Energetic ion, atom, and molecule reactions and excitation in low-current H_2 discharges: H_α Doppler profiles

Z. Lj. Petrović[1,2,*] and A. V. Phelps[1,†]

[1]*JILA, National Institute of Standards and Technology and University of Colorado, Boulder, Colorado 80309-0440, USA*

[2]*Institute of Physics, University of Belgrade, P.O. Box 68, 11080 Zenum Belgrade, Serbia*

(Received 30 July 2009; revised manuscript received 15 October 2009; published 2 December 2009)

Absolute spectral emissivities for Doppler broadened H_α profiles are measured and compared with predictions of energetic hydrogen ion, atom, and molecule behavior in low-current electrical discharges in H_2 at very high electric field E to gas density N ratios E/N and low values of Nd, where d is the parallel-plate electrode separation. These observations reflect the energy and angular distributions for the excited atoms and quantitatively test features of multiple-scattering kinetic models in weakly ionized hydrogen in the presence of an electric field that are not tested by the spatial distributions of H_α emission. Absolute spectral intensities agree well with predictions. Asymmetries in Doppler profiles observed parallel to the electric field at $4 \leq E/N \leq 20$ kTd result primarily from excitation by fast H atoms directed toward the cathode and diffusely reflected from the cathode. ($1\ \text{Td}=10^{-21}\ \text{V m}^2$) The effects of reflection of hydrogen particles and of changes with cathode material are modeled accurately without adjustable parameters. Maximum measured wavelength shifts result from acceleration of H^+ ions and charge transfer to fast H atoms. The Doppler profiles are consistent with models of reactions among H^+, H_2^+, H_3^+, H, and H_2 leading to fast H atoms and then fast excited H($n=3$) atoms.

DOI: 10.1103/PhysRevE.80.066401 PACS number(s): 52.20.−j, 52.80.Dy, 34.50.Gb

I. INTRODUCTION

Measurements are reported of the absolute spectral intensities for the Doppler profiles of the H_α line as a quantitative and noninvasive diagnostic of the velocity distributions of excited H atoms in multiple-scattering environment of low-current low-pressure discharges in hydrogen. Comparisons of the observed H_α profiles with a previously developed model [1,2] make possible the evaluation of otherwise unavailable energy and angular distribution properties of the energetic ions, atoms, molecules, and electrons. The present work approaches the complex problem of the kinetics of hydrogen discharges when multiple scattering and high electric fields are important by using the absolute, velocity dependent H_α emission in contrast to the recently published comparison of measured and predicted absolute spatial distributions of H_α emission [3]. In doing so, this paper makes quantitatively evident aspects of the collisional kinetics of energetic ions, atoms, and molecules of importance in the H_2 discharges, fusion edge plasmas, and geophysical plasmas cited below that are not made in our previous papers [1–3].

Before and since our proposal [1] of the importance of fast H atoms reflected from the cathode in the excitation of H_α lines, numerous authors have presented and interpreted observations of large far-wing Doppler broadening, also called "excess" Doppler broadening, in the cathode region of dc and rf glow discharges [4–22]. Contrary to these authors, we have chosen to use nearly uniform electric-field geometry and very low discharge currents to ensure the simplest possible experimental and modeling conditions. The first publication [1] in this series used illustrative spatial distribution and Doppler profile data to very briefly argue that the H_α emission in pure H_2 is primarily the result of collisions of fast H atoms produced by charge transfer of field accelerated H^+ ions and of fast H produced at the cathode by fast incident hydrogen ions and neutral species. The second paper [2] summarizes available cross section and surface scattering data and develops a multibeam model of the various ions and fast neutral species that predicts the absolute spatial dependence and line profile of the H_α emission. The third paper [3] provides experimental magnitudes and spatial variations of H_α emission over a wide range of pressures and electric field to gas density ratios E/N that successfully test several of the predictions of the model [2]. This approach is particularly useful for analysis of the dominant excitation processes but gives almost no information regarding the energies of the hydrogen neutral species. In the present paper, we report the measurement of the H_α Doppler profiles and use their comparison with the model of Refs. [1,2] to obtain velocity and angular distribution information, surface interaction data, and evidence of critical reaction pathways. Our discussion of previous work is limited to papers where comparison with the present Doppler profile work is particularly relevant and is not a historical review.

Early observations by Sternberg and co-workers [4,5] found asymmetrical far-wing Doppler broadening of the Balmer lines in dc glow and pulsed magnetron discharges in H_2. Assuming electron excitation of the H($n \geq 3$) atoms for fast excited atoms moving away from the cathode, they determined their apparent velocity distribution. Such an excitation sequence would cause the H_α signal to be proportional to the square of the electron current density, whereas we will show that the absolute magnitudes of our Doppler profiles agree with a model in which the emission is directly proportional to current density [2].

Cappelli *et al.* [6] correlated the far-wing H_α emission with the energy available to H^+ ions and with the phase of

*zoran@ipb.ac.rs

†avp@jila.colorado.edu

expected ion motion and particle reflection at the cathode of their 100 MHz rf discharge. They proposed excitation of the H_α by H^+. Baravian *et al.* [7] observed a similar far-wing broadening of H_α in higher frequency (13.56 MHz) rf discharges. Ayers and Benesch [8] found that the extent of the far-wing profiles varied with cathode material as expected for a surface dependent reflection of the energetic hydrogen species responsible for excitation. Our experiments and model are consistent these experimental observations, but not the proposed dominance of excitation by H^+.

Detailed observations and interpretations were made of Doppler profiles from dc discharges in H_2 by Bardeau and Jolly [9]. They observed asymmetric "far-wing" Doppler profiles parallel to the electric field and a dependence of symmetric far-wing Doppler profiles transverse to the discharge axis as a function of distance from the cathode. They argued that ions accelerated in the cathode fall were responsible for the excited atoms approaching the cathode and the associated red wing of their axial profile. Diffuse reflection of the incident ions or collisional removal of adsorbed gas as excited atoms in the $H(n=3)$ state were proposed as the source of the blue far wing of their axial profile, and an important source of both far wings of the transverse profiles. They separated the core excitation from the excitation in the far wings and argued that the decrease with distance of the far-wing excitation is characteristic of excited atoms produced at the cathode. Electron excitation and fast excited atoms approaching the cathode were proposed as the source of the central peak or "core" of the profiles. We have argued [1–3] that excitation at the cathode surface is not important in this type of experiment and so have a different explanation for their blue wing. The present paper makes these arguments quantitative.

Petrović *et al.* [1] reported the absolute, spatially dependent intensities of spectrally integrated H_α emission in a low-current uniform-field discharge in H_2 for two cathode materials. They also presented a spectral profile for H_α, arguing that it was the result of excitation in fast $H+H_2$ collisions. Using a very much simplified single-beam model, they showed that H_α excitation at the cathode surface in their experiments is negligible and cited evidence that the excitation of the fast $H(n=3)$ occurs primarily as a result of fast H production in charge-transfer collisions of H^+ with H_2, followed by fast H atom excitation in collisions with H_2. Here we provide important details of the previous experimental work and extend the analysis of the measurements to obtain absolute Doppler profiles, data for a cathode with low H atom reflectivity, and empirical angular distributions of excited atoms. We utilize an significantly improved "multibeam" model [2] to obtain absolute values.

