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Possibility of nonexistence of hot and superhot hydrogen atoms in electrical discharges

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Recently, the existence of extremely energetic hydrogen atoms in electrical discharges has been proposed in the literature with large controversy, from the analysis of the anomalous broadening of hydrogen Balmer lines. In this paper, the velocity distribution of H atoms and the profiles of the emitting atom lines created by the exothermic reaction $H_2^+ + H_2 \rightarrow H_3^+ + H + \Delta E$ are calculated, as a function of the internal energy defect ΔE. The shapes found for the non-Maxwell-Boltzmann distributions resulting in non-Gaussian line profiles raise serious arguments against the existence of hot and superhot H atoms as it has been proposed, at least with those temperatures.

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In the last 15 years the interpretation of the anomalous broadening of hydrogen Balmer lines in low-pressure electrical discharges has raised a large controversy in the physics community. In these recent years, dramatic broadening of Hα, Hβ, and Hγ lines has been observed in a variety of laboratories, either in pure H_2 or in specific gas plasma mixtures containing H_2, for different types of discharges [1–4]. The source of this line broadening has been attributed to Doppler effect, since other sources such as Stark effect and instrument broadening cannot explain the magnitude of the observed enlargement [2]. Once the broadened lines were detected in various laboratories, it was universally agreed to fit these lines with two or three Gaussians and to conclude about the existence of atoms with different temperatures from the full width at half maximum (FWHM). In particular, the existence of hot and superhot hydrogen atoms have been detected in a variety of discharge experiments. In Ref. [1], for example, cold (<0.2 eV), warm (<3 eV), and hot (>10 eV) atoms have been found. In other experiments the energies found were still larger [3,4]. However, at this point a formidable question raised in all minds: how can one neutral species in a plasma have temperatures as large as 300 000 K, while all other species, including electrons, have temperatures of less than 10 000 K?

The most obvious explanation for the existence of hot hydrogen atoms is the possibility of they may be created from molecular ions accelerated in the high electric field of the cathode fall region [3,5]. In Ref. [5], for example, H atoms are produced from charge transfer of H^+ ions accelerated at very high values of the electric field to gas density ratio E/N. The atoms could be created either due to collisions of the field accelerated hydrogen ions with the neutral hydrogen gas species or as a result of collisions between the accelerated ions and the cathode surface. Theoretical studies by modeling are able to explain the excitation of Hα Doppler profiles by fast H atoms mainly at high E/N values [6]. Modeling studies by Monte Carlo technique have also been reported in [7]. However, as pointed out in [1] the models cannot explain the presence of hot hydrogen atoms outside the sheath region of an RF plasma because there is no field in this region. An alternative explanation with large controversy has been advanced by Mills *et al.* [8] and pursued later on by Phillips *et al.* [1] invoking a new paradigm of quantum physics called by the authors as Classical Quantum Mechanics. This paradigm, applied to the line broadening phenomenon of hydrogen Balmer lines, postulates that the energy of H atoms may have its origin in a nonfield process that promotes a strange new species (hydrino) to a subground state. According to this model an ordinary hydrogen atom undergoing a catalysis step to form a hydrino H($\frac{1}{2}$) releases an energy of 40.8 eV.

This extraordinary broadening of the hydrogen Balmer lines is nowadays an intriguing phenomenon and apparently any definitive answer has not yet been found. In this letter, a different interpretation will be proposed. We simply question the validity of using the FWHM of the spectrum lines, whose profiles do not present a Gaussian shape, to infer about the existence of atoms with extremely high temperatures by fitting the lines with two or three Gaussians. In fact, using the standard procedure for deriving the temperature of emitting species from the Doppler broadening of spectral lines, a Gaussian profile needs to be assumed and this is indicative that the species have a Maxwell-Boltzmann (MB) distribution of velocities. However, collisions in which the internal energy of one or two colliding partners is converted to translational energy can affect the velocity distribution of both partners, and hence the Gaussian profiles of the lines emitted by them. As we will show in this letter, a non-Gaussian profile may serve as an indicator for a specific energy conversion from the internal modes of the colliding partners to the kinetic energy of the reaction products, but not to infer about the temperature of products calculated from the FWHM of the emitted lines. If the excited species are created as a result of a given exothermic reaction and if they radiate before undergoing thermalizing collisions, the corresponding emission line will present a non-Gaussian profile reflecting the kinetic energy exchange. However, the FWHM of these lines cannot be used to obtain the temperature of the velocity particle distribution of the emitting species.

