Shapes of atomic-hydrogen lines produced at a cathode surface

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The observation of extraordinarily wide wings on the spectrum lines of atomic hydrogen in emission at the cathode surface of an electric discharge is described. Actual line shapes in pure hydrogen manifest an articulation which divides the spectrum line into three distinct regions, each arising from a separate mechanism. Several novel discharge-source configurations have been developed in preceding experimentation, these falling into the general category of hollow cathodes. Three critical experiments have been performed to elucidate the process which gives rise to the extended far wings of the hydrogen lines and to determine their physical point of origin. Ultimately, it is concluded that the cathode surface itself is essential to the mechanism for producing the extreme velocities of the excited atoms which account for the distant extended wings.

I. INTRODUCTION

We have recently undertaken a set of experiments on the spectrum lines of atomic hydrogen as they are produced in the hollow cathode of an electric glow discharge. These studies have encompassed a detailed investigation of the shapes and shifts of Balmer and Paschen series lines in pure hydrogen and in mixtures of 1%, 5%, and 10% hydrogen in helium.

In a preliminary report on this work,[1] we called attention to the new effects which were observed in the Balmer series lines as manifested in a pure hydrogen discharge. There, we found that the hollow-cathode discharge exhibited highly articulated, threefold line shapes with an extraordinary wing development not observed in the positive column of the same discharge.

The principal spectrum presented in evidence of the phenomena in Ref. 1 was the H_α line shown in Fig. 1. This spectrum was observed with use of the hollow-cathode electric discharge source depicted in the upper portion of Fig. 2. The top trace in Fig. 1 shows the entire H_α line at low gain; the two middle traces, at increasing amplifications, bring out the intermediate wings; and the fourth (bottom) trace, at the highest gain, emphasizes the far wings. These latter extensive wings indicate the presence of excited hydrogen atoms with remarkably high velocities and, as such, demonstrates one of the major new effects under consideration.

In Ref. 1 we proposed a mechanism, dissociative excitation by electrons, for the production of the intermediate wings of the hydrogen lines (Fig. 1, third trace from the top). The process may be represented by the relation

$$e^- + H_2 \rightarrow H_2^* + e^- \rightarrow H + H^* + e^- + \text{kinetic energy}$$

Such transfers of kinetic energy to excited hydrogen atoms apparently had not been observed previously in electric discharges. However, several groups had noted similar effects in electron-beam experiments.[2–8] Following Ref. 1, two groups observed likewise effects in radiofrequency discharges.[9,10] The latter reference, Baravian *et al.*, included alternative explanations for the origin of their equivalence of our intermediate wings.

For the simplest case of dissociative excitation, that of monoenergetic transfer, the resulting emission line would be Doppler broadened into a rectangular line shape. Here in Fig. 1, however, a spread in the initial energy of excitation is followed by the smoothing effect of collisions prior to emission. Both contribute to the rounding of the idealized rectangular line shape associated with the underlying mechanism.

In our explanation of the development of the far wings in Fig. 1, we have recourse to two processes.[1] The first is the bombardment of hydrogen adsorbed onto the

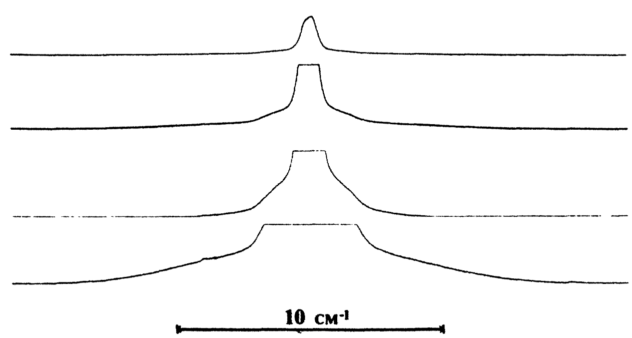

FIG. 1. H_α line at 656.28 nm as observed in the grazing configuration of the hollow cathode (Fig. 2, upper). The spectra are registered with gains of 1, 4, 10, and 20 (from top to bottom) in order to give optimal displays of the various regions of the articulated hollow-cathode line. The top trace shows the total line, the next two emphasize the intermediate wings, while the bottom trace is almost entirely taken over by the far wings. Note that this prototypical line from the grazing hollow cathode is quite symmetric. It is also conformably Gaussian and unshifted in wavelength to within the precision of the measurements. The traces are reproductions of original strip-chart recordings and the ordinates are proportional to photomultiplier current. In all spectra shown in this paper, wavelength increases to the right.

