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Relaxation behavior of rovibrationally excited H_2 in a rarefied expansion

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The evolution of the rotational and vibrational distributions of molecular hydrogen in a hydrogen plasma expansion is measured using laser induced fluorescence in the vacuum-UV range. The evolution of the distributions along the expansion axis shows the relaxation of the molecular hydrogen from the high temperature in the upstream region to the low ambient temperature in the downstream region. During the relaxation, the vibrational distribution, which has been recorded up to $v=6$, is almost frozen in the expansion and resembles a Boltzmann distribution at $T \approx 2200$ K. However, the rotational distributions, which have been recorded up to $J=17$ in $v=2$ and up to $J=11$ in $v=3$, cannot be described with a single Boltzmann distribution. In the course of the expansion, the lower rotational levels ($J < 5$) adapt quickly to the ambient temperature (≈ 500 K), while the distribution of the higher rotational levels ($J > 7$) is measured to be frozen in the expansion at a temperature between 2000 and 2500 K. A model based on rotation-translation energy transfer is used to describe the evolution of the rotational distribution of vibrational level $v=2$ in the plasma expansion. The behavior of the low rotational levels ($J < 5$) is described satisfactory. However, the densities of the higher rotational levels decay faster than predicted. © 2004 American Institute of Physics. [DOI: 10.1063/1.1807819]

I. INTRODUCTION

Relaxation of molecular rotation and vibration has attracted the attention of scientists for a long time, first of all, because it provides more insight into the fundamental behavior of rotation and vibration of molecules and also because of the nonequilibrium processes involved. The subject has been extensively studied theoretically. These theoretical studies are mainly aimed at determining cross sections or rate constants for rovibrational energy transfer in collisions. Both quasiclassical and quantum mechanical calculations have been performed to calculate the energy transfer of rotation,^{1,2} vibration,^{3–6} and rovibration.^{7,8}

However, the number of experimental studies of relaxation phenomena in H_2 is limited. The vibrational energy relaxation $v=1 \rightarrow 0$ has been measured by Kiefer and Lutz,⁹ Audibert *et al.*,^{10,11} and Dove and Teitelbaum¹² [reaction rate $k(v=1 \rightarrow 0) \sim 10^{-21} \text{ m}^3 \text{ s}^{-1}$ at 500 K]. More recently Kreutz *et al.*¹³ measured the vibrational energy relaxation of the $v=2$ state. However, all of these studies concerned the relaxation of the vibrational levels as a whole. The behavior of the individual rotational quantum levels was not considered. Rabitz and Lam,¹⁴ Gallagher and Fenn,¹⁵ and Meier, Ahlers, and Zacharias¹⁶ did study the rotational energy relaxation, but Rabitz and Lam, and Gallagher and Fenn only up to the $J=6$ level of the vibrational ground state in the work of Rabitz and Lam, and Gallagher and Fenn [$k(J=2 \rightarrow 0) \sim 5 \times 10^{-18} \text{ m}^3 \text{ s}^{-1}$ at 500 K] and only the relaxation of the $H_2(v=1, J=1)$ level in the work of Meier, Ahler, and Zacharias. Studies of the relaxation of higher rotational levels

with internal energies comparable to low rotational levels of the next vibrational state have not been reported yet, and neither have studies of the relaxation of rotational levels in vibrationally excited states other than $H_2(v=1, J=1)$. Such studies would enable experimental access to state-to-state reaction rates. In this paper, we will present an experimental study on the relaxation behavior of individual rotational levels, from low rotational levels to very high rotational levels in several vibrational states, that can finally lead to rotationally specific reaction rates.

The state-to-state reaction rates are, for example, important in negative hydrogen ion sources.^{17–20} In such sources rovibrationally excited hydrogen plays a key role, since the negative hydrogen ions is formed in the dissociative attachment (DA) reaction. And this reaction becomes five orders of magnitude more efficient when the rovibrational energy of the hydrogen molecule is increased to around 2.5 eV.^{21,22} Since in the plasmas used for the production of the H^- ion, the high rotational levels are usually enormously overpopulated,^{17,23–25} these high rotational levels play an important role in the production of the negative hydrogen ion. Knowledge of the behavior of the high rotational levels is therefore required.