Highly asymmetric far-wing emission from Doppler broadened Balmer series lines were observed along the axis of high-voltage hollow cathode discharges in pure H_2 by Lavrov and Melnikov [14]. These authors propose field accelerated negative-ion collisions with H_2 as the source of the observed "backward" moving fast $H(n=3)$ atoms producing the far-wing H_α asymmetry. Because of the high transparency of the hollow cathode to axially approaching ions and fast atoms, one expects a greatly reduced flux of reflected fast H atoms and the applicability of a model similar to that of Refs. [1,2] for cathodes with low reflectivity. We will show that at low-current densities the backward moving H atoms, produced by particle reflection at the cathode, explain the observed profiles quantitatively without the need for negative ions.

Konjević and co-workers [13,16,18–21,23–25] carried out extensive measurements of far-wing Doppler profiles from dc glow discharges. The contributions of Stark broadening to the core of the H_α profiles in these discharges was investigated in detail by Videnović *et al.* [16]. Using high-resolution measurements of the Balmer series profiles, this group determined the electric field in the cathode region [16,20]. The dependence on cathode material of the backscattered component of the far-wing H_α emission along the H_2 discharge axis was investigated [18]. The shift in the direction of the asymmetry with the direction of the electric field demonstrated by Šišović *et al.* [21] extends to glow discharges the observed dependence of the asymmetry on the direction of the electric field found at low currents in Ref. [1] and detailed in the present paper. Cvetanović *et al.* [20] provided relative spatially dependent intensities of the far-wing and core components, which have recently successfully been modeled [26]. The papers by Konjević and co-workers have argued for the importance of H_3^+ ions formed from collisions of H_2^+ with H_2 in H_α excitation. In our model [2], H_3^+ plays an important role in the ion kinetics at low E/N, but is not directly responsible for H_α production.

Babkina *et al.* [27] determined the energy spectrum of fast ground-state H atoms produced by various hydrogen ions when backscattered from a stainless-steel surface biased negatively with respect to a plasma source. They also observed the enhanced far wing of H_α emission produced by these atoms.

Of the many recent observations of enhanced far-wing H_α emission from rf and microwave discharges, only discharges in H_2 with sufficient time and/or spatial resolution provide useful information for verifying models and interpreting dc discharge results. Thus, observations by Cappelli *et al.* [6], Radovanov *et al.* [15], and by Gans *et al.* [17] showed the production of H_α by a flux of fast neutral particles leaving the instantaneous cathode at the time of arrival of the peak in ion flux. The more recent of these experiments confirm the importance of backscattered atoms in the excitation sequence and demonstrate the very short energy relaxation "lifetimes" of the population of high energy species in the reaction sequence. Thus, experiments with sufficient time and spatial resolution show that the mechanism of H_α far-wing production is consistent with that for the low-current dc discharges discussed in the present paper.

Very recently, Cvetanović *et al.* [28] used Monte Carlo techniques to calculate the H_α Doppler profiles observed normal and parallel to the surface. They show that the assumption of a cosine distribution of backscattered H atoms proposed in Ref. [1] gives good agreement of calculated and measured Doppler and spatial profiles for excited atoms leaving the cathode. See Sec. IV C of this paper.

An essential feature of the papers of Mills, Phillips, and co-workers [29] is their observation of nearly symmetric Doppler profiles for H_α under all discharge conditions and their interpretation of this symmetry in terms of a randomly directed thermal excitation process. Since we will show that our Doppler profiles can be highly asymmetric, their proposed excitation by a randomly directed "resonant transfer" collision does not apply to our experiment. Furthermore, we claim that the observed symmetry of H_α profiles in their rf experiments is the result of insufficient spatial and time resolution, reflection of emission by the glass walls, and the presence of rf sheaths at the insulating surfaces [30]. As a result, they cannot rule out the acceleration of hydrogen ions and subsequent reactions of Ref. [2] as the source of fast $H(n=3)$ atoms in pure H_2. Their observation of H_α far-wing broadening from microwave discharges has been brought into question by the inability of others [31,32] to reproduce the results and by the scarcity of information regarding sheaths in high power-density microwave discharges [33–35].

It is important to keep in mind that the experiments described in the present paper operate in the low-current diffuse or Townsend dark-discharge regime [36–38]. In this low-current density and low space charge-density limit the electric fields are not significantly perturbed from the nearly spatially uniform values defined by the external voltage and the large-diameter parallel-plane electrodes. As a result, one can calculate reasonably accurate ion, atom, molecule, and electron spatial distributions and energy distributions. The relative simplicity of this regime gives us a chance to test models [2] of H_α excitation and to discriminate against several of the alternative explanations cited above. Operation in this regime limits the current density to less than about 200 nA/cm^2 and severely limited the H_α signal and the useful spectral resolution in our measurements of the H_α Doppler profiles.

The apparatus features and model parameters essential to the present paper are briefly summarized in Secs. II and III. Section IV A discusses our procedure for placing the measured relative spectral distributions on an absolute scale for comparison with the predictions of the model; Sec. IV B discusses quantitatively the effects of changes in cathode material on the profiles; Sec. IV C presents the evidence for diffuse scattering of H atoms from the cathode and a wide angular distribution of angles for $H(n=3)$ atoms approaching the cathode; Sec. IV D shows that the maximum excited atom velocities are consistent with a scheme including H^+ accelerated by the electric field; and Sec. IV E shows the high sensitivity of the Doppler profiles to small changes in hydrogen density expected for excitation by multistep process. These topics were not been tested by comparison of experiment and model in our earlier spatial dependence paper [3]. Doppler profiles obtained by observations perpendicular to the electric field are available only from higher-current glow-discharge experiments and are not discussed in the present paper. See, for example Refs. [9,20].

II. EXPERIMENT

Figure 1 shows a schematic of the drift tube, monochromator, photomultiplier, and electrical circuit for the discharge. The low-current high-voltage drift tube is the same as that described previously [1,3,39,40]. One electrode is a

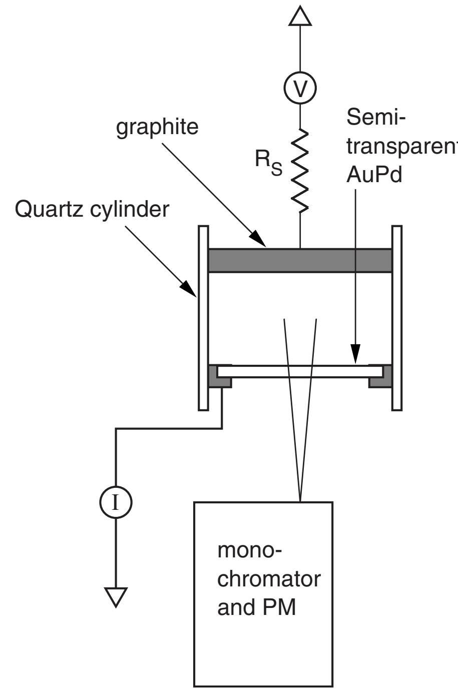

FIG. 1. Schematic of the drift tube, monochromator, photomultiplier, and electrical circuit for the discharge.

semitransparent film of 60% Au–40% Pd on a quartz window which is mounted in a stainless-steel ring. It is crucial to keep in mind that our observations are made through this semitransparent electrode, which may be either the cathode or the anode, rather than through the anode as in many other experiments [9,20]. The other electrode is vacuum-grade sintered graphite [41] attached to a terminal insulated for high voltages. The electrodes are 40 mm apart and 78 mm in diameter and provide a nearly uniform electric field. A quartz tube closely fitting the graphite electrode and appropriate insulators prevent long-path breakdown. The semitransparent electrode allowed observation of the spectral profiles parallel to the axis of the drift tube with a 1/4 m, f-5.5 monochromator. The wavelength scale and instrument resolution are determined by observing the Ne line at 659.9 nm from a Ne capillary lamp during each scan. The calibration is also tested using the H_α line from a low-current H_2 capillary lamp between data scans. Care is exercised to not overload the detection system and the optical geometry is preserved by scattering the lamp radiation from the graphite electrode. The spectral resolution was varied from 0.2 to 1.5 nm, full width at half maximum (FWHM). No impurity spectra were observed in the spectral scan between 200 and 700 nm presented in Fig. 2 of Ref. [3]. The sensitivity of the detection system is assumed to be constant over the small spectral range of the Doppler profile. Possible distortion of the Doppler profile data by light reflected from the electrodes has been discussed by Gemišić Adamov *et al.* [18]. We have analyzed our data neglecting the optical reflection from the graphite [42] and will cite evidence supporting this assumption in Sec. IV.

