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Formation of H(2*p*) and H(2*s*) in Collisions of Protons and Hydrogen Atoms with Hydrogen Molecules[*]

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Cross sections for emission of Lyman-α radiation owing to formation of H(2*p*) and H(2*s*) in collisions of 5–25-keV protons and hydrogen atoms with molecular hydrogen have been determined. The intensity of Lyman-α emitted spontaneously from H(2*p*) was measured at 54.7° or 125.3° with respect to the projectile beam in an essentially field-free collision chamber with an oxygen-filtered photometer calibrated by reference to previous results for H^+ on Ar. The narrow bandwidth of the oxygen filter allowed separation of the Doppler-shifted Lyman-α, emitted by H(2*p*) formed in electron capture by fast incident protons or collisional excitation of fast incoming hydrogen atoms, and the virtually unshifted Lyman-α emitted by the far slower H(2*p*) produced in dissociative excitation of H_2. The increase in intensity of Lyman-α when an electric field, oriented in the direction of the beam, was applied within the collision chamber has been used to derive separate cross sections for formation of H(2*s*) owing to projectile and dissociative excitation. The experimental configuration was designed to minimize the effect of polarization of the light emitted from H(2*p*) and H(2*s*), and, after small corrections for cascade effects, the data yield cross sections for population of these states. The total cross section for formation of H($n=2$) via projectile excitation exceeds that for dissociative excitation in either H^+ or H impact. H^+ is generally more efficient than H in the production of Lyman-α at low energies in projectile excitation and at all energies in dissociative excitation, and the cross section for formation of H(2*p*) usually exceeds that for H(2*s*). Scaling relationships from limiting high-energy-scattering theory are found to have only moderate success in relating our results to previous measurements involving excitation of H to the $n=3$ and 4 states in projectile excitation and as well as in dissociative excitation by other heavy particles.

I. INTRODUCTION

Processes that lead to the emission of light in collisions of energetic protons and hydrogen atoms with atomic and molecular gases have received increased attention recently because of their occurrence in proton auroras[1] and the interaction of the solar wind with planetary atmospheres. The energy range below 10 keV is of special interest in these events but has been relatively little explored, particularly for hydrogen-atom projectiles.[2]

Energetic H^+ and H excite the spectra of target gases as do incident electrons in auroras, but they also excite the atomic hydrogen-line spectrum which is the characteristic signature of a proton aurora. The hydrogen lines result from the formation of excited atoms (H^*) in capture collisions of energetic H^+ with atmospheric constituents (M)

$$H^+ + M \rightarrow H^* + M^+ , \qquad (1)$$

and in direct collisional excitation of fast atoms

$$H + M \rightarrow H^* + M. \qquad (2)$$

In previous papers we have reported the cross sections for emission of Lyman-α radiation in collisions of 1–25-keV H^+ and H with N_2 and O_2[3] and with the rare gases.[4] We related the observed emission cross sections in the presence and absence of an applied electric field to cross sections for population of H(2*p*) and H(2*s*) in processes (1) and (2). Molecular hydrogen is a simpler target than N_2 or O_2 and while not of great abundance in the earth's atmosphere at auroral altitudes, it is a prominent component of the atmospheres of the outer planets, and is an easier subject for theoretical study that would contribute to better understanding of experimentally determined cross sections and increased predictability of difficult-to-measure cross sections.

In addition to projectile excitation, processes (1) and (2), excited hydrogen atoms can be produced in collisions of energetic H^+ and H with H_2 by dissociative excitation of the H_2 target. Examples of such processes are

$$\underline{H}^+ + H_2 \rightarrow \underline{H}^+ + H^* + H, \qquad (3)$$

$$\underline{H}^+ + H_2 \rightarrow \underline{H}^+ + H^* + H^+ + e^- , \qquad (4)$$

$$\underline{H}^+ + H_2 \rightarrow \underline{H} + H^* + H^+ , \qquad (5)$$

for H^+ impact, and

$$\underline{H} + H_2 \rightarrow \underline{H} + H^* + H , \qquad (6)$$

$$\underline{H} + H_2 \rightarrow \underline{H} + H^* + H^+ + e^- , \qquad (7)$$

$$\underline{H} + H_2 \rightarrow \underline{H}^+ + H^* + H + e^- , \qquad (8)$$

$$\underline{H} + H_2 \rightarrow \underline{H}^- + H^* + H^+ , \qquad (9)$$

for H impact. The fast particle has been underlined, and an asterisk again denotes an excited atom. The Lyman-α radiation emitted by the fast hydrogen atoms that are excited in processes analogous to (1) and (2) is Doppler shifted when viewed at an angle other than 90° with respect to the direction of motion of the fast projectile. On the other hand the excited hydrogen atoms produced in dissociative processes, such as (3)-(9), are moving much more slowly than the fast projectiles, and the Lyman-α radiation emitted by them is virtually unshifted by the Doppler effect. By separating the shifted and unshifted components of the total Lyman-α radiation[5] emitted during H^+ or H bombardment of H_2 the cross section $\sigma_{PE}(2s)$ and $\sigma_{PE}(2p)$ for excitation of the fast projectiles and the dissociative excitation cross sections $\sigma_{DE}(2s)$ and $\sigma_{DE}(2p)$ can be obtained.

For hydrogen-atom impact on H_2 we are aware of only one previous study of the emitted Lyman-α radiation.[6,7] The total cross section for emission of Lyman-α from H(2p) was reported by Dahlberg *et al.*[6] in the energy range 12.5-140 keV. No separation of projectile excitation and dissociative excitation cross sections was attempted. Sellin has estimated $\sigma_{PE}(2s)$ for collisions of 15-keV H atoms from an experiment in which a proton beam was passed through H_2 under thick target conditions.[8]

For proton collisions, data are available over the broader energy range 0.35-200 keV.[6,8-20] Several determinations of $\sigma_{PE}(2s)$ have been reported.[13,16,19] Andreev *et al.*[15] used a spectrometer to separate the Doppler-shifted and unshifted components of Lyman-α radiation from both H(2s) and H(2p) for the impact of 10-35-keV H^+ on H_2. Hughes *et al.*[20] used the transmission characteristics of an oxygen-filtered photometer to separate the contributions to the total Lyman-α intensity owing to projectile and dissociative excitation of H(2p) for impact of 20-120-keV H^+.