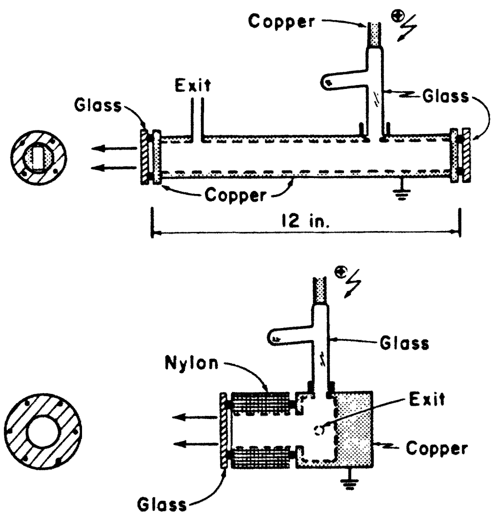

FIG. 2. Two hollow-cathode sources used in the present work. The upper one is designated the grazing configuration and the lower one the end-on configuration. In each case, the light emerges from the left and through a window sealed by an *O* ring. Light from the grazing configuration consists mostly of photons having skimmed along the copper walls, whereas light from the end-on configuration travels normal to the only active metal surface with which it can be involved. The angled glass tube provides for a view of the positive column (which fills the vertical glass tube) unobstructed by metal deposits. In each case, the flowing gas is introduced through a fitting attached to the copper tube at the top and is pumped out through the port marked "exit."

cathode walls by energetic ions and neutrals; this enables a hydrogen atom to acquire simultaneously electronic excitation and considerable kinetic energy. The second process is a similar acquisition of energy which may occur within the gaseous medium near the cathode wall. In either case, the mechanism is fueled by the transfer of energy from the cathode fall to positive ions.

We had previously fitted the far wings of the Balmer series lines to Doppler profiles and found the fit to be remarkably good. Other possible mechanisms resulted in line shapes which did not fit the far wings nearly as well. For example, the line shapes for Stark broadening by electrons and protons were computed using the tables of Vidal *et al.*[11] for a variety of plasma environments. However, the Gaussian shape clearly remained the better fit. We therefore concluded that the far wings were of Doppler origin and that the high electric field of the cathode fall region gave rise to highly energetic hydrogen atoms which emitted Doppler-shifted photons. The half-widths of the far wing profiles were then converted to mean kinetic energies of the emitting atoms. Table I gives the results and the corresponding transition probabilities for the Balmer lines. The decrease in kinetic energy down the Balmer series is explained by the larger number of eroding collisions associated with increasing lifetimes of the initial levels of the lines.

We have found, furthermore, that the ends of the far wings, defined as the points where the recorded signal descends into the noise, can be adequately specified to yield corresponding maximum observable atomic kinetic energies. For the H_α line in the grazing hollow-cathode configuration (Fig. 1), this value is 234 eV.

Following our reporting of the observation of the hollow-cathode lines, experiments were undertaken by Cappelli, Gottscho, and Miller (CGM) at AT&T Bell Laboratories.[9] Their investigations were conducted on an alternating radio-frequency discharge in hydrogen between plane parallel plates. By making observations through a hole drilled through one of the electrodes (the anode and the cathode alternately), they were able to probe fine details of the spatial distribution of the emission. Furthermore, they accumulated data similar to ours (which involved experiments on a dc discharge) through use of a boxcar integrator to process the incoming data. This latter device permitted essentially a stop-action framing of the various phases of the rf cycle. Accordingly, data could be obtained from any electric field strength condition which ranged from a maximum voltage applied in one direction through to an equivalent field pointed in the reverse direction.

The general morphology of the hydrogen lines observed by CGM is the same as ours. These lines are characterized by a central core, intermediate wings, and far wings. Their intermediate wings characteristics and interpretation of the mechanism (dissociative excitation) are essentially the same as ours.

