Luminescence cross sections in the low-energy collisions of H⁺, H₂⁺, and H₃⁺ ions with H₂

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Abstract. Luminescence cross sections for the optical emission of molecular hydrogen in the 200–600 nm spectral range and for the atomic Balmer-β line were measured for low-energy (≤1 keV) H⁺, H₂⁺, and H₃⁺ ions colliding with H₂ gas targets. Molecular hydrogen transitions between singlet states were observed for all the systems studied, while the emission continuum H₂(a-b) and discrete spectra associated with other transitions between triplet states appeared only in the H₂⁺ + H₂ collisions, where the spin conservation rule is fulfilled. Isotopic substitutions in the H₂⁺/D₂⁺ + H₂, D₂ system show that at E_lab = 1 keV, a dominant molecular luminescence mechanism is the collision-induced excitation (CIE) of the target.

1 Introduction

Electronic spectra of hydrogen molecule extend from vacuum ultraviolet (VUV), ultraviolet (UV), through the visible (VIS) spectral region, and into the infrared (IR) [1]. A detailed knowledge of many electronic transitions in H₂ reaches back almost a hundred years [2]. In the UV–VIS range, the most important spectral features of H₂ are a continuum due to the bound-free H₂(a ³Σ_g^+ – b ³Σ_u^+) transition in the 120–600 nm region [3] and a discrete spectrum in the 350–800 nm region, consisting of many lines (on the order of tens of thousands) [4]. The H₂(a ³Σ_g^+ – b ³Σ_u^+) continuum was observed in laboratories, first in discharges and later in experiments using electron beams bombarding H₂ [5]. Emission of the continuum was observed also in the collisions of ground state Ar⁺, Ne⁺, Kr⁺, Xe⁺, and metastable Ar⁺⁺ ions with H₂ [6] and in the collisions of metastable Ar⁺(³P₀,₁) atoms with H₂ [7]. The discrete parts of the H₂ VIS spectrum were mainly studied in discharges, and numerous electronic transitions were identified within the singlet and triplet systems [1,2,8]. A study of the multiline part of the H₂ spectrum under single-collision conditions is a challenge because these molecular lines appear very weak in comparison to atomic lines of the Balmer series and require long exposure times.

There is a great deal of interest in the application of H₂ emissions for the determination of conditions in various environments where collisions occur. Hydrogen continua appear in various spectral regions and their origins may differ: they can be due to recombination (Lyman, Balmer, and Paschen continuum), photoexcitation, or collision-induced excitation. The continua are of great interest in astrophysics (e.g., in the studies of solar flares [9], quasar emission [10], or in the observations of light from distant galaxies [11,12]). Spectroscopic analysis enables, for example, a determination of excitation mechanisms in galaxies [13] and a study of hydrogen molecular emission induced in a nebula by stellar winds [14]. Continuum emission serves also as a source of information in the spectral diagnostics of hydrogen-containing plasma [3,15,16]. There is currently some interest in collisional processes involving H₃⁺ in the context of astrophysical models [17].

Important parameters in modeling low-pressure hydrogen plasma conditions are the excitation cross sections, σ⁺, for H⁺ and H₂⁺ luminescence in the H_n⁺ + H₂ collisions. The σ⁺ data for hydrogen atomic lines of the Balmer series are available for higher collision energies [18], while for energies below 1 keV some of the most trusted data are derived by extrapolation [19]. Luminescence cross sections for Balmer-β emitted in the H_n⁺ + H₂ collisions at laboratory energies below 1 keV have been measured only once before [20] and were evaluated later to be incorrect by a factor of 30 [21]. Molecular hydrogen emission cross sections σ⁺ at low collision energies for the same systems were not known in 1992 [19] and we could not find anything in the literature published later; there are only measurements of σ⁺ for very small selected fragments of singlet spectra produced in H⁺ + H₂ collisions above E_lab = 150 keV [22].