In the present paper we report the results of a study of the emission of Lyman-α radiation in collisions of 1-25-keV H^+ and H with H_2. Cross sections for dissociative and projectile excitation have been separately determined for impact energies in the range 5-25 keV, while the total Lyman-α emission cross sections for both H^+ and H impact have been measured in the 1.5-25-keV range. Except in the work of Hughes *et al.*,[19] earlier determinations of $\sigma_{PE}(2s)$ and $\sigma_{DE}(2s)$ for an H_2 target have been carried out under the assumption of an isotropic angular distribution of the quench induced Lyman-α radiation. Recent calculations have demonstrated[21-24] that substantial, apparatus-dependent anisotropies in this radiation can exist and must be taken into account in measurements involving H(2s). Our measurements were carried out with an experimental configuration designed to minimize these effects. An abbreviated account of this work has been given elsewhere.[25]

II. EXPERIMENTAL PROCEDURE

Lyman-α radiation emitted during impact of protons and hydrogen atoms on molecular hydrogen was viewed at 65.7°, 90°, or 125.3° by an oxygen filtered photometer[3,4] which had been calibrated by normalization of our Lyman-α emission cross sections for 1-25-keV H^+ on Ar at each of these viewing angles to two previous absolute determinations of this cross section.[26,27] The apparatus used to prepare and detect the H^+ and H beams and bring them into collision with H_2 under thin-target conditions has been described in detail elsewhere.[28-30] Output pulses from the photometer were fed into a preamplifier, amplifier, and discriminator, and were counted with a scaler. Beam currents were measured with a digital charge integrator, and a differential capacitance manometer was used for target-pressure measurements. Matheson ultrapure H_2 was admitted to the scattering chamber at pressures in the range $1-5\times10^{-4}$ Torr. Using electron capture and stripping cross sections σ_{10} and σ_{01} for collisions of 1-25-keV H^+ and H with H_2[31,32] it can be shown[32a] that no more than 5% of the H^+ beam was converted to H and that less than 2% of the H beam was converted to H^+ by charge changing collisions upstream of the field of view of the photometer.

In a set of experiments in which the photometer viewed the interaction region at 90°, the transmission function A of the oxygen-filter was the same for Lyman-α emitted by fast H* formed in (1) and (2) or by slow H* produced by (3)-(9). The 90° measurements were carried out under essentially field-free conditions and, at any oxygen pressure, yielded an apparent emission cross section $Q(2p)$ which is related to the total cross section $Q_{90}(2p)$ for emission of Lyman-α from H(2p) at 90° by

$$Q(2p) = A\, Q_{90}(2p)\ . \tag{10}$$

The transmission function A for non-Doppler-shifted Lyman-α was determined by measuring the oxygen-pressure dependence of $Q(2p)$ for impact of H^+ or H on Ar with 0-, 100-, 150-, 200-, 300-, 400-, 500-, 600-, and 700-Torr O_2 in the filter. There are no Ar emission lines in the range of sensitivity of the unfiltered solar-blind photomultiplier.

A potential source of contamination of the Lyman-α $Q_{90}(2p)$ results is collisional excitation of the Lyman ($B\,^1\Sigma_u^+ - X\,^1\Sigma_g^+$) and Werner ($C\,^1\Pi_u - X\,^1\Sigma_g^+$) bands of H_2. Mumma and Zipf have recently reviewed the problem for electron impact on H_2 and pointed out[33] that several of these bands occur at the wavelengths of the oxygen-transmission windows.[34] Based on the spectral study[6] of the intensity of emission from H_2 induced by impact of 20–120-keV H^+ and H, as well as on less direct evidence reported by other groups,[10,19] these processes were not expected to lead to serious systematic errors in our experiments. This was confirmed in an auxilliary series of experiments in which the value of $Q_{90}(2p)$ deduced from measurements of $Q(2p)$ was shown to be independent of oxygen pressure over the range 0–700 Torr for both H^+ and H impact.

The total cross section $Q_{90}(2p)$ is related to the dissociative and projectile excitation cross sections by the equation

$$Q_{90}(2p) = [1 - \tfrac{1}{3}P_{\mathrm{DE}}(2p)]\,\sigma_{\mathrm{DE}}(2p) + [1 - \tfrac{1}{3}P_{\mathrm{PE}}(2p)]\,\sigma_{\mathrm{PE}}(2p)\,, \qquad (11)$$

where $P_{\mathrm{DE}}(2p)$ and $P_{\mathrm{PE}}(2p)$ are the polarization of Lyman-α radiation emitted by H(2p) formed via dissociative and projectile excitation. In general the angular distribution of electric dipole radiation is given by

$$I(\theta) = \frac{3I_T}{4\pi}\left(\frac{1 - P\cos^2\theta}{3 - P}\right)\,. \qquad (12)$$

Here, θ is the viewing angle, I_T is the total intensity, and the polarization $P = (I_\parallel - I_\perp)/(I_\parallel + I_\perp)$ is defined in terms of the intensities $I_\parallel$ and $I_\perp$ measured at 90° with respect to the reference axis having polarization parallel or perpendicular to that axis.