Concerning the far wings, we displayed data in Ref. 1 only for observations made perpendicular to the electric field. However, we made liberal use of the data taken

TABLE I. Hydrogen Balmer-line far-wing parameters for the hollow-cathode grazing configuration. The second column gives the values of the full width at half maximum. The trend in wave numbers is not monotonic because of the interplay between the dependences on atomic velocity and spectral line frequency. The third column furnishes the more essential quantities, the mean kinetic energies of the emitting atoms. They are calculated from the far-wing Doppler widths and the corresponding rms velocities. These are to be compared with the spectral lines transition probabilities as given in the fourth column.

Line	Linewidth (cm^{-1})	Mean energy (eV)	Transition probability (A) per 10^{-5} sec
H-α	9.94	107	441
H-β	12.46	92.5	84.2
H-γ	12.36	72.6	25.3
H-δ	12.06	61.7	9.7

from our observations along the field lines of the discharge, and we display some of these spectra in the present work. The principal difference between the CGM spectrum lines in pure hydrogen and ours is that theirs are somewhat more extensive in wavelength. This observation has been interpreted by CGM as being due to the pressure differences in the reported data, with our listed pressures running several times higher than theirs.

In addition to some variation of the hydrogen lines' features between the two sets of experiments, there is also a mild quantitative difference in interpretation of the underlying processes. As indicated above, we have suggested that the excitation-acceleration processes take place both in the gaseous discharge medium and on the cathode wall proper. Although we have concluded that the majority of the occurrences of excitation and acceleration takes place at the wall, CGM imply that most of such events occur within the gaseous medium. Quite possibly this underlying variation in perspective arises ultimately from the altered aspect of the experimental setup. It is interesting to note that Baravian *et al.*[10] do not observe extensive far wings, probably because they carry out their observations far from the electrodes unlike our observations and those of CGM. In this paper, we are presenting the results of further experiments which clarify the fundamental processes operative here and their relationship with the plasma-surface environment.

II. EXPERIMENTAL

All of the data of the present work were obtained from the spectra of atomic hydrogen in hollow-cathode discharges. Electrically, the experiments were carried out with constant dc voltages of 0.8–2 kV and with currents of 40–500 mA. All of the discharge tubes were supplied with overvoltages and 2550 ohms of series ballast resistance to stabilize the glow discharge. Gas pressures in the hollow cathode were in the 0.4–4.0 torr range. The levels of discharge pressure and applied voltage were governed primarily by the experimentally determined conditions most conducive to a stable discharge while maintaining a constant current. Spectrum lines for comparison were selected on the basis of obtaining scaled line heights for all of the lines' central peaks as nearly constant as practicable.

The measurements were made on a 5-m Jarrell-Ash spectrograph which has been converted to spectrometric operation through the addition of a lead screw-driven exit slit and a photomultiplier detection system. The grating is a 10-in., 300-groove/mm echelle blazed at 63°. Entrance and exit slits were set at 75 μm width to achieve a modest spectrometric wavelength resolving power on the order of 100 000 with a good signal-to-noise ratio. We wish to underscore the point that the favorable signal-to-noise ratio (which exceeds a value of 500 in the case of H_α) gives rise to an extensive dynamic range for the recorded signal, and it is this data quality advantage which has enabled us to discover the extended wing structure never previously observed (initially reported in Ref. 1).

Wavelength drive is achieved by turning the exit slit lead screw with a stepping motor whose power pulses are fed also into an up-down counter which registers the spectrometer wavelength. The diffraction grating is not rotated during the experiment. Spectra are graphed simultaneously at four different gains on four channels of Brush strip-chart recorders. Each channel emphasized a particular region of interest on the contour of the spectral line.

Two hollow-cathode sources, differently configured with respect to cavity shape and viewing aspects, were used in these experiments and are depicted in Fig. 2. The grazing hollow cathode, in the upper part of the figure, consists of a 12-in.-long water-cooled copper bar with a hollowed-out cavity of rectangular cross section and of dimension $1\frac{1}{4}\times\frac{3}{8}$ in. Glass windows, $1\frac{1}{2}$ in. in diameter abut Viton *O* rings, are supported by metal caps and provide a lengthwise view of the negative glow and the cathode fall in the cavity. Passage of the discharge from cathode to anode proceeds by way of a Pyrex tube seated into a hole in the copper bar. This tube is fitted with a protruding window for viewing the positive column and ends in a glass-to-Kovar seal. Here the Kovar constitutes the discharge anode and supports a fitting for connection to the pump-out section of this flowing system.

