VUV diagnostics of electron impact processes in low temperature molecular hydrogen plasma

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Abstract

Novel methods for diagnostics of molecular hydrogen plasma processes, such as ionization, production of high vibrational levels, dissociation of molecules via excitation to singlet and triplet states and production of metastable states, are presented for molecular hydrogen plasmas in corona equilibrium. The methods are based on comparison of rate coefficients of plasma processes and optical emission spectroscopy of lowest singlet and triplet transitions, i.e. Lyman band ($B^1Σ^+_u \rightarrow X^1Σ^+_g$) and molecular continuum ($a^3Σ^+_g \rightarrow b^3Σ^+_g$), of the hydrogen molecule in the VUV wavelength range. Comparison of rate coefficients of spin-allowed and/or spin-forbidden excitations reduces the uncertainty caused by the non-equilibrium distributions of electron energy and molecular vibrational level, which are typically known poorly in plasma sources. The described methods are applied to estimate the rates of various plasma processes in a filament arc discharge.

Keywords: plasma diagnostic, hydrogen plasma processes, VUV spectroscopy, filament arc discharge

(Some figures may appear in colour only in the online journal)
lifetimes of the lowest excited states are short and electron impact excitation cross sections from the ground state to those states are approximately an order of magnitude greater than excitation cross sections to upper electronic states. Therefore, the physical origin of the population density of the lowest excited states can be understood straightforwardly, and photon emission rate is linearly proportional to the electron impact excitation rate from the ground state.

Application of VUV emission for diagnostics of molecular hydrogen plasma processes such as ionization, dissociation and excitation is demonstrated in this paper. Instead of using information about the plasma parameters, i.e. density and temperature, the applied method is based on direct measurement of the VUV-emission rate, which is proportional to the electron impact excitation rate. Comparison of the rate coefficients results in a robust plasma diagnostic method requiring minimum knowledge of the plasma parameters. The method can be applied to obtain absolute numbers or relative changes of volumetric production rates through absolute or relative measurements of the VUV irradiance. The error caused by the electron energy distribution (EED) and molecular vibrational temperature is discussed.

The presented methods are applied for a set of previously presented VUV-irradiance measurements [11] of a filament driven negative hydrogen ion source, LIISA, at the JYFL accelerator laboratory. Estimated excitation and ionization rates based on saturation value (at >100 eV electron energy) of rate coefficients of vibrationally cold plasma have been presented and discussed briefly in the earlier study. In this study the analysis is carefully extended to account for different electron energy distribution functions (EEDFs) and vibrational temperatures. Furthermore, the dissociation rate of hydrogen molecules and the production rate of metastable hydrogen molecules (c^3Π_u state) are determined for the first time.

2. Processes affecting the population densities of excited electronic states of hydrogen molecules

The hydrogen molecule has two multiplet systems of electronic states, singlet and triplet, which differ in the orientation of the electron spins (S = 0 for singlet and S = 1 for triplet) governed by the Pauli exclusion principle. Radiative transitions between the electronic states are classified as optically allowed and optically forbidden. Optically allowed electron transitions are subject to the following selection rules: (a) change of the parity of the total wavefunction (g ↔ u), (b) conservation of the total spin quantum number, i.e. ∆S = 0, and (c) possible change of the total angular momentum quantum number, ∆Λ = 0, ± 1.

The selection rules affect the functional shapes of electron-impact excitation cross sections. However, due to electron exchange effects in electron-impact excitation collisions at low energies, these selection rules are not strictly preserved [12]. The most significant differences of electron-impact cross sections are found between singlet–triplet (∆S = 1) spin-forbidden excitations and singlet–singlet (∆S = 0) spin-allowed excitations. The excitation cross sections from the ground state (X^1Σ^+_g) to other singlet states (B^3Σ^+_u, C^3Π_u, B^1Σ^+_u, D^3Π_u, etc) are rather insensitive to the impacting electron energy in the range above 30 eV (figure 1). In the case of spin-forbidden transitions (∆S = 1), the electron impact excitation occurs via resonance processes. Therefore, the electron impact excitation cross sections from the ground state (X^1Σ^+_g) to the triplet states (b^3Σ^+_g, C^3Π_u, a^3Σ^+_g, etc) are peaked at <20 eV (figure 1).

Altogether the hydrogen molecule has several tens of electronic states [13]. In this study singlet states B^3Σ^+_u, C^3Π_u, EF^3Σ^+_g are taken into account. This is because the electron impact excitation cross sections of B^3Σ^+_u and C^3Π_u states correspond to over 75% of the total electron impact excitation cross section to singlet states, and cascading from the EF^3Σ^+_g state is the only significant effect involving upper states. Other singlet states either emit VUV light in a different wavelength range (e.g. D^3Π_u and B^1Σ^+_u), or the corresponding electron impact excitation cross sections are orders of magnitude lower (e.g. B^1Σ^+_g, D^3Π_u, G^1Σ^+_g) [12].

On the other hand, triplet states a^3Σ^+_g, b^3Σ^+_g, c^3Π_u, d^3Π_u and e^3Σ^+_g are taken into account in this study. This is due to lack of available cross sections for electron impact excitations to other triplet states. The lowest triplet state (b^3Σ^+_g) to which the radiative decay chains of a^3Σ^+_g, e^3Σ^+_g and d^3Σ^+_g states end is repulsive. The c^3Π_u state is partially metastable depending on the symmetry (c^3Π_u or c^3Π_u) [14]. The radiative lifetime

![Cross section vs. Electron energy](image-url)
of the metastable $^3\Pi_u$ state depends on the vibrational level and ranges from 1 ms ($\nu = 0$) to 10 $\mu$s ($\nu = 3$) [15, 16]. The $^3\Pi_u$ state is sensitive to electron impact de-excitation/ionization [17, 18] and collisional quenching [19].

Plasma emission spectroscopy yields information about population densities of molecules on excited states, which are affected by several processes. The diagnostics presented in this study are based on the premise that the VUV-light emission rate is equal to the electron impact excitation rate from the ground state to the corresponding electronic states (corona model). This sets the following limitations on the temporal resolution of the diagnostic as well as plasma parameters, which are fulfilled by most low temperature laboratory plasmas including hydrogen ion sources (see, e.g., [1, 20] and references therein).

(i) The shortest temporal scale that can be studied is on the order of 1 ns for singlet transitions and 100 ns for triplet transitions.

(ii) The plasma density is less than $10^{14}$ cm$^{-3}$.

(iii) The neutral gas pressure is under 500 Pa.

(iv) The ion temperature $T_i$ is lower than the electron temperature $T_e$.

The listed limitations do not concern the metastable $^3\Pi_u$ state, which is discussed thoroughly in sections 3.3 and 3.4. The best possible temporal resolution of the diagnostic method is limited by the radiative lifetime of the excited states (delay in spontaneous emission). The radiative lifetimes of the lowest singlet states ($B^3\Sigma^+_u$ and $C^3\Pi_u$) and lowest triplet states are under 1 ns and 10–40 ns respectively [16].

The plasma density is limited by the collisional de-excitation and ionization rate from the excited states. Significant collisional de-excitation of the $B^3\Sigma^+_u$ state requires the electron density to be $10^{14}$–$10^{16}$ cm$^{-3}$ [21]. For the $a^3\Sigma^+_g$ state the corresponding number is $10^{15}$ cm$^{-3}$ [17]. Since the cross sections of electron-impact ionization from the excited states ($B^3\Sigma^+_u$ and $a^3\Sigma^+_g$) are on the same order of magnitude (as a maximum) as the electron impact de-excitation cross sections [12], the given maximum plasma densities are also valid for ionization.

