Formation and relaxation of rovibrationally excited H₂ molecules due to plasma-surface interaction

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We report on the interaction of hydrogen atoms and molecules under high flux conditions with a cooled copper surface and its impact on gas phase densities and internal excitation of the molecules. These densities were measured by means of laser-induced fluorescence using tunable radiation sources in the vacuum-ultraviolet (vuv). While H atoms were detected by two-photon absorption laser-induced fluorescence, the necessary vuv radiation for the detection of rovibrationally excited H₂ molecules in the electronic ground state were produced by stimulated anti-Stokes Raman scattering. The results reveal a strong loss mechanism of H atoms and the formation of rovibrationally excited H₂ molecules due to surface interaction. The surface reaction probability of H atoms under high flux conditions on copper was estimated. Surface collisions are shown to have a profound influence on the density distribution of rovibrationally excited H₂ molecules: The distributions follow lower temperatures and are less Boltzmann-like, i.e., the distributions of the internal excitation of H₂ molecules differ more from thermodynamic equilibrium.

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I. INTRODUCTION

Hydrogen will play a vital role in future technologies ensuring our energy supply and reducing our dependence on limited fossil fuels. Used as an energy storage medium, it will be part of the so-called hydrogen economy [1]. In future nuclear fusion reactors hydrogen isotopes deuterium and tritium will be used as fuel [2]. However, the control of the interaction between plasma gas phase and surrounding surfaces in a fusion reactor is a challenging and until now unsolved technological task [3]. While hydrogen is fully dissociated and ionized in the core of a fusion plasma, hydrogen molecules were detected in the cooler parts close to reactor surfaces, such as the divertor region. These molecules are formed in rovibrationally excited states by association processes at surfaces [4–8] and can influence the condition and the stability of a fusion plasma [9,10].

Hydrogen containing plasmas are also widely used in applications such as the deposition of ultrahard diamondlike films or amorphous-microcrystalline silicon layers in solar cell production [11–13]. Hydrogen atoms are important for the formation of deposition precursors from injected monomers (e.g., SiH₂ from SiH₄) within the plasma gas phase, while on plasma facing surfaces hydrogen determines the surface chemistry, e.g., crystallization processes resulting in the formation of diamondlike structures [14].

Important parameters for plasma gas phase characterization are the densities of reactive species, such as ions and radicals, and their energies. These energies are kinetic energies as well as energies due to internal excitation. The internal excitation can be electronically, and, in case of molecules, due to vibration and rotation. Although the influence of rovibrationally excited molecules on the plasma gas phase and surface chemistry has been predicted, it is still a rather unexplored research field. For example, inelastic electron collisions are substantially enhanced if the molecules are rovibrationally excited [15]. Until now, descriptions and computational simulations of molecular plasmas often include a vibrational excitation, but usually neglect a rotational excitation of molecules [16].

However, it is well known that reaction rates depend on the total internal energy, i.e., on the vibrational state ν as well as the rotational state J of a molecule [17]. For instance, the rate coefficients for dissociative attachment of H₂ by inelastic electron collisions (H₂+e−→H⁺+H) are enhanced for vibrationally excited H₂ [18–21]. On the other hand, recent reports have revealed that dissociative attachment cross sections are enhanced by several orders of magnitude, if H₂ is in a rotationally excited state (ν,J)=(0,30) compared to the rovibrational ground state (0,0) [22]. Therefore, this enhancement by rotational excitation is of great relevance for the H₂ plasma chemistry.

Both, laboratory experiments and computational simulations, have demonstrated that hydrogen molecules can be formed by surface association processes, and that the released H₂ molecules are rovibrationally excited [23–27]. The excitation level of the product depends on the surface material and temperature. The products can be highly rotationally excited, while the distribution of their internal energies is far away from thermodynamic equilibrium [28].