Further interest can be found in the field of thin film deposition. In this field, for example, in the case of diamond deposition, often hydrogen plasmas are used.²⁶ To understand and improve the deposition processes a good understanding of the chemical kinetics is required. For a realistic description of processes such as dissociation, ionization, and dissociative attachment not only the ground state species should be considered but also the vibrationally and rotationally excited species.²⁷ Therefore vibrational and rotational

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population distributions are required and as well as knowledge of their relaxation behavior.

Also of interest are environments that are proton rich but have relatively low density. Examples of such environments are the outer regions of fusion plasmas and hydrogen plasma expansions. In such environments an important loss factor of protons is the charge exchange reaction with H_2 .^{28,29} This endothermic reaction is also greatly enhanced by internal energy of the H_2 molecule. These molecules are furthermore formed at the surfaces surrounding the plasma and have considerable internal energy in the form of rotation and vibration when leaving the surface. Again, knowledge of the behavior of the H_2^{IV} molecules is important.

Experimentally studying relaxation behavior, requires measurements of the rotational and vibrational populations. The most suited techniques are laser-based methods, because of their state-selective character. For hydrogen, proven techniques are coherent anti-Stokes Raman scattering (CARS),^{17,30} and the laser Schlieren technique.^{9,11,12} Due to the relatively high detection limits these techniques are limited to the lower vibrational states and to the lower rotational levels of these lower vibrational states. Furthermore the spatial resolution, in the case of CARS, is often limited, even in BOXCARS mode,³⁰ in which a crossed-beam arrangement is used. An advantage is the possibility of an absolute calibration. Alternative techniques to measure rotational and vibrational populations of molecular hydrogen are absorption spectroscopy^{23,24} and laser induced fluorescence (LIF).^{25,31} In the case of molecular hydrogen, the disadvantage of these techniques is that light in the vacuum-UV part of the spectrum has to be used. But, the advantage in the case of LIF is the high sensitivity of the technique. In the present case a detection limit of a few times 10^{13} m^{-3} was reached, which is several orders of magnitude better than 10^{17} m^{-3} reached with CARS.³⁰ Furthermore, the LIF method has the advantage of an excellent spatial resolution.

A well suited system to study relaxation is an expansion. In an expansion highly non-equilibrium conditions are encountered. The temperature, for example, undergoes drastic changes leading to large temperature gradients. The way the molecules react to the temperature gradients characterizes the relaxation of rotational and vibrational energy. In addition, the particles have a main velocity component along the expansion axis. So by recording the density distribution of the rovibrational energy levels as a function of the position along the expansion axis, the time dependent behavior of the relaxation of the rotational and vibrational energy can be studied.

The expansion, discussed in this paper, is a rarefied plasma expansion. The H_2^{IV} is most probably created in the nozzle of the source at the nozzle surface via surface recombination of the hydrogen atoms that are highly abundant in the plasma source. Subsequently, the plasma expands into a vacuum chamber. Very efficiently almost all of the ions and electrons are lost via charge exchange and subsequent dissociative recombination. As a consequence production of H_2^{IV} in the expansion via electron processes (e-V and E-V processes) is negligible, which is confirmed by the absence of molecular emission. Therefore, the expansion can be consid-

ered a rarefied gas expansion at an elevated temperature, which initially contains over 20% of rovibrationally excited H_2 and a few percent of hydrogen atoms. This environment proves well suited for the study of relaxation behavior of H_2^{IV} .