Electronic states can also be de-excited, e.g. via excitation transfer with neutral particles, charge exchange with ions and Penning ionization. The cross sections of these processes are, however, only known poorly [12]. Most of these de-excitation processes are resonant by nature and hence their cross sections could be large, but the required collision energies are on the order of a few electronvolts. Thus, they are negligible in low temperature plasmas, where the average energies of neutral particles and ions are low. Excitation transfer with neutral particles could limit the maximum neutral gas pressure. However, there are no cross section data available for excitation transfer of hydrogen molecules. The lower limit for the maximum neutral gas pressure ($T = 300$ K) can be estimated by using the excitation transfer cross section of the hydrogen atom (approximately $10^{-13}$ cm$^2$), which yields a pressure of 5 mbar assuming a 10 ns lifetime for the excited state. The given cross section is probably several orders of magnitude too large (and the calculated upper limit of the pressure too low), because of the vibrational distribution of the molecules and the Franck–Condon principle decreasing the excitation transfer probability of the molecule in comparison to the atom.

The applied model requires that the electron impact excitation is the dominant excitation process. This in turn requires that the ion temperature is lower than the electron temperature. The effects of photonic excitation and recombinaton on the population densities of excited molecules are negligible in comparison to corresponding effects in the case of atomic emission. Molecular hydrogen (laboratory) plasmas are optically thin for molecular emission, because the vibrational distribution of molecules and Franck–Condon principle result in a low probability of photon excitation. On the other hand, recombinaton of the hydrogen molecule leads mainly to dissociation of the molecule [12], i.e.

$$e + H_2^+ \rightarrow (H_2^{\ast \pi}; H_2^{\ast \Sigma^+}) \rightarrow H(1s) + H(n \geq 2),$$

which does not contribute to the population densities of excited molecules.

### 3. Estimating rate coefficients from VUV emission

A typical VUV spectrum of a hydrogen plasma is presented in figure 2. The spectrum can be divided into four different regions based on the origin of the radiation. Lyman-series (mainly Lyman-alpha) radiation is emitted by hydrogen atoms, while three dominant molecular transitions emit VUV light. These are Lyman and Werner bands, corresponding to transitions from the lowest excited singlet states ($B^3\Sigma^+_u$ and $C^3\Pi_u$) to the ground state, and a molecular continuum corresponding to the lowest transition between triplet states ($a^3\Sigma^+_g \rightarrow b^3\Sigma^+_u$). Because the lowest triplet state is repulsive, a continuum is observed instead of a band structure.

![Figure 2. VUV emission spectrum of a hydrogen plasma of an arc discharge with 840 W discharge power and 0.5 Pa pressure. The spectrum is not correlated for spectral transmittance.](image)

The Lyman-band and molecular continuum emissions are the most suitable transitions for the purpose of plasma diagnostics. This is because significant parts of Lyman-band and molecular continuum radiation are emitted in the ranges of 145–165 nm and 170–240 nm, including
negligible contribution from other transitions. Furthermore, the structures of Lyman-band and molecular continuum emissions do not depend (significantly) on the plasma parameters, and cascade effects from the upper states to \(B^1\Sigma_u^+\) state are well known, which allows straightforward estimation of the total emission from the measured signals in the specific ranges.

VUV emission can be used as a probe for the most important plasma processes, such as ionization rate, vibrational excitation rate to high vibrational levels, production rate of metastable \(c^3\Pi_g\) states, molecular dissociation rate and hot electron density. These rates are sensitive to distributions of electron energy and molecular vibrational level.

The vibrational distribution of neutral hydrogen molecules is not in thermal equilibrium, especially at high vibrational levels. However, a majority (>90%) of neutral molecules in typical laboratory plasmas are at the lowest vibrational levels (\(v \leq 4\)) (see, e.g., [22, 23] and references therein). This part of the distribution can be described reasonably well with the Boltzmann distribution, i.e. using a vibrational temperature \(T_{vb}\). The vibrational temperature of the lowest vibrational levels has been found to be between 100 K and 10 000 K (see, e.g., [23, 24] and references therein). These numbers are used as extremes when estimating the uncertainty of the presented diagnostic caused by the vibrational distribution. This is because the cross sections of electron impact ionization and excitation to electronic states are less than linearly proportional to the vibrational quantum number. Molecules also have rotational levels, which have a negligible effect on the discussed electron impact processes due to minimal energy exchange (≈0.01 eV) in transitions and long collision times (frozen rotation) [12].

The EEDFs of low temperature plasmas are typically non-Maxwellian. The distributions are often bi-Maxwellian at low pressures and Druyvesteyn-like at high pressures [25]. At high plasma density (and ionization degree), electron–electron collisions tend to drive the EEDF towards a Maxwellian [25]. Furthermore, superpositions of Maxwellian and flat (see definition later) distributions have been commonly found in filament arc discharges (e.g. [26–28]). When electron–electron collisions dominate in the entire energy range, the resulting EEDF is Maxwellian by definition. In hydrogen plasmas this is the situation only at low electron energies (\(E_e < 9\) eV). The EEDF at high electron energies is determined by elastic and inelastic collisions, the plasma heating method and electron confinement.

Typically only high energy electrons (\(E_e > 20\) eV) contribute to ionization and excitation to singlet states. For example, in the case of the EEDFs reported in [29–31], electrons above 20 eV contribute more than 99% to the ionization and 76–91% to the excitation to the \(B^1\Sigma_u^+\) state, although their density is only 1–3% of the total electron density in [29, 30] or 30% in [31]. Therefore, ionization and singlet state excitation rates can be described reasonably accurately by focusing only on the high energy part of the EEDF. Excitations to triplet states are most sensitive to the electron energy in the range of 10–20 eV.

The VUV-emission rate has been chosen for a closer study from a mathematical point of view to describe the distribution of electrons at energies exceeding the excitation and ionization thresholds (figure 3). At high energies the Maxwellian distribution and the tail of the bi-Maxwellian distribution can be described by the Boltzmann probability function

\[
f(E_e) = A e^{-E_e/k_B T_e},
\]

where \(A\) is a normalization factor, \(E_e\) is electron energy, \(k_B\) is the Boltzmann constant and \(T_e\) is electron temperature. The high energy tail of the EEDF is not described by a flat distribution.

\[
f(E_e) = \begin{cases} A : & E_e \leq E_{\text{max}} \\ 0 : & E_e > E_{\text{max}}. \end{cases}
\]

where \(A\) is a normalization factor and \(E_{\text{max}}\) is the end point (or maximum) energy of the plasma electrons, corresponding to the potential difference between the cathode and the plasma. The rate coefficients of these two distributions differ significantly. If the average energy of the distribution (\(\frac{1}{2}k_B T_e\) for Maxwellian distribution and \(E_{\text{max}}/2\) for the flat distribution) changes, the electron density at energies corresponding to the most sensitive range of the rate coefficients (\(6\) eV < \(E_e < 40\) eV, see discussion in sections 3.1–3.4) changes exponentially in the case of Maxwellian distribution and linearly in the case of the flat distribution.