Furthermore, surface interaction of hydrogen containing plasmas is a more general phenomenon. While the flux of hydrogen atoms and ions towards surfaces is very large in fusion experiments (10²²–10²⁴ m⁻² s⁻¹), the other extreme of the scale are very low flow conditions in interstellar media. There, molecules are formed by surface association on cold dust grains [29–31]. The interaction of hydrogen atoms with these surfaces is the dominant molecule formation process, where gas phase reactions play only a minor role due to low densities and low gas phase recombination cross sections. The flux conditions in our experiments are between these two extremes, i.e., a few orders lower than in fusion experiments, but still high compared to other experiments.
A common way to measure excited H₂ molecules is optical emission spectroscopy on the H₂ Fulcher band [5–8,32,33]. However, detailed knowledge of the excitation mechanisms is necessary to obtain electronic ground state \((X^1Σ_g^+)\) densities. Direct spectroscopic detection of H₂ molecules in the \(X^1Σ_g^+\) state is challenging, because transitions within this state are dipole forbidden and the energy gap to the first excited electronic state \(B^3Σ_u^+\) is large (\(\approx 10\) eV), i.e., these so-called Lyman transitions occur in the vacuum ultra-violet (vuv) spectral range. Various tunable vuv sources have been applied to H₂(\(v,J\)) detection [34–37]. Lower rovibrational states \((v = 2\) are detectable by means of coherent anti-Stokes Raman spectroscopy (CARS) [38–42], while stimulated anti-Stokes Raman scattering (SARS) has been applied successfully for the detection of higher rovibrational states with excellent sensitivity [43–48].

In this paper we report on the influence of surface collisions in a cascaded arc, i.e., in a thermal plasma source, on the distributions of rovibrationally excited H₂ molecules. An effect on the formation of rovibrationally excited H₂ in its electronic ground state is revealed by exposing surfaces to plasma under high flow conditions towards cooled copper surfaces with different areas. While the internal energy distributions of H₂ molecules are measured by means of SARS, additional measurements of the H atom densities by two-photon absorption laser-induced fluorescence (TALIF) indicate a fast formation of H₂ molecules by surface association.

II. EXPERIMENT

The plasma source has been described in detail elsewhere [49,50], and only a brief description is given here. Hydrogen gas flows with a flow rate of \(3000\) sccm \((1.25 \times 10^{21}\) s\(^{-1}\) \) under subatmospheric pressure of about \(9\) kPa into the plasma source, a wall-stabilized cascaded arc. The arc channel is \(4\) cm long with a diameter of \(4\) mm, a wall-stabilized cascaded arc. The arc channel undergoes a transition to subsonic flow formed downstream of the nozzle, where the plasma expansion occurs. Additional measurements of the H atom densities by two-photon absorption laser-induced fluorescence (TALIF) indicate a fast formation of H₂ molecules by surface association.

![FIG. 1. The plasma source, a cascaded arc, operated with nozzles of three different lengths. At the bottom is shown a scheme of the assumed processes within arc channel and nozzles.](image1.png)

![FIG. 2. The setup with the laser and anti-Stokes beam paths within the vuv spectrometer and the vacuum chamber (M, mirror; L, lens; BS, beam splitter; W, MgF₂ window; S, slit; PMT, photomultiplier tube).](image2.png)
in contact with the plasma after it left the arc channel. The AS beam focus as well as the laser focus for TALIF are positioned in the center of the expanding plasma jet 8 mm downstream of the nozzle exit, but still before the position \( z_M \) of the expansion shock front, which is given by

\[
z_M = 0.02 \sqrt{\frac{\Phi}{P_{\text{back}}} T_{\text{exit}}} A \text{ (in m)}
\]

with the gas flow \( \Phi \) in scs (standard cubic centimeter per second), background pressure \( P_{\text{back}} \), the mass \( A \) in amu, and the exit temperature \( T_{\text{exit}} \) in eV [55]. The exit temperature, as it will be shown later, depends on the nozzle length, and varies from 0.36 eV to 0.42 eV resulting for our conditions in shock positions between 13.0 mm and 13.5 mm. Therefore, all measurements are performed within the supersonic plasma expansion.

III. MEASURED AND SIMULATED \( \text{H}_2 \) DENSITY DISTRIBUTIONS

State densities of rovibrationally excited \( \text{H}_2 \) molecules measured with nozzles of three different lengths are shown in Fig. 4. The lines in the figures represent a model for the \( \text{H}_2(v,J) \) distribution that was used in the spectra calculation and that was fitted to the measured spectra. The points in the figures represent densities obtained from the integrated area under pronounced peaks in the measured spectra.