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In other systems, the same situation occurs. For example, the non-Gaussian profiles in noble gas afterglows observed in [9] result from dissociative electron-ion recombination of molecular ions Ne_2^+. In the case under analysis here, the energy gained by the hydrogen atoms responsible by the emission of broadened Balmer lines may have its origin in any exothermic reaction producing H atoms, such as

$$H_2^+ + H_2 \rightarrow H_3^+ + H + \Delta E, \quad (1)$$

which is exothermic by at least 1.56 eV [10] or by 1.17 eV according to [11]. However, there is a huge difference between the energy released by reaction (1) and the extremely high energies derived from the FWHM of Balmer lines. Nevertheless, we notice that the non-Gaussian profile of Hα line, for example, is only indicative that the distribution of H(n=3) atoms is not MB. Of course, we may always fit a non-MB distribution with different MB functions and derive different temperatures for them, but this does not mean that atoms with such temperatures had been really created.

A similar situation arises with the electron energy distribution function (EEDF) in pure N_2 discharges at relatively low values of the reduced electric field, typically for $E/N \leq 3 \times 10^{-16}$ V cm^2 [12]. In this case, the EEDF exhibits a nearly flat shape at electron energies ~0–2 eV and a sharply decrease at ~2–3 eV, due to a strong energy loss of electrons caused by the peak in the electron cross section for vibrational excitation. The strong maximum of $\sim 6 \times 10^{-16}$ cm^2 in the electron cross section $v=0 \rightarrow v=1$, at ~2–3 eV, constitutes a barrier for the electrons, avoiding they may reach high-energy regions. In consequence of this, the EEDF presents a characteristic shape that can be fitted by a MB distribution at 0–2 eV with very high temperature, but this does not mean that electrons with such high-energy exist. As a matter of fact, the electrons have only small energy in this zone. The global shape of the EEDF results from the normalization of the distribution as a whole. The non-MB distribution may be fitted by bimodal or trimodal MB functions at different zones but this must be used for practical purposes only. For example, in determining the electron rate coefficient of a given electron impact process by integrating the corresponding cross section with the EEDF. Thus, the same effect should occur with the non-Gaussian profiles of the hydrogen Balmer lines. Although these profiles may be fitted by multimodal Gaussian functions, it does not seem correct to assume that the temperatures derived from the FWHM of these Gaussians determine the existence of H($n \geq 3$) atoms with such temperatures.

With the aim of clarifying this point, we present in this paper a theoretical study based on [13], in which the three- and one-dimensional velocity distributions of the hydrogen atoms created by the exothermic reaction (1) are determined using energy conservation. Then, the profile of the Hα Balmer line is derived and the deviations relatively to a Gaussian profile are evaluated. To derive these expressions, let us consider reaction (1), in which a H_2^+ ion and a hydrogen molecule collide at temperature T, producing a H_3^+ ion and a hydrogen atom. The energy difference between the internal energies of two reactant species and product species is ΔE. Since $\Delta E > 0$ (exothermic reaction) any kinetic energies of the collision partners are able to produce the reaction and ΔE necessarily appears in the kinetic energies of the product species.

Let us consider the reaction $X_1 + X_2 \rightarrow X_3 + X_4$ to describe formally the reactive collision (1). Before the collision, the probability of finding the particles in a double three-dimensional velocity element is given by the product of two three-dimensional MB distributions. This probability can also be referenced to the center-of-mass frame, by defining the center-of-mass velocity and the relative velocity. At it is well known, as the Jacobian of the transformation of the double velocity element from the laboratory frame to the center-of-mass frame is unitary, the combined probability factors into a product of a distribution describing the center-of-mass motion and a distribution describing the relative motion. After the collision (1) takes place, the absolute value of the relative velocity $\mathbf{v}'$ is obtained from energy conservation,

$$\frac{1}{2}\mu v^2 + \Delta E = \frac{1}{2}\mu' v'^2, \quad (2)$$

where μ and μ' are the reduced masses of the two reactant and the two product species, $\mathbf{v}$ is the relative velocity before the collision, and v and v' denote the velocity absolute values. Since the energy defect ΔE is positive, the product species will have a relative kinetic energy in the center-of-mass frame larger than its initial value.

