Anomalous Doppler Broadening of Hydrogen Balmer Lines Caused by Exothermic Reactions

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INTRODUCTION

Large controversy is nowadays associated with the explanation of the anomalous Doppler broadening of hydrogen Balmer lines observed in many low-pressure electrical discharges.

In those experiments, it was observed extended far wings of the emission lines with central Gaussian shapes whose full-widths at half maximum (FWHM) allowed to find, in certain cases, kinetic energies of H atoms as large as \( \sim 50 \) eV, while the electrons have only few eV.

These experiments have been repeated with a large variety of cathode surfaces (Al, Cu, stainless steel) and mixtures of \( \text{H}_2 \) and \( \text{H}_2\text{O} \) with other gases (Ar-\( \text{H}_2 \), Ar-\( \text{H}_2\text{O} \), etc).

The explanation for this occurrence is based on the acceleration of \( \text{H}^+ \), \( \text{H}_2^+ \) and \( \text{H}_3^+ \) ions in the cathode sheath region followed by charge-exchange reactions, which produce fast atoms and slow ions. The \( \text{H}^+ \) ions can also be back scattered from the cathode under the form of fast atoms.

Even with these explanations, such high temperatures are difficult to justify and believe, in particular, due to the fact of they are much larger than the temperature of electrons.
It is well known that as the velocity distribution of a species follows a Maxwell-Boltzmann (MB) distribution, the corresponding 1D distribution takes the form:

$$F(v_z) = \frac{1}{\sqrt{\pi} v_0} \exp\left(-\frac{v_z^2}{v_0^2}\right),$$

with $v_0 = \sqrt{2K_B T/m}$, and the Doppler line shape of a spectrum line emitted by this species exhibits a Gaussian shape:

$$I(\lambda_0 \pm \Delta \lambda) = I_0 \exp\left(-\frac{\Delta \lambda^2}{\lambda_0^2 \frac{c^2}{v_0^2}}\right),$$

with $\Delta \lambda = (v_z/c) \lambda_0$, and where $\lambda_0$ denotes the central wavelength of the emission line. Then, the FWHM is given by:

$$\delta \lambda_{(1/2)} = 2 \Delta \lambda_{(1/2)} = \frac{2 v_0 \lambda_0}{c} \sqrt{\ln 2},$$

from which the temperature can be obtained.

However, in the case of the broadened profiles of the type of those observed experimentally, it is not obvious that they may be fitted by a series of Gaussian functions and to conclude about the existence of species with different temperatures. The entire distribution must be seen as a whole and not as a sobreposition of various MB distributions.
NON-GAUSSIAN PROFILES

With the purpose of evaluating the magnitude of the errors that have usually been committed, the 3D and 1D velocity distributions of H atoms created by the exothermic reaction:

\[ \text{H}_2^+ + \text{H}_2 \rightarrow \text{H}_3^+ + \text{H} + \Delta E , \]

with \( \Delta E = 1.56 \text{ eV} \), are calculated using energy conservation.

By considering the reaction:

\[ \text{X}_1 + \text{X}_2 \rightarrow \text{X}_3 + \text{X}_4 + \Delta E , \]

in the center-of-mass frame and transforming the velocity distributions to the laboratory frame, we obtain the following 3D velocity distribution of \( \text{X}_4 \equiv \text{H} \) species after the collision (see Phys. Rev. E 82, 2010, 035401-R):

\[
P(v_4) = \left( \frac{m_4}{2\pi k_B T} \right)^{3/2} \exp \left( - \frac{m_4 v_4^2}{2k_B T} \right) \left( \frac{m_3}{2\pi k_B T} \right)^{3/2} \exp \left( \frac{\Delta E}{k_B T} \right) 2\pi \\
\times \int_0^\infty \exp \left( - \frac{m_3 v_3^2}{2k_B T} \right) \frac{1}{2v_3 v_4} Z(v_3, v_4) \, v_3^2 \, dv_3 ,
\]

with \( Z(v_3, v_4) \) given by:
\[ Z(v_3, v_4) = (v_3 + v_4) \sqrt{(v_3 + v_4)^2 - 2 \Delta E/\mu'} - |v_3 - v_4| \sqrt{(v_3 - v_4)^2 - 2 \Delta E/\mu'} + \frac{2 \Delta E}{\mu'} \ln \left( \frac{|v_3 - v_4| + \sqrt{(v_3 - v_4)^2 - 2 \Delta E/\mu'}}{v_3 + v_4 + \sqrt{(v_3 + v_4)^2 - 2 \Delta E/\mu'}} \right) \]

and where \( \mu' = m_3m_4/(m_3 + m_4) \).

We easily verify that \( Z = 4v_3v_4 \) as \( \Delta E = 0 \), and \( P(v_4) \) transforms into a MB distribution.

Once the 3D velocity distribution is known, the 1D distribution can be easily obtained by numerical integration using cylindrical coordinates:

\[ F(v_z) = \int_0^\infty P(v_4) 2\pi v_\perp dv_\perp \]

being \( v_\perp = \sqrt{v_4^2 - v_z^2} \) the perpendicular velocity to the \( z \)-axis.
RESULTS AND DISCUSSION

3D velocity distribution of H atoms for $T = 500$ K and the values of the energy defect $\Delta E = 0$ (i.e. MB), 0.05, 0.1, 0.2, 0.5, 1 and 2 eV.

The distribution $P(v_4)$ rapidly changes from its MB shape as $\Delta E$ increases. The differences are significant even in the case of a low value of $\Delta E$ as small as 0.05 eV. The maximum of the 3D distribution, at $v_4 = 0$ in the case of a MB distribution, is rapidly pushed away towards higher energies as $\Delta E$ increases.
1D velocity distribution of H atoms, for the same conditions and notations as before.

In the case of $F(v_z)$ distributions, the increase of $\Delta E$ produces a strong reduction of the maximum of the distribution at the vicinity $v_z = 0$ and an enlargement at high velocities. The actual distributions are flatter and squarer than the best-fit MB distributions that we could plot.
Intensity of Hα Balmer line at the experimental conditions of a H₂ positive column with $[\text{H}_2^+]/[\text{H}_2] = 2 \times 10^{-5}$ and $[\text{H}]/[\text{H}_2] = 6.5 \times 10^{-4}$, calculated for $T = 500$ K and $\Delta E = 0$, 0.2 and 2 eV.

These lines are obtained by considering both collisions of momentum transfer and the exothermic reaction.
CONCLUSIONS

The profiles of the spectrum lines emitted by radiative species, produced in the sequence of an exothermic reaction before undergoing thermalizing collisions, do not present Gaussian shapes and the use of the FWHM of measured lines to derive the temperature of the distributions should be questioned.

In the case of a fit by a series of Gaussian functions, the FWHM of the individual Gaussians cannot be used to conclude about the existence of species with different temperatures because the distribution cannot be interpreted as a sum of various Gaussians.

However, it still remains opened the reasons behind the extraordinary enlargement of the spectrum Balmer lines as measured in many papers, since our calculations do not reveal such extension.

We believe that this may result from the particular shape of the cross section for a given exothermic reaction, since in this paper an energy-independent charge transfer cross section has been assumed.

Some particular features exhibited by the electron energy distribution functions (EEDF) in electrical discharges lead us to suspect that the same may occur with the H atoms.