Excitation by and Surface Reflection of Fast Hydrogen Atoms in Low-Pressure Hydrogen Discharges

Z. Lj. Petrović,[a] B. M. Jelenković,[a] and A. V. Phelps
Joint Institute for Laboratory Astrophysics, University of Colorado and National Institute of Standards and Technology, Boulder, Colorado 80309-0440
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Fast excited H atoms produced in collisions of fast H atoms with H_2 and observed by Doppler spectroscopy and quantitative radiometry are the dominant Hα source in low-current, low-pressure H_2 dc discharges. For heavy-metal cathodes, backscattered fast H atoms from incident H and H^+ atoms and H_2 and H_2^+ molecules excite most of the Hα. For graphite cathodes, backscattering is small and Hα is produced by electrons and by approaching fast H atoms produced by charge transfer in H^+-H_2 collisions and dissociation in H_2^+-H_2 and H_2-H_2 collisions. Excitation of Hα by ion collisions with H_2 and the cathode is small.

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Experimental evidence is presented for a new mechanism for the production of excited hydrogen atoms in which atomic collisions with surfaces and H_2 molecules play a crucial role. This mechanism is relevant to plasma-surface interactions, low-pressure electrical discharges used for plasma processing, fusion plasmas, surface physics, and hydrogen radiation from the atmospheres of the outer planets. The mechanism invokes the production of excited atoms in collisions of relatively low-energy (30 to 1500 eV) atomic hydrogen with H_2 gas and the production of backscattered H atoms in collisions of hydrogen atoms and molecules with surfaces. These experiments are the first to provide quantitative radiometry of the Doppler-shifted emission and the interpretation is the first to be consistent with measured atomic collision cross sections and with backscattering number and energy yields from surfaces. It is shown that previous explanations [1] are inconsistent with our experiment and that our model is consistent with the spatial distribution of emission obtained from high-current discharges [1].

Fast excited H atoms in the cathode regions of low-pressure electrical discharges in H_2 have been the subject of a number of recent investigations [1,2]. The hydrogen emission lines include "far wing" components from excited atoms approaching the cathode and, often, stronger components from excited atoms directed away from the cathode that cannot be explained by dissociative excitation of H_2 by electrons [1–3]. Published explanations [1] include the production of reflected, excited H atoms at the cathode by H^+ bombardment [4].

Our approach is to measure and model (a) the Doppler-broadened Hα profiles, (b) the magnitude and spatial distribution of the Hα emission, and (c) the change in line profile and spatial intensity with cathode material. A quantitative model based on the cross sections is shown to fit the data.

The measurements were made in a low-current, high-voltage, and uniform electric field H_2 discharge using the drift tube described previously [5]. One electrode is a semitransparent film of 60% Au–40% Pd. The other electrode is vacuum-grade, sintered graphite. The semitransparent electrode allowed observation of the spectral profiles parallel to the axis of the drift tube with a $\frac{1}{4}$-m monochromator. The full width at half maximum (FWHM) spectral resolution was 0.24 nm. The radial distribution of emission was uniform. The optical system [5] for the spatial scans used an interference filter peaked at 653 nm and slits set for a spatial resolution (FWHM) of ≈ 2 mm. The electrodes are 40 mm apart and 78 mm in diameter and, together with low current (< 10 μA), provide a nearly uniform electric field. The Hα emission was proportional to current.

Figure 1 shows the observed and calculated Hα line profiles for a H_2 discharge with the AuPd cathode at $E/n = 10$ kTd, $p = 20$ Pa $= 0.15$ Torr, an applied voltage of 2000 V, and a current of 10 μA. Here E is the electric field, n is the gas density, p is the hydrogen pressure, and 1 Td $= 10^{-21}$ V m^2. The relation between wavelength