The VUV-emission rate corresponds to the excitation rate of neutral molecules, if the plasma parameters are within the limits specified in section 2. Comparison of the rate coefficients of different processes allows estimation of their volumetric reaction rates from the measured VUV-emission rates of specific emission bands. The volumetric rate \(R\) of an electron impact process can be described as

\[
R = n_e n_o \int f(v) \sigma(v) dv = n_p n_e \langle v \sigma \rangle.
\]

Figure 3. Examples of EEDFs used in this study. Hot electron versions of distributions are used for calculating the rate coefficients presented in section 3.5 by renormalizing the \(E_e > 9\) eV part. The choice of 9 eV corresponds to the threshold energy of \(X^3\Sigma_u^- \rightarrow B^1\Sigma_u^+\) electron impact excitation for vibrational levels \(v \leq 4\).
where \( n_e \) is the electron density, \( n_n \) the neutral molecule density, \( f \) normalized electron velocity distribution function (EVDF), \( \nu \) the electron velocity and \( \sigma \) the cross section of the process. The term \( \langle \nu \sigma \rangle \) is the rate coefficient, and depends on the functional shapes of the EVDF and the cross section.

In molecular plasmas the volumetric rate of any given process depends on the vibrational distribution. The total volumetric rate can be calculated as a weighted average of the rate coefficients corresponding to individual vibrational levels. For a Boltzmann distribution the result can be written as

\[
R(T_{\text{vib}}) = n_e n_n \frac{\sum \langle \nu \sigma \rangle \exp\left(-\frac{E_i}{kT_{\text{vib}}}ight)}{\sum \exp\left(-\frac{E_i}{kT_{\text{vib}}}ight)} = n_e n_n \alpha(T_{\text{vib}}), \quad (5)
\]

where \( T_{\text{vib}} \) is the vibrational temperature, \( E_i \) is the energy of vibrational level \( i \) in the ground state and \( \langle \nu \sigma \rangle \) is the total excitation rate coefficient from the ground state vibrational level \( i \) to all possible vibrational levels of the upper state.

If the volumetric rate of a specific process \( R(\nu) \) can be determined, e.g. by measuring the volumetric emission rate of a specific band of VUV light, the volumetric rate of another process \( R(\nu \cdot 2) \) can be estimated from

\[
R(\nu \cdot 2) = \frac{n_e n_n \alpha_2(T_{\text{vib}})}{n_e n_n \alpha(T_{\text{vib}})} R(\nu), \quad (6)
\]

If the same neutral species \( (n_n) \) is involved in both processes, the electron and neutral densities cancel out. Thus, the volumetric rate \( R(\nu \cdot 2) \) can be obtained by multiplying the measured volumetric rate \( R(\nu) \) with the corresponding rate coefficients, i.e.

\[
R(\nu \cdot 2) = \frac{\alpha_2(T_{\text{vib}})}{\alpha(T_{\text{vib}})} R(\nu) = K_{2,1} R(\nu), \quad (7)
\]

where \( K_{2,1} \) is the ratio of the rate coefficients.

It is of note that the ratio of the rate coefficients, \( K_{2,1} \), is significantly less sensitive to changes of the EEDF (e.g. in terms of average electron energy or functional shape), and often to the vibrational temperature, than individual rate coefficients. The sensitivity of the \( K_{2,1} \) to the EEDF can be understood by studying the cross sections of the corresponding processes (figure 1) and their ratios at different electron energies. The rate coefficient ratio is sensitive to changes of the EEDF in the energy range where both the ratio of the cross sections changes significantly, and the absolute values of the cross sections are large. Typically the sensitive energy range is a narrow band close to the threshold energies. For example, when the excitation rate coefficients of similar types of transition (in terms of the selection rules) are compared, the sensitive energy range is 10–20 eV. In such cases (similar types of transition) the vibrational temperature dependence of \( K_{2,1} \) is reduced due to the similar dependences of the individual cross sections on it. Therefore, in some cases \( K_{2,1} \) is insensitive to the average electron energy, the shape of the EEDF and the vibrational temperature, although individual rate coefficients can vary by orders of magnitude within the same ranges of EEDF and vibrational temperature variations. Such situations are presented in sections 3.2–3.6, where the extreme values of \( K_{2,1} \) vary by less than 30% in comparison to their average values in the entire energy range of (both) EEDFs and vibrational temperatures.

There are several reviews about electron impact cross sections in low temperature hydrogen plasmas (e.g. [12, 32–35]). Data from [12] have been used in this study because they include the most complete critically assessed set of cross sections including fitting functions in analytic form.

### 3.1. Molecular ionization rate

Hydrogen molecules can be ionized by electron impact non-dissociatively via the \( H_2^+ (X^2\Sigma_g^+, \nu') \) state and dissociatively via the \( H_2^+ (X^2\Sigma_g^+, \nu') \) and \( H_2^+ (B^2\Pi_u^+, e') \) states [12]. The cross section of non-dissociative ionization is more than an order of magnitude larger (\( \nu = 0 \)) than the total cross section of dissociative ionization [12]. Hence, only non-dissociative ionization is taken into account in this study. The functional shapes of electron impact cross sections of ionization and spin-allowed excitations to the electronic states are similar. The molecular ionization rate can be estimated from the measured Lyman-band emission rate with equation (7) by estimating the ratio of the ionization and \( X^3\Sigma_g^+ \rightarrow B^2\Pi_u^+ \) excitation rate coefficients, \( K_{\text{ion,B}} \), plotted for different EEDFs and vibrational temperatures in figures 4 and 5.

In the case of \( K_{\text{ion,B}} \) the most sensitive range is 10–40 eV. The sensitivity in this range is mostly due to different threshold energies of the processes: 11.6 eV for \( B^2\Pi_u^+ \) excitation and 15.4 eV for ionization. In the case of the Maxwellian EEDF, there is a significant plasma temperature dependence of the rate coefficient ratio due to exponential nature of the EEDF in the range of 10–40 eV. In the case of the flat EEDF, the ratio of the rate coefficients does not depend strongly on the maximum energy of the distribution if \( E_{\text{max}} > 50 \) eV, which is typical in filament-driven arc discharges.

It can be concluded from figures 4 and 5 that the uncertainty of \( K_{\text{ion,B}} \) caused by the vibrational temperature is less...
than ±15%, if $T_{\text{vib}} = 6000$ K is used and the real vibrational temperature is in the range of 100–10 000 K. If the electron temperature can be estimated (or measured) with an accuracy of ±20%, which can be considered as a typical value [31], it causes an uncertainty of less than ±20% in $K_{\text{ion,B}}$. Hence, the total uncertainty of $K_{\text{ion,B}}$ is less than ±25% in the case of the Maxwellian EEDF. It must be emphasized that the flat distribution does not accurately describe the real EEDF. However, the uncertainty of the diagnostic results caused by such deviation can be described as a variation of (the effective) $E_{\text{max}}$ of an ideal flat EEDF. This can be demonstrated as follows: (1) choosing $K_{\text{ion,B}} = 2$ corresponds to an uncertainty of less than ±25% for $60 \text{ eV} < E_{\text{max}} < 250 \text{ eV}$ or (2) choosing $K_{\text{ion,B}} = 1.5$ corresponds to an uncertainty of less than ±35% for $35 \text{ eV} < E_{\text{max}} < 85 \text{ eV}$.