The model for the \( \text{H}_2 \) density distribution is a superposition of two different Boltzmann distributions of the vibrational states. Lower rotational states (\( J<7 \)) of each vibrational state follow a Boltzmann distribution described by a temperature of 700 K, i.e., close to the temperature of the gas in the background of the vacuum chamber. On the other hand, the higher rotational states follow a Boltzmann-like distribution with a much higher temperature between 2900 K and 4500 K. The distribution of the vibrational states can also be described by this temperature. Therefore, we will call this temperature \( T_{\text{vib}} \), although one should be aware of the fact that the term “temperature” may be inappropriate in case of non-Boltzmann distributions. Similar distributions were measured also by others and in other types of hydrogen discharges (see [56–58], and references therein). A special case is the first vibrational state (\( v=0 \)), for which the first rotational states have been reported in [41] to have a factor of 20 higher densities than expected from the trend in the higher vibrational states. This is probably due to mixing of the hot gas from the plasma source with the cool background gas, which populates the first rotational states of the \( v=0 \) state.

We want to emphasize the high rotational excitation we found for some of the excited \( \text{H}_2 \) molecules. Rotational excitation levels higher than \( J=20 \) were found in case of the short nozzles (6 mm and 16 mm), while for the long nozzle (30 mm) the densities of higher rovibrationally excited \( \text{H}_2 \) molecules were below the detection limit. The highest rovibrational excitations are only a few 0.1 eV below the dissociation limit at 4.5 eV.

While the SARS technique results in relative values for the density distribution of internal \( \text{H}_2 \) states, absolute \( \text{H}_2 \)
state densities are derived by comparison with the total H$_2$ density measured by means of Rayleigh scattering in a previous work [59]. By using a 16 mm long nozzle and the same process conditions as in the present work, the H$_2$ density was found to be 3.0 \times 10^{21} m^{-3} at a position 8 mm in front of the nozzle exit. For the nozzles with lengths of 6 mm and 30 mm the total H$_2$ densities were derived by comparison with this reference point. This results in total H$_2$ densities of 1.5 \times 10^{21} m^{-3} and 3.0 \times 10^{21} m^{-3} for the 6 mm and the 30 mm nozzle, respectively. The relative error of these densities is in the order of 50% due to power fluctuations of the AS beams.

### IV. MEASURED H ATOM DENSITIES

H atom densities measured by means of TALIF at the same position in the plasma jet are shown in Fig. 5. These values are in agreement with previous measurements performed with nozzle lengths of 6 mm and 16 mm [60], while we give here an additional result for the 30 mm nozzle. The values are summarized in Table I. Also given in the table are the total densities in the jet. Since the densities of ions, electrons, and electronically excited H atoms and H$_2$ molecules are orders of magnitude lower than ground-state atom and molecule densities, we neglect these species.

The dissociation degree, $n_{H} / (n_{H} + 2n_{H_2})$, was calculated for all three experiments (see Table I). Using the short nozzle (6 mm) the dissociation degree is around 50%, a value close to the dissociation degree inside the arc channel [41]. With the 16 mm nozzle we obtain a value of 10%, that was reported also in [59]. On the other hand, using the longest nozzle of 30 mm length, the dissociation degree is less than 1%. This clearly indicates a strong loss mechanism of H atoms inside the nozzle channel (see Sec. VI).

### V. TEMPERATURES INSIDE THE NOZZLE AND IN THE PLASMA EXPANSION

The kinetic gas temperatures have been calculated from the linewidths of the measured H$_2$ (vuv-LIF) and H (TALIF)....

**TABLE I.** Summary of H$_2$ and H densities measured 8 mm in front of the nozzle and the corresponding dissociation degree.

