Broadening of hydrogen lines produced by $H_2^+ + H_2 \rightarrow H_3^+ + H$ reaction with an energy-dependent cross section

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The non-maxwellian character of velocity atom distributions responsible for an excessive broadening of Balmer lines observed in hydrogen discharges at low and moderate fields is investigated. For this purpose we analyse the effects on line broadening produced by an exothermic reaction creating H atoms, such as: $H_2^+ + H_2 \rightarrow H_3^+ + H + \Delta E$, with ΔE = 1.56 eV. The reactant species are assumed with different temperatures and the actual reaction cross section [1] is simulated considering a cutoff energy at 1 eV. The results are given as a function of the temperature of H_2^+ ions and of the cutoff energy of the cross section. The profiles obtained for the H_α line are significantly flatter and squarer than a Gaussian function avoiding that a temperature for the H atoms may be safely determined from the full width at half maximum of these lines.

Recently, anomalous H_α line broadening has been observed in different laboratories using a large variety of experiments, both in pure H_2 and in specific mixed gas plasmas, produced by DC, RF and microwave discharges. The spectral lines are composed of two components, a central line, which is only modestly broadened, and lateral wings which may be dramatically broadened. It is universally agreed that the broadening must be Doppler broadening. Other sources of line broadening such as Stark effect and instrument broadening are easily eliminated as they cannot explain the magnitude of the observed broadening, nor are these alternative explanations consistent with the fact of only hydrogen spectral lines are selectively broadened. The electron density required to explain the observed enlargement by Stark effect would be larger by orders of magnitude than the density of atoms. The emission profiles and the spatial distributions of H_α have been predicted from a kinetic collisional model of energetic hydrogen atoms, molecules and ions for the cathode region of a low-pressure, weakly ionized discharge in pure H_2, and these results have been successfully compared with a variety of experiments.

However, the generality of the models proposed cannot explain the line broadening detected away from the high field region. Indeed, hot H atoms have also been detected in regions where it is generally understood that the field is quite weak, such as it is the case of the positive column of a DC discharge, an abnormal glow discharge, and outside the sheath region of an RF discharge. Also in microwave plasmas the broadening of H_α line has been detected. In certain cases a modest broadening but clearly selective (*i.e.* confined only to the H-atom spectrum) has been observed.

With these facts in mind, we have recently tried to answer these interrogations by choosing a different line of investigation. We have investigated the effects produced by an exothermic reaction producing H atoms in the velocity distribution for this species and thus in the broadening of H_α line [2,3]. We have considered to illustrate this effect the case of reaction $H_2^+ + H_2 \rightarrow H_3^+ + H + \Delta E$, in which, the product species share the energy ΔE = 1.56 eV. Of course this reaction cannot explain the extraordinary enlargement of the lines measured in regions of high field gradient but it may bring some light to the situations where the field is relatively weak. With a reaction of this type is possible to study the modifications produced on the velocity distributions and line profiles of H atoms, as well as the effects of determining Doppler temperatures from these modified profiles can be then evaluated and discussed. However, the species produced by the above reaction have isotropic distributions, so that the model is surely invalid as anisotropic processes dominate the excitation of the Balmer lines.

In this contribution we will update our previous investigations by eliminating some restrictions: *i)* the temperatures of both colliding partners, H_2^+ and H_2, are assumed different from each other, in line with the fact of the temperatures of ions are normally larger, although the velocity distribution still continues to be isotropic; *ii)* the probability of the above reaction producing H atoms is assumed energy-dependent, although using an approximate procedure to maintain the essence of our model; *iii)* the contributions of other reactions for the enlargement of the H_α line are also investigated.