The rovibrational population leaving the plasma source^{30,31} shows a remarkable similarity with rovibrational distributions measured in other plasma environments.^{17,23-25} The higher rotational levels ($J \geq 5$) in all of the aforementioned studies are overpopulated, usually even by orders of magnitude. Although the measurements are performed in different experiments, under very different experimental conditions (pressure, temperature, electron density, and electron temperature) the distributions are stunningly similar. The mentioned distributions also compare well with rovibrational distributions of H_2 produced in surface recombination studies.³²⁻³⁴ In these studies the high rotational levels are also overpopulated, which may point to surface recombination as an important production mechanism for the H_2^{IV} in plasma environments.

In this paper rotational and vibrational distributions of hydrogen in a plasma expansion will be presented. Rotational levels up to $J = 17$ will be shown and vibrational levels up to $v = 6$. The rotational distributions will be shown to be non-Boltzmann, and the evolution of the rovibrational distribution in the plasma expansion, in other words the relaxation behavior, will be discussed. A first ansatz has been made to explain the evolution of the rovibrational distribution using a master-equation type model based on rotational-translational (R-T) energy transfer.

II. EXPERIMENT

The experiment to measure the rovibrationally excited H_2 in the plasma expansion facility³⁵ is presented in detail in a preceding paper³¹ and will be briefly described in the following section.

A. Plasma source

The rovibrationally excited hydrogen H_2^{IV} is studied in a hydrogen plasma, which is created in the plasma source, a high current cascaded arc. The arc channel with a diameter of 4 mm and a length of 50 mm is formed by the central holes in four insulated cascade plates. The plasma is created by a dc current ($\sim 60 \text{ A}$, 9 kW) in hydrogen gas flowing through the channel with three standard liters per minute (slm). The arc channel is connected to a vacuum vessel via a nozzle with a constant diameter of 4 mm. The pressure in the source is $\sim 13 \text{ kPa}$ and in the vessel the pressure is kept at constant values ranging from 20 to 100 Pa. The expansion from the plasma source into the vacuum vessel is depicted schematically in Fig. 1.

In the cascaded arc the plasma is ionizing and the ionization degree is estimated to be 2%–3%. The dissociation degree is estimated between 50% and 100%. When the power input ends, i.e., at the beginning of the copper nozzle, the plasma becomes recombining and the plasma gets in contact with the nozzle surface. Surface recombination at this nozzle surface decreases the dissociation degree by over one order of magnitude. This surface recombination of hydrogen

FIG. 1. Schematic representation of the arc source, the vacuum vessel and the rarefied plasma expansion.

atoms leads to the very efficient production of rovibrationally excited hydrogen molecules, as was already observed by others.^{36,37} It also reduces the amount of hydrogen atoms leaving the plasma source. Moreover, the H^+ ions in the recombining plasma undergo charge exchange with H_2 forming H_2^+ and H_3^+ . These ions recombine very rapidly, leading to a decrease of the ionization degree in the nozzle and the first few millimeters of the expansion of several orders of magnitude. This results in an ionization degree of well below 10^{-5} .

B. Rarefied expansion

Due to the large pressure difference between the plasma source and the vacuum vessel, the hydrogen plasma expands supersonically into the vacuum chamber, as is depicted in Fig. 1. In the first part, the silent zone, the plasma is accelerated, and both temperature and density decrease rapidly. Due to the charge exchange and recombination processes explained in the preceding section, the ionization degree drops drastically. Furthermore, the dissociation degree has dropped below 10%, so that the expansion is that of a hot gas. The plasma expansion has changed into a gas expansion, with this difference that the temperature of the expansion is still high (in the order of 1000 K) and that it contains a considerable amount of H_2^v molecules and still some hydrogen atoms.