The end-on hollow cathode depicted in the lower part of Fig. 2 is also machined out of a piece of solid copper stock. In this case, both the internal and external cross sections are round rather than rectangular. The single glass window, pressed against an *O* ring, is positioned $2\frac{1}{2}$ in. from the cavity of the discharge to reduce the speed of the buildup of copper sputtered from the cathode surface. Within the cylindrical volume of the end-on hollow cathode, the side wall is recessed to form a chamber with a diameter of $2\frac{1}{2}$ in. and a viewing aperture (on the left) of $1\frac{1}{2}$ in. Thus radiation from the end wall of the cathode proceeds directly out of the cavity, while radiation from the side wall is blocked off. Only radiation emitted in a direction nearly normal to the cathode surface is able to attain direct egress from the end-on configuration. The arrangements for gas handling, pump out, and water cooling are effectively the same for both cathode configurations.

III. THREE CRITICAL RESULTS

A. Blue-shifted lines

Figure 3 presents six recordings of the H_β line as it is produced in the two hollow cathodes. For both cathode configurations, the line is presented at gains of 1, 4, and 20, to emphasize the three regions of interest, namely, the central core of the line, the intermediate wings, and at 20$\times$, the far wings.

It will be observed that the central core (1$\times$) of this line has much the same appearance in either the grazing or the end-on configuration of the hollow cathode. The same may be said for the intermediate wings (4$\times$) as well. The striking difference here lies in the far wings which show a pronounced shift to the blue in the end-on

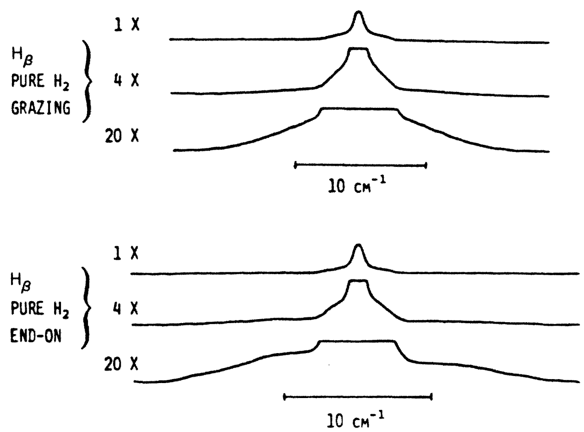

FIG. 3. These six traces are presented to illustrate the differences in the appearance of lines from the grazing and end-on configurations of the hollow cathode (Sec. III A). Each example is shown at gains of 1, 4, and 20 (top to bottom) emphasizing the central core, the intermediate wings, and the far wings, respectively. The shift to shorter wavelength of the far wings is readily apparent. These spectra as well as those of the next two figures have been manually digitized from original strip-chart recordings on an Altec AC-90-C digitizer and subjected to horizontal scaling where necessary.

configuration in contrast to the case of the grazing configuration where the far wings may be represented by a pure, unshifted Gaussian line shape.

We had alluded to the general features of the blue shift in a previous paper.[1] There we indicated that we were quite surprised to discover that most of the emitting atoms are moving *toward* the observer while the electric field is directed in the opposite sense. When we realized that most of the high velocity excited hydrogen atoms were moving away from the cathode wall, we were led to the conclusion that the wall itself constitutes the major source of energetic excited atoms. Figure 3 is consistent with that circumstance. If the major fraction of the energetic atoms are either driven from the wall (and simultaneously excited) or are reflected from the wall (and simultaneously excited), the far wings of Fig. 3 seem well accounted for. The modifying effect of collisions would serve to fill in the red wing of the line (as also in the case of the grazing configuration). Furthermore, whatever excitations arise from within the gaseous medium would also be expected to favor the populations of excited atoms heading toward the cathode wall.