The principal source of noise in these measurements of H_α emission is the fluctuations in the current from the cooled photomultiplier (Hamamatsu R928), with a typical background of ≈360 counts/s. With our highest resolution of 0.2 nm FWHM, ≈430 counts/s were obtained at the H_α peak. Using a scan rate of 0.005 nm/s, the average count rate is recorded at intervals of 4 s and later normalized to the average current for that interval. This data is smoothed 3 times with 3-point averaging before plotting. Because of the low signal to noise, the current dependence of the H_α emission profiles is not investigated. We rely on the demonstrated linearity of the spatial distribution of H_α emission in this apparatus [3] and utilize discharge currents up to 12 μA [43].

III. DOPPLER PROFILE PARAMETERS

The geometry appropriate to the calculation and observation of the H_α profiles is shown in Fig. 11 of Ref. [2]. Part (a) shows the geometry for viewing along the discharge electric field, while part (b) shows the geometry for viewing at right angles to the electric field. We consider emission from a thin slab perpendicular to the axis of the drift tube. In the calculation of the excited atom density, the slab is assumed large enough in the direction perpendicular to the electric field so that any loss of excited atoms out of the field of view of the monochromator is balanced by excited atoms entering the field of view. Reference [2] discusses an approximate allowance for the loss of fast atoms and molecules to the quartz wall. We calculate the contribution to the photon flux resulting from emission by an $H(n=3)$ atom at a wavelength shift from line center, $\Delta\lambda$, corresponding to the component of velocity of the excited atom toward or away from the observer. Except as noted, the calculated H_α profiles are folded into a triangular approximation to the monochomator transmission function, with a width determined from the experimental reference lines.

Because of its importance in the calculation of the Doppler profiles for comparison with experiment in this paper, we review the procedure in Ref. [2] for simulating the departures of the angular distribution of $H(n=3)$ atoms from that of beams directed along the electric field. A range of angular distributions is accommodated by assuming that the excited H atoms have a normalized angular distribution $G(\theta)$ per unit solid angle given by

$$G(\theta) = (1+b)\cos(\theta)^b/(2\pi), \qquad (1)$$

for $0 \le \theta \le \pi/2$ and zero for $\pi/2 \le \theta \le \pi$. For atoms approaching the cathode, the polar angle θ is measured from the normal directed toward the cathode. For backscattered atoms, θ is the polar angle with the normal directed away from the cathode. The constant b is chosen to fit experiment. The distribution of Eq. (1) changes from sharply peaked (beamlike) along the surface normal for $b \gg 1$ to a nearly uniform distribution over a hemisphere for $b \ll 1$. We find that $b=0.6$ gives a reasonable fit to the backscattered angular distribution for H atoms isotropically incident on Ni at 450 eV and 4 keV calculated by Eckstein and Verbeek [44]. Our use of this value assumes that these calculations also simulate our situation of a more normally directed distribution incident on a polycrystalline, rough surface [17]. For the conditions of the present paper, we will find it best to assume

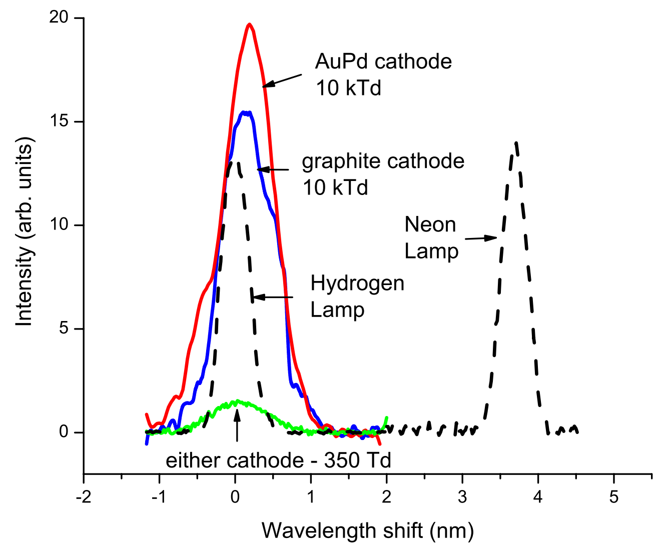

FIG. 2. (Color online) Moderate resolution H_α profiles observed parallel to the electric field of low-pressure low-current H_2 discharges. The solid curves show experimental data for an AuPd cathode and a graphite cathode for $E/N=10.5\pm0.1$ kTd, $p=0.14\pm0.01$ Torr, and a spectral resolution of 0.4 nm FWHM. The small curve is representative of the profiles obtained with $E/N=350$ Td and $p=0.8$ Torr for both discharge polarities. The dashed curves are reference lines from the hydrogen and neon lamps scattered off the anode. The hydrogen lamp reference line is obtained with the drift tube voltage set to zero.

a relatively broad distribution ($b\approx1$) for approaching excited atoms. It is important to keep in mind that the only fitting parameters we apply to the kinetics model are the parameter b for excited H atoms approaching the cathode and the magnitude factor used to place the experiments on an absolute scale. The choice of b is discussed further in Sec. IV C.

IV. H_α EMISSION PROFILES

In this section we present experimental H_α line profiles emitted by excited $H(n=3)$ atoms produced in our drift tube filled with pure H_2 and utilize them to test various aspects of the model of Ref. [2]. We obtained H_α profiles only when looking along the electric field and parallel to the axis of the drift tube. Because of the very small discharge currents required for a uniform electric-field drift tube [43,45], our spectral resolution and signal-to-noise ratio are much poorer than in the many recent experiments utilizing the high electric fields and current densities in the cathode regions of dc glow discharges [9,18,20]. Thus, the narrow "core" of the Doppler profile, resulting mostly from electron excitation, is often not resolved in our experimental data.

