Application of molecular convergent close-coupling cross sections in a collisional radiative model for the triplet system of molecular hydrogen

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Abstract
Collisional radiative (CR) models for molecular hydrogen are of high relevance for performing qualitative and quantitative analysis of excited-state population densities measured in plasmas or predicting the dependence of plasma emission on parameter variations. Although the development of such models for H₂ started decades ago, major uncertainties still exist regarding the most important set of input parameters, namely the cross sections for electron-impact excitation. The deviations between cross sections from different datasets are particularly pronounced in the energy region close to the threshold energy, strongly increasing the uncertainty of CR models applied to low-temperature plasmas. This paper presents experimental validation of a set of newly calculated non ro-vibrationally resolved electron-impact cross sections calculated for the triplet system of H₂ using the molecular convergent close-coupling method in the adiabatic-nuclei formulation. These cross sections are implemented into a CR model based on the flexible solver Yacora. A first comparison of CR calculations with the different datasets to experimentally-determined population densities is performed at a planar ICP discharge for varying pressure (between 1 and 10 Pa) and RF power (between 700 and 1100 W). For the experimentally-accessible electron temperature and density range (2.5–10 eV and 1.8–3.3 × 10¹⁶ m⁻³, respectively), very good agreement between the model and experiment is obtained using the new data set, in contrast to previously used cross sections.

Keywords: collisional radiative model, molecular hydrogen, electron-impact excitation cross sections, low-temperature, low-pressure plasma, plasma spectroscopy

(Some figures may appear in colour only in the online journal)

1. Introduction

Hydrogen molecules play an important role in low-temperature, low-pressure plasmas related to numerous applications and research areas. Prominent examples are plasma processing, i.e. the modification of surface properties by the impact of a plasma (see for example [1–3]) and the
field of fusion research (molecules appear in the cold plasmas at the edge of magnetically confined fusion experiments [4] or in the divertor [5]). In all of these fields, plasma diagnostics are an invaluable tool for characterizing the plasma and understanding basic physical effects [6–9].

A diagnostic method often applied due to its rather simple setup is optical emission spectroscopy (OES) [6, 10]. Spectroscopic measurements directly yield the intensity of a transition, and by applying the Einstein coefficient the population densities of excited states can be obtained. In order to determine plasma parameters (as the electron temperature \( T_e \), electron density \( n_e \), and the densities of the ground states of one or more particle species) from such measurements, population models predicting the dependence of excited-state population densities on the plasma parameters are required. By matching population densities calculated with the population models to measured ones, the plasma parameters can be determined [10].

The type of population models providing the broadest application range (between very low and very high electron densities) are collisional radiative (CR) models [11]. Usually, this type of model is applied to plasmas with a collision rate too high for corona models but too low for local thermodynamic equilibrium (LTE). Nevertheless, CR models intrinsically include the corona model and for high collision rates, their results converge to the population distributions predicted by LTE.

CR models solve the rate equations for all excited states of the atom or molecule implemented in the model [11]. These rate equations balance the probabilities for populating and depopulating the excited states. Combining the rate equations for all excited states results in a system of coupled ordinary differential equations. The uncertainty of the model predictions strongly depends on the error bars of the reaction probabilities used as input for the model. For some simple atoms (for example hydrogen or helium), a well-benchmarked set of reaction probabilities is available and very reliable and well-benchmarked CR models exist (see for example [12–15]). However, in the case of molecules, the more complex structure and additional ro-vibrational degrees of freedom makes the calculation or measurement of reaction probabilities much more difficult. Although molecular hydrogen is the simplest neutral molecule, cross sections from different literature sources for specific electron-impact excitation reactions are in substantial disagreement [14], particularly in the low-energy region close to the reaction threshold. These disagreements can result in large uncertainties in plasma parameters determined using CR models for low-temperature hydrogen plasmas.

One application for such models is the molecular Fulcher-\( \alpha \) band emission \((d^3 \rightarrow a^3)\) which, in combination with an atomic hydrogen emission line, is a standard tool for determining the ratio of atomic to molecular hydrogen [16]. This ratio is correlated to the respective particle fluxes and its knowledge can be essential for understanding basic properties of hydrogen plasmas interacting with surfaces [17]. Thus, it is highly desirable to reduce the uncertainties in the molecular cross sections applied in the CR models (especially in the low-energy region) in order to significantly reduce the uncertainty in the model application.