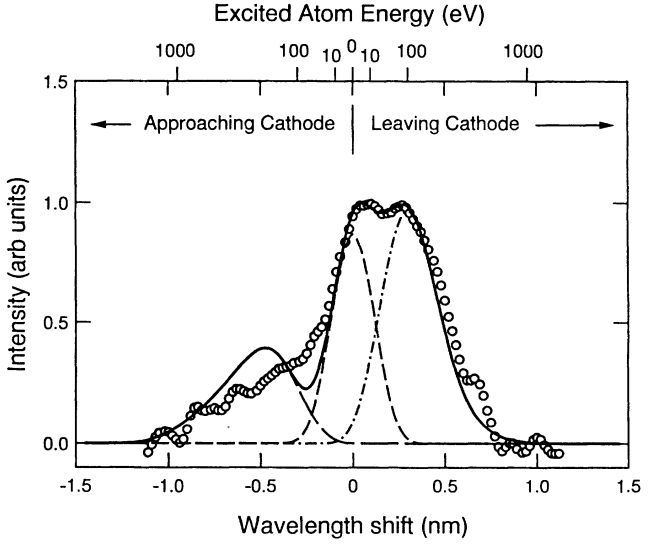

FIG. 1. Spectral profiles for the Hα line observed parallel to the axis of a low-pressure, low-current H_2 discharge at $E/n = 10$ kTd and 20 Pa.

shift $\Delta\lambda$ and H atom energy ϵ for atoms directed parallel to the tube axis is $\Delta\lambda(\text{nm}) = 0.03\epsilon^{1/2}$, where ϵ is in eV. The circles show the experimental profile, while the dashed curves represent distinguishable components of the profile and are the result of fits to the data to be described. The solid curve shows the sum of the calculated components. The short-dashed curve centered about $\Delta\lambda = 0$ is an analytical fit to the instrument function. The area under this curve represents excited atoms which are moving too slowly to produce an observable Doppler shift. The long-dashed and dot-dashed curves at negative and positive $\Delta\lambda$ show our estimates of the components of the profile representing fast excited atoms approaching the cathode and directed away from the cathode, respectively. The areas under the components assigned to excited atoms approaching the cathode (approaching component), not moving significantly, and directed away from the cathode (leaving component) are in the ratios 1:1.1:2.4. Thus, more than one-half of the excited atoms are directed away from the cathode. The energies corresponding to the mean wavelength shifts of the approaching and leaving components are 330 and 170 eV, respectively. Similar data are obtained at other E/n. When the electrode voltages were reversed such that the cathode was graphite, the areas under the components were in the ratios 1:0.5:0.3, i.e., the leaving component was reduced by a factor of 8.

Spatial variations of the Hα emission coefficient observed at 90° to the tube axis are shown in Fig. 2 for very nearly the same E/n and pressure as for Fig. 1. The normalized emission coefficient is the rate of photons emission per unit length of discharge divided by the gas density and the total current [5]. The Hα spatial profiles were made absolute by normalizing experimental emission signals for $E/n = 300$ Td to published theoretical electron excitation coefficients [6]. Because of the large spread in the available rate coefficients [7] for collisional quenching of Hα emission, the absolute values shown are uncertain to $\pm 40\%$.

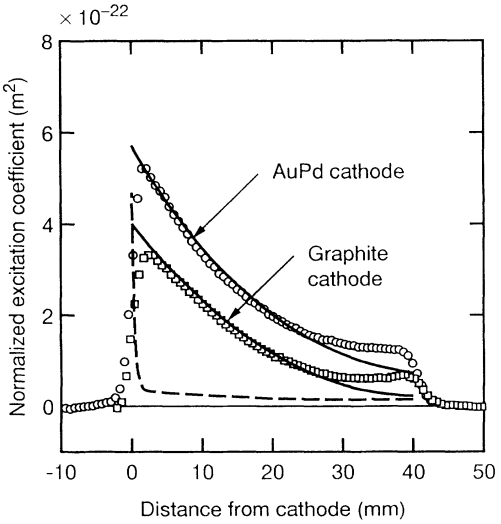

FIG. 2. Spatial dependence of the calculated and measured Hα excitation coefficient for self-sustained discharges in H_2 with Au-Pd and graphite cathodes for the same conditions as Fig. 1.

Our interpretation of the observed spectral distribution of Hα emission is that the excitation in the far wings of Fig. 1 is the result of collisions between fast H atoms and H_2. Excitation by fast atoms dominates collisional excitation by ions and electrons because of much larger cross sections [5,8] for excitation by neutrals at the typical ion, fast neutral, and electron energies and because of the larger neutral fluxes [5,9]. If the leaving component of Hα excitation ($\Delta\lambda > 0$) were caused by H^+ ions reflected from the cathode, the emission would be confined to a few mm of the cathode because of the slowing down of the ≈ 170 eV H^+ ions by the applied electric field. Also, the probability of reflection of a H^+ ion from the surface as H^+ is small [4,10].