Representative spectral emission data from our drift tube and from reference lamps in the vicinity of the H_α line are shown in Fig. 2. The solid curves show measured H_α profiles at near optimum observing conditions of $E/N=10$ kTd and 0.15 Torr, i.e., at near our highest usable discharge voltage (2000 V) and resultant largest expected Doppler shift and at near our maximum H_α signal as discussed in Ref. [3]

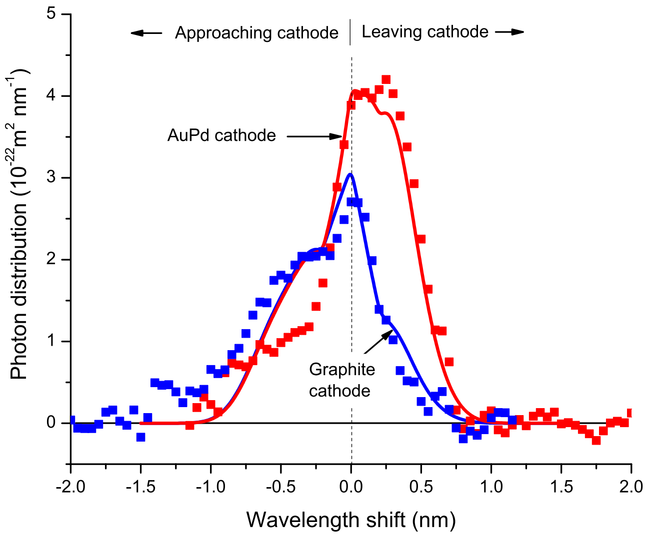

FIG. 3. (Color online) High resolution spectral profiles for the H_α line observed parallel to the electric fields of a low-pressure low-current H_2 discharge at $E/N = 10.5 \pm 0.2$ kTd, $p = 0.15 \pm 0.001$ Torr, and a resolution of 0.2 nm FWHM. The points are experimental data and the solid curves are results from the model of Ref. [2]. The experimental data for the graphite cathode is reversed in this plot so as to place emission from excited atoms moving toward the cathode at negative wavelength shifts, as is the case for the AuPd cathode.

(1 Td$=10^{-21}$ V m^2 and 1 Torr$=133$ Pa). We note that the Doppler shift for $H(n=3)$ atoms is approximately $\Delta\lambda = 0.03(\epsilon)^{0.5}$ nm, where the H atom energy ϵ is in eV. The data for the AuPd cathode is obtained looking through the cathode toward the graphite anode, so that $H(n=3)$ atoms moving toward the cathode appear at negative wavelength shifts and $H(n=3)$ atoms moving away from the cathode appear at positive shifts. The curve for the graphite cathode is obtained by reversing the discharge voltage, so that excited H atoms moving toward the cathode appear at positive wavelength shifts. The dashed curves of Fig. 2 show profiles from light scattered from hydrogen and neon lamps that serve as references for wavelength calibration and determining the spectral resolution. In Fig. 2, the nominal FWHM resolution is 0.4 nm for the lamps and the $E/N=10$ kTd data.

At $E/N < 1$ kTd the H_α spectral profile obtained for either the AuPd or graphite electrode acting as the cathode was the same shape as the reference profile and, as expected for excitation by electrons, the spatial distributions for either polarity were the same in magnitude and shape. Such data is shown in Fig. 2 for $E/N=350$ Td and 0.8 Torr (310 V) using slit widths twice those used for the high E/N scans, but otherwise the same detection sensitivity as for the data at $E/N=10$ kTd.

We are particularly concerned with testing models for the far wings of the H_α profiles, such as those for high E/n in Fig. 3. Because of the low estimated ion densities ($\sim 10^6$ cm^{-3}) and much lower electron densities at our low discharge currents, one can completely neglect ion- and electron-induced collisional Stark broadening [46]. Similarly, the Stark splitting caused by the applied electric field of ≤ 500 V/cm can be neglected [47] in our experiments. The low gas densities rule out significant pressure broadening [48]. The contribution of dissociative excitation by electrons to the Doppler line profile [49] is included in the model [2], although it is not distinguishable because of the relatively low spectral resolution used in the present experiments.

A. Determination of absolute spectral emission

In this section we are concerned with the determination of the scale factor required to place the experimental Doppler profiles on an absolute scale for comparison the results of the model of Ref. [2]. We normalize the Doppler profiles measured at high E/N to the absolute emission data obtained in Ref. [3] for the same parameters. In particular, the spatial average of the absolute values of the experimental total H_α apparent excitation coefficient calculated from the $E/N = 10$ kTd, 137 mTorr curve for the AuPd cathode of Fig. 4(b) of Ref. [3] is 3.3×10^{-22} m^2. We multiply the measured relative spectral intensities by a scale factor such that the integral of the experimental profile for the AuPd cathode in Fig. 3 equals the axially averaged absolute excitation coefficient from our spatial data. This scale factor is the same for the data obtained with the graphite cathode of Fig. 4, but varies with the monochromator resolution as expected. We consider the agreement of absolute values quite remarkable and well within our error estimate, e.g., $\pm 20\%$.

B. Dependence on cathode material

In this section we examine the effects of changes in the cathode material of the drift tube on the H_α profiles and the ability of the model of Ref. [2] to quantitatively predict the profiles. Figure 3 shows our highest-resolution profiles (FWHM$=0.2$ nm) for the H_α line observed at a high E/N of 10.5 kTd and a low pressure p of 0.15 Torr. The relative experimental data (points) for the AuPd and graphite cathodes are multiplied by the same scaling factor so as to place them on the absolute scale for comparison with the absolute value predicted by the model. In this plot and in the remainder of this paper, the experimental plots for the graphite cathode have been reversed so that positive wavelength shifts represent excited atoms moving away from the cathode and negative shifts represent excited atoms moving toward the cathode. The model calculations of this section were carried out with the values of b to be adopted in Sec. IV C.

The experimental data of Fig. 3 for emission by excited H atoms (points) shows generally good agreement with the predictions of the model (curves) of Ref. [2]. The high degree of asymmetry of the Doppler profile at this and other high E/N is consistent with the assumption of the model [1,2] that the number of reactions, inelastic, and elastic collisions in the sequence leading to excitation is insufficient to randomize the directions of the $H(n=3)$ atoms produced. Although the details of this fortunate circumstance are not quantitatively understood, the result is that highly asymmetric H_α lines can be approximately modeled by treating separately the species approaching and leaving the cathode [2]. The larger spread toward high velocities for $H(n=3)$ approaching the cathode (negative wavelength shifts in our case) than for excited atoms leaving the cathode is also consistent with the model

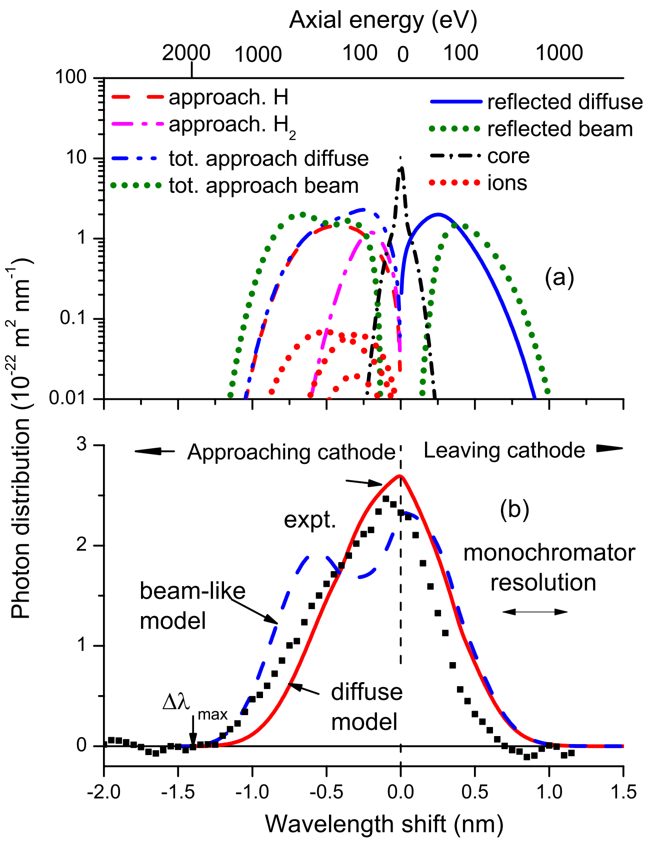

FIG. 4. (Color online) (a) Calculated contribution of excitation by various species to excitation of H_α Doppler profile. (b) Comparison of our lower resolution experiment with results of model for beamlike and for diffuse angular distributions of H(n=3) atoms approaching the cathode. The smooth curves are calculations after folding in the instrumental resolution of 0.4 nm FWHM. The points are experimental data. For these plots E/N=10 kTd, p=0.15 Torr, and cathode is graphite.