Figure 1 shows the intensity of H_α Balmer line calculated using our model in the case of an energy-independent cross section, *i.e.* for a cutoff energy $E_0 \rightarrow \infty$, a common temperature T = 500 K for H_2^+ ions and H_2 molecules, and the following values of the energy defect ΔE of the exothermic reaction considered in this paper: 0 (*i.e.* MB distribution); 0.2 eV; 2.0 eV. Also plotted in figure 1 are the best fitted Gaussian functions to the calculated flatter profiles. Since the fitting is made in the bottom of the distribution, the area limited by the gaussians significantly exceed the area under the flatter profiles. In the case of the broadest profile with ΔE = 2.0 eV, the circunscrit area is about 13% only of the area under the fitted Gaussian, with this latter being adjusted on the base of the flat profile. The temperature of the fitted Gaussian is 7453 K. It is worth noting here that the broadened profiles shown in figure 1 correspond only to the lateral wings of a real spectrum. If other collisions where also included in the model, in particular the collisions of momentum transfer, profiles with a shape close to the measured spectrum would be then obtained [2].

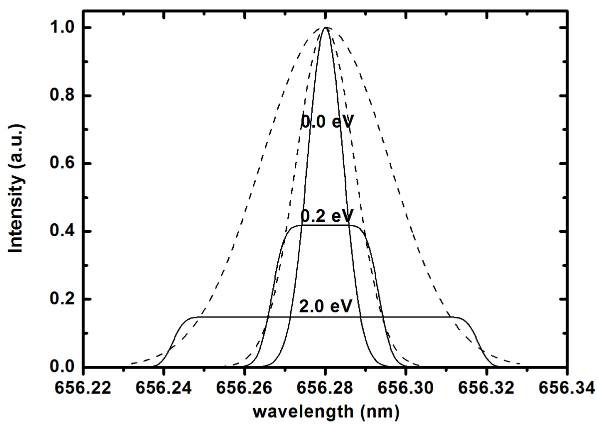

Fig. 1: Intensity of the Doppler H_α line for the same reaction as before but considering the energy defects ΔE = 0, 0.2 and 2.0 eV, an energy-independent cross section and a common temperature T = 500 K for H_2^+ ions and H_2 molecules. The broken curves are the best fitted Gaussian profiles at the bottom of the distributions for ΔE = 0.2 and 2.0 eV.

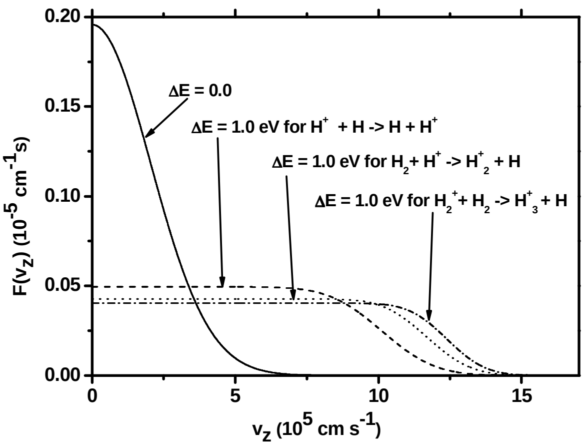

Fig. 2: One-dimensional component velocity distribution of H atoms, as a function of the z component of the velocity. Three different reactions involving collisions of H^+ and H_2^+ ions are considered.

As can be seen in figure 2, there is a strong departure of the MB distribution (ΔE = 0.0 eV) for the three pathways with ΔE = 1.0 eV. As the masses of the colliders increase the tail of the 1D distribution function significantly enlarges.

Conclusion

In this work the energy variation of the cross section is taken into account in the model, although assuming a constant probability up to a given cutoff energy and a null-probability beyond this value. The results are explored in terms of the parameters: temperature of H_2^+ ions and cutoff energy of the reaction cross section, keeping constant the temperature of molecular hydrogen and the energy transferred to both product partners.
Three different reactions involving H^+ and H_2^+ ions were investigated and the effects produced on the 1D distribution have been evaluated. However, other collisional processes need to be included in order the model may properly describe the broadening profiles. Here, we want just to call attention for the strongly non-Gaussian profiles so obtained.

References

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