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2 Experimental

The vacuum part of the experimental apparatus consisted of three large (ca. 100 l) chambers pumped differentially (the arrangement is shown in Fig. 1 of Ref. [23]). In the first chamber, a hot-cathode Colutron ion source was installed on a 3D-adjustable mount. Hydrogen ions were generated from H₂ gas (Linde, purity 99.999%) or D₂ gas (Linde, purity 99%) at a relatively very high ion source pressure of 60 Pa, to minimize the amount of H₂⁺ metastables [24]. The anode-to-cathode voltage \( U_A \) was kept mostly at 100 V, and occasionally set at 50 V to test a possible influence of residual metastable states of H₂⁺ ions. Ions were extracted from the source by a 1000 V potential and transported to the second vacuum chamber, where they were mass-selected by a magnetic field separator. The first two vacuum chambers were independently pumped by two 1200 l/s oil diffusion pumps equipped with liquid nitrogen traps. Subsequently, the ions were transported to the third chamber, passing through electrostatic lenses and a retarder, where they were slowed down to a required energy before entering the collision cell. The collision chamber was pumped by two parallel 1400 l/s and 450 l/s turbomolecular pumps that provided a background pressure about \( 10^{-3} \) Pa during the measurements.

A schema of the collision cell as seen from above is shown in Figure 1. The cell (C) is cylindrical, with the beam slit (S) 1 mm wide and 8 mm high. The observation window (W), made of MgF₂, was mounted at the bottom, while a flexible tube supplying target gas was attached at the top of the cell. Hydrogen target gas was admitted into this 30 cm long, 2.5 cm i.d. tube, which simultaneously connected the scattering cell to an MKS Baratron capacitance manometer (head type 398 HD). The ion beam was collected in a Faraday cup (F) insulated from the collision cell (C). The available beam energies were in the 20–1000 eV range, with corresponding beam currents of 1–40 nA for H⁺, 10–200 nA for H₂⁺, and 5–180 nA for H₃⁺, respectively. Ion currents were recorded continuously with a Keithley picoammeter and computer-averaged. The ion beam path in the collision cell was \( x = 66 \) mm, but only the region between \( x_1 = 6 \) mm and \( x_2 = 18 \) mm from the entrance slit was observed by the optical detection system. The bottom of the Faraday cup (F) was located relatively far away from the observation zone to avoid some background emission created by hydrogen ion beams bombarding a metal surface.

In most of our measurements, the target pressure was kept below 0.20 Pa, because in this range the luminescence intensity increased linearly with target gas pressure, while the ion beam current at 1 keV was attenuated by only 2–3% at \( x = 66 \) mm. Of the three ion projectiles, the total collision cross section at 1 keV is the largest for H₂⁺ + H₂ (8 × 10⁻²⁰ m² [19]). The mean free path at 0.20 Pa is then more than 20 cm and our experiment fulfills single collision conditions for all three systems studied. Higher target gas pressures (up to 2.0 Pa) were also applied for H₂⁺ + H₂ collisions, to record molecular luminescence spectra with better resolution. Under these conditions, the intensity of light increased linearly with pressure, despite attenuation of the ion beam current up to 40% at \( x = 66 \) mm, a behavior that indicates some luminescence contribution from secondary collisions. We have recorded fragments of better-resolved (0.18 nm FWHM) molecular spectra for the H₂⁺ + H₂ collisions at 1000 eV with both 0.19 and 2.0 Pa target gas pressures and found no important differences in the appearance of the spectra, apart from intensity variations (<50%) of some lines. To improve the signal-to-noise ratio and gain a 10-fold advantage in light collection time (the spectrum in the 350–600 nm range is compiled from 11 partially overlapping spectra of 46 nm span), we recorded the better resolved spectra at 2.0 Pa.

The luminescence from collision cell was reflected by an aluminum mirror toward the entrance slit of a spectrograph. The optical arrangement of our experiment is presented in Figure 1 of reference [25]. Luminescence spectra were recorded with a 1024-channel “Mepsicron” detector attached to a modified McPherson 218 spectrograph, which was equipped with 150, 300, 1200, and 2400 L/mm interchangeable snap-in gratings blazed at various wavelengths. The detector is sensitive only in the 200–600 nm spectral range. Its sensitivity profile was determined using a standard Osram Wl17 G tungsten ribbon lamp and a Hamamatsu L656K deuterium lamp [26]. The recorded luminescence signal at 0.19 Pa target gas pressure was from 1 to 30 cts/s, depending on the ion beam energy and the optical slit width used. The detector dark count rate was about 3 cts/s. The time necessary for collection of a luminescence spectrum varied from 20 min to 6 h. For H₂⁺ + H₂, the luminescence spectra above 380 nm were always recorded with a cut-off filter absorbing light λ < 380 nm, to avoid a contribution of UV-light in the second order of a grating. At collision energies above 300 eV, some background light consisting mainly of the Balmer-β line was observed without target gas in the collision cell. The light disappeared completely when the ion beam was directed away from the collision cell; therefore, our conclusion is that this was caused by a beam neutralization on the edges of the entrance slit to the collision cell. The background light at collision energy of 1 keV did not exceed 20% of the luminescence recorded with target gas present and it was subtracted during cross section measurements.