[1,2]. Thus, the excited H atoms leaving the cathode are the result of collisions of ions, atoms, or molecules with the cathode, some of which are backscattered as lower energy H atoms [2,44] and produce lower velocity H(n=3) atoms. For the conditions of the AuPd cathode of Fig. 3, average wavelength shifts of −0.38 and 0.31 nm are calculated for the axially directed velocities of H(n=3) approaching and leaving the cathode and correspond to axially directed energies of 158 and 104 eV, respectively.

An important feature of Fig. 3 is the large decrease in H_α emission caused by excited atoms leaving the cathode when the cathode material is changed from a thin film of AuPd to graphite. We see that this change is in very good agreement with predictions of the model [2]. This reduction in emission by excited atoms leaving the cathode is the result of the much lower probability that a fast incident hydrogen ion, atom, or molecule will be reflected as a fast H atom from graphite than from AuPd. See Ref. [2] for details.

The experimental data of Fig. 3 shows a noticeably larger magnitude at Δλ from −0.3 to −0.9 nm for H(n=3) approaching the graphite cathode than for the AuPd cathode. Because of a lower electron yield per ion [50], one expects a somewhat higher discharge operating voltage (2050 versus 2000 V) at very nearly constant pressure for the graphite cathode, as was the case with the spatial scans in Fig. 7 of Ref. [3]. However, for this small change in discharge voltage and essentially no change in pressure, the model predicts very little change in the H_α emission profile at negative wavelength shifts. The assumption of a larger optical reflection from the graphite surface would increase this discrepancy. Thus, we cannot account for the observed difference and propose that some parameter changed more than recorded. In Sec. IV E, we will consider a case where the small change in discharge parameters is significant.

C. Angular distribution of excited atoms

We next consider the choice of the empirical approximate angular distribution for the H(n=3) atoms approaching the cathode that replaces the narrow beam approximation, i.e., $b\to\infty$ in Eq. (1), used in the model of Ref. [1]. This is done by adjusting values for b in Eq. (1) to obtain a reasonable fit to the experimental Doppler profiles for the H_α line. Figure 4 shows a comparison of calculated H_α profiles with extreme values of the parameter b for the excited atoms, i.e., the beamlike value of b=100 giving a beam width of 13° FWHM and a diffuse distribution value of b=1 giving a cosine distribution. Figure 4(a) shows the components of the Doppler profile predicted by the model [2] for E/N=10 kTd and p=0.15 Torr for the graphite cathode. This figure shows the small contributions of excitation by ions by the dotted (red) curves for H^+, H_2^+. and H_3+ with progressively lower magnitudes and smaller wavelength shifts. The dotted (olive) curves for approaching and leaving excited atoms are calculated assuming b=100, while the remaining curves are calculated using b=1. The set of curves shown in Fig. 12(a) of Ref. [2]. are calculated for the case of an AuPd cathode for otherwise very similar discharge conditions and show the much larger contribution of reflected fast H atoms.

In Fig. 4(b) we compare experimental data with a spectral resolution of 0.4 nm FWHM with predictions of the model of Ref. [2] for E/N=10 kTd, p=0.15 Torr, and a graphite cathode. We show the lower resolution data because of its much higher signal-to-noise ratio. The dashed curve shows the sum of the components for the beamlike model (b=100) for the excited H atoms produced by H atoms and H_2 molecules approaching the cathode (negative shifts), and have used the recommended [2] value of b=0.6 for the excited H atoms leaving the cathode (positive shifts). The solid curve is calculated for b=1 for excited atoms approaching the cathode and b=0.6 for H(n=3) leaving the cathode. Each calculated curve is convoluted with a triangular function with a FWHM of 0.4 nm to simulate the instrument function. The maximum wavelength shift attainable by an H^+ ion and exciting H(n=3) near the anode for the applied voltage of 2000 V is indicated by $\Delta\lambda_{max}$.

The fit of experiment to the beamlike model with b=100 at shifts from −1.0 to $-\Delta\lambda_{max}$ in Fig. 4(b) is good, but is poor for shifts from −1.0 nm to line center. On the other hand, the fit of the experimental data to the model using the diffuse angular distribution (b=1) for Δλ from −0.5 to 0 nm is very good. Similarly, the fit is very good [51] using b

=0.6 for positive Δλ. A mixture of effective angular distributions for approaching H(n=3) is expected for the axial profile because of the increasing effects of angular scattering as the ions and fast atoms and molecules move from anode to cathode and because of the expected narrowing of the differential scattering cross sections as the energy of the particles increases. One notes that the excited atoms with wavelength shifts approaching that expected for an H^+ ion at the applied voltage are by definition the result of beamlike motion from anode to cathode parallel to the electric field, as well as evidence of excitation collisions very close to the cathode. Unless otherwise specified, we will show model results utilizing the simplifying assumption of b=1 for excited atoms approaching the cathode. Obviously, these assumptions should be replaced by mathematically accurate models utilizing yet-to-be-determined differential scattering cross sections for the various collision processes in the excitation sequence.

We note that the assumption of an optical reflection coefficient of 5% results in obviously negative values for the corrected spectral emissivity at wavelength shifts $\delta\lambda$ from +0.5 to +1 nm in Fig. 4(b). This supports our neglect of optical reflection from the graphite electrode.

D. Dependence on voltage

Figure 5 shows H_α profiles obtained at various discharge voltages and demonstrates the dependence of the profiles on the energy available to the ions and, through collisions, to the excited atoms. Here we have used the parameter $V_d = E/N \times Nd$ so as to emphasize the upper limit to the available H(n=3) energy. The E/N vary from 4 to 20 kTd at an approximately constant pressure of 0.16±0.03 Torr. Figure 5(a) shows samples of profiles for the AuPd cathode. Unfortunately, the available data for the AuPd cathode covers only part of the range of Δλ expected for excited atoms approaching the cathode with the maximum applied voltage of 3500 V. The data of Fig. 5(b) for the graphite cathode is obtained with reversed polarity and is available over the complete range of Δλ expected for approaching excited atoms. The points in Fig. 5 are the predictions of the model of Ref. [2] using b=1 for approaching H(n=3) and b=0.6 for leaving H(n=3). The calculations show good agreement with experiment, e.g., the model predicts the systematic increase in wavelength spread as the discharge voltage increases and the decrease in signal for leaving excited atoms with the graphite cathode.

Next, we consider the increase in the extent of the wings of the profiles of parts (a) and (b) of Fig. 5 as the discharge voltage is increased. The results of visual extrapolation of the data to zero at negative shifts are shown in Fig. 6, where the square points are the maximum shifts for the graphite cathode and the round points are for the AuPd cathode as estimated from data such as that of Fig. 5. The round points with arrows are lower limits to the maximum shift resulting from the limited records. The lines are calculated maximum shifts assuming that the velocity of the H(n=3) atoms are the same as the parent H^+, H_2^+, or H_3^+ ions accelerated across the whole discharge gap so as to reach velocities corresponding to the applied voltage. This comparison of measured and calculated maximum frequency shifts is consistent with the proposal of Refs. [1,2] that the reaction sequence responsible for the far wings of the H_α is such that H^+ is a major contributor to the production of the higher velocity H atoms and, subsequently, for the H(n=3).