A recently published cross-section set [8] is the source of most of the cross sections used to model these H_2 discharges. At the E/n and pressure of Figs. 1 and 2, H^+ ions are formed by electron- and heavy-particle-induced dissociative ionization and by collisional dissociation of H_2^+. About half of the H^+ ions undergo charge-transfer collisions with H_2 to produce fast H and slow H_2^+ before reaching the cathode. The fast H atoms lose a significant fraction of their speed in H-H_2 inelastic collisions in about 30 mm. Dissociative excitation of H by electrons is included in the component of the profile represented by the instrument function in Fig. 1, since the maximum energy of the H atoms is ≈ 10 eV [3].

Ground-state H_2^+ ions are calculated to reach a steady-state drift velocity and energy distribution in ≈ 3.7 mm with an effective "temperature" for the one-dimensional Maxwellian [11] of $T_+ \approx 180$ eV. Here we have used one of the lower values [12] for the charge-transfer cross section for H_2^+ in H_2 in order to fit our experiment. No transport coefficients measurements have been reported for H_2^+ in H_2 at the E/n of interest, so we cannot test this choice under drift tube conditions. The H_2^+ ions in the ground vibrational state dissociate in ≈ 25 mm. The rate of conversion of H_2^+ to H_3^+ is negligibly small at the ion energies of interest here [8]. A H_2 molecule with the same energy as that of the H_2^+ is formed on each H_2^+-H_2 charge-transfer collision. The possibility of significant vibrational excitation [8] of the H_2^+ introduces an uncertainty of as much as 50% to these cross sections.

The line profile for fast excited H atoms approaching the cathode is shown by the left-hand portion of the long-dashed curve of Fig. 1. Beam experiments [13] show that the relative production of excited H atoms with small energy losses and small angular scattering in H-H_2 collisions increases with decreasing energy ϵ to nearly 100% at $\epsilon \approx 2000$ eV. We extrapolate this result to the

30–1500 eV of the present experiments. Because of the long mean free paths for large-angle scattering [8], the velocities of fast H^+ ions and H atoms approaching the cathode are nearly normal to the cathode. A fast-H-atom energy distribution consistent with the wavelength dependence of the line profile for $\Delta\lambda < -0.5$ nm in Fig. 1 has a high energy component that varies as $(1500-\epsilon)^2$. Such a distribution is produced by H^+ ions which are formed uniformly in the gap by electrons [5] and are neutralized by charge transfer as they cross the gap. The consistent distribution also has a low-energy component with $T_+ \approx 90$ eV, such as is produced by dissociation of the higher energy H_2^+ with a temperature of ≈ 180 eV. Preliminary results of Vrhovac *et al.* [14] for unidentified hydrogen ions are consistent with the sum of these H^+ and H_2^+ ion energy distributions. The total H atom energy distribution is multiplied by the energy-dependent $H+H_2 \rightarrow H\alpha$ excitation cross section [8], weighted to take into account the spatial distribution discussed below, and folded into the instrument function to obtain the spectral intensity distribution shown in Fig. 1. The relative experimental data are scaled to fit the calculated profile at the peak. The calculated $H\alpha$ line profile of Fig. 1 for excited atoms approaching the cathode is in good agreement with experiment except near $\Delta\lambda = 0.3$ mm, where there is structure in the calculated profile. Our preliminary investigation suggests that the discrepancy is caused by our neglect of velocity loss and of angular scattering during excitation.

The calculation of the spectral distribution for the leaving component of the profile of Fig. 1 depends on the distribution in energy and angle for backscattered H^+ and H. Experiment and theory [4,10] show that for incident H^+, H, H_2^+, and H_2 the backscattered species are almost entirely H atoms, that the H atom number and energy yields increase with target atomic mass, and that the distribution in energy of the backscattered H atoms increases with energy for low incident energies. For simplicity, we have used a distribution of backscattered atoms proportional to the H atom energy, i.e., a distribution with an average energy of 67% of the incident energy [4,10]. As suggested by experiment [4,10], we have used a number yield R_N of 60% per incident H and H^+ for both the high- and low-energy groups of our model. We use $R_N = 1.2$ per incident H_2 and H_2^+ [4,10]. In accordance with theory [10] for energies at 30 and 300 eV, we use a $\cos^2\Theta$ angular distribution of backscattered atoms, where Θ is the polar angle. The relative magnitudes of the calculated approaching and leaving components in Fig. 1 take into account the spatial distributions discussed below. Fitting the relative magnitudes of the leaving and approaching components of the profile in Fig. 1 required only a 30% adjustment in the fluxes obtained using the cross sections discussed above.