3.2. Excitation rate to $B^1\Sigma_u^+$ and $C^1\Pi_u$ states

The vibrational distribution of low temperature molecular hydrogen plasmas is not in thermal equilibrium (see, e.g., [22, 23] and references therein). The fraction of molecules at high vibrational levels affects the rates of several plasma processes, e.g. the volume production of negative hydrogen ions through dissociative attachment [1]. It has been concluded [1, 36] that most of the vibrational excitations populating states $\nu \geq 5$ are preceded by electron impact excitation to the $B^1\Sigma_u^+$ and $C^1\Pi_u$ singlet states. Radiative transitions from the given excited electronic states to the ground state populate high vibrational levels, when the vibrational level changes in the electronic transition according to the Franck–Condon principle [13]. By assuming that transitions between vibrational levels in electron impact excitation to electronic states follow the Franck–Condon factors it can be calculated that 63–67% of the (de-)excitations emitting in the Lyman band and 46–49% emitting in the Werner band lead to ground state vibrational levels $\nu \geq 5$. Approximately 15% of transitions from $B^1\Sigma_u^+$ and $C^1\Pi_u$ states lead to such high vibrational levels (vibrational continuum) that the molecule dissociates instantly [37]. The corresponding dissociation rate does not depend strongly on the electron energy or vibrational temperature of the molecules.

The total excitation rate to $B^1\Sigma_u^+$ and $C^1\Pi_u$ states can be estimated from the measured Lyman-band emission with equation (7) by comparing the total excitation rate coefficients to the $B^1\Sigma_u^+$ and $C^1\Pi_u$ states with the excitation rate coefficient to the $B^1\Sigma_u^+$ state. The ratio of the rate coefficients, $K_{BC,B}$, is plotted for different vibrational temperatures and EEDFs in figures 6 and 7.

The rate coefficient ratio is only weakly sensitive to variations of the EEDF in the range of 10–20 eV. This can be explained by the similarity of the functional shapes of the cross sections and threshold energies (figure 1). For example, using median values of $K_{BC,B} = 1.64$ for the Maxwellian EEDF or $K_{BC,B} = 1.79$ for the flat EEDF cause corresponding uncertainties of less than ±10%, if the real electron temperature is in
the range of 3 eV–25 eV or the effective $E_{\text{max}}$ is in the range of 30 eV–250 eV. On the other hand, using $T_{\text{e vib}} = 6000$ K causes an uncertainty of less than $\pm 4\%$ to $K_{BC}$ if the real vibrational temperature is in the range of 100–10 000 K. Therefore, the total uncertainty corresponding to the selected median values of $K_{BC}$ (in respective ranges of EEDF vibrational temperature variations) is less than 11\%.

3.3. Maximum production rate of metastable hydrogen molecules

The metastable state ($c^3\Pi_u$) of the hydrogen molecule has an important role in molecular hydrogen plasmas. Metastable molecules have lower ionization potentials and different electronic transition probabilities than ground state molecules. Therefore, the existence of metastable molecules allows ionization and de-excitation by lower energy electrons, which in turn complicates plasma diagnostics based on triplet transitions. Metastable states can also affect the production of negative hydrogen ions [1].

From the diagnostics point of view there are significant uncertainties related to the metastable $c^3\Pi_u$ state. Different symmetries of the $c^3\Pi_u$ state ($c^3\Pi_u^0$ and $c^3\Pi_u^+$) have significantly different lifetimes. The lifetime of the $c^3\Pi_u^0$ state is 6.2 ns; i.e., only the $c^3\Pi_u^0$ state can be considered metastable [16]. There are only a few studies on the $c^3\Pi_u^+$ state, with significant discrepancy between calculations and experiments [16]. The $c^3\Pi_u$ state is argued to be metastable without any distinction between the parities of the wavefunction ($c^3\Pi_u$) in the electron impact cross section data ([12] and references therein). Because there are no cross section data on electron impact excitation to the $c^3\Pi_u^0$ state, the $c^3\Pi_u$ state is assumed to behave as the metastable $c^3\Pi_u^0$ state. Moreover, experiments and theoretical calculations about electron impact excitation cross sections from the ground state $X^1\Sigma^+_g$ to the $c^3\Pi_u$ state differ by a factor of 2–3 [12]. There is also a significant difference between calculated cross sections, e.g. in [12] and [38].

From the point of view of molecular continuum emission there are three different types of triplet state. The lowest triplet state, $b^3\Sigma_u^+$, is repulsive, and electron impact excitation to this state leads to non-radiative dissociation. Triplet states $a^3\Sigma_u^+$, $d^3\Pi_u$ and $c^3\Sigma_u^+$ lead to emission within the molecular continuum. The metastable state $c^3\Pi_u$ can either spontaneously decay, transform to a radiative triplet state ($a^3\Sigma_u^+$) by electron impact de-excitation or collisional quenching, drift to the wall of the plasma chamber or be ionized by electron impact. Therefore, the contribution of the metastable molecules to the molecular continuum emission depends on the plasma parameters and the dimensions of the plasma chamber.

The volumetric production rate of metastable molecules ($c^3\Pi_u$) can be estimated from the measured volumetric emission rate of the molecular continuum ($a^3\Sigma_u^+ \rightarrow b^3\Sigma_u^+$) radiation and the ratio of the rate coefficients of excitation to metastable states and total excitation to triplet states leading to molecular continuum emission. The minimum production rate of metastable molecules can be estimated if most of the excitations to the $c^3\Pi_u$ state are assumed to eventually emit a photon within the molecular continuum (e.g. via collisional quenching or decay to $a^3\Sigma_u^+$). The maximum of the metastable state production rate corresponds to the situation in which all metastable states decay without photon emission in the molecular continuum. Because of the large cross section of electron impact excitation from the ground state to the $c^3\Pi_u$ state, there is approximately a factor of two difference between these two extremes.

The uncertainty caused by such approximations (extreme cases) can be reduced by comparing the transition probabilities of different processes affecting the population density of the $c^3\Pi_u$ state. Typically, the most significant de-excitation processes are electron impact de-excitation, collisional quenching with neutral particles and collision with the wall of the plasma chamber, as discussed in [39]. The radiative lifetime of the $c^3\Pi_u$ state depends on the vibrational level and ranges from 1 ms ($\nu = 0$) to 10 $\mu$s ($\nu = 3$) [19]. These radiative lifetimes correspond to de-excitation transition probabilities of $10^3$ s$^{-1}$ ($\nu = 0$) and $10^5$ s$^{-1}$ ($\nu = 3$), respectively. The collisional quenching rate coefficient of the $c^3\Pi_u$ state in collisions with hydrogen molecules at 300 K is $1.88 \times 10^{-9}$ cm$^3$ s$^{-1}$ [19]. This means that the transition probability of collisional quenching depends on the neutral gas pressure as $4.7 \times 10^5$ s$^{-1}$ Pa$^{-1}$. The rate coefficient of the most significant electron impact de-excitation process (the superelastic transition $c^3\Pi_u \rightarrow b^3\Sigma_u^+$) is on the order of $10^{-5}$ cm$^3$ s$^{-1}$ regardless of the electron temperature [17]. Thus, collisional de-excitation is significant if the neutral gas pressure is more than $2 \times 10^{-3}$ Pa and/or the electron density is more than $10^{15}$ cm$^{-3}$ for $c^3\Pi_u$ ($\nu = 0$) or 0.2 Pa and/or $10^{13}$ cm$^{-3}$ for the $c^3\Pi_u$ ($\nu = 3$) state. Furthermore, the $c^3\Pi_u^+$ state de-excites due to wall collisions [39]. This is a significant process in small plasma sources at low neutral gas pressure and electron density, because the average thermal velocity of hydrogen molecules ($T = 300$ K, 1.9 mm $\mu$s$^{-1}$) corresponds to a distance of some centimeters during the radiative lifetime of the $c^3\Pi_u^+$ state.