B. Hydrogen lines in a helium atmosphere

The prevailing conditions for this experiment are very similar to those of Sec. III A. For present purposes, we simply substitute a flowing premixed combination of hydrogen and helium in a 1 to 99 ratio by volume for the pure hydrogen of the experiment above. The results are presented in Fig. 4. The line produced in the grazing hollow-cathode configuration is shown in the middle three traces, while the line emitted from the end-on arrangement is shown in the four traces below, with the

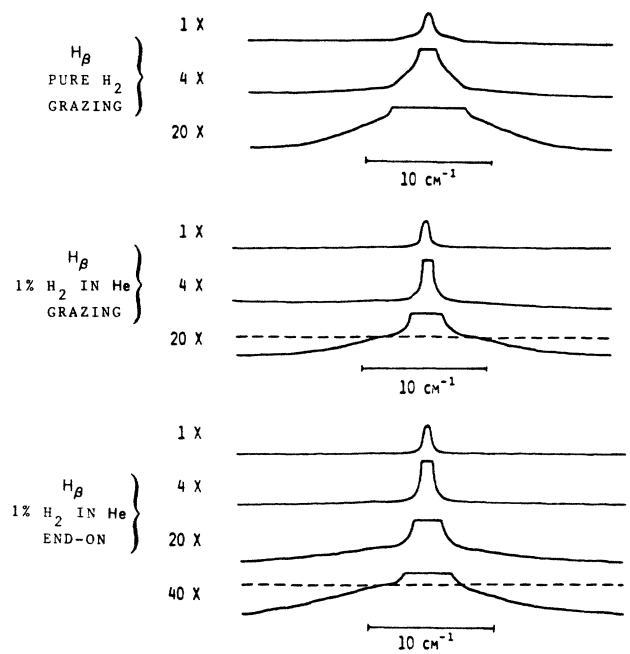

FIG. 4. These six traces are presented to illustrate the similarities and differences between H_β lines at 486.13 nm generated in pure hydrogen and in a predominantly helium atmosphere (Sec. III B). The top three traces are of pure hydrogen, the bottom six are from hydrogen in helium. The mode of presentation is the same as that of Fig. 3. The points to be noted are the lack of intermediate wings in the helium atmosphere but the persistence of the far wings which are equally extensive in pure hydrogen and in 99% helium. The data was digitized and scaled as in the previous figure.

added 40× enhancement provided to bring out the detailed behavior of the far wings.

A comparison of all the 4× traces of Figs. 3 and 4 will reveal that the *intermediate* wings of the H_β line are completely lacking in the helium atmosphere. This latter circumstance should not be unexpected if our previous explanation of the intermediate wing mechanism, dissociative excitation of hydrogen molecules, is to be accepted. In an atmosphere composed predominantly of helium, recombination of hydrogen atoms into molecules is unlikely once dissociation has taken place. Thus in such a dc discharge, hydrogen molecules will be present near the cathode only briefly following the establishment of the glow, and the intermediate wing mechanism will not be operative.

The *far* wings of H_β in the helium atmosphere are quite evident in Fig. 4 and, while they are not of quite the same intensity relative to the central peak as those in pure hydrogen, they attain the same extent in the frequency domain. This latter parameter turns out to be susceptible to quite precise determination. The procedure is to seek out the two points on either side of the spectrum line where the signal first discernibly rises above the noise. If we define these two points as the limits of the far wings, it is possible, as a result of the very large signal-to-noise ratio of the present experiment, to specify the limits of the far wings to a precision of about $\frac{1}{3}$ cm^{-1}. In any case, the far wings are present (and equally extensive as those in pure hydrogen) and the intermediate wings are gone. Note that the decided blue shift of the far wings in the end-on configuration is present in the helium atmosphere as well.

The insensitivity of the extent of the far wings to the character of the discharge carrier gas strikes us as an essential fact regarding the mechanism of the energy transfer to the emitting hydrogen atoms. In particular, we believe that it serves to support our original contention that a considerable proportion of the excitation and energization process for the emitting atoms takes place at the cathode wall.

C. Facing a rubber wall

Shortly after we began associating the extensive far wings of the hydrogen lines with the cathode fall region of the discharge, the question arose as to whether the far wing phenomenon is dependent upon the material composing the cathode wall. Accordingly, we devised an experiment to test the dependence of the data on cathode composition. In this experiment, we used the identical discharge tube in the grazing configuration (Fig. 2, top) but with an electroplated layer of nickel over the copper throughout the entire surface available to the discharge. The effect on the hydrogen lines was negligible.