In excited states of the hydrogen molecule, the spin of the two electrons can be either paired or non-paired, resulting in the existence of two multiplet systems: a singlet system and a triplet system. The ground state \( X^1 \) of \( \text{H}_2 \) belongs to the singlet system. Spontaneous transitions interconnecting these two systems are forbidden (as they require a spin exchange) and thus for low-pressure plasma applications it is possible to use separate CR models for the singlet and the triplet system. This paper gives an insight into the status of a CR model for the triplet system of molecular hydrogen based on the solver Yacora [14] and the different sets of input reaction probabilities used in this model up to now. The reason behind focusing on the triplet system is that it includes the two electronic states \( d^3 \) and \( a^3 \), the upper states of the Fulcher-\( \alpha \) transition and the \( \text{H}_2 \) UV continuum respectively [18, 19], the latter being another emission band very suitable for application in plasma diagnostics.

Next, a comprehensive set of electron-impact cross sections for the triplet system of \( \text{H}_2 \) is introduced. It has been generated using the molecular convergent close-coupling (MCCC) method in the adiabatic-nuclei (AN) formulation [20–22]. This method produces accurate collision data over the entire range of incident energies, including the critical region close to the excitation threshold. The calculated cross sections are implemented into the CR model for the triplet system of \( \text{H}_2 \). Due to the flexible character of Yacora, the set of input data can be easily switched and thus it is ideally suited for comparative investigations concerning the impact of different input cross sections on the calculated population densities.

Finally, population densities of the electronically excited states \( d^3 \) and \( a^3 \) have been determined experimentally in a planar ICP setup by means of emission spectroscopy. These two states are those with the highest diagnostic relevance in the triplet system of molecular hydrogen. The obtained results are compared to those calculated with the CR model applying different sets of electron-impact cross section for benchmarking purposes.

2. The Yacora model for the triplet system of \( \text{H}_2 \)

In molecular CR models the presence of rotational and vibrational levels implies a large number of rate equations to be solved. In addition, the number of reactions interconnecting the excited states is much larger in molecules than in atoms. While a CR model for the hydrogen atom usually includes a few thousand reactions, the number of reactions in a full model for \( \text{H}_2 \) (including the ro-vibrational levels) can be larger by several orders of magnitude. In order to reduce the required effort or to make the construction of molecular CR models even possible at all, the structure of the molecule is often simplified, e.g. by neglecting the rotational and/or the vibrational splitting of the electronically excited states. This is done as well in the Yacora model for the triplet system of the hydrogen molecule used within this study: the model includes the ground state \( X^1 \), and all electronic states of the
triplet system up to the principal quantum number \( p = 10 \) but without the ro-vibrational levels. Although this model is not capable of determining the ro-vibrational population of excited states, it can be used—in combination with results of plasma diagnostics—for determining plasma parameters like the electron temperature and the electron density.

Figure 1 shows a simplified energy level diagram of the hydrogen molecule. The orange box encompasses the states which are implemented in the present CR model. Shown for principal quantum numbers of up to \( p = 3 \) are the states resulting from the different possible orbital angular momentum projections of the electrons. For higher principal quantum numbers, the splitting into different angular momentum projections is not included. The energy shown in the figure for the different states is equivalent to the energy of the respective lowest-energy ro-vibrational level. Indicated in red in figure 1 are the Fulcher-\( \alpha \) transition and the \( H_2 \) UV continuum, neglecting the ro-vibrational structure.

The lowest state in the triplet system, \( b^3 \), is repulsive, i.e. the potential energy curve of this state is non-binding and it does not form a potential well. A molecule excited or de-excited into and staying in this state will dissociate into two hydrogen atoms in the atomic ground state.

The lowest vibrational level \( v = 0 \) of the \( c^3 \) state is metastable, i.e. decay via spontaneous emission to energetically lower levels is possible only via electric quadrupole or magnetic dipole radiation with very low transition probabilities. Therefore, this state has a relatively large radiative lifetime of around 1 ms [23]. Alternatively, de-excitation can also occur via collisions with molecules in the ground state (quenching) [24]. The vibrational levels with \( v > 0 \) can radiate into the \( a^3 \) state [25] but due to the small energy difference the transition probability is small. The effective radiative lifetime of the \( c^3 \) state is \( 9.5 \times 10^{-5} \) s which is about four orders of magnitude larger compared to the lifetime of the \( a^3 \) state [25]. Due to the metastable character of \( c^3 \) (\( v = 0 \)) this state can reach large population densities and thus it can be significant for excitation of energetically higher states in the triplet system, for example the upper state of the Fulcher-\( \alpha \) transition [26].

Details on the Yacora CR model for \( H_2 \) are already described elsewhere [14], and therefore only a brief summary is given here. All implemented reactions interconnecting the excited states implemented in the model and the reference for the reaction probabilities are contained in table 1. The model focusses on application in low-pressure plasmas, i.e. excitation of electronic states by collisions with heavy particles is neglected. Yacora converts reaction probabilities that are defined as cross sections into rate coefficients using an electron energy distribution function defined by the user of the model. Within the scope of the present work, a Maxwell distribution is used.