In order to separate the contributions owing to projectile and dissociative excitation, experiments were carried out in which the photometer viewed the interaction region at 54.7° or 125.3° and a technique originated by Stebbings *et al.*[5] was employed. For H* in the keV energy range, the Doppler shift in Lyman-α viewed at these angles is substantial in comparison with the bandwidth[35] of the oxygen filter. On the other hand, consideration of the potential curves[36] for the excited states of H_2^+ and H_2 which correlate with $H(n=2) + H^+$ or $H(1s) + H(n=2)$, respectively, suggests that H* formed in processes (4), (5), (7), and (9) will have kinetic energies in the 4–12 eV range, while those formed in processes (3), (6), and (8) will have $E \lesssim 1$ eV. Therefore, Lyman-α radiation due to dissociative excitation of H* is essentially unshifted, and the transmission of the oxygen filter for Lyman-α radiation emitted by fast H* will be considerably less than for slow H*. This difference in absorption can be used to obtain the cross section for each process. At any oxygen pressure, the 54.7° or 125.3° experiments yield an apparent emission cross section

$$\sigma(2p) = A\,\sigma_{\mathrm{DE}}(2p) + B\,\sigma_{\mathrm{PE}}(2p)\,, \qquad (13)$$

where B is the transmission function for Doppler-shifted Lyman-α radiation. It is important to note that, according to Eq. (12), these results are effectively independent of polarization as $\cos^2\theta = \frac{1}{3}$ for 54° 44′ and 125° 16′.

The transmission function B for Doppler-shifted Lyman-α radiation was determined at each impact energy by measuring $\sigma(2p)$ for the impact of H^+ on Ar at the same O_2 pressures employed in the determination of A. Since the O_2 filter window is most transparent at a wavelength slightly longer than that of unshifted Lyman-α radiation, the transmission of the filter at fixed O_2 pressure for Lyman-α emitted from H* of a given energy is greater at 125.3° than at 54.7°. In our experiments, the energy range studied at 54.7° was 5–15 keV, while, for a viewing angle of 125.3°, measurements were made for 10–25-keV H^+ and H impact.

Once the transmission functions A and B had been determined, the value of $\sigma(2p)$ for collisions of H^+ or H with H_2 was measured at the same oxygen pressures. Values of $\sigma_{\mathrm{DE}}(2p)$ and $\sigma_{\mathrm{PE}}(2p)$ were then calculated using a linear least-squares-fitting procedure which employed the theoretical treatment of Eq. (13) at the eight nonzero O_2 pressures.

For studies of H(2s) formation by the precesses in Eq. (1)–(9), an electric field was applied within the collision chamber in a direction parallel or antiparallel to that of the beam. The field was generated by application of a voltage of the same magnitude, but of different sign, to a pair of parallel plates oriented perpendicular to the beam direction. The plates were coated with cadmium to minimize reflection of Lyman-α and each had a 0.375-in.-diam hole to allow the beam to pass through without striking any surfaces. Lyman-α emitted from a portion of the beam track midway between the plates was viewed at 54.7° or 125.3° with respect to the beam and the electric field direction using the photometer with its oxygen cell evacuated. This experimental configuration minimizes the effects of the polarization of quench-induced radiation from H(2s) for which the reference axis in Eq. (12) is the direction of the applied electric field. In this configuration, both quenching plates were completely blocked from the viewing zone of the photometer. The field needed to quench H(2s) was determined by increasing the applied voltage until no further enhancement of the Lyman-α signal could be detected with further increases in voltage. Care was taken to demonstrate that the magnitude of the saturation voltage and the enhancement of the signal owing to electric field quenching were unchanged when the direction of the field was switched from parallel to antiparallel with respect to the beam direction.

The difference $\sigma(2s)$ determined at 54.7° or 125.3° between the apparent cross section $\sigma(2s+2p)$, measured with the electric field on and $\sigma(2p)$ measured with the field off is related to the cross sections for emission from H(2*s*) owing to projectile and dissociative excitation as

$$\sigma(2s)=\sigma(2s+2p)-\sigma(2p)=A\,\sigma_{DE}(2s)+B\,\sigma_{PE}(2s)\ . \tag{14}$$

Values of $\sigma_{DE}(2s)$ and $\sigma_{PE}(2s)$ were determined by the same least-squares procedure as described for the treatment of emission cross sections for H(2*p*).

The errors in the Lyman-α emission cross sections can be estimated by consideration of the uncertainties in the values of $\sigma(2p)$, $\sigma(2s)$, A, and B. Based on contributions of $\lesssim 5\%$ from measurements of the beam current and photometer counts and $\lesssim 2\%$ from nonlinearities in pressure measurements, the relative error in either $\sigma(2p)$ or $\sigma(2s+2p)$ is $\lesssim 7\%$. The subtraction required to obtain $\sigma(2s)$ results in an additional source of error in the cross sections for emission of Lyman-α from H(2*s*). Defining the ratio Y as the number of photometer counts with an applied electric field to the number of counts in the absence of a field, it can be shown that the subtraction in Eq. (14) leads to a fractional error of $\approx (Y+1)^{1/2}/(Y-1)$ times the fractional error in the number of counts with the field off. We estimate that uncertainties in A and B induce *relative* errors of about 5–10% in the dissociative excitation cross sections and about 10–15% in the cross sections for projectile excitation. The *absolute* cross sections for hydrogen-atom impact have an additional uncertainty of about ±10% owing to errors in the neutral beam detection technique,[28]— which would not affect a comparison of any of the four H-impact cross sections, but which would have to be considered when comparing H$^+$ and H results. All of our *absolute* values have an additional error owing to uncertainties in the Lyman-α emission cross section for H$^+$+ Ar given as ~ 25–30% by Andreev *et al.*[27] and ±45% by Pretzer *et al.*[26]

