Balmer Emissions Induced by H_2^+ and H_3^+ Impact on Molecular Hydrogen*

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(Received 13 May 1963)

Absolute cross sections for the production of H_α, H_β, and H_γ emissions by H_2^+ and H_3^+ impact on molecular hydrogen have been measured for ion energies up to 130 keV. Emissions resulting from dissociative electron capture by the fast ion or from dissociative excitation of the fast ion are Doppler shifted from emissions resulting from dissociative excitation of the target gas, allowing separate measurements of these emissions.

I. APPARATUS

BEAMS of H_2^+ and H_3^+ ions from a 145-keV positive ion accelerator are magnetically analyzed and enter a differentially pumped collision chamber. Spectroscopic observation of the collision region is made at a 30° angle, allowing Doppler-shifted emissions from fast hydrogen atoms to be resolved from the Doppler-unshifted emissions from the target hydrogen. A calibrated JaCo 500-mm Ebert scanning spectrometer provides spectral analysis. Further description of the apparatus can be found in a previous paper.[1]

II. RESULTS AND DISCUSSION

The Balmer emissions H_α, H_β, and H_γ resulting from collisions of H_2^+ and H_3^+ with H_2 were measured and the cross sections for production of these radiations determined.

Our definition of the cross section follows from $N=\sigma\rho F$, where N is the number of photons emitted per cubic centimeter, σ is the cross section, ρ is the molecular density in the chamber, and F is the ion flux.

In the pressure range of a very few microns, all the emissions were found to be linear with pressure and current.

In the case of H_2^+ impact, data below 20 keV were less accurate than at the higher energies since the beam current drops at low energies. No attempt was made to obtain data with H_3^+ ions below 20 keV.

Absolute measurements should be accurate to within about 40% while relative measurements should be better.

A. Doppler-Unshifted Radiations

We have plotted in Fig. 1 the cross sections for the Doppler-unshifted emissions versus the velocity of the ion. Included in the figure are the results for proton impact[1] and some higher energy data taken previously for H_2^+ and H_3^+ impact.[2] However, the data on which Ref. 2 are based were not extensive and were complicated by chamber impurities not present in this experiment.

The possible mechanisms producing the unshifted Balmer radiations include:

$$\underline{H}_2^+ + H_2 \rightarrow [\underline{HH}^+] + H + H^*, \tag{1}$$

$$\underline{H}_2^+ + H_2 \rightarrow [\underline{HH}] + H^* + H^+, \tag{2}$$

$$\underline{H}_2^+ + H_2 \rightarrow [\underline{HH}^+] + H^* + H^+ + e, \tag{3}$$

with similiar reactions possible for H_3^+ impact. The brackets indicate the possibility of dissociation of the primary ion, or resulting molecule in the case of charge transfer, mechanism (2).

Mechanisms (2) and/or (3) would not seem to be dominant contributors since Afrosimov *et al.*[3] have measured secondary (slow) proton production by these ions on molecular hydrogen and found it to be small. They found a maximum cross section of 5×10^{-17} cm^2 for H_2^+ impact at 2×10^8 cm/sec. In the case of H_3^+ impact, however, the slow H^+ production failed to peak in their energy range, which was comparable to ours, but appeared to be about 3.5×10^{-17} cm^2 for velocities between 3×10^8 and 4×10^8 cm/sec. If mechanisms (2) and/or (3) were dominant and if our measurements are to be at all compatible with those of Afrosimov *et al.*, it would require nearly 100% excitation of the hydrogen atoms which are freed from the resulting slow protons. Despite the fact that their curves for slow proton production peaked at roughly the same energy as our unshifted Balmer emissions for H^+ and H_2^+ impact we must choose mechanism (1) as the most probable one.

If the principal mechanism for production of these emissions depends only on the net ion charge for equal velocity ions, then the H^+, H_2^+, and H_3^+ curves should be similar. Indeed, we find that at the lower velocities the curves overlap within experimental error. However, for velocities greater than the velocity at which the maximum occurs in the H^+ curve, the three curves are quite different. The H^+ curve peaks at about 15 keV,

* Supported by the National Science Foundation and the Air Force Cambridge Research Laboratories.

[1] R. H. Hughes, Sabrina Lin, and L. L. Hatfield, Phys. Rev. **130**, 2318 (1953).

[2] R. H. Hughes, J. Opt. Soc. Am. **51**, 696 (1961).

[3] V. V. Afrosimov, R. N. Il'in, and N. V. Fedorenko, Zh. Eksperim. i Teor. Fiz. **34**, 1398 (1958) [translation: Soviet Phys.—JETP **7**, 968 (1958)].