A scaling of the measured luminescence intensity necessary to derive absolute cross sections was determined by performing measurements for the Balmer-β line in the He⁺ + H₂ reaction at 700 eV [27]. In the course of our experiments, the volume of luminescence region observed in the collision cell and the solid angle of collection of light were the same as in the reference reaction. The calibration factor for σ⁺ was checked using another luminescent...
reaction, namely, $\text{H}^+ + \text{N}_2$ at a beam energy of 1000 eV [28] and we found a very small discrepancy between the results of both normalizations.

Experimental uncertainties of $\sigma^*$ in the excitation functions presented below are standard deviations from averages of 10–15 measurements at each collision energy. Systematic errors are certainly present. First of all, they may stem from uncertainty of the value of $\sigma^*$ determined in reference [27], which we take as a reference (there is only a limited discussion of this problem in Ref. [27], where uncertainties in relative cross sections are estimated to be 10% or less). The absolute values for Balmer-$\beta$ may contain systematic errors due to the manufacturers’ scaling of electronic instruments measuring ion intensity and target gas pressure. The values of $\sigma^*$ for the $\text{H}_2^+$ emission may have additional systematic error resulting from uncertainty of the detector sensitivity curve which served for correction of the recorded spectra. We estimate that this latter error should not exceed 20%.

3 Luminescence spectra

Luminescence spectra resulting from collisions of $\text{H}_n^+$ with $\text{H}_2$ at 1 keV beam energy are shown in Figure 2.

The spectra are corrected for wavelength-dependent sensitivity of the detection system. Atomic lines $\text{H}_\beta$ and $\text{H}_\alpha$ of the Balmer series stand out in all three spectra. In the neighborhood of the Balmer series, numerous densely packed rovibronic lines of $\text{H}_2$ appear. The wavelengths of $(v',v'')$ bands belonging to the strongest electronic singlet transition $\text{H}_2(\text{GK 3$a'\Sigma_g^+ - B 2p\sigma$ $\Sigma_u^+$})$ are marked in Figure 2a (GK has been earlier denoted as G [1,2]). The lowest bound triplet state of molecular hydrogen is $\text{H}_2(c 2p\pi^2\Pi_u)$, which is metastable ($\tau = 95 \mu s$ [29]). Slightly higher, by just 0.023 eV [29], lies the $\text{H}_2(a 2s^3\Sigma_g^+)$ state, which has a much shorter radiative lifetime, reported as $\tau = (10.45 \pm 0.25) \text{ ns}$ from experiment [30] and as $\tau = 8.8 \text{ ns}$ from theory [29]. This state decays to the repulsive $\text{H}_2(b 2p\sigma^3\Sigma_u^+)$ state and the spectrum associated with this transition is the most intense one, extending from $\lambda 120$ nm to about $\lambda 600$ nm [3]. A large part of the continuum can be seen in Figure 2b (note that the detection efficiency falls to zero below $\lambda 190$ nm, with the onset of absorption of light in air). So-called 0-0 bands, i.e., the wavelengths of $(v' = 0 \rightarrow v'' = 0)$ for numerous other triplet transitions from higher states down to the $a$ and $c$ states [1] are marked in Figure 2b (the energy of the upper electronic state increases toward shorter wavelengths). Among the triplet transitions in Figure 2b, one can recognize relatively intense bands in the $\lambda 560$–$610$ nm region. The emissions below $\lambda 460$ nm, expected to be much weaker than those from lower triplet states, are obscured by singlet transitions and could not be identified. The spin-conservation rule permits formation of $\text{H}_2^+$ triplet states only for the $\text{H}_2^--\text{H}_2$ system and the validity of this rule is confirmed in Figure 2, where the triplet transitions are absent for the $\text{H}_2^+$ and $\text{H}_3^+$ ion projectiles.