III. EXPERIMENTAL RESULTS

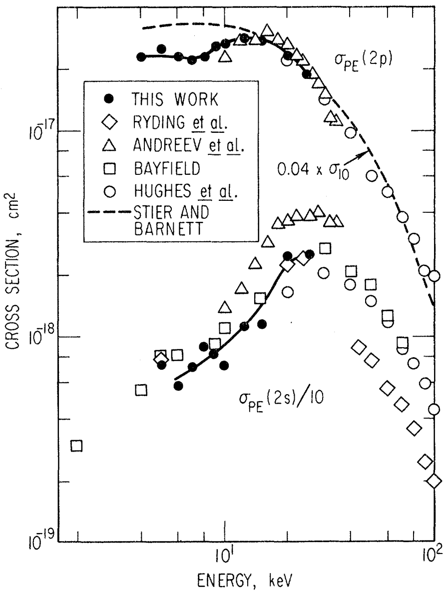

FIG. 1. Cross sections for emission of Lyman-α radiation owing to projectile excitation of H(2*p*) and H(2*s*) in collisions of 2–100-keV protons with H$_2$. Values of $\sigma_{PE}(2s)$ have been divided by 10 and σ_{10} has been multiplied by 0.04. Data are from Ryding *et al.*, Ref. 13; Andreev *et al.*, Ref. 15; Bayfield, Ref. 16; Hughes *et al.*, Ref. 19 for $\sigma_{PE}(2s)$ and Ref. 20 for $\sigma_{PE}(2p)$; and Stier and Barnett, Ref. 31.

Figure 1 gives our Lyman-α cross sections for projectile excitation of H(2*p*) and H(2*s*) owing to electron-capture collisions of protons with H$_2$, and compares our work with the results of previous studies. Also shown is the total electron-capture cross section σ_{10} of Stier and Barnett.[31] The cross section $\sigma_{PE}(2p)$ is nearly energy independent in the range 5–10 keV, rises gradually to a maximum at ~15 keV, and then falls rapidly at higher energies. On the other hand, $\sigma_{PE}(2s)$ is substantially smaller than $\sigma_{PE}(2p)$ at lower energies, increases monotonically in the 5–25-keV energy range, and is $\gtrsim \sigma_{PE}(2p)$ at $E \gtrsim 20$ keV. The agreement between our values of $\sigma_{PE}(2p)$ and those reported by Andreev *et al.*[15] is very good. This is a necessary condition as the cross sections reported in all three studies are normalized to the value of $\sigma_{PE}(2p)$ for H$^+$+ Ne reported by Andreev *et al.*[27] While the agreement in energy dependence of $\sigma_{PE}(2s)$ reported by different groups[13,15,16,19] is also good, a wide spread exists in the absolute values of $\sigma_{PE}(2s)$ determined at each energy. This variation in magnitude may reflect systematic errors inherent in some of the determinations of $\sigma_{PE}(2s)$. While our experimental configuration minimizes effects owing to anisotropy of quench-induced Lyman-α radiation,[21–24] application of an electric field parallel or antiparallel to the beam axis results in a perturbation of the energy of the incoming protons which could be a problem when $\sigma_{PE}(2s)$ changes rapidly with energy, as it does for H$_2$ target, and could also lead to an additional Doppler shift in the Lyman-α radiation from fast H*. While reversal of the field direction never resulted in changes of greater than 10% in $\sigma_{PE}(2s)$, the potential problem still remains. Bayfield avoided the latter problem by employing an "external" quenching method[16] in which the electric field was applied downstream of the collision chamber; however, as the Lyman-α detector did not view the quenching region at the optimum angle, a polarization correction[21–24] should be applied to his work and the seemingly good agreement between the magnitude of Bayfield's and our $\sigma_{PE}(2s)$ may be fortuitous owing to systematic errors in each work. Andreev *et al.*[15] applied a quenching field within the collision chamber at 90° with respect to both the

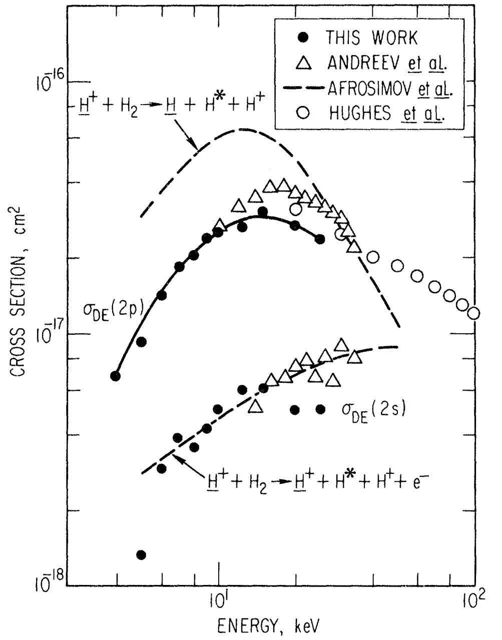

FIG. 2. Cross sections for emission of Lyman-α radiation owing to dissociative excitation of H($2p$) and H($2s$) in collisions of 4–100-keV protons with H_2. Broken lines represent the upper bounds to the cross section for emission of Lyman-α radiation owing to the processes indicated. Data are from Andreev *et al.*, Ref. 15; Afrosimov *et al.*, Ref. 38; and Hughes *et al.*, Ref. 20.

H^+ beam and the direction of observation. While the correction owing to polarization of quench-induced Lyman-α radiation under these conditions is probably small, a Seya-Namioka spectrometer such as they employed can have substantially different transmission for the Lyman-α components $I_\parallel$ and $I_\perp$[37] and hence errors could have been induced in $\sigma_{PE}(2s)$ if the polarization of the radiation from Stark-quenched H($2s$) for proton impact on H_2 were markedly different from that in the measurements used for detector calibration. Hughes *et al.*[19] employed an external quenching field and applied an experimentally determined polarization correction to the intensity of quench-induced Lyman-α radiation; and hence their values of $\sigma_{PE}(2s)$ should be least influenced by the types of systematic error discussed above.