Our present model underestimates the unshifted component of the profile shown by the fitted, short-dashed curve in Fig. 1 by an order of magnitude. Because of the small Doppler shifts, this component is attributed to electron excitation and is not of primary concern in this Letter. Possible reasons for the discrepancy are that our nonequilibrium electron model [5] severely underestimates the number of electrons near the threshold for $H\alpha$ excitation and/or underestimates the yield of backscattered electrons from the anode.

We next consider the absolute values of the spatially dependent $H\alpha$ excitation coefficient data of Fig. 2. The spatial distribution of the component of the excitation caused by approaching fast H is assumed to depend on the square of the distance from the anode, as was found experimentally [5] for Ar. Such a distribution is consistent with the fact that from one to three collisions are required to produce the fast H. For the component representing fast H atoms leaving the cathode, we use the attenuation length for inelastic collisions [8] at the energy of the mean of the Doppler shift. The magnitudes of the products of H atom flux and excitation cross section are given by integrals over wavelength of the components of the calculated $H\alpha$ profiles. The upper solid curve of Fig. 2 for the AuPd cathode shows the calculated $H\alpha$ spatial profile including the contributions of approaching and backscattered fast H atoms, H^+ ions, and electrons. The contribution of electron-H_2 collisions is calculated using published cross sections [6] and an approximate model [5]. The result is too small, $< 2\%$ at the cathode, to show well. The contribution of H^+-H_2 collisions at the cathode is $< 5\%$ of the total excitation. The ratio of the spatially integrated leaving component to the spatially integrated approaching component is the same as the ratio for the spectrally integrated leaving and approaching components of Fig. 1. The fit of the model to experiment in Fig. 1 is good except near the anode. The predicted excitation by backscattered and secondary electrons from the anode has the correct spatial dependence but is too small by about an order of magnitude. Investigation of this problem is continuing. Note that resolution of this discrepancy in favor of increased electron excitation might also resolve the discrepancy in the magnitude of the unshifted component discussed in the previous paragraph.

The lower solid curve of Fig. 2 is calculated by reducing the assumed yields of backscattered fast H atoms for graphite to $R_N = 0.2$ for incident H and H^+ and 0.1 for incident fast H_2 and H_2^+. These R_N values yield agreement with the factor-of-8 reduction in the leaving component calculated from the spectral profiles. The low H atom yields for incident H atoms is typical of experiments for graphite loaded with hydrogen [10]. We have not found data for H_2 (or H_2^+) incident on graphite.

We next show that the spatial distribution and magnitude of the signal predicted using the previously favored model [1,2] are inconsistent with our experiment. The dashed curve of Fig. 2, calculated for the conditions of Figs. 1 and 2, shows the emission resulting from excited atoms emitted from the cathode as the result of H^+ strik-

ing the cathode and from collisions of H^+ ions with H_2. The calculation uses the quenching cross section obtained by interpolation between our unpublished thermal data and high-energy measurements [7,15], the mean of radiative lifetimes calculated [16] for the $n=3$ levels in the average electric field of 500 V/cm of between 7 and 17 ns, and a velocity calculated from the measured mean $\Delta\lambda$ for the leaving component. The calculations use a value of 0.005 excited H per incident H^+ as an upper limit to an extrapolation of measured absolute and relative yields [4] to our energies.

Finally, we give an example of the agreement of our model with results obtained in higher-current discharges. Although the electric fields in higher-current dc discharges and dc-biased rf discharges are spatially nonuniform [1,2], the electric-field magnitudes and excited H lifetimes near the cathode are often comparable with ours. Thus, the experimental spatial dependence of $H\alpha$ emission near the cathode found by Barbeau and Jolly [1] agrees well with our model and not with the rapid attenuation expected for excited fast atoms. We therefore propose that our basic explanation of the generation of $H\alpha$ emission, including the far wings of the Doppler profiles, applies to the earlier experiments [1,2]. Obviously, more detailed investigations are needed to test the applicability of our model to rf discharges, etc.

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[a]Permanent address: Institute of Physics, Belgrade, Yugoslavia.

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