A spectrum recorded for $\text{H}_2^++\text{H}_2$ with better spectral resolution is presented in Figures 3–5. One can identify rovibronic lines of transitions between electronic singlet states: $\text{H}_2(\text{GK 3$d\sigma$ $\Sigma_g^+ - B 2p\sigma$ $\Sigma_u^+$}),$ $\text{H}_2(\text{I 3$\pi$$^1\Pi_u - B 2p\sigma$ $\Sigma_u^+$}),$ and $\text{H}_2(\text{H$\Pi$ 3$s\sigma$ $\Sigma_g^+ - B 2p\sigma$ $\Sigma_u^+$}). The $\text{H}_2(\text{GK-B})$ transition appears clearly for all three ion projectiles $\text{H}_2^+$, the other two transitions could not be identified for $\text{H}_2^+$ and $\text{H}_2^+$ due to lower intensity of molecular luminescence. The wavelengths of $(v',v'')$ bands in $\text{H}_2(\text{GK-B})$ are marked in Figures 3–5. References [2,31] describe the $\text{R}_2$ (A463.403 nm) rotational line of $\text{H}_2(\text{GK-B})$ $(v' = 0, v'' = 0)$ as the strongest in the molecular spectrum of hydrogen in the VIS. The observed triplet transitions in the $\lambda 560$–$610$ nm range (Fig. 5) are due to emissions from the $\text{H}_2(g 3d\sigma$ $\Sigma_g^+),$ $h 3s\sigma$ $\Sigma_g^++ i 3d\pi$ $\Pi_g, j 3d\delta$ $\Delta_g)$ states to the $\text{H}_2(c 2p\pi^3\Pi_u)$ state and contain a small part of the Fulcher band $\text{H}_2(d 3p\pi$ $\Pi_u - a 2s^3\Sigma_g^+)$, which extends above $\lambda 600$ nm.
Fig. 3. Luminescence spectrum recorded at 1 keV beam energy for $H_2^+ + H_2$ in the $\lambda$190–392 nm region; resolution 0.5 nm (up to $\lambda$375 nm) and 0.18 nm FWHM (above $\lambda$375 nm); target gas pressure 2.0 Pa. The spectrum is corrected for sensitivity of the optical detector.

Fig. 4. Luminescence spectrum recorded at 1 keV beam energy for $H_2^+ + H_2$ in the $\lambda$372–490 nm region (resolution 0.18 nm, target gas pressure 2.0 Pa). The peak of $H_\beta$ reaches 31500 cts. The spectrum is corrected for sensitivity of the optical detector. Positions of the strongest rovibronic lines of the GK-B, I-B, and HH-B electronic transitions in $H_2$ molecule are shown as full circles, triangles pointing up, and triangles pointing down, respectively.

The mechanism of excitation of the Balmer-$\beta$ line likely varies with collisional system. For $H^+ + H_2$ (see the energy diagram in Fig. 6, left column), among exit channel leading to $H_\beta^*$, the lowest one involves electron transfer to the projectile, while collisional dissociation of the target with simultaneous excitation of $H_\beta^*$ is more endoergic. For $H_2^+ + H_2$ (the middle column in Fig. 6), the lowest $H_\beta^*$ product channel corresponds to proton transfer from the projectile ion to the target. More endoergic channels, namely, collisional dissociation of the projectile and collisional dissociation of the target can also produce $H_\beta^*$. To check which pathway is more effective at 1 keV ion beam energy, we have measured the $D_\beta/H_\beta$ intensity ratio for $H_2^+ + D_2$ and $D_2^+ + H_2$ systems using isotopic spectral shift. The ratio is equal to $(0.36 \pm 0.03)$ and $(1.13 \pm 0.05)$, respectively.
This seems to indicate that the excited hydrogen atom arises more often from the projectile than from the target, reflecting energy ordering of the product channels. A similar trend for this reaction was observed in [21] for H₂ ionization, where the projectile and target atoms were distinguished by Doppler shift of atomic lines. For the H₂⁺ + H₂ system, the lowest energy levels are given in the right column in Figure 5. Exit channels associated with excitation of Balmer-β lines are more endoergic than in the case of two other projectile ions. The lowest channel here is associated with collisional dissociation of the target; a slightly higher channel corresponds to rather complicated (and therefore less probable) ejection of an excited atom by H⁺ projectile ion. Measurements of Dβ/Hβ intensity ratio for H₂⁺ + D₂ and D₂⁺ + H₂ systems gave (0.91 ± 0.05) and (0.82 ± 0.05), respectively. The similarity of these results indicates that very likely the excitation of the Balmer-β line occurs here via some even higher channels, corresponding to more complete collisional dissociation into atoms.