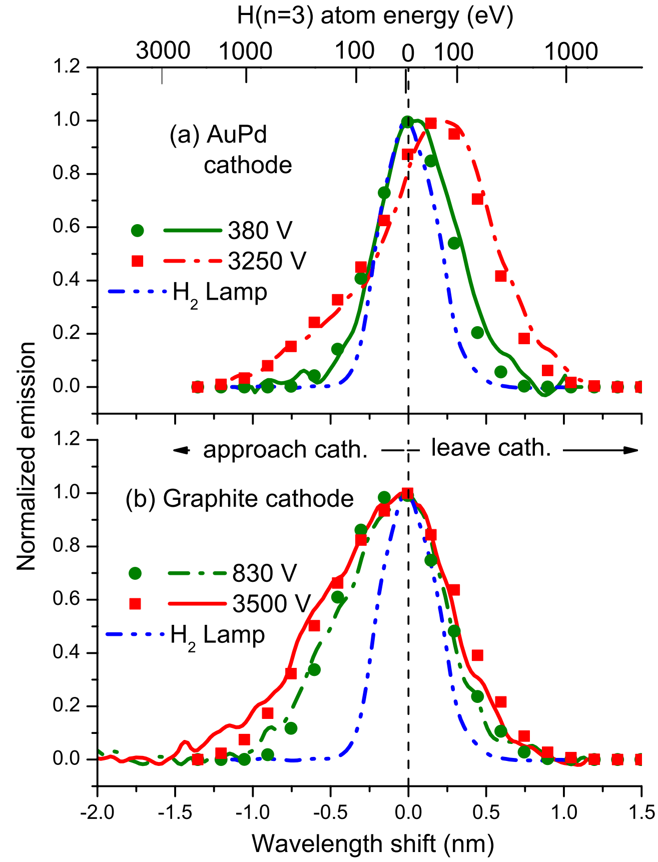

FIG. 5. (Color online) Examples of H_α profiles viewed along electric field at various applied voltages and E/N from 4 to 20 kTd for pressures of 0.16±0.03 Torr. The curves are experiment and the points are model results after folding in the instrumental resolution of 0.4 nm FWHM. The profiles are normalized to their peak values. Part (a) is for an AuPd cathode. Part (b) is for a graphite cathode.

The relatively large fraction of high energy H^+ ions indicated by ones ability to extrapolate the data of Fig. 5 to velocities corresponding the applied voltage is surprising. An extension of the kinetics model [2] to include a realistic electron-induced yield of H^+ from the anode [51] fails to increase significantly the measured profiles at the highest negative shifts.

E. Sensitivity to discharge parameters

Figure 7 illustrates the sensitivity of the H_α profiles to changes in gas density (pressure) and electric field and the ability of the model [2] to predict these changes. The profiles shown by the solid curves are obtained by observing parallel to the electric field for AuPd cathode at E/N=10.2 kTd and p=0.14 Torr and for a graphite cathode at E/N=10.4 kTd and p=0.15 Torr. These data are for a low resolution of 0.4

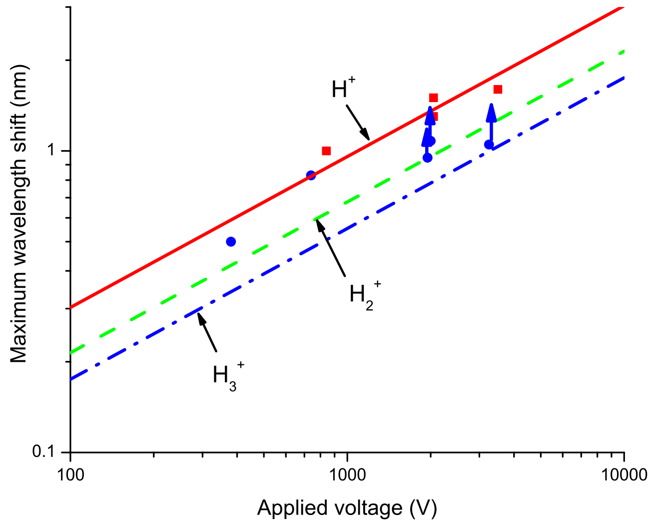

FIG. 6. (Color online) Maximum negative Doppler shift versus voltage between electrodes. The circular points are the maximum shifts for the AuPd cathode estimated from data such as shown in Fig. 4(a). The square points are maximum shifts for the graphite cathode from data such as in Fig. 4(b). The lines are calculated maximum shifts for H(n=3) produced from H^+, H_2^+, and H_3^+ versus the experimental applied voltage. The points with arrows are lower limits from Fig. 4 resulting from the limited wavelength range of the data.

nm FWHM so as to increase the signal to noise. We are primarily concerned with the experimental difference between these two profiles (red curve) and its comparison with the difference in profiles predicted by the model (red squares). The large experimental difference profile for $\Delta\lambda > 0$ is caused by the change in cathode material. If the discharge voltage and pressure were the same for both cathodes, the model predicts no change in the photon production for negative $\Delta\lambda$ beyond -0.1 nm. Therefore, most of the observed difference for $\Delta\lambda < 0$ nm is the result of the small change in discharge operating conditions. We see that the model predicts the observed changes at positive and negative $\Delta\lambda$ rather well. This example emphasizes the necessity for accurate measurements of the voltage and gas pressure. The high sensitivity of the experiment and model to the change in hydrogen pressure in this example is the result of the multistep sequence of reactions and excitation events determining the concentrations of ions, atoms, and molecules in a low-pressure hydrogen plasma.

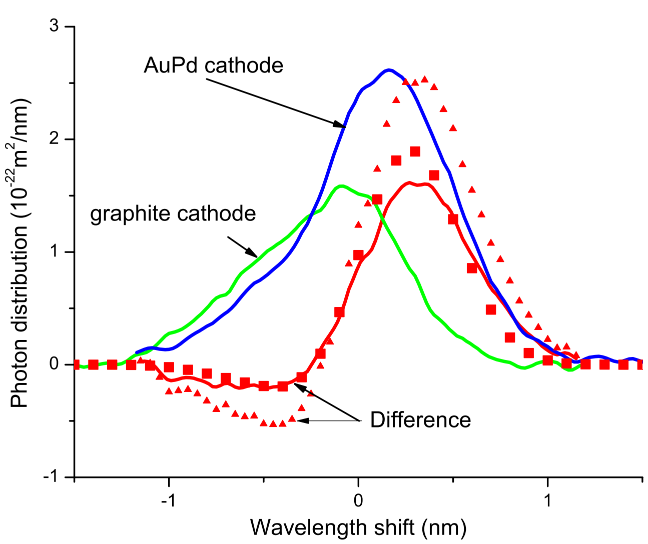

FIG. 7. (Color online) H_α profiles viewed parallel to the electric field for AuPd cathode at E/N=10.2 kTd and p=0.14 Torr and graphite cathode at E/N=10.4 kTd and p=0.15 Torr. The resolution is 0.4 nm FWHM. The experimental curves (solid) are scaled by a common factor to fit the absolute calculated difference values (points). The square difference values are calculated assuming negligible optical reflection from the graphite, while the triangular points are obtained assuming 10% optical reflection.