On the other hand, using spherical coordinates the probability of finding the particle of mass μ, in the three-dimensional velocity element $\mathbf{d}^3\mathbf{v}$, is giving by

$$P(v)\,\mathbf{d}^3\mathbf{v} = \left(\frac{\mu}{2\pi k_B T}\right)^{3/2} \exp\left(-\frac{\mu v^2}{2k_B T}\right) v^2 dv \sin\theta\, d\theta\, d\phi. \quad (3)$$

Inserting Eq. (2) in Eq. (3) to replace v with v' and making the substitution $v\,dv = (\mu'/\mu)\,v'dv'$ obtained by differentiation of Eq. (2), we obtain the probability of finding the particle of mass μ' in the velocity element $\mathbf{d}^3\mathbf{v}'$,

$$P(v')\,\mathbf{d}^3\mathbf{v}' = \left(\frac{\mu'}{2\pi k_B T}\right)^{3/2} \exp\left(-\frac{\mu' v'^2}{2k_B T}\right) \exp\left(\frac{\Delta E}{k_B T}\right) \times \sqrt{1 - \frac{2\Delta E}{\mu' v'^2}}\, v'^2 dv' \sin\theta\, d\theta\, d\phi. \quad (4)$$

Since the center-of-mass distribution is not observable, we must convert it back to the laboratory frame and express the distribution in terms of the velocities $\mathbf{v}_3$ and $\mathbf{v}_4$ of two product species. Because the probability of finding the ensemble of two particles in the center-of-mass velocity element $\mathbf{d}^3\mathbf{V}$ is unchanged with the collision and using again the invariance of the products of velocity elements from the center-of-mass frame to the laboratory frame, we obtain for the combined probability of the two product species,

$$P(v_3,v_4)\,\mathbf{d}^3\mathbf{v}_3\,\mathbf{d}^3\mathbf{v}_4 = \left(\frac{m_3}{2\pi k_B T}\right)^{3/2}\left(\frac{m_4}{2\pi k_B T}\right)^{3/2}\exp\left(-\frac{m_3 v_3^2}{2k_B T}\right) \times\exp\left(-\frac{m_4 v_4^2}{2k_B T}\right)\exp\left(\frac{\Delta E}{k_B T}\right) \times\sqrt{1-\frac{2\Delta E}{\mu'(v_3^2+v_4^2-2(\mathbf{v}_3\cdot\mathbf{v}_4))}}\,\mathbf{d}^3\mathbf{v}_3\,\mathbf{d}^3\mathbf{v}_4. \quad (5)$$

Converting to spherical coordinates and integrating Eq. (5) over v_3, θ_3, ϕ_3, θ_4 and ϕ_4, the probability of finding the hydrogen atoms, i.e., the particles of velocity v_4, in the three-dimensional velocity element $4\pi v_4^2 dv_4$ is given by

$$P(v_4)\,4\pi v_4^2\,dv_4 = \int_0^\infty\left(\int_0^\pi P(v_3,v_4)\sin\theta_4\,d\theta_4\right)\times v_3^2\,dv_3\left(\int_0^{2\pi}d\phi_4\right)4\pi v_4^2\,dv_4 = \left(\frac{m_4}{2\pi k_B T}\right)^{3/2}\exp\left(-\frac{m_4 v_4^2}{2k_B T}\right)\chi(v_4)\,4\pi v_4^2\,dv_4, \quad (6)$$

where $\chi(v_4)$ is a factor accounting for the non-MB characteristics of the velocity distribution,

$$\chi(v_4) = \left(\frac{m_3}{2\pi k_B T}\right)^{3/2}\exp\left(\frac{\Delta E}{k_B T}\right)2\pi\int_0^\infty\exp\left(-\frac{m_3 v_3^2}{2k_B T}\right)\times\left\{\int_0^\pi\sqrt{1-\frac{2\Delta E}{\mu'[v_3^2+v_4^2-2(\mathbf{v}_3\cdot\mathbf{v}_4)]}}\sin\theta_4\,d\theta_4\right\}\times v_3^2\,dv_3. \quad (7)$$

By choosing $\mathbf{v}_3$ along the z axis, we may write $(\mathbf{v}_3\cdot v_4)=v_3 v_4\cos\theta_4$. The integral over θ_4 is easily performed by replacing $\xi=\cos\theta_4$ and making the substitution $x^2=v_3^2+v_4^2-2v_3v_4\xi$. Equation (7) is then easily integrated and we obtain from Eq. (6) the following three-dimensional velocity distribution of H atoms produced by reaction (1),

$$P(v_4) = \left(\frac{m_4}{2\pi k_B T}\right)^{3/2}\exp\left(-\frac{m_4 v_4^2}{2k_B T}\right)\left(\frac{m_3}{2\pi k_B T}\right)^{3/2}\exp\left(\frac{\Delta E}{k_B T}\right)2\pi \times\int_0^\infty\exp\left(-\frac{m_3 v_3^2}{2k_B T}\right)\frac{1}{2v_3 v_4}Z(v_3,v_4)\,v_3^2 dv_3, \quad (8)$$