In the next experiment, the cathode surface of the *end-on* configuration of Fig. 2 was subjected to alteration. The procedure was to coat all of the cathode wall within the line of sight with rubber, namely, with General Electric red high-temperature silicone rubber RTV106. As may be noted in Fig. 2, the discharge can still be maintained onto copper side walls which, however, have been purposely recessed to remain in eclipse during observation. The recorded emission, then, comes from a hollow-cathode discharge with all active cathode surfaces concealed and with all surfaces visible to the detector coated.

The results of this experiment, shown in Fig. 5, are quite striking. The upper four traces display the H_α line from the RTV-treated end-on hollow cathode divided, as before, into four segments of varying amplifications to emphasize different regions of the spectrum line structure. In the bottom trace, we would expect the far wings to appear most prominently since the central peak and the intermediate wings were driven off scale and out of the picture. It will be appreciated that the far wings are virtually lacking here even though the central peak and the intermediate wings are similar in height and structure compared with those in the lower four traces from the untreated copper cathode. (The intermediate wings are, in fact, slightly enhanced in this viewing of the rubberized surface.) The latter traces show the central peak and the intermediate wings are as usual and the far wings are large, broad, and blueshifted.

What is indicated by this experiment, then, is that the far wings appear only when the active cathode wall is directly in the line of sight. The central peak and the intermediate wings may be generated near the cathode surface, but the far wings are largely produced at the cathode surface.

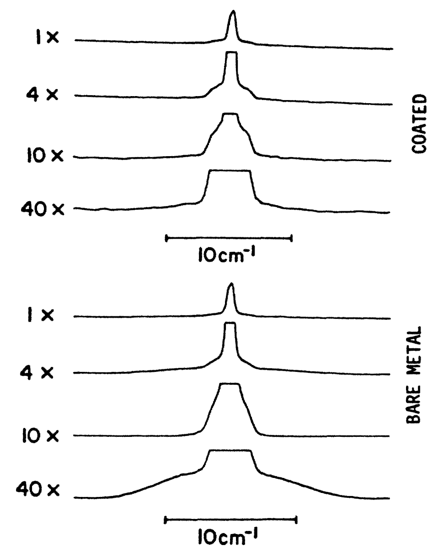

FIG. 5. H_α lines at coated and bare metal cathode surfaces. These eight traces are presented to illustrate the effect of concealing the active cathode surface with a coating of silicone rubber (Sec. III C). In the four upper traces the cathode is, in fact, coated with RTV to the detriment of the far wings which are virtually lacking in the 40× trace where they normally appear most prominently. This is to be contrasted with the bottom-most trace (40×). In the lower four traces, nothing is changed from the conditions of the upper four except that the cathode surface is uncoated (bare metal). Here the far wings are broad and prominent at 40× in contrast to those above.

IV. CONCLUSION

When we first noticed the remarkable development of the far wings of the hydrogen lines,[1] we immediately considered the possibility of their having arisen as an artifact related to, say, diffraction grating imperfection. It was hard to believe that such a striking phenomenon in so simple a system as a glow discharge in hydrogen could have escaped attention until the reporting of Ref. 1. However, after performing experiments which ruled out experimental causes for the observed far wings, we went on to find them to be quite ubiquitous, arising in both hollow-cathode configurations of Fig. 2, remaining strong through a switch of cathode surface material from copper to nickel, and persisting in a predominantly helium atmosphere.

One possible reason for the historical delay in the discovery of the far wings is that most discharge emission studies had been directed toward the region of the positive column. The cathode surface was avoided unless particular spectral features were sought, typically the atomic lines of metallic elements with which the cathode surface had been impregnated. In the case of our investigation, the cathode fall region is deliberately being probed and only there do the extended far wings appear and not in the positive column. We take this circumstance as a primary indication that the cathode surface itself gives rise to the extended far wings.

Follow-up experiments by CGM (Ref. 9) and Baravian *et al.*,[10] both using rf discharge excitation, also lend support to the view that the far wings originate from high velocity excited hydrogen atoms at the cathode surface. CGM made their observations directly through the electrodes and therefore obtained both intermediate and far wings in their atomic hydrogen spectra. Baravian *et al.*, on the other hand, carried out their observations far from the electrodes and did obtain intermediate wings but no extensive far wings.