The triangular points (red) in Fig. 7 show the difference calculated from the experimental profiles when we assume a reflection coefficient of 10%. We argue that this much larger discrepancy with the model is evidence that the optical reflection from the graphite is significantly less than 10% and can be neglected.

V. DISCUSSION

The agreement of the shape and magnitude of measured and calculated H_α Doppler profiles presented Figs. 3–5 and in Fig. 7 provide strong confirmation of the model predictions [1,2] of the dominance of acceleration and charge transfer of H^+ followed by excitation of H_α by fast H atoms approaching the cathode and for excitation by H atoms resulting from the reflection at the cathode of hydrogen ions and atoms as fast H atoms. Thus, Figs. 4–6 and the accompanying arguments show that the component of the Doppler profile produced by excited H(n=3) atoms approaching the cathode extends to velocities corresponding to acceleration of H^+ to the applied voltage and is independent of cathode material. Figures 3 and 5 and the associated discussion show that the components of the Doppler profile emitted by excited H atoms moving away from the cathode are strongly dependent on cathode material, have the expected significantly lower mean velocity than the component approaching the cathode, and have a velocity distribution peaked at low velocities as expected for H atoms diffusely reflected from the cathode. The comparison of experimental and model results of Fig. 7 show the high sensitivity of the Doppler profile to small changes in hydrogen density and provide strong evidence for of the multistep sequence of collisions determining the concentrations of ions, atoms, and molecules in a low-pressure hydrogen plasma. It is important to keep in mind that the experimental results in Figs. 3, 4, and 7 are absolute spectral intensities and agree with the magnitudes predicted by the model to within the estimated experimental uncertainties of ±20%. In spite of this agreement, it is recognized that the model of Ref. [2] applied here is approximate and would benefit from more detailed calculations. Steps in that direction are the exploratory calculations of Petrović and Stojanović [22] and of Cvetanović *et al.* [28], which still lack the unavailable differential scattering cross sections.

There has been much speculation regarding the role of the ions H^+, H_2^+, and H_3^+ in the production of the large broadening observed in the wings of the H_α line, often called "excess broadening" [1,2,4–22]. Our experimental observations are consistent with the model predictions that direct excitation by these ions is small compared to excitation by the neutral fast H atoms and fast H_2 molecules. Additional modeling will be required to determine the applicability of this conclusion to the other plasma devices cited. Of course, the presence of fast neutral atoms and molecules is the result of energy gain from the electric field by the H^+ and H_2^+ ions and their subsequent charge-transfer collisions with the background H_2. It is difficult to verify experimentally the predicted role of the H_3^+ known to be formed rapidly in collisions of low energy H_2^+ with H_2 [52].

The Doppler profiles presented in this paper show many of the features observed for profiles obtained from glow discharges dominated by the cathode fall [6–9,11,15,20]. Although the discharge conditions at these higher currents differ in many respects from ours, the E/N in the cathode fall of these discharges [20] are comparable with the higher values in our drift tube. We have confirmed the applicability of the present interpretation by successfully extending the approximate model of Ref. [2] to several of these discharges. We have not extended the model to rf discharges. The failure of our H_α broadening experiments to support the interpretations of various discharge experiments and their use to support the energy generation and "hydrino" model of Mills [29] has been outlined [35].

The measurement and interpretation of Doppler broadened spectral lines provides a noninvasive technique for determining certain averages over the velocity distribution of the emitting atom. In our experiment, the observation from a single direction limits the information obtained to a component of the excited atom velocity along the line of sight. As a result, we cannot distinguish between excited atoms with a low velocity in the axial direction and those moving mostly perpendicular to the observer, i.e., those moving radially. Thus, we recognize that our choice of a diffuse angular distribution is not a unique solution to fitting the low velocity portion of the H_α Doppler profile. An example of an alternate hypothesis is that our model for the energy and spatial distributions of ions, atoms, and molecules results in a deficiency of low energy $H(n=3)$ atoms. Because we did not obtain Doppler profiles for a significant range of pressures at fixed E/N, we are unable to test for the expected change in angular scattering with gas density. For example, at significantly lower pressures than ours, the profiles should tend to take on a beamlike character while still showing the spread in excited atom energies resulting from production at various points in the drift tube. At significantly higher pressures and the same E/N as ours, the asymmetry and wavelength extent of the profiles should disappear because of multiple scattering and quenching. At present, there is insufficient differential scattering cross-section data available to predict this transition.

ACKNOWLEDGMENTS

We would like to acknowledge the contributions of B. M. Jelenković, who participated in the closely related experiments cited. We benefited greatly from numerous helpful suggestions and the loan of equipment by A. Gallagher. We gratefully acknowledge J. D. Krakover, J. Feeney, R. Hart, T. Brown, and R. A. Mitchel for help with the personal computer. The experimental work during 1989–90 was supported in part by the Air Force Wright Laboratories, the National Institute of Standards and Technology, and the U.S.-Yugoslavia Joint Board (Project No. 926). Preparation of this paper by A.V.P. was supported in part by JILA, while Z.Lj.P. was supported by the Ministry of Science of Serbia (Project No. MNTRS141025). We thank D. Alchenberger for advice on reflectivity measurements.

[1] Z. Lj. Petrović, B. M. Jelenković, and A. V. Phelps, Phys. Rev. Lett. **68**, 325 (1992).

[2] A. V. Phelps, Phys. Rev. E **79**, 066401 (2009). The exponent in Eq. (8) of this reference should be b not (b+1).

[3] Z. Lj. Petrović and A. V. Phelps, Phys. Rev. E **80**, 016408 (2009).

[4] M. Kajzer and Z. Sternberg, *Yugoslav Symp. and Summer School on Phys. of Ionized Gases*, edited by B. Navinsek, Hercegnovi, July 1970 (Inst. J. Stefen, Ljubljana, 1970).

[5] K. Prelec and Z. W. Sternberg, Fizika (Zagreb) **8**, 37 (1977).

[6] A. L. Cappelli, R. A. Gottscho, and T. Miller, Plasma Chem. Plasma Process. **5**, 317 (1985).

[7] G. Baravian, Y. Chouan, A. Ricard, and G. Sultan, J. Appl. Phys. **61**, 5249 (1987).

[8] E. L. Ayers and W. Benesch, Phys. Rev. A **37**, 194 (1988).

[9] C. Barbeau and J. Jolly, J. Phys. D **23**, 1168 (1990); Appl. Phys. Lett. **58**, 237 (1991).

[10] Z. Lj. Petrović and A. V. Phelps, *Proceedings of the International Seminar on Reactive Plasmas*, edited by T. Goto (Nagoya University, Nagota, 1991), p. 351.

[11] S. A. Bzenić, S. B. Radovanov, S. B. Vrhovac, Z. B. Velikić, and B. M. Jelenković, Chem. Phys. Lett. **184**, 108 (1991).

[12] Z. Stokić, M. M. F. R. Fraga, J. Božin, V. Stojanović, Z. Lj. Petrović, and B. M. Jelenković, Phys. Rev. A **45**, 7463 (1992).

[13] M. Kuraica and N. Konjević, Phys. Rev. A **46**, 4429 (1992).

[14] B. P. Lavrov and A. S. Melnikov Opt. Spektrosk. **75**, 1152 (1993) [Opt. Spectroc. **75**, 676 (1993)]; Opt. Spektrosk. **79**, 922 (1995) [Opt. Spectroc. **79**, 842 (1995)].