The ratio of the total rate coefficient of electron impact excitation to the metastable state ($c^3\Pi_u$) and the total rate coefficient of electron impact excitation to the molecular continuum radiative states ($a^3\Sigma_u^+ \rightarrow d^3\Pi_u$, $e^3\Sigma_u^+ \rightarrow$ with/without $c^3\Pi_u$), $K_{c\Pi_uMC}^\text{total}$ and $K_{c\Pi_uMC}^\text{total}$, is plotted for different EEDFs in figures 8 and 9. The insensitivity of the rate coefficient ratio to the EEDF can be explained by similar functional shapes and threshold energies of the processes. The contribution of different vibrational levels is not taken into account due to the lack of numerical data [12, 38]. However, it can be argued that, because increasing vibrational level decreases the threshold energies and increases the cross sections almost identically for electron impact excitation from the ground state to any triplet state [38], the effect of vibrational temperature on $K_{c\Pi_uMC}$ is almost negligible (of the same order as in figures 6 and 7).

Using median values of $K_{c\Pi_uMC}^\text{total} = 0.60 K_{c\Pi_uMC}^{\text{total}} = 1.55$ (Maxwellian EEDF) and $K_{c\Pi_uMC}^\text{total} = 0.56 K_{c\Pi_uMC}^{\text{total}} = 1.26$ (flat EEDF) causes an uncertainty of less than 17\% if the
3.4. Molecule dissociation rate via triplet state excitation

There are several processes which lead to molecule dissociation in hydrogen plasmas, e.g. dissociative electron attachment, recombination, ionization, excitation to triplet states, excitation to singlet states at a high vibrational level and processes of molecular hydrogen ions [12]. The significance of each process depends on the plasma parameters. Unfortunately, there are no reliable experimental data for the cross sections of molecule dissociation, as discussed in [33]. It has been argued that electron impact excitation to triplet states is the main dissociative channel for the hydrogen molecule [33, 34].

The minimum dissociation rate of the molecules by the lowest, repulsive, triplet state $b^3\Sigma_g^+$ can be estimated from the measured molecular continuum emission. In this case, the rate coefficient of electron impact excitation to all triplet states is compared to the rate coefficient of electron impact excitation to the states emitting a photon within the molecular continuum. It can be argued that all of the electron impact excitations to the $c^3\Pi_u$ state lead to the dissociation of the molecule, because both radiative and collisional de-excitation of $c^3\Pi_u$ lead mainly to the $b^3\Sigma_g^+$ state.

Two extremes of the rate coefficient ratios can be considered by assuming that either all ($K_{\text{triplet,MC}_{\text{max}}}$) or none ($K_{\text{triplet,MC}_{\text{min}}}$) of the metastable states lead to molecular continuum emission. There is approximately a factor of two difference between these extremes. The coefficient ratios $K_{\text{triplet,MC}_{\text{max}}}$ and $K_{\text{triplet,MC}_{\text{min}}}$ are plotted for Maxwellian and flat EEDFs in figures 8 and 9. The error analysis discussed in section 3.3 for the production rate of metastable $c^3\Pi_u$ is also valid for the dissociation rate of hydrogen molecules discussed in this section.

3.5. Hot electron density

The density of hot electrons ($E_e > 9$ eV) can be negligible in comparison to the total electron density of the plasma. However, it is the only part of the EEDF which produces (positive) ions and electrons from the neutral gas. Therefore, the diagnostic of this population is important, especially from the point of view of applications, e.g. optimizing the performance of ion sources. The mean of $X^3\Sigma_g^+ \rightarrow B^3\Sigma_g^+$ electron impact excitation is rather insensitive to the electron energy, which allows estimation of the hot electron density. When the density of neutral molecules $n_1$ is known and the ionization degree is low enough not to affect the neutral density, the hot electron density can estimated with

$$n_e = \frac{R_{\text{Ly-band}}}{n_1\langle v\sigma \rangle},$$

where $R_{\text{Ly-band}}$ is the measured (volumetric) emission rate of Lyman-band radiation and $\langle v\sigma \rangle$ is the rate coefficient. The rate coefficient for Maxwellian and flat EEDFs is presented in figures 10 and 11.
It can be concluded from figures 10 and 11 that the uncertainty of \( \langle v \sigma \rangle \) caused by the vibrational temperature varies from 40\% \((T_e = 3\text{ eV})\) to 20\% \((T_e = 24\text{ eV})\) in the case of the Maxwellian distribution and from 21\% \((E_{\text{max}} = 35\text{ eV})\) to 13\% \((E_{\text{max}} = 250\text{ eV})\) in the case of the flat distribution if \( T_{\text{vib}} = 6000\text{ K} \) is used and the real vibrational temperature is in the range of 100–10 000 K. If the electron temperature can be estimated (or measured) with an accuracy of \( \pm 20\% \), it causes an uncertainty of less than \( \pm 15\% \) in \( \langle v \sigma \rangle \). Using the median value of \( \langle v \sigma \rangle = 1.6 \times 10^{-8}\text{ cm}^3\text{ s}^{-1} \) causes an uncertainty of less than \( \pm 33\% \) if the effective \( E_{\text{max}} \) is in the range of 30–250 eV. Thus, the total uncertainty of \( \langle v \sigma \rangle \) is less than \( \pm 43\% \) for the Maxwellian EEDF and less than \( \pm 39\% \) for the flat EEDF in the described situations.

3.6. Error analysis

The presented methods to analyze reaction rates in molecular hydrogen plasma are based on absolute measurements of the volumetric emission rates of specific emission bands. There are several sources of error affecting the estimated absolute reaction rates:

(i) measurement technique
(ii) overlapping emission bands
(iii) coverage of emission band by the measurement
(iv) cascade from upper states
(v) deviation of the assumed EEDF from the real one
(vi) estimation of the vibrational distribution
(vii) effect of other plasma processes e.g. collisions of metastable molecules
(viii) uncertainty of the cross sections
(ix) validity of the assumptions listed in section 2.

In an earlier paper [11], it was estimated that the uncertainty of the measured volumetric emission rates of a specific emission band in a specific wavelength range is less than 18\% (the experimental setup is described briefly in section 4). This error covers both the error of the measurement itself (item (i)) and the overlap of the emission bands (item (ii)) in the selected wavelength ranges of 145–170 nm for the Lyman band and 170–240 nm for the molecular continuum.

The measured ranges of Lyman-band and molecular continuum emission do not cover the entire emission band. The coverage can be estimated by studying synthetic emission spectra. The synthetic spectrum can be calculated, if the vibrational distribution of the upper state and the Franck–Condon factors governing the change of vibrational level in electronic transitions are known. The vibrational distribution of the \( B'\Sigma_u^+ \) state can be estimated by using distributions described in [40] or by assuming that the vibrational temperature of ground state hydrogen molecules is between 0 and 10 000 K and that vibrational excitation in the electron impact excitations to the \( B'\Sigma_u^+ \) electronic state follows the Franck–Condon factors (first order approximation). Using the aforementioned vibrational distributions for the \( B'\Sigma_u^+ \) state and Franck–Condon factors from [13] yields that the range of 145–170 nm covers 38–43\% of the total Lyman-band emission. Using the synthetic spectrum of the molecular continuum from [24] yields that the range 170–240 nm covers 59–62\% of the total molecular continuum emission if the vibrational temperature of the neutral gas is in the range of 0–9000 K. If median values (40\% and 61\% respectively) are used, the variation of the correction factors corresponds to uncertainties of 5\% and 3\% for Lyman-band and molecular continuum emissions, respectively.