Up to now, two different sets of cross sections for electron-impact excitation from the ground state to the states with principal quantum number \( p = 2 \) or \( p = 3 \) have been available. The cross sections from Miles et al [27] have been calculated by semi-empiric methods based on experimental information and phenomenological extensions of the Born approximation into the low-energy region. The data from Janev et al [23] represents a summary of different measurements and calculations.

The datasets of [27] and [23] do not include collisions with excited states or excitation of states with \( p > 3 \), and hence when using these datasets it is necessary to obtain reaction probabilities for the aforementioned processes elsewhere. For collisions between states within \( p = 2 \), connecting \( p = 2 \) with \( p = 3 \), and for excitation of states with \( p > 3 \), rate coefficients from [28] are used. They represent estimations based on data for hydrogen-like atomic ions and the hydrogen atom. This data was applied to the molecule since up to now no appropriate input data was available. Cross sections for electron-impact de-excitation have been deduced from the electron-impact excitation cross sections by applying the detailed balance principle.

For electron-impact ionization, the cross sections from [29], calculated using the Gryzinski method [33, 34] are used. The effective Einstein coefficients calculated in [25] by averaging the Einstein coefficients for the individual levels are used as probabilities for spontaneous emission.

| Process                      | Reaction                              | Reference |
|------------------------------|---------------------------------------|-----------|
| Electron-impact excitation    | \( H_2(i) + e^- \rightarrow \) [27] or [23] together | [27], [23] |
| Electron-impact de-excitation | \( H_2(j < i) + e^- \) with [28], or MCCC | [28], [23] |
| Ionization                   | \( H_2(i) + e^- \rightarrow \) [29] | [29] |
| Spontaneous emission         | \( H_2(i) \rightarrow \) [25], see text | [25] |
| Quenching with \( H_2 \)     | \( H_2(c^3 \text{ or } a^3) + H_2 \rightarrow 2H_2 \) [24], see text | [24] |
| Charge exchange with \( H^+ \) | \( H_2(i) + H^+ \rightarrow \) [30], see text | [30] |
| Dissociative attachment      | \( H_2(i) + e^- \rightarrow \) [31, 32], see text | [31, 32] |
Additionally included in the model are the following loss channels for excited molecular states: de-excitation (quenching) of the states $c^3$ and $a^3$ by collisions with the molecular ground state, charge exchange of $H^+$ with excited states of $H_2$, and dissociative attachment of electrons to excited states of $H_2$. The reaction probabilities for the latter three processes are taken from [24], [30] and [31, 32], respectively. Finally, electric quadrupole and magnetic dipole radiation of $c^3$ is taken into account, based on the lifetime given in [23]. Other alternative de-excitation channels for $c^3$, e.g. diffusion, are not included.

Due to the high relevance of electron-impact excitation from the ground state in low-pressure plasmas, the accuracy of the respective cross sections is a critical point. As described in [14], the differences between cross sections from [27] and [23] are large, particularly close to the threshold energy; depending on the excited state, deviations up to factors significantly larger than ten occur. The reason is that both data sets are not fully based on a quantum mechanical treatment taking into account both the projectile and target wave functions as well as the scattering amplitude in an energy range including the low-energy region. It is not possible in a straightforward manner to define one of the two sets to be more accurate, resulting in a significant uncertainty in CR model results for molecular hydrogen.

Exchanging the input data with cross sections deduced using theoretical techniques accurate both close to the threshold energy and at high energies is desirable. Up to now, this was possible only for some selected transitions, mostly using data based on the R-matrix method [35].

The comprehensive set of MCCC cross sections applied in the Yacora CR model for the triplet system of $H_2$ includes electron-impact excitation from $X^1$ to $p = 2$ and $p = 3$, within $p = 2$ and for $p = 2 \rightarrow p = 3$, as well as de-excitation from $p = 2$. For the first time ever, a CR model for molecular hydrogen is based (up to $p = 3$) on a comprehensive set of input cross sections for electron-impact excitation where all cross sections have been determined specifically for the hydrogen molecule and using the same technique.