4 Luminescence cross sections: Balmer-β line

The luminescence cross sections were obtained from the sums of photons attributed to the Balmer-β line. Only the spectra obtained for low (0.19 Pa) target gas pressure were used in cross section measurements. To collect these spectra, we used a low spectral resolution (4.0 nm FWHM).

4.1 H⁺ + H₂

The excitation function for production of Hβ is presented in Figure 7. The σ(Hβ) value increases monotonically from 0.0035 × 10⁻²² m² at 200 eV to 0.028 × 10⁻²² m² at 1000 eV. It can be compared with σ(Hα) = 0.07 × 10⁻²² m² at 1200 eV, which can be derived from Figure 1 of reference [33]. Reference [20] at 1 keV gives σ(Hβ) = 0.009 × 10⁻²² m², three times lower than our result. The discrepancy may be due to important differences in experimental arrangements and procedures. In reference [20], ion current was four orders of magnitude higher than in the present work, light was collected on the ion beam axis using an original calibration of emission intensity, and target gas pressure was measured with an ionization gauge. The results of [20] were evaluated later [21] to be too low by a factor of 30, which is true at 3 keV, but seems exaggerated for collision energies below 1 keV. For the Balmer series, the review of Phelps [19] gives only the values of σ(Hα) from reference [21] and extrapolates them below 1.5 keV down to 100 eV. Assuming that the ratio of intensities Hα/Hβ in this collision energy range is about 5 [20], one obtains σ(Hβ) = 0.5 × 10⁻²² m² at 1 keV. Our result is then about 20 times lower than the extrapolation made by Phelps.

4.2 H₂⁺ + H₂

In the present work, σ(Hβ) = 0.125 × 10⁻²² m² at 1 keV and σ* decreases toward lower collision energies (see Fig. 7). To compare this with earlier results, we took the extrapolations of reference [19] for H₂ cross sections measured above 2 keV [21] and assumed an H₂/Hβ intensity ratio of 5. In this way, one obtains σ(Hβ) = 0.5 × 10⁻²² m² at 1000 eV, four times higher than our result. Reference [20] gives measured σ(Hβ) = 0.04 × 10⁻²² m² at 1 keV, three times lower than our result. The latter discrepancy probably has the same causes as given in Section 4.1, namely, different experimental arrangements and procedures.

4.3 H₃⁺ + H₂

The excitation function is presented in Figure 7. At 1 keV we have measured σ(Hβ) = 0.146 × 10⁻²² m². Phelps [19] used the experimental data above 3 keV for H₂α [21] and extrapolated the excitation function toward lower
energies. Assuming an $H_\alpha/H_\beta$ intensity ratio equal to 5, one obtains an estimate $\sigma^*(H_\beta) = 1.3 \times 10^{-22}$ m$^2$ at 1000 eV [19]. Our experimental result is about an order of magnitude lower than this estimate by extrapolation.

The excitation functions for $H_2^+ + H_2$ and $H_3^+ + H_2$ are somewhat different, probably reflecting the differences in mechanisms of production of atomic luminescence in both cases. The formation of $H_\beta$ in $H_2^+ + H_2$ collisions occurs in the lowest exit channel $H_3^+ + H_2$, endoergic by 11 eV and corresponding to the proton transfer that leaves the $H$ atom of the projectile excited (see Fig. 6, middle column). As the excitation function shows, the Balmer series in this case can be observed from the lowest collision energy $E_{\text{lab}} = 20$ eV, which in the center-of-mass frame corresponds to $E_{\text{CM}} = 10$ eV. This small (1 eV) deficiency of energy can be supplied from the collision energy spread caused by thermal motion of the target gas (Chantry effect [34]).