The present investigation has included the results of three experiments particularly designed to characterize the origin of the extended far wings. The first experiment (a) entails a comparison of atomic hydrogen line spectra from two hollow-cathode sources of differing design. The grazing and end-on configurations provide lines of sight parallel and perpendicular to the cathode wall, respectively. While the far wings of spectral lines in the grazing configuration are unshifted and Gaussian, those in the end-on configuration are distinctly shifted to the blue. Thus experiment (a) demonstrates that the excited hydrogen atoms retain a velocity distribution which is skewed away from the cathode surface.

The second experiment (b) involves substituting a gaseous mixture of hydrogen and helium in a 1 to 99 ratio by volume for the pure hydrogen of the basic investigation. The far wings of H_β in the helium atmosphere are observed to be equally extensive in the frequency domain as those in pure hydrogen. Thus experiment (b) demonstrates that the extreme velocities attained by the excited hydrogen atoms are largely independent of the mass of their gaseous collision partners in the discharge.

The third set of experiments (c) tests whether or not the far wing phenomenon is dependent upon the material composing the cathode wall. First, nickel was electroplated onto the interior of the grazing hollow cathode as an alternative conductor to copper. The atomic hydrogen line shapes remain effectively the same as before. In the second of these experiments, the portion of the end-on cathode wall within the line of sight was coated with high-temperature silicone rubber RTV106. The recorded emission shows that the far wings are found to be virtually lacking in intensity relative to the central peak and the intermediate wings when compared with those of the untreated copper cathode. The latter experiment demonstrates that the development of the far wings depends on the maintenance of the *active* cathode surface specifically within the line of sight.

All of these observations are consistent with the conclusion that the cathode wall itself is responsible for producing high velocity excited hydrogen atoms whose Doppler-shifted photons comprise the extended far wings. In addition, we have noted that the retained kinetic energy of the energetic emitting atoms increases with the Einstein A coefficient. Degradation of the initial kinetic energy continues throughout the radiative lifetime of the excited atoms. The high collision rate to which the fastest atoms are subjected serves not only to drain off energy, but also steadily randomizes the direction of the velocity retained in those atoms. While most atoms are excited and accelerated at the cathode surface, most likewise undergo collisions prior to emission of a Balmer photon.

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[1]W. Benesch and E. Li, Opt. Lett. **9**, 338 (1984).

[2]R. S. Freund, J. A. Schiavone, and D. F. Brader, J. Chem. Phys. **64**, 1122 (1976).

[3]J. A. Schiavone, K. C. Smyth, and R. S. Freund, J. Chem. Phys. **63**, 1043 (1975).

[4]T. Ogawa and M. Higo, Chem. Phys. Lett. **65**, 610 (1979).

[5]M. Higo and T. Ogawa, Chem. Phys. **44**, 249 (1979).

[6]M. Higo and T. Ogawa, Chem. Phys. Lett. **75**, 271 (1980); **52**, 55 (1980).

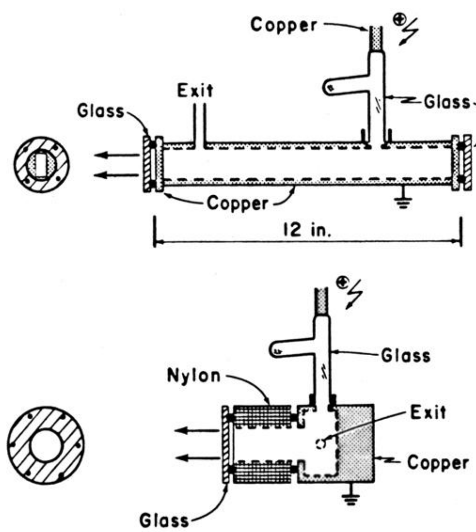
[7]T. Ogawa, J. Kurawaki, and M. Higo, Chem. Phys. **61**, 181 (1981).

[8]M. Higo, S. Kamata, and T. Ogawa, Chem. Phys. **66**, 243 (1982).

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

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

[11]C. R. Vidal, J. Cooper, and E. W. Smith, Astrophys. J. Suppl. Ser. **25**, 37 (1973).



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