After several centimeters a stationary shock wave is formed,³⁸ i.e., the density and temperature increase and the velocity decreases. Behind the Mach disk of the shock structure the flow is subsonic and approximately isobaric. At the sides of the expansion, there are large recirculation flows. This recirculation implies long residence times of the order of 1 s in the vacuum vessel. The remaining hydrogen atoms enter this recirculation flow and collide frequently with the vessel wall, where they associate, forming additional H_2^v molecules. However, the number of these newly formed molecules is too small to be of influence on the number of H_2^v molecules in the expansion flow. The surface recombination does have an effect on the H atom density in the flow as depicted in Fig. 4, where the axial dependence of the H atom density is shown. Due to the surface recombination, the H atom density in the background is lower than in the expansion—the remaining density results from the diffusion

FIG. 2. Schematic representation of the experimental arrangement. In the figure, M stands for mirror, L is a lens, W is a window, S is a slit, BS is a beam splitter, and PD is a photodiode.

of H atoms out of the expanding flow into the background. This effect is extensively described by Mazouffre *et al.*^{39,38}

The collisional mean free path is several millimeters in the subsonic part of the flow. In the shock region the mean free path is even larger, in the order of the size of the expansion structure. In this rarefied flow, the relaxation behavior of H_2^v , which was produced in the nozzle, is studied. Due to the high velocity, the number of collisions in the supersonic part of the flow is too low to have an effect on the relaxation. In other words, apart from the expansion no effect was observed on the H_2^v densities. The relaxation, therefore, takes place mainly in the subsonic part of the flow and only measurements in this region will be discussed.

C. Diagnostical method and optical system

The rovibrational population of the ground state H_2 molecule is measured using LIF on the Lyman band ($X^1\Sigma_g^+ \leftrightarrow B^1\Sigma_u^+$). The hydrogen molecule is excited to the B state using a laser in the vacuum-UV range, i.e., with wavelength between 120 and 160 nm. Since such laser systems are not available, these short wavelengths are obtained by frequency shifting via a Raman gain process called stimulated anti-Stokes Raman scattering (SARS).⁴⁰ The experimental setup is shown schematically in Fig. 2. A frequency-tripled Nd:YAG (yttrium aluminum garnet) laser is used to pump a dye laser. The output beam with wavelength between 430 and 470 nm is frequency doubled in a BBO crystal resulting in 8 ns pulses of up to 12 mJ between 215 and 235 nm. This laser beam is focused into a Raman cell filled with 1.2 bar of hydrogen at 77 K. In the cell the SARS process takes place, and up to ten so-called anti-Stokes (AS) beams are produced, of which each beam is subsequently shifted up in frequency by 4155.19 cm^{-1} . Using the SARS process, tunable, narrow band laser radiation can now be produced in the range between 50 000 and 85 000 cm^{-1} . All of the produced AS beams are focused into the detection volume at the same time. The induced fluorescence is imaged onto a slit

FIG. 3. A typical measurement. The upper signal is a part of the m-LIF spectrum of rovibrationally H_2 . Of several transitions the lower level is indicated. Note the dynamic range of the spectrum in the inset. The middle graph is the interference signal of the Fabry-Pérot etalon, and the lower signal is the TALIF spectrum of nitric oxide. The frequency is expressed in terms of the doubled beam of the dye laser.

mask of $1 \times 0.5 \text{ mm}^2$ and is detected by an electronically gated photomultiplier tube (PMT). The combination of the size of the slit mask and the laser beam waist result in a detection volume of 2.10^{-10} m^3 . The fluorescence signal is corrected for the power of the anti-Stokes, used for the excitation. The AS power is measured by splitting of part of the laser beams immediately after the Raman cell and selecting the correct anti-Stokes by a monochromator. The resulting AS beam is attenuated and the power is measured by a PMT.

When the wavelength of the dye laser is scanned, all the AS beams are scanned simultaneously and can excite the H_2 molecules. The LIF spectrum is therefore the addition of the LIF spectra that arise from the excitation of the hydrogen molecules by the individual anti-Stokes. This technique is called multiplexed-LIF (m-LIF).³¹ It increases the peak density in the spectra, thus increasing the amount of obtained information. However to identify the peaks in the spectra, the wavelength has to be known accurately. This is achieved by both linearizing the wavelength scale and calibrating the wavelength absolutely. To linearize the wavelength scale, part of the remnant dye laser fundamental beam led through a Fabry-Pérot etalon. The resulting fringe pattern is used to linearize the wavelength scale. Another part of the remnant dye laser fundamental beam is used to excite nitric oxide in a reference cell via a two-photon transition of the γ band. The resulting two-photon absorption laser induced fluorescence (TALIF) spectrum is well known from literature,⁴¹ and can be used to calibrate the wavelength absolutely. In Fig. 3 a typical measurement is depicted, showing part of the m-LIF spectrum of H_2^{ν} , the interference signal of the Fabry-Pérot and the TALIF signal of nitric oxide as function of the frequency of the doubled dye laser beam. In the inset of the