### 3. MCCC cross sections for electron-impact excitation of the triplet system

The convergent close-coupling (CCC) method is an *ab initio* approach to solving the electronic scattering problem which has been applied extensively to studies of light- and heavy-projectile scattering on a wide variety of atomic targets. An important feature of the method is its ability to provide accurate cross sections for all incident energies. This is achieved by performing a large close-coupling expansion of the total scattering wave function, which accounts for coupling between all important reaction channels including ionization. The MCCC method extends the same techniques to molecular targets, and has been applied to electron and positron scattering on molecular hydrogen and its cation [20, 36–39]. For a review of electron, positron, proton, and antiproton scattering on both atomic and molecular hydrogen using the CCC and MCCC methods, see [40]. A detailed discussion of the MCCC method can be found in [21], with details specific to the spheroidal-coordinate implementation utilised in the present MCCC calculations given in [22].

The AN method is utilized, allowing the electronic scattering calculations to be performed independently at a number of different internuclear separations, with the dependence on nuclear vibrational motion reintroduced afterwards. This method provides more accurate near-threshold cross sections than the simpler fixed-nuclei approach which neglects vibrational motion. The non-vibrationally-resolved cross sections for scattering on the $v = 0$ level of the $X^1$ state to each state in the $p = 2$ and $p = 3$ spectra have been taken from [36]. The remaining fully vibrationally-resolved cross sections presented in [36] will naturally allow the extension of the present work to a vibrationally-resolved CR model later. The cross sections for scattering on the $v = 0$ levels of the $c^3$ and $a^3$ states have been taken from [41].

The accuracy of the MCCC method has been demonstrated recently by the outstanding agreement between theory and experiment for the fundamental $X^1 \rightarrow b^3$ transition in $H_2$, where there have previously been significant discrepancies between different calculations and measurements [42]. In addition, new R-matrix calculations of electron scattering on the $X^1$ state of $H_2$ were found to agree very well with MCCC results [43]. An overall uncertainty of 10% has been estimated for the MCCC cross sections, taking into account errors due to the target structure and convergence of the scattering calculations, as well as the use of the AN approximation. The AN MCCC method can be readily extended to include rotational excitations as well, which will allow future studies to consider rotationally- and vibrationally-resolved modelling.

The differences between the sets of cross sections from [23, 27] and the MCCC calculations are exemplarily assessed in figure 2 for the excitation from the ground state $X^1$ into the states $a^3$ (upper state of the $H_2$ UV continuum), $c^3$ (which can have a high relevance for populating other triplet states) and $d^3$ (upper state of the Fulcher-$\alpha$ transition).

In the whole energy range there is a factor of below two ($a^3$), about two ($c^3$) and seven ($d^3$) difference between the cross sections from [27] and [23]. For excitation of the $a^3$ state, the data from [27] and [23] is almost identical and the MCCC cross section lies below. The MCCC cross section for excitation of the $c^3$ state is in absolute value closer to the cross section from [27], while for $d^3$ it is closer to the data from [23]. For higher collision energies, i.e. in the Born regime, the cross sections from the different sources are parallel to each other. The fact that for the states $a^3$, $c^3$ and $d^3$ significant differences in the agreement between the MCCC data with the cross sections from [27] or [23] can be seen demonstrates that the assumptions and simplifications made for determining the previously used cross sections may have resulted in an acceptable accuracy for single excitation processes but not for the full set of cross sections. Close to the threshold energy $E_{\text{thr}}$—indicated in figure 2 by vertical dashed lines—differences in the shape are apparent, in particular for the excitation process $X^1 \rightarrow d^3$.

Taking into account the good accuracy of the MCCC cross sections in this energy range (when using the AN approach),
Figure 2. Cross sections from [23, 27] and the MCCC data for electron-impact excitation of the states a, c and d from the ground state in the hydrogen molecule. Indicated by the vertical dashed lines is the threshold energy for excitation of the three states.

Figure 3. Rate coefficients for electron-impact excitation from c into the states of p = 3 from [28] and calculated using the MCCC cross sections, assuming a Maxwell EEPF.

rate coefficients occur. For the excitation channel c → d, i.e. excitation of the upper state of the Fulcher-α transition, significant deviations are seen (for T_e = 1 eV the MCCC based rate coefficient is 42% smaller than the previously used data, for T_e = 100 eV almost 70%). Therefore, a direct and significant impact of exchanging the input data on the model results for the d state is expected.

4. Basic dependencies

In order to illustrate the impact of the different sets of input data, CR model results based on the excitation cross sections from [23, 27] and the MCCC cross sections are compared for a broad range of the electron temperature T_e (1–100 eV), the electron density n_e (10^{16}–10^{20} m^{-3}) and the ground state density n(X_1) (10^{18}–10^{22} m^{-3}). These ranges include the parameters of typical low-pressure, low-temperature plasmas close to the divertor of fusion machines or in smaller laboratory-scale experiments, see for example [44–46]. Special focus is put here again on the a, c and d states.