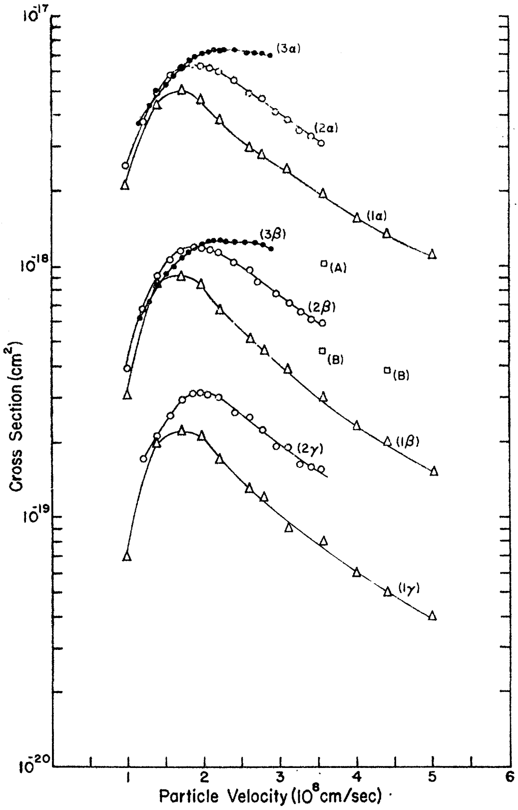

FIG. 1. Unshifted Balmer emissions: (3α), (2α), (1α)—H_α for H_3^+, H_2^+, and H^+ impact, respectively; (3β), (2β), (1β)—H_β for H_3^+, H_2^+, and H^+ impact, respectively; (2γ), (1γ)—H_γ for H_2^+ and H^+ impact, respectively. (A) H_β for H_3^+ impact (Ref. 2); (B) H_β for H_2^+ impact (Ref. 2). The H^+ impact data are from Ref. 1.

the H_2^+ at about 35 keV, and the H_3^+ at about 80 keV.

Molecular ion impact might be expected to produce greater dissociative excitation of the target hydrogen than proton impact for the following reasons: (1) The presence of the electron(s) in the molecular ion permits more effective excitation of triplet repulsive states by the process of electron exchange since the proton is restricted to exciting singlet repulsive states by the spin conservation rule; (2) in close collisions the screening of the total nuclear charge of the ion by the orbital electron(s) may not be particularly effective; and (3) naively treating the H_2^+ and H_3^+ ions as H^+ plus H, and H^+ plus 2H, respectively, one would expect considerable excitation due to the neutral component—for instance, Bates and Griffing[4] have shown with the Born approximation that H impact excitation of H atoms is comparable to H^+ impact at lower velocities. This rather simple model fails to explain our curves.

B. Doppler-Shifted Radiations

The cross sections for the Doppler-shifted radiations versus velocity are plotted in Fig. 2 along with data from Refs. 1 and 2.

The mechanisms possible for the production of these radiations include:

$$\underline{H_2}^+ + H_2 \rightarrow \underline{H} + \underline{H}^* + H_2^+, \quad (4)$$

$$\underline{H_2}^+ + H_2 \rightarrow \underline{H}^* + \underline{H}^+ + [HH], \quad (5)$$

$$\underline{H_3}^+ + H_2 \rightarrow [\underline{HH}] + \underline{H}^* + H_2^+, \quad (6)$$

$$\underline{H_3}^+ + H_2 \rightarrow [\underline{HH}^+] + \underline{H}^* + [HH]. \quad (7)$$

We have omitted mechanisms that produce slow protons for the reasons previously given under A.

The H_2^+ impact curves exhibit a principal maximum at about 10 keV. The curves show further small structure at higher velocities, which are within experimental

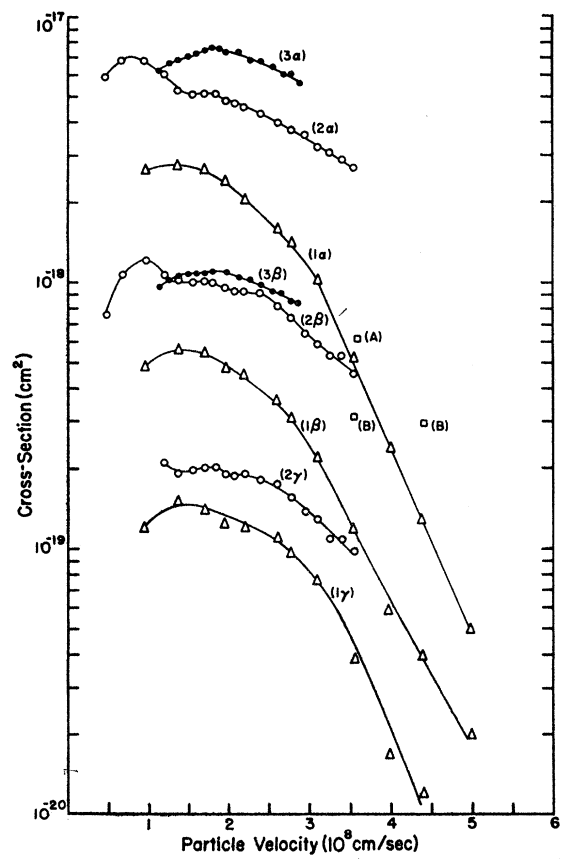

FIG. 2. Shifted Balmer emissions: (3α), (2α), (1α)—H_α for H_3^+, H_2^+, and H^+ impact, respectively; (3β), (2β), (1β)—H_β for H_3^+, H_2^+, and H^+ impact, respectively; (2γ), (1γ)—H_γ for H_2^+ and H^+ impact, respectively. (A) H_β for H_3^+ impact (Ref. 2); (B) H_β for H_2^+ impact (Ref. 2). The H^+ impact data is from Ref. 1.