H_2^{ν} spectrum a part of the spectrum is enlarged to show the dynamic range within a scan. Spatially resolved measurements are performed by moving the plasma source with respect to the laser excitation and observation zone.

D. H_2^{ν} densities

To determine the densities of rovibrationally excited hydrogen molecules, excitation spectra have been recorded in the wavelength range between 115 and 145 nm. The spectra have been corrected for the excitation efficiency (Einstein coefficient, laser energy, and transmission through the optics in the excitation branch) and for the wavelength dependent detection efficiency (window transmission, mirror reflectivity, and quantum efficiency of the PMT). The latter three have been individually measured by the manufacturer. This procedure leads to relative densities of hydrogen in the different rovibrational levels. These relative densities have been calibrated using previously performed CARS measurements.³⁰ These measurements show overlap with the presented m-LIF measurements at the $H_2(X)$ ($v=2$, $J=3$) state. Using the m-LIF technique with the present setup, H_2^{ν} levels can now be probed along the rotational and vibrational ladder, having rotational and vibrational energies from around 0.7 eV up to the dissociation limit at 4.5 eV. This means densities can be measured of levels having energies higher than that of the vibrational state $v=1$, and rotational level $J=4$. The lowest densities, that can be detected are in the order of a few times 10^{13} m^{-3} . The error in the relative densities is $\approx 30\%$. The error in the absolute densities is estimated to be around 50%.

To check possible saturation in the LIF measurements, a radiative model has been used. Basically the rate equation, or Bloch equations in this case, has been solved for all the transitions used in the measurements. The model showed that with the laser powers used, no saturation occurs for any of the recorded transitions.

E. Boltzmann distribution

Rotational and vibrational distributions at thermodynamic equilibrium are characterized by a Boltzmann distribution. The relative populations of a rotational Boltzmann distribution at a temperature T_{rot} are given by

$$P_J^{\text{Boltz}} = \frac{1}{Q_{\text{rot}}} g_N (2J+1) \exp(-E_J^{\text{rot}}/kT_{\text{rot}}), \quad (1)$$

where Q_{rot} is the rotational partition function, $2J+1$ is the statistical weight of the rotational level, k is the Boltzmann constant, and E_J^{rot} is the energy of the rotational level. For H_2 the degeneracy of the nuclear spin g_N is given by $2N+1$, where N is the quantum number of the nuclear spin; in this case, $N=0$ for para-hydrogen (even J) and $N=1$ for ortho-hydrogen (odd J). So ortho-hydrogen has three times more statistical weight. In a so-called Boltzmann plot, the density divided by the degeneracy, n/g is plotted semilogarithmically as a function of the energy. For a thermal population, it yields a straight line, of which the slope is inversely proportional to the temperature.

FIG. 4. The axial density distribution of H atoms and of ground state and rovibrationally excited H_2 molecules in a hydrogen plasma expansion. The H_2 densities are measured using Rayleigh scattering and the H atom densities are measured using two-photon absorption laser induced fluorescence. The densities of H_2^v are multiplied by 50. The numbers denote the different regions of the expansion: 1 is the supersonic, undisturbed part, 2 denotes the shock region, and 3 is the subsonic part. The background pressure was 20 Pa.