Recent cross section data of electron impact excitation to the \( EF'\Sigma_u^+ \) state [41] imply that 9–15\% of the total Lyman-band emission is caused by cascade from the \( EF'\Sigma_u^+ \) state in the case of the studied EEDFs. Synthetic spectra \((T_{\text{vib}} = 100–10 000\text{ K})\) imply that the measured signal (145–170 nm) includes 31–34\% of the total cascade effect. Thus, 86–93\% of the measured signal is caused by direct excitation to the \( B'\Sigma_u^+ \) state. Using a median value (89.5\%) for the correction includes a relative uncertainty of 4\% (estimated similarly to the previous paragraph). Cascading from upper states also affects the molecular continuum. Without accurate cross sections the correction due to the cascade contribution (from states which are
not taken into account in this study) to molecular continuum emission can not be estimated accurately. However, it can be argued that the cascade effect is small (i.e. <10%), because the cross sections of electron impact decrease significantly as a function of the main quantum number.

The total uncertainty caused by items (i)–(iv) could be reduced at least by a factor of two with improved calibration of the photodiode and more detailed analysis of overlapping emission bands, filter transmission and stray emission.

The uncertainty caused by estimating the EEDF and vibrational temperature (items (v) and (vi)) are discussed in sections 3.1–3.5. The uncertainty is 11%–25% in the case of listed plasma processes and 26%–43% in the case of the hot electron density. These values correspond to situations in which the vibrational distribution of the plasma is unknown and only a rough approximation of the EEDF is available. Therefore, detailed knowledge of the EEDF and vibrational distribution would reduce these uncertainties significantly.

The lack of experimental data on relevant cross sections is problematic [12, 33]. The calculations of the cross sections have become more accurate, but experimental studies include uncertainties of several tens of percent especially at low electron energies [33]. Moreover, there is a variation from several tens of percent up to a factor of 2–3 between calculations, especially in the case of excitation to triplet states [12, 38]. The presented diagnostics of plasma processes is mostly sensitive to relative error between the cross sections due to the comparison of rate coefficients. The absolute error of the cross sections does not have a significant effect on the diagnostic results if the main contribution is systematic error, which is similar for each cross section. The uncertainty caused by the cross section data can not be estimated accurately based on the available data, but it can be argued that it is probably comparable to or larger than the total uncertainty caused by items (i)–(vi).

Deviations from the assumptions made in section 2 can be considered a minor source of error. This is because typical ion source plasmas are within the range of these assumptions by a great margin (orders of magnitude) [1, 20].

4. An example of plasma analysis

Absolute and relative VUV emission have been measured earlier from the filament-driven arc discharge negative ion source, LIISA [11] (figure 12). The plasma chamber (diameter 9 cm, length 31 cm) is made of copper, but it is coated with tantalum due to the evaporation of the filament. The arc discharge power was varied in the range of 140–840 W by adjusting both the arc current between 4 and 12 A and the arc voltage between 35 and 70 V. The presented values were measured at the plasma chamber pressure of 0.35 Pa, which corresponds to 5 sccm feed rate of hydrogen gas\(^1\). The relative VUV emission was not observed to depend significantly on the pressure in the range between \(1.2 \times 10^{-3}\) mbar and \(2.0 \times 10^{-2}\) mbar [11]. The total electron density of a similar ion source [43] has been measured to be always below \(10^{12}\) cm\(^{-3}\). Thus, the requirements for the diagnostics described in section 2 are valid in the studied ion source.

The measurements were made with a VUV-irradiance meter, which consists of a factory calibrated photodiode (IRD-inc SXUV20BNC) and optical bandpass filters of specific wavelength ranges—Lyman band (161 nm, FWHM 20 nm) and molecular continuum (180 nm, FWHM 40 nm). The device was looking into the plasma along an axial line of sight through the extraction aperture (diameter 9 mm) of the ion source from a distance of approximately 1.5 m. The photodiode (an effective area collimated to 3.14 mm\(^2\)) observed a plasma volume of approximately 20 cm\(^3\) out of the 2340 cm\(^3\) total volume of the plasma chamber. The transmittances of the

\(1\) The optimum plasma chamber pressure is presented incorrectly in [11]. The correct plasma chamber pressure is 0.35 Pa (measured with a Pirani gauge including up to a factor of 2 uncertainty [42]) instead of 0.17 Pa. The gas feed rate of 15 sccm was estimated in [11]. The value of 5 sccm is experimentally verified.
the filters were measured using a spectrometer, which consists of a monochromator (McPherson model 234/302) and a photomultiplier (ET Enterprises 9406B) and utilizing the ion source as a light source. The background signals caused by the stray transmittance and overlapping of adjacent emission bands were taken into account, and the corresponding uncertainty due to such corrections was included in the total uncertainty. Thus, the presented values (table 1) correspond to Lyman-band and molecular continuum emission in the wavelength ranges of 145–170 nm and 170–240 nm, respectively. The average wavelengths in table 1 correspond to energy-weighted average wavelengths of the (corrected) emission in the given wavelength range.

The confinement of primary electrons (emitted by the filament) in the multicusp magnetic field of filament arc discharges is known to be effective (see, e.g., [25, 44]). The same conclusion has been derived from the VUV-emission data obtained with the LIISA ion source. It has been observed that the arc power is efficiently absorbed in inelastic collisions between primary electrons and neutrals [11]. Furthermore, it has been observed that Lyman-band radiation is linearly proportional to the arc discharge power, while the molecular continuum radiation is mainly proportional to the arc discharge current in the entire parameter range. Therefore, it is convenient to transform the measured irradiance values to average volumetric emission rates in the line-of-sight volume and normalize the results to the arc power (Lyman band) or the arc current (molecular continuum) as presented in table 1.

The EEDF of the hot electron component in filament arc discharges is best described by the flat distribution discussed in section 3. Such a distribution has been observed experimentally and deduced numerically (see, e.g., [26–28]). Furthermore, the electron energies can not exceed the potential difference of the filament and the plasma, i.e. the Maxwellian distribution would be a non-physical representation of the high energy tail.

The estimated volumetric rates and hot electron densities in the line-of-sight volume are presented in table 2. The total emission rate of the Lyman band (direct excitation to $B^3\Sigma_u^+$ state) and molecular continuum are calculated by using the equation

$$R_{\text{tot}} = R_{\text{meas}} k_{\text{cov}}$$  \hspace{1cm} (9)$$

where $R_{\text{meas}}$ is the measured photon emission rate (table 1), $k_{\text{cov}}$ is a correction factor taking into account the coverage of the measurement compared to the total emission and $k_{\text{cas}}$ is a correction factor taking into account the cascade effect. Values of 0.4 (Lyman band) and 0.6 (molecular continuum) have been used for $k_{\text{cov}}$, and 0.895 (Lyman band) and 1 (molecular continuum) for $k_{\text{cas}}$ as discussed in section 3.6. The volumetric rates were calculated from equation (7) by using rate coefficient ratios from figures 5, 7 and 9. The dissociation rate and vibrational excitation rate to $\chi^2\Sigma^+_u (\nu > 5)$ via electronic excitation to $B^3\Sigma_u^+$ and $C^3\Pi_u$ states are calculated by using the fractions between the measured and total rates discussed in section 3.2. The hot electron densities are estimated with equation (8) by using the rate coefficient from figure 11 and neutral gas density corresponding to 0.35 Pa pressure at room temperature. The variation of the values in each cell corresponds to the variation of applied arc voltages ($E_{\text{max}}$).