Cross sections for dissociative excitation of hydrogen atoms in H^+ impact on H_2 are shown in Fig. 2, along with the results of similar experiments at higher energies. Also shown in Fig. 2 are cross sections measured in charged-particle coincidence experiments.[38] As the latter results also contain a contribution from dissociative ionization of H_2 via the repulsive $2p\sigma_u$ state of H_2^+ to yield H^+ + H($1s$), they must be taken as upper bounds to the cross sections for processes (4) and (5). Both $\sigma_{DE}(2p)$ and $\sigma_{DE}(2s)$ increase steadily in the 5-15-keV range, and then fall off gradually as the impact energy is increased from 15 to 25 keV. In our experiments, the magnitude of $\sigma_{DE}(2p)$ for proton impact is always nearly 5 times that of $\sigma_{DE}(2s)$. Our results and those of previous workers are in

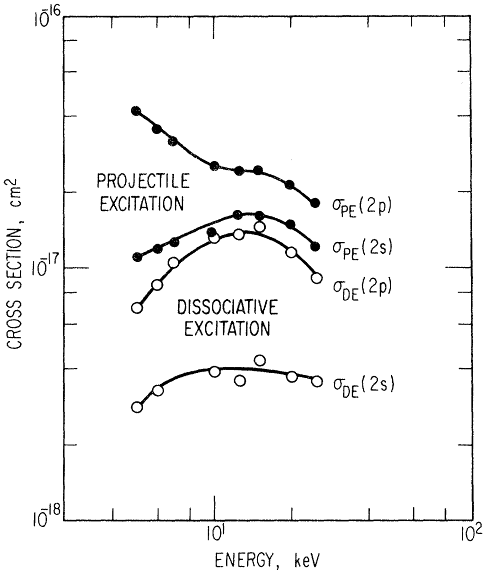

FIG. 3. Cross sections for emission of Lyman-α radiation owing to projectile and dissociative excitation of H($2p$) and H($2s$) in collisions of 5–25-keV hydrogen atoms with H_2.

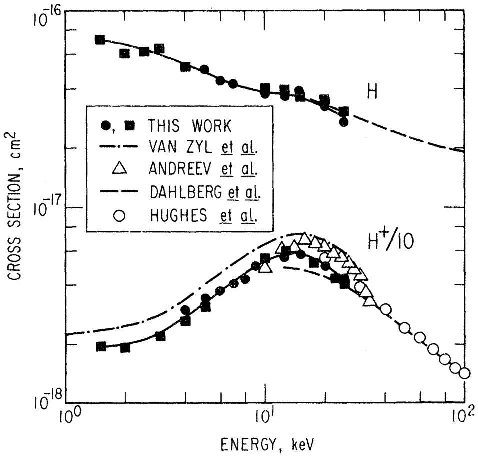

FIG. 4. Total cross section for emission of Lyman-α radiation owing to projectile and dissociative excitation of H($2p$) in collisions of 1–100-keV protons and hydrogen atoms with H_2. For this work, the solid circles represent the sum $\sigma_{tot}(2p) = \sigma_{PE}(2p) + \sigma_{DE}(2p)$, while the solid squares represent values Q_{90}. For the previous studies, $\sigma_{tot}(2p)$ is given by the open symbols and $Q_{90}(2p)$ is given by the broken lines. The results for proton impact have been divided by 10. Data are from van Zyl *et al.*, Ref. 14; Andreev *et al.*, Ref. 15; Dahlberg *et al.*, Ref. 6; and Hughes *et al.*, Ref. 20.

satisfactory agreement within experimental error. Owing to the errors induced in the determination of $\sigma_{DE}(2s)$ via the subtraction in Eq. (14), the relative fractional error in this cross section is about twice that for $\sigma_{DE}(2p)$.

Figure 3 shows our results for impact of hydrogen atoms on H_2. Inspection of the cross sections for the individual emission processes shows that H(2p) formed in collisional excitation of the incoming fast hydrogen atom is the most important source of Lyman-α radiation in the energy range we studied. Both in dissociative and projectile excitation of H*, the cross section for emission from H(2p) is greater than that for emission from H(2s), the effect being more pronounced for the former process; however, the observation that $\sigma_{PE}(2s)$ is greater than $\sigma_{DE}(2p)$ at all energies emphasizes the dominance of collisional excitation of fast incoming H atoms over dissociative excitation of H_2 as a source of excited hydrogen atoms. The value of $\sigma_{PE}(2s)$ at 15 keV estimated by Sellin[8] lies about an order of magnitude below our curve.

A useful test of the procedure used to separate the contributions from slow and fast H* is the comparison, given in Fig. 4, of the total cross section $\sigma_{tot}(2p)=\sigma_{PE}(2p)+\sigma_{DE}(2p)$ for emission of Lyman-α from H(2p) in H^+ and H impact with the value $Q_{90}(2p)$ which we obtained in an independent set of measurements. The agreement between these two quantities is seen to be excellent. Inspection of Eq. (11) shows that this is necessary condition if *both* $P_{DE}(2p)$ and $P_{PE}(2p)$ are small. Measurements of the polarization of Lyman-α radiation from H^+ excitation of H_2 by Kauppila *et al.*[17] imply that this is indeed the case for $P_{DE}(2p)$. Further evidence for a small degree of polarization in dissociative excitation collisions comes from the measurements of polarization of H_α from collisions of 45–700-eV He^+ with H_2 reported by Nathan and Isler[39a] and the observation by Ankudinov *et al.*[39b] of zero polarization of H_α from these collision partners in the 10–30-keV energy range. We are unaware of any direct measurement of $P_{PE}(2p)$ for H^+ impact on H_2; however, based on the similarity of other features of $\sigma_{PE}(2p)$ for H_2 and targets for which polarization data are available,[40] $P_{PE}(2p)$ for H_2 is not expected to be large in the range 5–25 keV.