The measured distributions in this paper will show clear deviations from a Boltzmann distribution. The low detection limit combined with the large dynamic range enable measurements of rotational levels having energies, which are much higher than the energies of the rotational states in the next vibrational level. These high rotational levels exhibit both a high degeneracy (increasing with J to values above 100) and a large energy spacing between the levels, leading to different behavior compared to the lower rotational states. It will show that only the lower rotational levels have a thermal distribution. The higher rotational levels are much higher populated than thermal and exhibit a more vibrational-like behavior.

III. ROTATIONAL RELAXATION BEHAVIOR

To study the behavior and importance of rovibrationally excited H_2 in a plasma jet, H_2^v densities are measured as a function of position in the jet. In Fig. 4 the axial distributions of the density of several rotational levels of $H_2(v=2)$ are plotted together with that of the total H_2 density. The total H_2 density has been measured using Rayleigh scattering of the 230 nm laser. In Fig. 4 the different regions of the expansion have been denoted by numbers. The supersonic expansion is denoted by 1, the stationary shock region by 2, and the subsonic part by 3.

In the supersonic part of the expansion the density of the level $J=1$ decays slower than the densities of higher rotational levels. The rotational distribution tries to adapt to the rapidly decreasing temperature, and therefore there is a redistribution of density over the different rotational levels. The lowest rotational levels ($J=0,1$) gain some extra density in this process. Therefore, in the expansion the $J=1$ level decreases slower than the other rotational levels.

In the subsonic part the behavior of the $H_2(v=2)$ densities deviates substantially from the total H_2 density. The total H_2 density rises slightly, because in the subsonic flow the static pressure is constant and the temperature decreases

FIG. 5. The axial density dependence of several rovibrationally excited H_2 molecules in a hydrogen plasma expansion. The levels $v=2$, $J=1$, 7, 13, and $v=3$, $J=11$ are shown. The background pressure was 20 Pa.

due to heat conduction to the vessel walls. The $H_2(v=2)$ densities, on the other hand, decrease, meaning that the H_2^v loss processes are more efficient than the production processes in this region. Also the behavior of the various rotational levels of $v=2$ differ. The densities of the higher rotational levels decrease more rapidly than the lower ones. This is depicted clearly in Fig. 5. In this figure the rotational levels $J=1$, 7, and 13 of the $v=2$ and the $J=11$ of the $v=3$ are shown. It is clear from the figure that in the $v=2$ the $J=7$ and $J=13$ decrease much faster in the subsonic part than the $J=1$, but the $J=13$ decreases less strong than the $J=7$. This clearly indicates that the relaxation process for H_2 is more complicated than just a Boltzmann distribution with a slope that is quickly adapting to the ambient temperature.

Usually relaxation processes are very fast and complete relaxation occurs within typically ten gas kinetic collisions, but for H_2 the number of gas kinetic collisions needed for rotational relaxation of the lower rotational levels is more in the order of 500. This is related to the energy spacing between the various rotational levels. In most other gases the rotational constant $B < 2 \text{ cm}^{-1}$, whereas for the light H_2 molecule B is 60 cm^{-1} . In addition, the nuclear spin of H_2 prohibits transitions between *ortho*- and *para*-hydrogen, so between even and odd J , giving rise to the rotational selection rule $\Delta J = \pm 2, \pm 4, \dots$. This increases the energy gap for rotational transitions even more. For comparison the typical thermal energy in the subsonic region of the plasma expansion is $kT = 350 \text{ cm}^{-1}$. This is much larger than the rotational energy differences for most gases, but it becomes significantly smaller than the spacing between the levels of *ortho*- and *para*- H_2 (except the spacing between $J=0$ and $J=2$, e.g., $\Delta E_{v=2} = 319 \text{ cm}^{-1}$). Therefore many collisions are needed to adapt even the lower rotational levels ($J < 5$) to the ambient temperature, giving rise to long relaxation times. The relaxation times for higher rotational levels are even much longer. The number of collisions occurring in the subsonic part of the expansion is ~ 200 at a background pressure of 20 Pa. This leads to a relaxation length of $200 \times 2 \text{ mm} = 400 \text{ mm}$. So, by studying the density evolution of the rotational levels in the axial direction, one studies the relaxation as function of the number of collisions.