with the factor $Z(v_3,v_4)$ given by

$$Z(v_3,v_4) = v_+\sqrt{v_+^2-2\Delta E/\mu'} - |v_-|\sqrt{v_-^2-2\Delta E/\mu'} + \frac{2\Delta E}{\mu'}\ln\left(\frac{|v_-|+\sqrt{v_-^2-2\Delta E/\mu'}}{v_+ + \sqrt{v_+^2-2\Delta E/\mu'}}\right) \quad (9)$$

and where $v_+=(v_3+v_4)$ and $v_-=(v_3-v_4)$. We easily verify that Eq. (9) gives $Z=4v_3v_4$ as $\Delta E=0$. In this case, Eq. (8) transforms into a MB distribution.

Equation (8) can be numerically integrated over v_3. When the arguments of the square roots of Eq. (9) are negative, which occur as the final relative kinetic energy is not sufficient to achieve the reaction, the square roots are replaced by zero. The integration over v_4 velocities satisfies to the normalization condition $\int_0^\infty P(v_4)\,4\pi v_4^2\,dv_4=1$. Once the three-dimensional velocity distribution is known, the one-dimensional distribution can also be obtained by numerical integration using cylindrical coordinates,

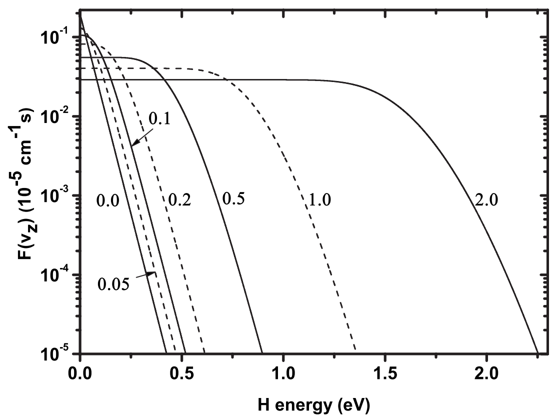

FIG. 1. One-dimensional component velocity distribution of H atoms created by the reaction $H_2^+ + H_2 \rightarrow H_3^+ + H$, as a function of energy of H atoms, calculated for $T=500$ K and the values of the energy defect $\Delta E=0$ (i.e., Maxwell-Boltzmann), 0.05, 0.1, 0.2, 0.5, 1, and 2 eV.

$$F(v_z) = \int_0^\infty P(v_4)2\pi v_\perp dv_\perp \quad (10)$$

being $v_\perp=\sqrt{v_4^2-v_z^2}$ the perpendicular velocity to the z axis. This latter distribution obeys to the normalization condition $\int_{-\infty}^{\infty}F(v_z)\,dv_z=1$.

Figure 1 shows the one-component velocity distribution of H atoms, $F(v_z)$, calculated from Eq. (10), with $T=500$ K, and different values of the energy defect of reaction (1) in the range $\Delta E=0-2$ eV, as a function of the energy-component of H atoms, $E_z=\frac{1}{2}m_4 v_z^2$. In this representation, a MB distribution is given by a straight line with negative slop. It is clearly visible from this figure that a small ΔE value as low as 0.5 eV is large enough to produce a strong deviation relatively to a MB distribution. Furthermore, if we fit each of these distributions by bimodal MB functions, the fitted MB to the low-energy part of H-atom distribution has an extremely high temperature, while that of the high-energy part has a much lower temperature. Thus, we cannot conclude that the atoms really have the temperatures of these MB distributions. The temperatures obtained by fitting the actual distribution by multimodal MB distributions should be used only for practical purposes. For example, in determining the rate coefficient of a given reaction induced by atom impact, as the cross section for such process is known.

It follows from this analysis that if instead we have opted for plotting $F(v_z)$ in a linear scale, as function of the one-component velocity v_z, we could evaluate the deviations relatively to Gaussian profiles. In this case the distribution would have a Gaussian shape for $\Delta E=0$ and broader and squarer shapes more and more pronounced as ΔE increases. Since the Doppler emission lines are linked with the $F(v_z)$ distributions, the profiles of hydrogen Balmer lines may be assumed as having approximately the same shape. The intensity profiles of the Hα line, assuming that the upper emitting state H(n=3) has the same velocity distribution as the H atoms produced by reaction (1), can be easily determined by making the replacement $v_z \rightarrow \Delta\lambda = (v_z/c)\lambda_0$, with $\lambda_0 = 656.28$ nm representing the central wavelength, and plotting $I(\lambda_0 \pm \Delta\lambda)$ as a function of v_z in a linear scale.