In order to use the results of these experiments to discuss the processes which can directly form H(2p) in collisions of H^+ and H with H_2, we must demonstrate that cascade effects do not influence substantially the observed emission cross sections. According to the electric-dipole selection rules, the 3s and 3d levels are connected to H(2p) and the 3p level is connected to H(2s) by an allowed transition in the absence of an applied electric field. Owing to the relatively long H(3s) radiative lifetime in field-free space, only ~ 27% of 5-keV H atoms, ~ 17% of those with 15-keV kinetic energy or ≈ 12% of the 25-keV H(3s) formed via projectile excitation under our experimental conditions could radiate H_α followed by Lyman-α before moving downstream from the field of view of the photometer. On the other hand, ~ 96% of 5-keV H(3d), ~ 85% with 15 keV, and 75% with $E = 25$ keV could yield H_α followed by Lyman-α in the photometric viewing zone. Consideration of the short lifetimes of H(3p) toward H_α and Lyman-β transitions shows that 12% of 3p hydrogen atoms will yield H(2s) at all impact energies studied in our experiments.

Based on these considerations and the values of $\sigma_{PE}(3s)$, $\sigma_{PE}(3p)$, and $\sigma_{PE}(3d)$ for 10–100-keV proton impact on H_2 reported by Hughes *et al.*,[41] we conclude that the cascade correction to $\sigma_{PE}(2p)$ is ≈ 5–7% and, that in the absence of an applied electric field, (3p-2s) transitions are responsible for no more than 2% of the 2s H atoms which are formed. Preliminary values[42] of the cross sections for projectile excitation of the $n = 3$ sublevels for collisions of 10–35-keV H with H_2 indicate that, in our experiments, the cascade correction for $\sigma_{PE}(2p)$ in hydrogen atom impact on H_2 is no more than 5% and that no more than 2% of H(2s) is formed via cascade from H(3p) when no electric field is applied.

The cascade contributions to the dissociative excitation cross sections must be calculated in a slightly different manner. While there is some uncertainty in the kinetic energy of H* formed in dissociative excition, consideration of the radiative lifetimes of the 3s and 3d sublevels and the cross sections for quenching of H_α radiation[43] by molecular gases at thermal energies leads to the conclusion that nearly all H(3s) and H(3p) produced in this process will make a radiative transition to H(2p) followed by emission of a Lyman-α photon before being quenched by H_2. Furthermore, for low-kinetic-energy H* this will take place in the field of view of the photometer, so that the cascade contribution to $\sigma_{DE}(2p)$ is $\sigma_{DE}(3s)+\sigma_{DE}(3d)$. Similarly, when one takes account of the short lifetime of H(3p) and the branching ratio for transitions from this state, one can estimate that about 12% of the 3p hydrogen atoms formed via dissociative excitation will make an H_α transition to H(2s); hence we can estimate the cascade contribution to $\sigma_{DE}(2s)$ as ~ 0.12 $\sigma_{DE}(3p)$. For proton impact on H_2, the value of $\sigma_{DE}(3p)$[15] deduced from the Lyman-β measurements can be used to estimate that the cascade contribution to $\sigma_{DE}(2s)$ is no more than 5%. This result, in conjunction with the total cross section[44] for emission of H_α owing to dissociative excitation, implies that the cascade correction to $\sigma_{DE}(2p)$ is $\lesssim$ 15% in the keV energy range. We are unaware of measurements of $\sigma_{DE}(n=3)$ for collisions of H with H_2.

Recently reported cross sections for destruction of energetic[45] and thermal[46,47] H(2s) in collisions with H_2 can be used to show that, under our experimental conditions, the metastable atoms will exit from the photometer's field of view before being quenched; hence, collisional quenching of H(2s) cannot lead to an erroneously large value of $\sigma_{DE}(2p)$ and $\sigma_{PE}(2p)$. At thermal energies, the cross sections for collisional quenching of H(2p) are quite large,[48] but at the pressures employed in this work, spontaneous radiation will occur before collisional quenching. Even if the cross sections in the keV range are as large as those at thermal energies, collisional quenching would not affect our determination of $\sigma_{PE}(2p)$.

IV. DISCUSSION

A. Projectile Excitation

The shape of the cross-section curves for $\sigma_{PE}(2p)$ and $\sigma_{PE}(2s)$ for electron-capture collisions of protons with molecular hydrogen and the increase in the ratio $\sigma_{PE}(2s)/\sigma_{PE}(2p)$ with increasing impact energy are similar to the results obtained for N_2,[3,14,19,49] O_2,[3,19,49] and CO,[50] the only other diatomic targets for which Lyman-α data are available. The values of $\sigma_{PE}(2s)$ are comparable for all four targets, while $\sigma_{PE}(2p)$ is smaller for H_2 than for N_2, O_2, and CO by about a factor of 2. For collisional excitation of atomic-hydrogen projectiles, the energy dependence of $\sigma_{PE}(2p)$ is similar to that observed for N_2, O_2, and CO as well as for all of the rare gases except Xe[4] and is only 10–20% smaller in magnitude than the values reported for N_2 and O_2,[3] however, the cross section for excitation of incoming H atoms to the 2s state has a maximum at ~ 12.5 keV for an H_2 target, but decreases monotonically with increasing energy in the 1–25-keV energy range for collisions with other diatomic targets. At the low end of our energy range, the values of $\sigma_{PE}(2p)$, $\sigma_{PE}(2s)$, and $\sigma_{PE}(n=2)$ for hydrogen-atom bombardment exceed those for proton impact by about 50–75%. As the collision energy increases, the values for H^+ and H become comparable at 20, 10, and 15 keV, respectively, and at larger impact energy, protons are more effective than hydrogen atoms in production of Lyman-α radiation owing to projectile excitation. This behavior differs somewhat from that observed previously for diatomic targets, where both $\sigma_{PE}(2p)$ and $\sigma_{PE}(2s)$ for H-atom impact were greater than or equal to those for H^+ bombardment over our entire energy range.