Figure 4 shows the calculated population density of these three states, normalized by the ground state density, versus the electron temperature. The electron density is fixed to 10^{17} m^{-3}, a typical value for low-pressure laboratory experiments, and the electron temperature.

The general trend of the population densities with increasing T_e is defined mainly by the rate coefficients for electron-impact excitation: a strong increase at low temperatures, followed by a flat region and a slow decline for high temperatures. The population densities for the a state are up to a factor of ten larger than the ones for d. This is a direct effect of a larger cross section (and hence rate coefficient) for excitation from the ground state. Although a and c have a comparable energy, c is overpopulated by a factor of about 100 compared to the a state, demonstrating that the large

the applicability of the CR model for H_2 in particular to low-temperature plasmas (where the average energy of the plasma particles can be close to or below the threshold energy, i.e. the different shape of the cross sections in this energy region can have a significant effect) should benefit from using these more reliable cross sections.

Figure 3 demonstrates the high relevance of using, for the first time in a CR model of H_2, a comprehensive set of input cross sections for electron-impact excitation, including p → p = 3. The figure shows rate coefficients for excitation from c into the six states of p = 3 calculated by convolution of the MCCC cross sections with a Maxwell electron energy probability function (EEPF), compared with the rate coefficient previously used in the CR model for these six excitation channels. Due to the lack of more detailed data, the rate coefficient from [28] for electron-impact excitation c → p = 3, not considering the splitting of the p = 3 states caused by different angular momentum projections, was divided by six to represent an average over the six p = 3 triplet states (assuming a uniform distribution of the excitation probability). This scaled rate coefficient is shown in the figure by the bold black line. Depending on the final state of the excitation process and the electron temperature, deviations by a factor of up to ten between the previously used data and the MCCC based
The effective radiative lifetime of the $c^3$ state affects its population over the whole investigated $T_e$ range.

As expected from the comparison of the rate coefficients from the different data sets, the calculated normalized population densities are very similar for all three input data sets in the case of the $a^3$ state. Also for the $c^3$ state, the results using the MCCC data or those from [27] are close whereas those from [23] are higher. For $d^3$ the population density calculated using the MCCC cross sections is closer to the result based on the data from [23] over the whole investigated electron temperature range.

When comparing figure 2 with the figures shown in this section, it has to be kept in mind that figure 2 presents the input cross sections used in the CR model while the rate equations solved by the CR model are based on rate coefficients. The fact that for example for $T_e > 50$ eV the population density for $c^3$ calculated using the MCCC cross sections is almost identical to the result based on the cross sections from [27] but the results deviate noticeably for lower temperatures can be attributed to the different shape of the cross sections. Furthermore, it points out an important issue: the fact that the calculated population densities are not parallel to each other means that even if a CR model using one of the available sets of input cross sections succeeds in describing population densities measured for a specific plasma, it may fail in case of a significantly different electron temperature. Therefore, validating a CR model should always be done over a wide range of plasma parameters.

Figure 5 shows the normalized population densities of the $a^3$, $c^3$ and $d^3$ states versus the electron density for $T_e = 5$ eV and $n(X^1) = 10^{20}$ m$^{-3}$. For the $a^3$ and $d^3$ states, dashed lines indicate the results of the corona-model approximation (i.e. balancing electron collision excitation from the ground state with spontaneous emission), which cannot be applied for $c^3$ since the relevance of radiative de-population is small due to its large effective radiative lifetime.

The normalized population densities increase linearly with $n_e$ up to $n_e \approx 3 \times 10^{16}$ m$^{-3}$, in very good agreement with the corona model. This illustrates a regime where the rate of the dominant populating process (electron-impact excitation) is proportional to $n_e$ while the rate for the dominant de-populating process (spontaneous emission for $a^3$ and $d^3$, quenching for $c^3$) does not depend on $n_e$. However, already for $n_e > 3 \times 10^{16}$ m$^{-3}$ slight deviations from the linear behaviour can be seen, i.e. the validity of the corona approximation breaks down at relatively low electron densities, demonstrating that the application of a CR model is mandatory for a large range of $n_e$. 

![Figure 4](image1.png)

**Figure 4.** Normalized population density of the three states $a^3$, $c^3$ and $d^3$ calculated using the cross sections from [23, 27] and the MCCC cross sections over a broad range of the electron temperature.

![Figure 5](image2.png)

**Figure 5.** Normalized population density of the three states $a^3$, $c^3$ and $d^3$ calculated using the cross sections from [23, 27] and the MCCC cross sections over a broad range of the electron density. The dashed lines indicate results obtained using the corona model for $a^3$ and $d^3$. 