[15] S. B. Radovanov, K. Dzierżęga, J. R. Roberts, and J. K. Olthoff, Appl. Phys. Lett. **66**, 2637 (1995).

[16] I. R. Videnović, N. Konjević, and M. M. Kuraica Spectrochim. Acta, Part B. **51**, 1707 (1996).

[17] T. Gans, V. Schulz-von der Gathen, U. Czarnetzki, and H. F. Döbele, Contrib. Plasma Phys. **42**, 596 (2002).

[18] M. R. Gemišić Adamov, B. Obradović, M. M. Kuraica, and N. Konjević, IEEE Trans. Plasma Sci. **31**, 444 (2003).

[19] N. Konjević, G. Lj. Majstorović, and N. M. Šišović, Appl. Phys. Lett. **86**, 251502 (2005).

[20] N. Cvetanović, M. M. Kuraica, and N. Konjević, J. Appl. Phys. **97**, 033302 (2005).

[21] N. M. Šišović, G. Lj. Majstorović, and N. Konjević, Eur. Phys. J. D **32**, 347 (2005); **41**, 143 (2007).

[22] Z. Petrović and V. Stojanović, in *Proceedings of the 5th Serbian Conference on Spectral Lines Shapes in Astrophysics*, edited by L. C. Popović and M. S. Dimitrijević (Memorie della Società Astronomica Italiana, Triste, 2005), Vol. 7, p. 172.

[23] M. Kuraica and N. Konjević, Phys. Scr. **50**, 487 (1994).

[24] M. Gemišić Adamov, M. M. Kuraica, and N. Konjević, Eur. Phys. J. D **28**, 393 (2004).

[25] G. Lj. Majstorović, N. M. Šišović, and N. Konjević, Phys. Plasmas **14**, 043504 (2007).

[26] A. V. Phelps, Bull. Am. Phys. Soc. **53**, 41 (2008).

[27] T. Babkina, T. Gans, and U. Czarnetzki, Europhys. Lett. **72**, 235 (2005).

[28] N. Cvetanović, B. M. Obradović, and M. M. Kruaica, J. Appl. Phys. **105**, 043306 (2009). Although this calculation uses different $H+H_2$ elastic cross sections than that of Ref. [2], we do not expect to result in major differences in results. They derive an energy distribution for the H atoms leaving the cathode that is consistent with their experimental H_α profile rather than calculating it from first priciples as is the present paper.

[29] J. Phillips, C.-K. Chen, K. Akhtar, B. Dhandapani, and R. Mills, Int. J. Hydrogen Energy **32**, 3010 (2007); R. L. Mills and K. Akhtar, *ibid.* **34**, 6465 (2009).

[30] J. Phillips and C.-K. Chen, Int. J. Hydrogen Energy **33**, 7185 (2008).

[31] S. Jovičević, M. Ivković, N. Konjević, S. Popović, and L. Vušković, J. Appl. Phys. **95**, 24 (2004).

[32] S. Jovičević, N. Sakan, M. Ivković, and N. Konjević, J. Appl. Phys. **105**, 013306 (2009).

[33] G. M. Batanov, V. A. Ivanov, I. A. Kossiy, and K. F. Sergeichev, Fiz. Plazmy **12**, 552 (1986) [Sov. J. Plasma Phys. **12**, 317 (1986)].

[34] A. Hallil, O. Zabeida, M. R. Wertheimer, and L. Martinu, J. Vac. Sci. Technol. A **18**, 882 (2000).

[35] A. V. Phelps, J. Appl. Phys. **98**, 066108 (2005).

[36] M. J. Druyvesteyn and F. M. Penning, Rev. Mod. Phys. **12**, 87 (1940).

[37] B. N. Klyarfeld, L. G. Guseva, and A. S. Porkrbvskaya-Soboleva, Zh. Tekh. Fiz. **36**, 704 (1966); [Sov. Phys. Tech. Phys. **11**, 520 (1966)].

[38] A. V. Phelps, Z. Lj. Petrović, and B. M. Jelenković, Phys. Rev. E **47**, 2825 (1993).

[39] B. M. Jelenković and A. V. Phelps, Phys. Rev. A **36**, 5310 (1987).

[40] A. V. Phelps and B. M. Jelenković, Phys. Rev. A **38**, 2975 (1988).

[41] Vacuum grade POCO graphite, Poco Graphite, Inc., 300 Old Greenwood Rd., Decatur, Texas 76234, USA.

[42] Recent measurements by one of the authors (Z.Lj.P.) for unpolished POCO graphite, which had not been exposed to discharges, gave 6% reflectivity. Our use of H_2 discharge cleaning and the resultant layer of sputtered graphite reduces the reflection, while sputtered Au, Pd, and/or stainless steel on the graphite could increase the reflection.

[43] B. M. Jelenković and A. V. Phelps, in *Swarm Studies and Inelastic Electron-Molecule Collisions*, edited by L. C. Pitchford, B. V. McCoy, A. Chutjan, and S. Trajmar (Springer-Verlag, New York, 1985) p. 113. This work with D_2 found ~10% distortion of the spatial distribution of emission when the current was raised to 10 μA. Because of higher ion drift velocities in H_2, the electric field distortion for H_2 discharges is expected to become significant only for higher currents than for D_2.

[44] W. Eckstein and H. Verbeek, in *Data Compendium for Plasma-Surface Interaction*, edited by R. A. Langley *et al.* (International Atomic Energy Agency, Vienna, 1984), p. 12.

[45] Our maximum discharge current densities are 2×10^{-11} A/m^2 compared to 4×10^{-6} A/m^2 for a typical dc glow discharge [18] used in H_α Doppler studies.

[46] C. Stehlé, J. Quant. Spectrosc. Radiat. Transf. **44**, 135 (1990).

[47] C. C. Havener, N. Rouze, W. B. Westerveld, and J. S. Risley, Phys. Rev. A **33**, 276 (1986).

[48] J. F. Kielkopf, J. Chem. Phys. **62**, 3784 (1975); N. F. Allard, J. F. Kielkopf, R. Cayrel, and C. van't Veer-Menneret, Astron. Astrophys. **480**, 581 (2008). We have found no experimental data for $H(n=3)$ broadening by H_2 and so use typical values for other neutral and nonresonant species.

[49] R. S. Freund, J. A. Schiavone, and D. F. Brader, J. Chem. Phys. **64**, 1122 (1976); K. Ito, N. Oda, Y. Hatano, and T. Tsuboi, Chem. Phys. **21**, 203 (1977).

[50] A. V. Phelps and Z. Lj. Petrović, Plasma Sources Sci. Technol. **8**, R21 (1999).

[51] The model of Ref. [2] has been extended to include H^+ produced at the anode by electron impact on adsorbed H_2. The expected yield [53] of H^+ per incident electron for a monolayer coverage of H_2 on a tungsten anode is $\sim10^{-9}$. Assuming an extremely large H^+ yield of 0.01 per electron for our dirty AuPd operated as an anode and using $b=100$, the calculated profile shows a roughly 5% increase in the total H_α at negative wavelength shifts relative to that at positive wavelength shifts.

[52] A. V. Phelps, J. Phys. Chem. Ref. Data **19**, 653 (1990); **20**, 1339 (1991); **23**, 153 (1994).

[53] T. E. Madey and J. T. Yates, Jr., J. Vac. Sci. Technol. **8**, 525 (1971).