Hughes *et al.* have pointed out[20] that at high energies, and for $n = 2–4$, the cross sections $\sigma_{PE}(ns)$ for electron-capture collisions of H^+ with a number of targets including H_2 follow the n^{-3} scaling law predicted by Born calculations.[51] They also showed that the ratio $\sigma_{PE}(3s)/\sigma_{PE}(2s)$ follows this relationship surprisingly well down to 20 keV, their lowest impact energy, and that the ratio $\sigma_{PE}(3p)/\sigma_{PE}(2p)$ of cross sections for excitation of H(np) is fairly constant, but lower by a significant amount in their energy range, than expected from the n^{-3} relationship. Extension of these comparisons to lower energies shows even more surprisingly that the n^{-3} scaling law works fairly well for the ratio of cross sections for projectile excitation to the 3s and 2s states at energies as low as ≈ 7 keV; however, as $\sigma_{PE}(3p)$ decreases rather rapidly at $E \lesssim 20$ keV, the $\sigma_{PE}(3p)/\sigma_{PE}(2p)$ ratio is no longer constant at lower energies.

Comparison of $\sigma_{PE}(2p)$ and $\sigma_{PE}(2s)$ with the total electron-capture cross section σ_{10} as in Fig. 1 shows that for $E \gtrsim 15$ keV, roughly 4% of all charge-transfer collisions form H(2p), but that no comparable constant relationship is apparent for collisions which yield H(2s). Similar behavior has been noted for electron capture by protons for a number of other target gases.[19,20,50] The observation that $\sigma_{PE}(2p)$ is less than $0.04\,\sigma_{10}$ for $E \leq 15$ keV and that $\sigma_{PE}(2s)/\sigma_{PE}(2p)$ falls off rapidly with decreasing energy, as well as the nature of the failure of the n^{-3} scaling law at lower energies all emphasize that the fraction of electron-capture collisions leading to H* decreases with decreasing impact energy.

Figure 5 shows the ratio of the emission cross sections to the stripping cross section σ_{01} for hydrogen atoms incident upon H_2 and several other simple gases. We had previously shown that for impact of 1–25-keV H on a number of collision partners,[4,50] the magnitude and energy dependence of the relative probability of promotion to the $n = 2$ sublevels and removal an electron is rather insensitive to the identity of the target. For a molecular-hydrogen target, $\sigma_{PE}(2p)/\sigma_{01}$ and $\sigma_{PE}(n=2)/\sigma_{01}$ are similar in energy dependence but somewhat greater in magnitude than for the other target gases (the curves for Ne, Ar, and Kr,[4] not given in Fig. 5, show the same energy dependence but lie between those for He and H_2); however, the ratio $\sigma_{PE}(2s)/\sigma_{01}$ is nearly constant for H_2 in the 5–10-keV energy range, and exhibits a significant difference from the behavior of the other target gases which we have studied.

It has often been assumed that the cross section for collision processes involving a hydrogen molecule is equal to twice the cross section for that process with an atomic-hydrogen target; however, even at energies $\gtrsim 100$ keV it has been shown that the ratios $\sigma_{10}(H_2)/\sigma_{10}(H)$[52,53a] and $\sigma_{01}(H_2)/\sigma_{01}(H)$[53b] for H^+ and H collisions with H_2 and H fail to reach a limiting value of 2.0, and, at $E \lesssim 10$ keV, it was found[52] that $\sigma_{10}(H)$ is greater than $\sigma_{10}(H_2)$. Comparison of our values of $\sigma_{PE}(2p)$ for proton impact on H_2 with the values for an atomic-hydrogen target shows that the cross section for electron cap-

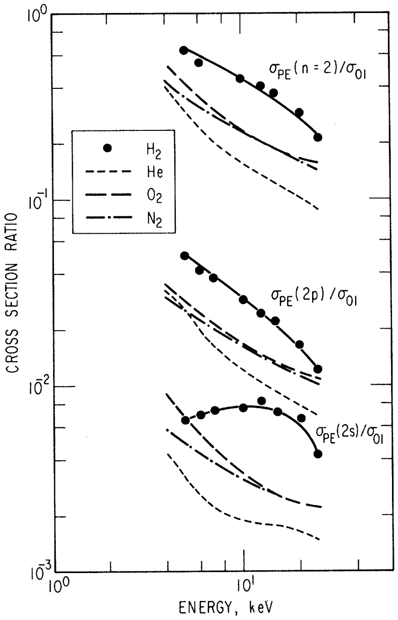

FIG. 5. Ratio of $\sigma_{PE}(2s)$, $\sigma_{PE}(2p)$, and the sum $\sigma_{PE}(n=2) = \sigma_{PE}(2s) + \sigma_{PE}(2p)$ to the stripping cross section σ_{01} of Stier and Barnett (Ref. 31) for impact of 2–25-keV hydrogen atoms on H_2, He, O_2, and N_2. Projectile excitation cross sections for He were taken from Ref. 4, while those for O_2 and N_2 were taken from Ref. 3. Ratios involving $\sigma_{PE}(2p)$ and $\sigma_{PE}(2s)$ have been divided by 10 and 20, respectively.

ture into the 2*p* state for an H target exceeds that for H_2 by 15–75% in the 4–25-keV energy range. A similar result for electron capture into the 2*s* state at low impact energies was reported by Bayfield.[54] Only for $E \gtrsim 70$ keV does the H_2 molecule approach the limiting behavior of two H atoms for $\sigma_{PE}(2s)$.[13,54]

B. Dissociative Excitation

The features of dissociative excitation of hydrogen atoms to the $n=2$ sublevels in collisions of H^+ and H with H_2 can be summarized as follows: (i) The total probability of formation of $H(n=2)$ is less than in projectile excitation collisions at each energy which we studied. For H impact, the ratio $\sigma_{DE}(n=2)/\sigma_{PE}(n=2)$ is ~ 0.2 at 5 keV, and never exceeds 0.5. In H^+ impact, this ratio is ~ 0.35 at 5 keV, ~ 0.9 at 10 keV, and ~ 0.6 at 25 keV. (ii) Formation of H(2*p*) is more probable than formation of H(2*s*) by about a factor of 5 in H^+ impact and by about 2–4 in H impact. At most energies, protons are more effective than hydrogen atoms in causing dissociative excitation. The only exception to this generalization is for formation of H(2*s*), where $\sigma_{DE}(2s)$ for H-atom impact exceeds that for H^+ impact at $E \lesssim 8$ keV. At projectile energies above 10 keV, the values of both $\sigma_{DE}(2p)$ and $\sigma_{DE}(2s)$ for H^+ impact are roughly twice those for H bombardment.