With further increasing electron density, the population densities for $c^3$ and $d^3$ flatten because de-population by electron collisions becomes dominant. Due to the small energy difference between $c^3$ and $a^3$, collisional de-population of $c^3$ predominantly feeds into $a^3$. As a result, the population density of $a^3$ increases with $n_e$ even for high electron densities. This result illustrates that the metastable $c^3$ state has to be taken into account when calculating excited-states population densities in the triplet system.

Again, the population densities for $d^3$ calculated using the different sets of input data are not parallel to each other: for $n_e > 10^{18}$ m$^{-3}$ the population density calculated using the MCCC cross sections approaches the result based on the cross section from [27]. In contrast, for $n_e < 10^{11}$ m$^{-3}$ it is closer to the results based on the cross sections from [23].

Concerning the evaluation of spectroscopic measurements of the Fulcher-$\alpha$ transition, knowledge about the population channels of the upper $d^3$ state is very important: only when direct excitation from the ground state is dominant can the gas temperature of the plasma be determined [47]. Figure 6 summarizes the relative importance of the following types of populating processes with varying ground state density for the $d^3$ state:

- Direct excitation (via electron collision from the ground state), figure 6(a).
- Stepwise excitation (mainly via electron collisions from $c^3$), figure 6(b).
- Cascading (from energetically higher states), figure 6(c).

The calculations have been carried out for the different sets of cross sections and for the typical plasma parameters already used in figures 4 and 5: $n_e = 10^{17}$ m$^{-3}$, $T_e = 5$ eV. The upper $x$-axis gives the gas pressure corresponding to the ground state density for a molecular temperature of 1000 K.

The only processes included to the CR model with a reaction rate depending on the ground state density are quenching of the $e^3$ and $a^3$ states. For $n(X^1) < 10^{19}$ m$^{-3}$ the quenching rates for these two states are negligible compared to collisional de-population and, for $a^3$, spontaneous emission. In contrast, when increasing $n(X^1)$ significantly above $10^{19}$ m$^{-3}$, quenching becomes the dominant de-populating channel of $c^3$, reducing the large effective lifetime of this state. Consequently, the relative importance of direct excitation of $d^3$ increases (figure 6(a)) while the importance of stepwise excitation decreases (figure 6(b)).

The relative importance of the three types of populating processes depends strongly on the set of input excitation cross sections. This dependence is caused by a sensitive interplay of the rates for the different channels depopulating $c^3$ with the ones for direct and stepwise excitation of $d^3$. The relevance of stepwise excitation is lowest (less than 10%) when using the MCCC cross sections but it can reach more than 50% for low $n(X^1)$ values when using the data from [27]. As stated before, when using the cross sections from [27] and [23], reaction probabilities for electron collisions $p = 2 \rightarrow \ldots$ are estimated using the rate coefficients of [28], which are based on data for hydrogen-like atomic ions and the hydrogen atom. These data have a high uncertainty, and switching to MCCC cross sections specifically calculated for these transitions suggests that the relevance of the stepwise excitation has been strongly overestimated in the past.

When using the cross sections from [27], cascading is relevant and increases from a relative contribution of about 10% up to about 17% with increasing ground state density. When the data from [23] or the MCCC cross sections are applied, the contribution of cascading is significantly below 10% over the whole ground state density range and may be negligible, depending on the desired accuracy.

As mentioned above, the methods currently applied for determining the gas temperature assume that direct excitation is the dominant populating process for $d^3$. This is the case for varying the ground state (see figure 6(a)) and also for the $T_e$ variation done for figure 4 and for the $n_e$ variation done for figure 5. If, however, for a specific set of plasma parameters the relevance of direct excitation is reduced to a level where it is no longer dominant, simple scaling of vibrational and rotational populations is not possible and application of a fully vibrationaly resolved CR model is mandatory for evaluating the gas temperature.

![Figure 6. Relative relevance of three different types of populating processes for $d^3$: (a) direct excitation, (b) stepwise excitation and (c) cascading.](image-url)
5. Comparison of the CR model results to experimentally determined population densities

In order to check which set of input data for the CR model results in the best representation of experimentally determined population densities, measurements have been carried out at a low-pressure, low-temperature hydrogen discharge at a well-diagnosable planar inductively coupled plasma. The discharge vessel consists of a cylindrical stainless-steel vessel with a diameter of 15 cm and a height of 10 cm. The RF is coupled to the plasma through a planar coil sitting on top of a dielectric window (RF frequency 2 MHz, max. power 2 kW). As diagnostic methods, a radially-movable Langmuir probe can be inserted and emission spectroscopy is conducted at radial lines of sight in the optical (OES) and vacuum UV (VUV) spectral range (see figure 7 for the arrangement of the diagnostics). For OES, the spectrometer is calibrated with an Ulbricht sphere as secondary radiation standard. The resulting error for the determined intensities is 10%. Concerning the VUV spectrometer, the relative sensitivity is determined with a deuterium arc lamp whereas the intensity calibration is transferred from the visible to the VUV spectrometer by measuring emission lines of a Helium discharge simultaneously with both spectrometers. This yields an intensity error of 22% (detailed information on the VUV calibration can be found in [48]). For the pressure range of the present investigations, the EEPF in the discharge follows a Maxwell distribution.