<table>
<thead>
<tr>
<th>Nozzle length</th>
<th>Total density (m$^{-3}$)</th>
<th>H$_2$ density (m$^{-3}$)</th>
<th>H density (m$^{-3}$)</th>
<th>Dissociation degree (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6 mm</td>
<td>4.7 \times 10^{21}</td>
<td>1.5 \times 10^{21}</td>
<td>3.2 \times 10^{21}</td>
<td>51.6</td>
</tr>
<tr>
<td>16 mm</td>
<td>3.6 \times 10^{21}</td>
<td>3.0 \times 10^{21}</td>
<td>6.2 \times 10^{20}</td>
<td>9.4</td>
</tr>
<tr>
<td>30 mm</td>
<td>3.0 \times 10^{21}</td>
<td>3.0 \times 10^{21}</td>
<td>4.3 \times 10^{19}</td>
<td>0.6</td>
</tr>
</tbody>
</table>
line profiles. They are listed for the axial position $z=8$ mm in Table II together with the vibrational $H_2$ temperatures at the same position derived from the distributions in Fig. 4. While $T_{\text{kin}}$ is comparable for both, $H_2$ molecules and $H$ atoms, the values for $T_{\text{vib}}$ of $H_2$ are about 4 times higher. Therefore, the plasma is far off from thermodynamic equilibrium. There are much more high rovibrationally excited $H_2$ molecules as one would expect from the kinetic temperature, indicating a strong production of these high excited molecules, e.g., due to surface association processes. However, the kinetic temperature is determined due to the Doppler shift in the direction of the laser beam path. Therefore, we measured the kinetic temperatures perpendicular to the direction of the expansion. It is well known from earlier measurements \cite{61,62} and theory \cite{63} that the parallel temperature stays constant at a value higher than the perpendicular temperature, while the perpendicular temperature decays in the expansion due to adiabatic cooling.

 Apparently, the kinetic temperature as well as the vibrational temperature decay with increasing nozzle length due to a heat flow from the plasma towards the water cooled nozzles. Since densities and temperatures were measured downstream of the nozzles at $z=8$ mm, the question arises, whether this also gives information about the conditions and developments inside the nozzles. We calculated the temperature at the nozzle exit using the well-known temperature development at the center axis of an expanding hot gas and/or plasma,

$$T(z) = \frac{T_{\text{exit}}}{(1 + z^2/z_0^2)^{\gamma/2}},$$

where $\gamma$ is the adiabatic index (heat capacity ratio), $z$ is the distance from the nozzle, and $z_0$ is introduced to take into account that the expansion starts already inside the nozzle, i.e., slightly before the nozzle exit. For a straight nozzle, $z_0$ is in the order of the nozzle radius (here, 2 mm). The adiabatic index $\gamma$ would be 1.3 for a pure molecular $H_2$ gas at these temperatures, but we use 1.7, a value that was found for $H_2$/H containing hydrogen hot plasma expansions in [51].

With Eq. (2) the exit temperatures were found to be 4700 K, 3650 K, and 2450 K for the 6 mm, 16 mm, and 30 mm nozzle length, respectively. These values are very close to the vibrational temperatures of the molecules (see Table II), which indicates that $T_{\text{vib}}$ and $T_{\text{kin}}$ are in equilibrium, if we assume that the vibrational temperature does not change between the nozzle exit and $z=8$ mm in the expansion. Such a relaxation behavior of rovibrationally excited $H_2$ molecules was investigated previously [57]. It was found that the decay rate of a rotational state increases with the rotational number until $J=7$, but stays constant for higher rotational states [57]. Therefore, the vibrational temperature “freezes” and stays constant during the gas phase expansion.

On the other hand, the vibrational temperatures, given by the distributions in Fig. 4, decrease with increasing nozzle lengths. The hydrogen plasma is not only cooled inside the nozzles, but the shapes of the distributions change and become more non-Boltzmann-like with increasing nozzle length. The higher rotational states ($J>6$) are faster depopulated than the lower states.

Within the gas phase only molecule-molecule and, less important due to lower atom densities, molecule-atom collisions contribute to the redistribution of the internal energies of $H_2$ molecules [41,57,64,65]. The situation inside the nozzles is different. There, the internal energies of $H_2$ are redistributed not only by gas phase reactions and collisions, but also by molecule-surface collisions and the production of rovibrationally excited $H_2$ due to surface association [25–27]. Wall cooling was also found to be the dominant cooling mechanism in a recombining plasma [66], as well as for rovibrationally excited $H_2$ produced on a heated filament [42]. In [67] it was shown that by surface collisions an internal (rotational) energy of $H_2$ can be converted even into translational energy. However, the exact nature of the cooling processes inside the nozzles remains unknown and further investigations are necessary.