Comparison of the Lyman-α emission cross sections with the results of coincidence experiments[38] allows us to comment on the relative contributions of processes (3)–(5) in collisions of H^+ with H_2. Inspection of Fig. 2 shows that, at low energies, the curve representing the upper bound to the cross section for process (4) is similar in magnitude to $\sigma_{DE}(2s)$ and is substantially smaller in absolute value than $\sigma_{DE}(2p)$. Since this curve contains a component of undetermined magnitude owing to dissociative ionization through the repulsive $2p\sigma_u$ state of H_2^+ to yield $H(1s) + H^+$, we see that dissociative ionization without electron capture must make only a minor contribution to the total $H(n=2)$ formed at low impact energies. It is of interest to note that $\sigma_{DE}(2p)$ and $\sigma_{DE}(n=2)$ are similar in shape to the limiting curve for process (5). Although the magnitude of the limiting cross section for process (5) exceeds the value of $\sigma_{DE}(n=2)$ at low energies, this also contains a contribution from dissociation through the $2p\sigma_u$ state of H_2^+ and hence we cannot rule out process (3) as a major source of $H(n=2)$ at this end of our energy range.

As the impact energy is increased, the limiting cross section for dissociative ionization with electron capture reaches a maximum at ≈ 12 keV and then drops rapidly, while the limiting cross section for simple dissociative ionization rises steadily. It appears that at $E \gtrsim 60$ keV, the latter process would be the more probable. It is important to note that with increasing impact energy $\sigma_{DE}(n=2)$ becomes a steadily increasing fraction of the sum

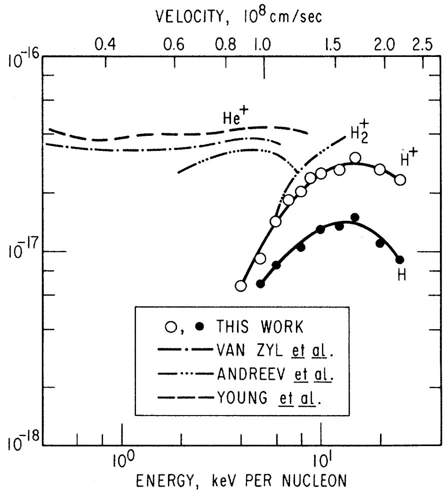

FIG. 6. Comparison of the dissociative excitation cross section $\sigma_{DE}(2p)$ for the impact of H^+, H, H_2^+, and He^+ on H_2. Abscissa gives *E* for H^+ and H, $\frac{1}{2}E$ for H_2^+, and $\frac{1}{4}E$ for He^+. Data are from van Zyl *et al.*, Ref. 14; Andreev *et al.*, Ref. 15; and Young *et al.*, Ref. 55.

of the two limiting cross sections. The observation that, at $E \gtrsim 50$ keV, $\sigma_{DE}(n=2)$ *exceeds* the total of the limiting curves for (4) and (5) is persuasive evidence for the increasing importance of process (3) at high impact energies.

For dissociative excitation of $H(n=2)$ in collisions of hydrogen atoms with H_2, none of the processes (6)–(9) can be ruled out on the basis of existing cross-section measurements. Based on the values of σ_{0-1}[32] reported for these collision partners, process (9) is not expected to play an important role at high impact energies. We must await further mass analysis and coincidence experiments in order to make more definitive statements about the mechanism of dissociative excitation in hydrogen-atom bombardment of H_2.

Our cross sections for dissociative excitation of H_2 are compared with results obtained for H_2^+[14] and He^+[55] impact in Fig. 6, where we have plotted $\sigma_{DE}(2p)$ as a function of incident particle velocity. At high impact energy, the Born approximation implies that this cross section should depend only on the relative velocity of the collision partners, and indeed this has proven to be a fairly good scaling relationship for target excitation by 0.15–1.00-MeV hydrogen projectiles.[56] In our energy range, we see that scaling by relative velocity brings the H_2^+ results into fairly good agreement with $\sigma_{DE}(2p)$ for H^+ impact. This is also the case for dissociative excitation of H_2 to yield Balmer α, β, and γ radiation by H^+, H_2^+, and H_3^+ projectiles.[57] For He^+ impact, however, the energy dependence of $\sigma_{DE}(2p)$ is markedly different than for the hydrogen projectiles, demonstrating that the ionization potentials of the species involved and other details of the interaction potential play a large role at our low impact energies.

Although it is not meaningful to compare our results via relative velocity scaling with electron impact measurements of dissociative excitation cross sections, we note that behavior similar to property (ii) is exhibited in electron impact, for which it has been shown[58] that, in the 50–6000-eV energy range, $\sigma_{DE}(2p) \approx 2\sigma_{DE}(2s)$.

As for projectile excitation, the concept of the equivalence of a hydrogen molecule to a pair of hydrogen atoms is not particularly useful in our energy range for dissociative excitation collisions. Comparison of the target excitation cross section $\sigma_{tar}(2p)$[5] for the process

$$\underline{H}^+ + H \rightarrow \underline{H}^+ + H(2p) , \qquad (15)$$

with $\sigma_{DE}(2p)$ for the impact of H^+ on H_2 shows that the cross section for excitation of a free hydrogen atom via process (15) actually exceeds that for dissociative excitation of H_2. The ratio $\sigma_{tar}(2p)/\sigma_{DE}(2p)$ is ≈ 3 at 5 keV, falls to a minimum of $\simeq 15$ at 12.5 keV and rises to ~2 at 25 keV.

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