These distributions have been obtained in the case of H atoms only suffer collisions dictated by reaction (1). However, if other collisions were also included, in particular the collisions of momentum transfer, profiles with a shape close to the measured spectrum lines would be obtained. For this purpose, we use the cross section of reaction (1) indicated in [14] to calculate a rate coefficient for this reaction. We obtain $k_1 = \langle v\sigma(E)\rangle \sim 2.5\times 10^{-9}$ cm^3 s^{-1}, which is a value close to 2.11×10^{-9} cm^3 s^{-1} reported in [15]. On the other, the rate coefficient for elastic collisions may be estimated considering hard sphere collisions $k_{col} = \pi d^2\sqrt{8K_BT/(\pi\mu)}$, with d=1 Å and $\mu = m_H/2$, giving $k_{col} = 6.46\times 10^{-12}\sqrt{T}$ cm^3 s^{-1}, with T in K. The number of collisions of both types, per volume unity and time unit, are $[H_2^+]$ $[H_2]$ k_1 and $[H]^2$ k_{col}, so that the spectrum emission lines, as both types of collisions are included, can be roughly estimated by considering a weighted combination of the modified I_1 and nonmodified I_{col} spectra due to reaction (1), as follows: $I(\lambda) = \xi I_1 + (1-\xi) I_{col}$, with $\xi = \delta(H_2^+)k_1/(\delta(H_2^+)k_1 + \delta(H)^2 k_{col})$, and where $\delta(H_2^+) = [H_2^+]/[H_2]$ and $\delta(H) = [H]/[H_2]$ denote the ionization and the dissociation degrees. When the collisions with molecules are also efficient for thermalization, we should consider δ(H) instead of $\delta(H)^2$ in the expression for ξ. Since $\nu_{col} \sim 2.8\times 10^6$ s^{-1} at p=1 Torr and T=500 K, while the lifetime of Hα line is $\nu_{rad} \sim 6.3\times 10^7$ s^{-1}, we may assume that H(n=3) radiates before thermalizing collisions.

Figure 2 shows the spectrum emission of Hα line calculated for the experimental conditions of the positive column of a hydrogen glow discharge reported in [16]: p=1 Torr, I=30 mA, T=500 K, $[H] = 1.25\times 10^{13}$ cm^{-3} and $n_e = 3.85\times 10^{11}$ cm^{-3}. Assuming $[H_2^+] \sim n_e$, we obtain $[H_2^+]/[H_2] = 2\times 10^{-5}$ and $[H]/[H_2] = 6.5\times 10^{-4}$. The spectra are calculated for ΔE=0.2 and 2 eV, being the nonbroadened line ΔE=0 also plotted for comparison. The extended lateral wings obtained for ΔE=2 eV, that is for a value close to 1.56 eV reported in [10], are remarkable. Measured spectra with this shape have been obtained in [16], which at that time have also been interpreted as indicative of the presence of hot atoms. Finally, we notice that we have assumed in these calculations an energy-independent cross section for reaction (1). However, in the case of a decreasing cross section with energy [13], the velocity distribution of the product species in the center-of-mass frame would become narrower and the observable spectrum would be even more rectangular than it is predicted here.

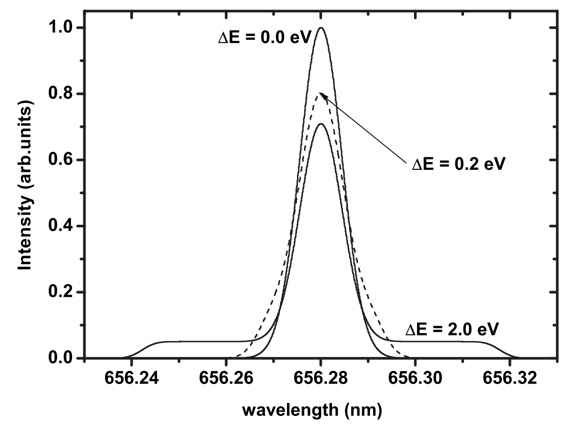

FIG. 2. Intensity of Hα Balmer line at the experimental conditions of a H_2 positive column with $[H_2^+]/[H_2] = 2\times 10^{-5}$ and $[H]/[H_2] = 6.5\times 10^{-4}$, calculated for T=500 K and ΔE=0, 0.2 and 2 eV.

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