From the Langmuir probe, spatially-resolved values for the electron temperature and density are obtained. These profiles show the typical textbook behaviour: constant over the radius and decreasing close to the wall for \( T_e \) and a Bessel profile for \( n_e \) with the maximum in the centre of the vessel. In order to use these results for CR modelling purposes, averaging over the spectroscopic line of sight is performed. The corresponding results are summarized in figure 8 for a variation of the pressure between 1 and 10 Pa at fixed generator power of 700 W. The observed trends correspond to the ones expected from global textbook models (see e.g. [49]): a decrease of \( T_e \) with increasing pressure, and an increase of \( n_e \).

Concerning the comparison between experimentally determined population densities and those derived from CR modelling using the different input data sets, special focus is again put on the \( a^3 \) and \( d^3 \) states. From the spectroscopic measurements of the first four diagonal vibrational transitions of the Fulcher-\(\alpha\) transition, the population density of the \( d^3 \) state is derived as described in [50]. Similarly, the density of the \( a^3 \) state is derived from the continuum emission recorded between 180 and 300 nm following [19].

In general, the comparison can be performed in two different ways. First, the direct approach where the Langmuir probe data and the ground state \( H_2 \) density is used as fixed input for the CR model and the resulting calculated molecular population densities are compared to the experimentally determined ones. In this approach, the \( H_2 \) density is calculated with the ideal gas law from the pressure and the gas temperature, which has been determined according to [51]. For the present experimental investigations, the density of \( X^1 \) is determined to values between \( 1.3 \times 10^{20} \) and \( 1.1 \times 10^{21} \) m\(^{-3}\), i.e. exactly in the range where collisional de-excitation by heavy particles becomes relevant (see figure 6). It should be noted that the reduction of the \( H_2 \) density by dissociation processes is neglected [52, 53], which means that the calculated molecular population densities must be considered as an upper limit.

Figure 9 shows the comparison of population densities obtained for the \( d^3 \) state from the experimental measurements (pressure variation between 1 and 10 Pa at fixed RF power and for a power variation between 700 and 1100 W at 1 Pa) together with the results of the CR modelling according to the first approach carried out with the three different sets of input cross sections. The population densities are plotted as a function of \( T_e \) on the x-axis, but it should be noted that \( n_e \) and the ground state density also vary for the data points. In general, the measured and calculated population densities increase with the electron temperature, independent of the set of input cross sections used in the CR model. The population densities from the CR model using the MCCC cross sections slightly overestimate the experimental population densities by about 20% to 50%, whereas the calculations based on the input data of [23] overestimate the measurements by about a factor of two.
Figure 9. Comparison of measured population densities of the d3 state to the ones calculated with the CR model Yacora H₂ using cross section from either [23, 27] or the MCCC data. The results have been obtained for a pressure variation at 700 W and for a power variation at 1 Pa.

Figure 10. Comparison of measured population densities of the a3 state to the ones calculated with the CR model Yacora H₂ using cross section from either [23, 27] or the MCCC data. The results have been obtained for a pressure variation at 700 W and for a power variation at 1 Pa.

Figure 11. Density ratio of atomic to molecular hydrogen determined via fitting the experimentally obtained population densities with the CR model using cross sections from either [23, 27] or the MCCC data. The results have been obtained for a pressure variation at 700 W and for a power variation at 1 Pa.

In contrast, the calculated densities based on the data of [27] underestimate the measured ones by a factor of two to three. The population densities derived for the a3 state from the experimental measurements as well as those determined from CR modelling according to the first approach are summarized in figure 10. Similar to the d3 state, the population densities increase with the electron temperature (the reduction observed between 5.7 and 8.8 eV is caused by a reduction of the gas pressure). CR modelling overestimates the experimentally determined population densities for all three sets of input data, but the amount of overestimation varies: by a factor of 1.3–1.8 for the MCCC data or for the input from [27] and by a factor of 1.8–2.6 when using the input from [23].