Figures 4 and 6 of reference [19] contain measured $\sigma^*(H_\alpha)$ for $H_2^+ + H_2$ and $H_3^+ + H_2$ in the 2–10 keV collision energy range [21]. The luminescence cross sections for $H_3^+$ projectiles at these energies are always about 20% higher than for $H_2^+$. Below 2 keV, the values of $\sigma^*(H_\alpha)$ for both collision systems were extrapolated and at 750 eV, the numbers differ by a factor of 4.6 in favor of the $H_3^+$ precursor [19]. The relative intensity $(H_\alpha)/(H_\beta)$ is approximately constant around $E_{\text{coll}} \sim 1$ keV (as measured in numerous experiments); therefore, the trends in excitation functions for $H_\alpha$ and $H_\beta$ should be very similar. Our results for $H_\beta$ disagree with the extrapolations made in reference [19]. From Figure 7, one can see that at $E_{\text{coll}} = 750$ eV both projectiles have the same $\sigma^*(H_\beta)$ (contrary to the claim made in Ref. [19]) and from this energy on, the slightly higher yield of $H_3^+$ projectiles confirms the trend observed in reference [21] at higher collision energies. It seems a plausible explanation that the intensity of the Balmer-β line for $H_3^+ + H_2$ is slightly higher than for $H_2^+ + H_2$ above 1 keV, because in this energy range a complete dissociation into excited atoms plays a bigger role. This mechanism favors a system with more hydrogen atoms (in this case $i = 5$ vs. $i = 4$, which is close to the observed factor 1.2).

5 Molecular luminescence cross sections $\sigma(H_2^*)$

5.1 $H^+ + H_2$

In our studies at low target gas pressure (0.19 Pa), the $H_2^+$ emission can be clearly recognized only in the spectral region around $H_\beta$ and $H_\gamma$, where the strongest bands of $H_2$ (G-K-B) are located. Beyond the 400–560 nm region, molecular luminescence was indistinguishable from the background recorded without target gas. In the literature we could not find absolute cross sections for excitation of UV–VIS luminescence of a hydrogen molecule induced by $H^+$ impact at 1 keV. There are only approximate cross sections at collision energies $\geq 150$ keV [22], concerning two fragments of discrete molecular spectra of $H_2$, namely, the $H_2$(G-B) (0,0) and $H_2$(I-B) (0,0) bands measured with 1.6 nm bandpass filter at $\lambda 463.2$ nm and $\lambda 417.6$ nm, respectively. The cross sections at 150 keV are about $1 \times 10^{-24}$ m$^2$ for each band and the excitation functions rapidly decrease when the collision energy becomes higher. Our measurements give $\sigma(H_2^*) = 0.17 \times 10^{-22}$ m$^2$ at 1 keV. The excitation function is presented in Figure 8; it rises slowly with ion beam energy. Molecular hydrogen luminescence for $H^+ + H_2$ was earlier observed in VUV [35], and the cross section for emission of Lyman bands around $\lambda 160$ nm, on the rising part of the excitation function, measured at 20 keV was found to be $\sigma(H_2^*) = 3.4 \times 10^{-22}$ m$^2$ [35].
5.2 $\text{H}_2^+ + \text{H}_2$

Our result for luminescence cross section is $\sigma(\text{H}_2^*) = 3.0 \times 10^{-22} \text{ m}^2$ at 1 keV (see Fig. 8) and of this value we attribute 75% to the triplet $\text{H}_2(\text{a-b})$ continuum, 15% to all transitions between singlet states producing discrete emission in the $\lambda 380$–560 nm region, and 12% to the triplet discrete spectra in the $\lambda 560$–610 nm spectral range. This cross section can be compared only with $\sigma(\text{H}_2^*) = 10 \times 10^{-22} \text{ m}^2$ measured for excitation of the triplet continuum $\text{H}_2(\text{a-b})$ when 15 eV electrons bombarded $\text{H}_2$ [36].