Vibrational temperatures of 100 K and 10 000 K have been used to demonstrate the effect of the vibrational temperature. The maximum density of metastable molecules can be calculated from the estimated production rate and average lifetime of the metastable states. The plasma parameters (density and neutral gas pressure) are in the range where, in principle, all of the de-excitation processes listed in section 3.3 affect the effective lifetime of the $C^3\Pi_u$ state. However, the maximum effective lifetime of the $C^3\Pi_u$ state can be estimated to be 26 $\mu$s, which corresponds to the time of flight of a thermal hydrogen molecule across the radius of the plasma chamber (5 cm). Hence, a typical maximum production rate of $1.1 \times 10^{16}$ s$^{-1}$ cm$^{-3}$ with 10 A arc current corresponds to a maximum density of $4 \times 10^{14}$ cm$^{-3}$ molecules excited to the

| Emission band | $\langle \delta \rangle$ | Emission power | Photon emission |
|---------------|-----------------|----------------|-----------------|
| Lyman band/$P_{\text{arc}}$ | 160 nm | 40 mW kW$^{-1}$ cm$^{-3}$ | $3.3 \times 10^{16}$ kW$^{-1}$ s$^{-1}$ cm$^{-3}$ |
| Mol. Cont./$I_{\text{arc}}$ | 195 nm | 0.55 mW A$^{-1}$ cm$^{-3}$ | $5.4 \times 10^{14}$ A$^{-1}$ s$^{-1}$ cm$^{-3}$ |

Note: Relative error for emission power is ±10%.

Table 2. Calculated reaction rates of different processes and hot electron densities.

| Process | Vibrational temperature | Rate |
|---------|-------------------------|------|
| Ionization | 100 K | $8$–$15$ | $1 \times 10^{16}$ kW$^{-1}$ s$^{-1}$ cm$^{-3}$ |
| Excitation ($B^3\Sigma_u^+ \rightarrow C^3\Pi_u$) | 100 K | $13$–$14$ | $1 \times 10^{16}$ kW$^{-1}$ s$^{-1}$ cm$^{-3}$ |
| Excitation ($\nu > 5$) | 100 K | $7.4$–$7.8$ | $1 \times 10^{16}$ kW$^{-1}$ s$^{-1}$ cm$^{-3}$ |
| Dissociation ($B^3\Sigma_u^+ \rightarrow C^3\Pi_u$) | 100 K | $1.9$–$2.0$ | $1 \times 10^{16}$ kW$^{-1}$ s$^{-1}$ cm$^{-3}$ |
| Dissociation (via $b^3\Sigma_u^+$, min.) | 100 K | $1.8$ | $1 \times 10^{15}$ A$^{-1}$ s$^{-1}$ cm$^{-3}$ |
| Dissociation (via $b^3\Sigma_u^+$, max.) | 100 K | $4.2$ | $1 \times 10^{15}$ A$^{-1}$ s$^{-1}$ cm$^{-3}$ |
| $c^3\Pi_u$ states, min. | 100 K | $0.5$ | $1 \times 10^{15}$ A$^{-1}$ s$^{-1}$ cm$^{-3}$ |
| $c^3\Pi_u$ states, max. | 100 K | $1.1$ | $1 \times 10^{15}$ A$^{-1}$ s$^{-1}$ cm$^{-3}$ |
| Hot electron density | 100 K | $5.7$–$8.5$ | $1 \times 10^{10}$ kW$^{-1}$ cm$^{-3}$ |
| 10 000 K | $4.1$–$5.7$ | $1 \times 10^{10}$ kW$^{-1}$ cm$^{-3}$ |

Note: Variation of the rates corresponds to 35–70 eV maximum energies of the flat EEDF. The rates have been normalized with the arc power or arc current depending on their responses to these parameters.
The most significant state. The dissociation of the molecule
for which 20 \( \times \) 1.5 leads to approximately 0.4% of
ion source parameters (arc voltage 70 V, arc current 12 A); i.e.,
molecules dissociate only 1.5–3 times more frequently via triplet
states than singlet states. The results are consistent with
the explanation given in [11]. There, the conclusion was that
during the thermalization process each electron emitted by the
filament passes through the optimum energy range for triplet
excitation, which explains the molecular continuum radiation
being proportional to the arc current.

5. Discussion

The principles of robust and straightforward diagnostics
electron impact processes in low temperature molecular
hydrogen plasmas have been presented in this study. The
method could contribute significantly to the development of
plasma and ion sources, since the effects of mechanical
modifications, for example, could be connected directly to the
changes of reaction rates in the plasma. Similar information
could be obtained by measuring the plasma parameters (neutral
gas density, electron density and EEDF) and applying
collision radiative models.

The presented methods include significantly smaller uncertainty
than calculating the reaction rates from the measured plasma parameters. This is because applying the presented method does not require any information about the electron and neutral densities and because the rate coefficient ratio \( K_{2,1} \) (equation (7)) is less sensitive to the electron temperature
than the rate coefficient \( \alpha_{ei} \) itself. The most significant difference in the uncertainties of different methods is caused by the electron temperature dependence of \( K_{2,1} \) and \( \alpha_{ei} \). This is demonstrated in figure 13, showing the normalized ratio
of ionization and \( B^3 \Sigma_u^+ \) excitation rate coefficients \( K_{ion,B} \) and
normalized ionization rate coefficient \( \alpha_{ei} \), as a function of the electron temperature. Although \( K_{ion,B} \) is the most sensitive
\( K_{2,1} \) coefficient (discussed in this study) to the variation of the electron temperature, it changes only by an order of magnitude in the range of 3 eV \( < T_e < \) 25 eV, while \( \alpha_{ei} \) varies

### Table 3. The average number of single molecules to undergo a certain process.

| Process                      | Vibrational temperature |
|------------------------------|-------------------------|
|                              | 100 K       | 10000 K  |
| Ionization                   | 73–141      | 61–117   |
| Excitation \( (B^3 \Sigma_u^+, C \Pi_u^a) \) | 121–129     | 115–123  |
| Excitation \( (\nu > 5) (B^3 \Sigma_u^+, C \Pi_u^a) \) | 70–74       | 67–70    |
| Dissociation \( (B^3 \Sigma_u^+, C \Pi_u^a) \) | 18–19       | 17–18    |
| Dissociation (via \( b^3 \Sigma_u^a \)), min. | 1.7         | \( \Lambda \)^{-1} |
| Dissociation (via \( b^3 \Sigma_u^a \)), max. | 3.9         | \( \Lambda \)^{-1} |
| \( c^3 \Pi_u \) states, min. | 0.5         | \( \Lambda \)^{-1} |
| \( c^3 \Pi_u \) states, max. | 1.0         | \( \Lambda \)^{-1} |

Note: The numbers have been normalized with the arc power or arc current. The calculated numbers assume a homogeneous and isotropic plasma emission distribution occupying the whole chamber. This assumption overestimates the values by not more than 50%, as explained in [11].