For a description of the processes inside the nozzles we need to know the development of the temperature. We assume that the temperature inside the nozzles follow an exponential decay,

$$T(z) = T_0 e^{-z/z_{\text{temp}}},$$

where $T_0$ is the temperature at the end of the arc and $z_{\text{temp}}$ is the distance at which the temperature declines by 1/e. Both parameters are assumed to be the constant for all three types of nozzles. Their values were fitted to match the values for the temperatures at the nozzle exits and result in $T_0 = 5500$ K (0.45 eV) and $z_{\text{temp}} = 37$ mm.

The resulting temperature developments inside and outside the nozzles are shown in Fig. 6. The exit temperature depends on the nozzle length and influences the exit velocity $c_0 = \sqrt{2k_B T_{\text{exit}}/m}$, which is 5700 m/s for the 6 mm nozzle, 5000 m/s for the 16 mm nozzle, and 4100 m/s for the 30 mm nozzle.

VI. SURFACE ASSOCIATION AT THE NOZZLE SURFACE

The loss of hydrogen atoms inside the nozzle depends on the nozzle length as shown in Table I. Several possible mechanisms for the loss of H atoms inside the nozzle are discussed in [60]. Volume loss due to three-body recombination of H atoms is very unlikely under our conditions, since its time constant is around 2 ms inside the arc channel, because the maximal densities are in the order of $10^{22}$ m$^{-3}$ and the rate coefficient is $5\times10^{-44}$ m$^3$s$^{-1}$ [60]. On the other hand, flow velocities around 5000 m/s result in a residence time of only 2 $\mu$s in a nozzle of 10 mm length.
Surface association of H atoms forming H2 molecules is supposed to be the most probable process. Similar to the discussion of the temperature development in Sec. V the density \(n_{\text{ext}}\) of H atoms at the nozzle exit was calculated using the known decay in the plasma expansion [55,68],

\[
n(z) = \frac{n_{\text{ext}}C_0}{z^2 + z_0^2},
\]

where \(z_0\) is again in the order of the nozzle radius, see Eq. (2). The resulting H densities at the nozzle exits are summarized in Table III.

In a next step we will give an estimate of the surface reaction probability of H atoms on the nozzle surface, i.e., the cooled copper material. Therefore, we assume a viscous flow, which is reasonable since the mean free path \(\lambda_{\text{mfp}}\) is two orders of magnitude lower than the nozzle dimensions (4 mm) under our conditions. The mean free path is calculated using a hard sphere model with an effective collision area of \(3 \times 10^{-14} \text{m}^2\) [69] and a typical density of \(10^2 \text{ m}^{-3}\). This results in \(\lambda_{\text{mfp}} = 0.03 \text{ mm}\).

The loss of H atoms due to diffusion to H atoms towards the surface of the nozzle and with a surface reaction probability \(\alpha\) is given for a cylindrical geometry by

\[
\frac{1}{K_{\text{wall}}} = \tau = \frac{\lambda_0^2}{D} + \frac{V}{A} \frac{2(2-\alpha)}{\bar{v} \alpha},
\]

where \(\lambda_0\) is the diffusion length, \(D\) is the diffusion coefficient, \(\bar{v}\) is the mean kinetic velocity, \(\tau\) is the lifetime of H atoms, and \(V/A\) is the volume-to-surface area ratio [70,71].

**TABLE III.** Temperatures and H and H2 densities at the nozzle exits.

<table>
<thead>
<tr>
<th>Nozzle length</th>
<th>(T_{\text{exit}}) (K)</th>
<th>([H]_{\text{exit}}) (m(^{-3}))</th>
<th>([H_2]_{\text{exit}}) (m(^{-3}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>6 mm</td>
<td>4700</td>
<td>(3.3 \times 10^{22})</td>
<td>(2.9 \times 10^{22})</td>
</tr>
<tr>
<td>16 mm</td>
<td>3650</td>
<td>(9.5 \times 10^{21})</td>
<td>(7.2 \times 10^{22})</td>
</tr>
<tr>
<td>30 mm</td>
<td>2450</td>
<td>(5.8 \times 10^{20})</td>
<td>(1.3 \times 10^{21})</td>
</tr>
</tbody>
</table>