Experimental cross sections are available for the $\text{H}_2^* (\text{a-b})$ continuum emission between $\lambda 170$ nm and $\lambda 360$ nm for Ar$^+ + \text{H}_2$ colliding at $E_{\text{CM}} = 19$ eV and for metastable Ar$^{++} + \text{H}_2$ at $E_{\text{CM}} = 0.5$ eV. The values are believed to be accurate within a factor of 3 and they are equal to $0.04 \times 10^{-22} \text{ m}^2$ and $1.4 \times 10^{-20} \text{ m}^2$, respectively [6]. For both argon ions colliding with $\text{H}_2$, production of triplet states is allowed by the spin-conservation rule. The enormous $\text{H}_2^*(\text{a-b})$ luminescence cross section for Ar$^{++} + \text{H}_2$ is explained by an accidental resonance of the metastable states of Ar$^{++}$ with molecular excited levels of $\text{H}_2$ [6].

We have measured relative luminescence cross sections for various isotopic combinations of the diatomic projectile ion–target systems. The results are collected in Table 1. Additional spectra recorded with higher resolution at 1 keV show that molecular lines associated with the isotope used as a target greatly outnumber those arising from the projectile. This indicates that at this collision energy, collision-induced excitation (CIE) of the target dominates over charge transfer.

5.3 $\text{H}_3^+ + \text{H}_2$

The cross section for molecular hydrogen emission observed for this system is $\sigma(\text{H}_3^*) = 0.33 \times 10^{-22} \text{ m}^2$ at 1000 eV. There is no recognizable molecular emission below 200 eV collision energy, and at higher energies, the excitation function slowly rises with $E_{\text{coll}}$ up to 1 keV (see Fig. 8).

6 Conclusions

Luminescence spectra observed in the collisions of $\text{H}_n^+$ ions with $\text{H}_2$ at energies up to 1 keV show important differences caused by the spin properties of the projectiles. The $\text{H}_2^+ + \text{H}_2$ system fulfills the spin conservation rule permitting formation of electronically excited $\text{H}_2^*$ triplet states and this leads to a considerably larger molecular luminescence cross section. The measured cross section for molecular $\text{H}_2^*$ emission for $\text{H}_2^+ + \text{H}_2$ at 1 keV is $\sigma(\text{H}_2^*) = 3 \times 10^{-22} \text{ m}^2$, an order of magnitude higher than for the other two projectiles. Triplet emissions of $\text{H}_2^*$ excited in $\text{H}_2^+ + \text{H}_2$ collisions dominate the spectrum in the $\lambda 200$–600 nm region, contributing about 87% of the light. The remaining 13% of emission is from singlet $\text{H}_2^*$ states. This fraction of the value of the entire $\sigma(\text{H}_2^*)$ from $\text{H}_2^+ + \text{H}_2$ is approximately equal to $\sigma(\text{H}_2^*)$ of luminescence produced in the $\text{H}_3^+ + \text{H}_2$ system, where the excitation of triplet transitions is forbidden. This indicates that both molecular projectiles excite singlet molecular states of hydrogen with similar yield.

The Balmer-$\beta$ emission cross sections at 1 keV are on the order of $10^{-23} \text{ m}^2$ for $\text{H}_2^+$ and $\text{H}_3^+$ projectiles, while for $\text{H}^+$ they are about five times lower. Below $E_{\text{coll}} = 750$ eV, the $\sigma^*(\text{H}_3^*)$ cross section for $\text{H}_2^+$ projectile is slightly larger than for $\text{H}_3^+$, at higher collision energies the ordering reverses. Isotopic substitutions show that for $\text{H}_2^+ + \text{H}_2$, a dominant mechanism of luminescence at 1 keV is CIE of the target.

The velocities of $\text{H}_n^+$ ions at 1 keV are between 250 and 440 km/s, overlapping with typical velocities of solar winds, which are in the 200–400 km/s range [37]. Therefore, luminescence cross sections obtained in the present work can be useful for making estimates of light intensity produced in collisions of solar wind with hydrogen molecules. The presence and relative strength of the UV emission continuum or VIS triplet emissions can be used as a simple indicator of $\text{H}_2^+$ participation in the populations of stellar winds.

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Author contribution statement
Both authors contributed equally to the paper.

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