As already explained in the introduction, the Fulcher-α band emission in combination with an atomic hydrogen emission line is a standard tool for determining the ratio of atomic to molecular hydrogen [16]. Thus, in the second approach, the measured band intensities are fitted with the molecular CR model via varying the input parameters (electron temperature and the density of the considered species) implicitly considering the effect of dissociation processes and again taking into account the total gas density calculated with the ideal gas law from the pressure and the gas temperature. Additionally, measured emission of the atomic Balmer lines Hα to Hγ is fitted using a benchmarked CR model for atomic hydrogen [14]. Here, the experimentally determined values of the electron temperature and density can be compared to the one obtained from the CR model fits. Performing this fitting procedure shows that the experimentally determined electron temperature and density values are matched very well (within 10%) when the MCCC data is used. With the input from [27], much higher $T_e$ (between 15% and more than 60% higher) and $n_e$ values (up to a factor of three higher) are required. In contrast, using the input from [23] requires electron temperatures and densities both being about 20% lower than the experimental ones. Such significant deviations can have a strong impact on the results of evaluating plasma diagnostics like OES using the CR model results. The difference of the determined population densities arising from the different input sets is mapped directly onto the determined ratios $n(H)/n(H_2)$. Figure 11 shows the density ratio determined from the different sets of cross sections. The highest density ratio is obtained when using the data from [23], the lowest when using the input of [27] whereas the result of the MCCC data is in between. A confirmation, which result is correct cannot be given because an independent measurement of the ground state densities of H or H₂ is not
available at the used experimental setup. However, the good agreement between the experimentally obtained electron temperatures and electron densities to the one from CR modelling in the case of the MCCC data suggests that these cross sections can be considered more reliable. The huge spread of the determined ratios \( n(H)/n(H_2) \) (up to a factor of ten) highlights again the relevance of a reliable set of cross section data.

Disregarding the discrepancy of the experimental and modelled electron temperature and density values evident in the second approach when using the cross sections from [23] and [27], the obtained ratios of atomic to molecular density can still be used in order to correct the \( H_2 \) density used for calculating the emission band intensities in the first approach. The results using the cross sections of [27] (not shown here) remain virtually unchanged, as the atomic to molecular density ratio is very low. The intensities determined with the MCCC data are reduced between 10% and 40% for the Fulcher-\( \alpha \) transition and between 10% and 30% for the continuum, i.e. the results move closer towards the experimentally determined ones. The same trend is apparent for the cross sections of from [23], where the reduction of the intensities is between 10% and 90% (Fulcher-\( \alpha \)) or between 15% and 50% (continuum). Nevertheless, the best match between experiment and CR modelling is still obtained for the MCCC input.

It should be noted, that this comparison with experimental data is carried out in a broad \( T_e \) range, but the \( n_e \) range is limited to the low-density region of \( n_e \leq 3 \times 10^{16} \text{ m}^{-3} \). As can be seen in figure 5, the collisional depopulation by electrons is not yet relevant in this range. Therefore, a detailed comparison of the different data sets in an electron density range significantly above \( 3 \times 10^{16} \text{ m}^{-3} \) will be carried out in future work.

6. Conclusions

The new set of MCCC cross sections for electron-impact excitation of the hydrogen molecule represents a substantial improvement in accuracy over the previously available data-sets. A non-vibrationally resolved CR model for the triplet system of \( H_2 \), based on the flexible solver Yacora, was applied for benchmarking the MCCC cross sections at a low-pressure, low-temperature hydrogen discharge (\( T_e \) range: \( \approx 2.5-10 \text{ eV} \), \( n_e \) range: \( 1.8-3.3 \times 10^{16} \text{ m}^{-3} \)): total population densities of the \( d^2 \) and the \( a^2 \) states measured by OES were compared to predictions of the CR model, based on plasma parameters from a Langmuir probe. Three different sets of input cross sections were used: the MCCC cross sections and alternatively two previously available sets of cross sections from literature. The agreement between observation and predictions is very good for the MCCC cross sections while significant deviations are seen for the two other cross section sets.

This successfully performed benchmark indicates that the uncertainty of \( H_2 \) CR model results will be significantly reduced when using the MCCC cross sections as input. The accuracy of plasma parameters, e.g. the ratio of atomic to molecular hydrogen, determined using such CR models will drastically improve, opening the door towards extending the physics insight in a wide range of plasma experiments. In this context, future work will be directed towards extending the benchmark to a wider range of electron densities.

Similar investigations to those presented in this publication are also planned for the singlet system. The MCCC cross section will also enable for the very first time constructing a model for the singlet and the triplet system including excited state-excited state electron-impact reactions connecting the two multiplet systems. Furthermore, the models can be extended to deuterium and implementing vibrationally or ro-vibrationally resolved cross sections in future CR models or corona models will enable a much-improved interpretation of the vibrational or ro-vibrational structure of \( H_2 \) emission bands.

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