### Table 4. The average number of ionizations, excitations, dissociations and productions of metastable states per kilowatt of arc discharge power or electrons emitted by the filament.

| Process                      | Vibrational temperature |
|------------------------------|-------------------------|
|                              | 100 K       | 10000 K  |
| Ionization                   | 15–30       | 13–24    |
| Excitation \( (B^3 \Sigma_u^+, C \Pi_u^a) \) | 25–27       | 24–26    |
| Excitation \( (\nu > 5) (B^3 \Sigma_u^+, C \Pi_u^a) \) | 15          | 14–15    |
| Dissociation \( (B^3 \Sigma_u^+, C \Pi_u^a) \) | 3.8–4.0     | 3.6–3.8  |
| Dissociation (via \( b^3 \Sigma_u^a \)), min. | 0.6         | events/arc |
| Dissociation (via \( b^3 \Sigma_u^a \)), max. | 1.3         | events/arc |
| \( c^3 \Pi_u \) states, min. | 0.15        | events/arc |
| \( c^3 \Pi_u \) states, max. | 0.35        | events/arc |

Note: The calculated numbers assume a homogeneous and isotropic plasma emission distribution occupying the whole chamber. This assumption overestimates the values by not more than 50%, as explained in [11].

c\(^3\)\(\Pi_u\) state. This in turn corresponds to approximately 0.4% of
the neutral gas density at 0.35 Pa at room temperature.

The total reaction rates can be compared to the neutral gas
density, the gas feed rate and the number of electrons emitted
by the filament. This allows estimation of the average number
of different reactions experienced by a single molecule during
the time it spends in the plasma chamber (table 3) and
the average number of different types of inelastic collision caused
by a single electron emitted by the filament (table 4). The
total reaction rates can be estimated assuming a homogeneous
and isotropic plasma emission profile. This overestimates
the obtained values by less than 50% [11].

The gas feed rate of 5 sccm corresponds to \( 2.1 \times 10^{18} \)
molecules s\(^{-1}\). Comparing this number to the total number of
molecules in the chamber (0.35 Pa of ideal gas, \( N = 2.6 \times 10^{17} \)
molecules) yields an average passage time of 83 ms through
the plasma chamber. This means that each molecule undergoes
on average several tens of ionization and singlet state
excitation reactions and dissociates several times (table 3).

It is possible to estimate the energy efficiency of the plasma
source by comparing the total reaction rates to the heating
power and the number of electrons emitted by the filament.
This is presented in table 4. Each kilowatt of discharge power
produces approximately \( 1.3–3.0 \times 10^{20} \) electrons and ions per
second via ionization corresponding to 20–40 A of electrical
current. Approximately the same number of neutral molecules
are excited to singlet states per kilowatt of discharge power.
The molecular continuum emission is proportional to the arc
current, and therefore it is reasonable to compare the molecule
dissociation rate and the production rate of metastable \( c^3 \Pi_u \)
states to the number of electrons emitted by the filament. It
turns out that every electron emitted by the filament dissociates
on average 0.6–1.3 molecules via triplet states and excites
0.15–0.4 molecules to the metastable state. The dissociation
rates via triplet and singlet states are comparable under typical
ion source parameters (arc voltage 70 V, arc current 12 A); i.e.,
molecules dissociate only 1.5–3 times more frequently via triplet
states than singlet states. The results are consistent with
by almost three orders of magnitude. For the other processes studied in this paper the difference is even more significant. The coefficient $K_{\text{ion,b}}$ is more sensitive to the variation of the vibrational temperature than $(\sigma v)_{\text{ion}}$. However, for other processes, $K_2$ is less sensitive to vibrational temperature than $(\sigma v)$ due to similar dependences of the rate coefficients on the vibrational temperature.

Based on the error analysis presented in section 3.6 it is justified to claim that the main sources of uncertainty for determining the ionization rate and total excitation rate to $B^1\Sigma_u^+$ and $C^1\Pi_u$ states are uncertainties of measurement (relative uncertainty $\pm 18\%$), the coverage of the measured emission ($\pm 5\%$), cascade effects ($\pm 4\%$) and determining the coefficients $K_{\text{ion,b}}$ and $K_{\text{RC,b}}$ ($\pm 25\%$) within the limits of EEDF and vibrational temperature variations discussed in sections 3.1 and 3.2.

Applying the general law of error propagation for the independent error sources, it can be argued that with the presented methods it is possible to measure the ionization rate and total excitation rate $B^1\Sigma_u^+$ and $C^1\Pi_u$ with an accuracy of $32\%$ or better. This number does not take into account the uncertainty of the cross section data. The effects of both metastable states and discrepancies in cross section data (e.g. in [12] and [38]) do not allow us to make a general statement about the uncertainty of diagnostic results based on molecular continuum emission. However, the EEDF, the vibrational distribution and the density of metastable molecules are often characteristic properties of the given plasma source. Therefore, the listed uncertainties mostly affect the systematic error of the VUV diagnostic. It is possible to measure relative changes with significantly higher accuracy in comparison to absolute values, which is often more important for practical development of plasma sources.

Several simulation codes have been developed for molecular hydrogen plasmas during the last decades, e.g. [23] and references therein. The presented diagnostics of the reaction rates could be a powerful tool to benchmark the simulation codes, as introduced in [45]. The VUV emission is a consequence of the most significant plasma processes (with the largest cross sections), which have been taken account by most of the codes. Therefore it should be possible to extract the volumetric VUV emission rates as simulation outputs. Comparison of the simulations and the VUV spectroscopy could validate input parameters of the simulations, e.g. the functional shape of the hot part of the EEDF and/or the vibrational distribution. The presented diagnostics could allow development of a new type of plasma simulation in which the measured reaction rates of hot electron processes (ionization, dissociation and vibrational excitation rates) could be used as a parameter and the simulation could focus on cold electron processes such as plasma diffusion, recombination and dissociative electron attachment.

The presented methods have been applied to analyze a filament arc discharge. Although the plasma parameters depend on the mechanical design of the plasma source, some results can be generalized. It is well known that the confinement of primary electrons emitted by the filament is good in multicusp arc discharges and that their energy dissipates mainly in inelastic collisions with neutrals. Therefore, the reaction rates normalized with respect to the arc power and the arc current (table 4) should be general properties of this type of plasma source.

The excitation rate to vibrational levels ($\nu \geq 5$) via electron impact excitation to $B^1\Sigma_u^+$ and $C^1\Pi_u$ states was estimated earlier by Graham [9] to be on the order of $10^{13}$ cm$^{-3}$ s$^{-1}$ kW$^{-1}$. This is approximately an order of magnitude lower than the estimated value given in this paper. The deviation is probably caused by the difference in the confinement of the primary electrons, since the apparatus used in [9] does not contain a multicusp magnetic field. The density of metastable $c^3\Pi_u$ states in a multicusp ion source was measured earlier to be on the order of $10^{10}$ cm$^{-3}$ kW$^{-1}$ [39]. This is approximately two orders of magnitude lower than the upper limit estimated in this study. The difference is probably caused by uncertainties related to the estimate presented in this study, i.e., (a) the applied cross section is the total cross section to $c^3\Pi_u$ states, (b) the contribution of $c^3\Pi_u$ state to the molecular continuum emission, (c) the estimated maximum effective lifetime of the $c^3\Pi_u$ state and (d) the assumption of homogeneous and isotropic plasma emission profile. Thus, the estimated maximum $c^3\Pi_u$ density presented in this study is consistent with the measured value given in [39].

The benefits of VUV spectroscopy arise from the quantum mechanical properties of the hydrogen molecule. Processes such as excitation to triplet states leading to molecule dissociation and excitation to singlet states leading to production of high vibrational levels in the ground state are directly related to the properties of the hydrogen molecule orbitals and Franck-Condon principle. Although these properties are not valid for other elements, there are often interesting (chemical) phenomena related to electronic excitations and forbidden transitions, e.g. the production of the metastable helium [46]. Therefore, it should be possible to utilize the same principle, namely the comparison of the rate coefficients with similar functional shapes, for other plasmas as well.

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