The measured \(\lambda_{\text{mfp}}\) for the three different nozzles are \(7.6 \times 10^{-3} \text{ m}\) (6 mm nozzle), \(8.2 \times 10^{-4} \text{ m}\) (16 mm nozzle) and \(8.3 \times 10^{-4} \text{ m}\) (30 mm nozzle), again assuming a cylinder [70]. The diffusion coefficient is \(D = \frac{3}{5} \bar{v} \lambda_{\text{mfp}} = 0.3 \text{ m}^2 \text{s}^{-1}\), while the mean kinetic velocity is \(\bar{v} = \sqrt{\frac{k_B T}{m}}\) \(= 10^4 \text{ m/s}\), and \(V/A\) is \(10^{-3} \text{ m}\) for all three nozzles.

The development of \(\lambda_{\text{mfp}}\), \(D\) and \(\bar{v}\), and thus with Eq. (5) the loss rate \(k_{\text{wall}}\) of hydrogen atoms, were calculated at each position within the nozzles. While pressure and temperature determine the total density at each position, the H atom loss rate \(k_{\text{wall}}\) changes the ratio between \(n_{H_2}\) and \(n_H\). Here, we assume that the surface reaction probability \(\alpha\) in Eq. (5) lead to a loss of H atoms and the formation of H\(_2\) by surface association. Surface sticking, reflection, and desorption of H atoms are neglected, because these mechanisms do not change the H density within the nozzles under steady-state conditions.

Free parameters in this simple model are the dissociation degree in the arc, i.e., the values of \(n_{H_2}\) and \(n_H\) at the start of the nozzles, and the surface reaction probability \(\alpha\). We found that only a dissociation degree of 0.99 (almost fully dissociated hydrogen plasma) and a surface reaction probability of \(\alpha = 0.32\) lead to H and H\(_2\) densities as they are summarized in Table III. The resulting developments of the H and H\(_2\) densities inside and outside the nozzles are shown in Fig. 7.

Although we found strong losses of H atoms inside the nozzles due to surface association, the predicted formation of high rovibrationally excited H\(_2\) molecules [25–27] is not visible in the distributions shown in Fig. 4. The reason is the redistribution of the internal energy of H\(_2\) due to molecule collisions with the cooled copper surface of the nozzles and molecule-molecule collisions within the gas phase. Therefore, the decay of the vibrational and rotational temperatures is stronger than the production of high rovibrationally excited H\(_2\), and thus this production is not directly measurable.

The measured H and H\(_2\) densities are reproduced well in the model with a mean relative error of 24%. The main contribution to this error is the difference in the density of H\(_2\) for the 30 mm nozzle, which is probably due to the rather large relative error of the H\(_2\) densities measured by SARS. Without this data point the relative error is only 13%. We also calculated the dependence of this relative error on the fit parameters \(\alpha\) and the dissociation degree. The result is shown in Fig. 8. Clearly visible are the minima at the mentioned values.

The value for \(\alpha\) is in the same order of magnitude found by others, which is e.g., 0.5 for H/D association on Cu(111) surfaces [25]. However, these experiments were performed with low atomic fluxes on a cleaned and well-defined Cu surface that was cooled to 100 K and was fully covered with H/D atoms. On the other hand, the surface inside the nozzle...
in our experiments is much hotter and exposed to an enormous heat flux and particle flow. In this respect, the similarity in the results is astonishing.

VII. CONCLUSIONS

Distributions of the internal energy of rovibrationally excited H₂ molecules have been measured by vuv-LIF in an expanding thermal H₂ plasma, using stimulated anti-Stokes Raman scattering (SARS) for the production of the vuv radiation. The H₂(ν, J) distributions differ from a Boltzmann distribution and depend strongly on the exposure time of the hot gas to a cooled copper surface. The relaxation of excited H₂ molecules due to surface collisions is faster than the relaxation in the gas phase found in earlier experiments. The temperatures are the lower the longer the gas-surface interaction lasts. TALIF measurements of H atom densities using nozzles of various lengths reveal a strong H atom loss depending on the surface exposure time inside the nozzles, in agreement with increasing H₂ densities. A high surface association rate was found for H atoms on cooled copper surfaces. The association rate is close to values found by others, although our copper surfaces were much hotter.

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