[4] D. R. Bates and G. Griffing, Proc. Phys. Soc. (London) **A66**, 961 (1953).

error but are reproducible and, therefore, we assume are real.

Sweetman[5] has measured the cross sections for the reactions (a) $H_2^+ \rightarrow H+H$ (charge transfer) and (b) $H_2^+ \rightarrow H+H^+$ (dissociation) from 100 keV to higher energies. At 100 keV he finds cross sections of about 5×10^{-17} and 6×10^{-17} cm^2 for reactions (a) and (b), respectively. This means that 2.9, 0.5_4, 0.1% of the sum of reaction events (a) and (b) result in H_α, H_β, and H_γ emission, respectively. These fractions are considerably larger than the fraction of the corresponding Balmer emissions resulting from electron capture by protons in hydrogen.[1]

The H_3^+ impact curves exhibit a single broad maximum at about 50 keV. We assume that these curves are the result of mechanisms (6) and (7). (Afrosimov *et al.*[3] found that total charge transfer peaked at 40 keV for H_3^+ impact on H_2.)

ACKNOWLEDGMENTS

The authors wish to thank Darrell Bolding, Bill Evans, and David Kay for their aid in making the calculations and in obtaining the data.

[5] D. R. Sweetman, Proc. Roy. Soc. (London) **A256** 416 (1960).

PHYSICAL REVIEW VOLUME 131, NUMBER 6 15 SEPTEMBER 1963

Multiple Excitation and Ionization of Inner Atomic Shells by X Rays*

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(Received 5 April 1963)

Reinvestigation of the region of the argon K absorption edge has revealed a new resonance absorption structure followed by a new continuum. These new features may be interpreted as arising from double-electron-excitation processes involving an M electron as well as the K electron. The first new resonance line lies about 22 eV above the first line in the previously observed single-electron-excitation resonance structure. No additional resonance structure was found in the region from zero to about 50 eV.

INTRODUCTION AND EXPERIMENT

THE x-ray absorption spectrum of gaseous argon in the region of the K edge (about 3.2 keV) has been reinvestigated with an automatic two-crystal vacuum spectrometer. A new absorption-edge structure was observed. This structure, interpreted as evidence for multiple-electron excitation and multiple ionization is discussed qualitatively in terms of a few particular two-electron transitions.

The details of the apparatus and techniques of two-crystal spectrometry have been presented elsewhere.[1] A few essentials are, however, pertinent in this discussion.

A platinum-plated copper anode served as the source of continuous x rays. The x-ray tube was operated at 14.3 kV and 54 mA. A pair of calcite crystals (having a parallel-position width of 10.1 sec of arc for $\lambda=1.54$ Å radiation) was used. A gas cell 1.00-in. long with 0.001-in. beryllium windows and filled with research-grade argon was used as the absorber. The gas cell was filled to different pressures for the recording of different parts of the curve in Fig. 1. For the KM region of interest, the pressure was 213 mm Hg. The beam intensity with the gas cell evacuated (I_0) was 500 counts per sec. Intensity measurements for the region of interest were taken at intervals of 10 sec of arc (0.094 eV) by rotating the first crystal. A krypton-filled proportional counter was used to measure the intensity.

The absorption data, Fig. 1, represent the average of four complete passes through the wavelength region of interest. The ordinate values are in arbitrary absorption units proportional to $\ln(I_0/I)$, where I_0 is the incident and I is the transmitted intensity. The data have been corrected for instrumental effects such as background intensity and the several resolving power perturbations.[1,2] The resolving power correction does the following: (1) yields narrower lines and edges, (2) alters the degree of asymmetry, (3) enhances significantly the relative absorption contrast, and (4) shifts slightly the measured energy position of each structural component. Even though the spectral window is very narrow in this experiment ($\lambda/\Delta\lambda \approx 11\,000$), this correction is very important if detailed analysis is to be made of, or relative to, the K excitation.

* Supported by the Air Force Office of Scientific Research [under Contract 49(638)-402], by the National Science Foundation (under Grant No. 9639), and by the Advanced Research Projects Agency through the Materials Science Center at Cornell.

[1] The apparatus and techniques used in this experiment are discussed in detail by H. W. Schnopper, Ph.D. thesis, 1962, Cornell University (to be published).

[2] L. G. Parratt, Rev. Mod. Phys. **31**, 616 (1959); and J. O. Porteus, J. Appl. Phys. **33**, 700 (1962).