground state ($X^1\Sigma_g^+, 0$): (a) copper HC and (b) titanium HC. Discharge conditions: same as in figures 3 and 4.

Thus, only values of the rotational temperature derived from the population of Q branch vibrational state $\nu' = 0$ were recalculated to determine $T_0$ of the ground vibronic state $X^1\Sigma_g^+(\nu = 0)$ at different radial position, see the upper part of figure 6. The results in figure 6 show that both temperatures, $T_0$ and $T_{rot}$ (Q branch; $\nu' = 0$), change along HC diameter with a bending point at the radial position $r = 0.9$ mm. Here, one should note that the radial temperature profiles are measured only up to $r = 1.8$ mm, because intensities of first five lines in a Q-branch are too weak to allow accurate temperature measurement.

Figure 6: Radial distributions of the rotational temperature measured from Q-branch $\nu' = \nu'' = 0, 1, 2$ of the Fulcher-$\alpha$ band system and the rotational temperature $T_0$ recalculated from the population of Q branch $\nu' = 0$ for the ground vibronic state $X^1\Sigma_g^+(\nu = 0)$. Experimental conditions: copper hollow cathode discharge in H$_2$ at $p=3$ mbar; $I=45$ mA; $U=454$ V.
In accordance with above described model of low pressure hydrogen discharge [15], the translational gas temperature is expected to be twice as large as the rotational one of an excited state, see equation (2), where rotational constants of excited and ground vibronic states are related as $2B_{\nu' \nu} = B_{X0}$. In our case, the temperature recalculated from equation (2) for the ground vibronic state $X^1\Sigma_g^+(\nu = 0)$ is also two times larger than the rotational temperature of excited state $d^3\Pi_u^-$.

Although the population density distribution over vibrational levels in gas discharge plasmas has usually non-Boltzmann character, the Boltzmann plot technique is widely used for rough estimation of vibrational temperature $T_{vib}$ or vibrational population distribution [14, 24]. The vibrational temperature is routinely determined from the measurement of the relative intensities of bands in a well-developed system.

The highest precision is achieved if the used bands are free from overlap. According to (3), apart from band intensities, the relative band transition must be available. For required relative H$_2$ transition probabilities and vibrational term data, see [25].

Radial intensity distributions for vibrational bands of the Fulcher-α system ($d^3\Pi_u^- \rightarrow a^3\Sigma_g^+$ electronic transition; Q-branch $\nu' = \nu'' = 2$ and $\nu' = \nu'' = 3$; spectral lines from Q1 to Q5) are shown in figure 7a. The maximum radial distance from the axis ($r=2.1$ mm) is determined by the intensities of the branch, which for higher radius become too weak to allow accurate vibrational temperature measurement. To determine $T_{vib}$ of the H$_2$ molecule in excited state, integral intensities of these two bands are introduced in equation (3).

The distribution of $T_{vib}$ in excited state al along HC diameter follows profile with shape similar to the one for rotational temperature, see figure 7, but with the bending point located now at the radial position $r=1.2$ mm, see figure 7b. The dependence of average vibrational temperature upon HC wall temperature shows that vibrational temperature does not change significantly with HC wall temperature range, in particular if one takes into account the change of HCGD voltage.

![Figure 7](image.png)

**Figure 7:** (a) Radial intensity distribution of the Fulcher-α system ($d^3\Pi_u^- \rightarrow a^3\Sigma_g^+$ electronic transition; Q-branch $\nu' = \nu'' = 2$ and $\nu' = \nu'' = 3$ and (b) Calculated vibrational H$_2$ temperature distribution. Experimental conditions: titanium HC discharge in pure H$_2$ at $p=4$ mbar; $I=90$ mA; $U=400$V.
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