FIG. 6. The rotational distribution of the vibrational state $v=2$ at several positions along the jet center of a hydrogen plasma expansion. The background pressure was 20 Pa.

Figure 6 is an example of a relaxation process in progress. In this rotational Boltzmann plot, rotational distributions of $H_2(v=2)$ are shown at various positions along the jet centerline of an hydrogen plasma expansion. The background pressure is 20 Pa. For most gases, a decrease in the ambient temperature would result in a steeper slope of the Boltzmann plot within ten collisions, or a few millimeters in the subsonic part of the expansion, since $\Delta E \ll kT$, but not with H_2 . Then it takes much longer, as can be seen in Fig. 6. At 20 mm the distribution is nonthermal, i.e., not a straight line. The lower rotational levels have adapted to the low ambient temperature of around 1250 K, and this temperature decreases in the course of the expansion to 400 K at 400 mm. But the higher rotational levels ($J > 9$) are distributed according to a temperature of 3200 K, irrespective of the position in the plasma expansion. Even after 400 mm, i.e., ≈ 200 collisions, this part of the distribution has the same shape, whereas the absolute density has decreased by ≈ 2 orders of magnitude. Because the energy gap between the rotational levels is very large, the rate coefficients for rotational transitions of these levels are very small, both the excitation to higher levels and deexcitation to lower levels. Therefore the total rate is low, whereas the loss rates for the intermediate and lower levels are higher. This results in a kind of stagnation of the densities in the higher levels, as can be seen in Fig. 6. The levels $J=0-4$ adapt fairly quickly to the ambient temperature, and the levels $J \geq 9$ remain distributed according to the high temperature. The levels $J=5-7$ are intermediate levels and decrease more rapidly than $J=9$. As a result, an inversion can be seen between the levels $J=7$ and 9. This inversion is located at the energy of the next vibrational level (see section IV).

A similar rotational relaxation has been observed for $H_2(v=3)$. In Fig. 7 rotational distributions of $H_2(v=3)$ are shown at various position in a hydrogen plasma expansion, at a background pressure of 100 Pa. At this background pressure the number of collisions per unit of time, i.e., per unit of distance along the z axis, are higher, so the relaxation process is faster; in other words, the population should adapt more quickly to changes in the temperature. This is true for the lower rotational levels relax, which adapt relatively fast.

FIG. 7. The rotational distribution of the vibrational state $v=3$ at several positions along the jet center of a hydrogen plasma expansion. The background pressure was 100 Pa.

At 50 mm they are distributed according to a temperature of around 500 K. But the higher rotational levels, $J \geq 7$, are located on a line representing a much higher temperature of 2200 K. In the course of the subsonic part of the expansion the relative decrease in density of the rotational levels with $J \geq 7$ is approximately the same. This results in a constant shape of the density distribution, while the absolute densities decrease by more than three orders of magnitude. This effect is studied in more detail in the following section, where a master-equation type model based on rotation-translation coupling will be presented. The decrease of the density of the high rotational levels at 100 Pa of the $v=3$ is an order of magnitude higher than the decrease of the high rotational levels at 20 Pa of the $v=2$.

In Fig. 8 some of the measured H_2^{TV} levels are plotted a function of the total internal energy, i.e., rotation + vibration. Since the figure covers the vibrational levels $v=2-6$, it is clear that the stagnation is located at the energy of the next vibrational level. Furthermore it becomes more clear that for both $v=2$ and $v=3$, the high rotational levels are distributed at a temperature in the same order of the vibrational temperature.

FIG. 8. The density per statistical weight of some of the measured H_2^{TV} levels as function of the total internal energy (rotation+vibration) at an axial position of 50 mm and a background pressure of 20 Pa.

IV. ROTATIONAL RELAXATION MODEL

To explain the evolution of the rotational distribution in the plasma expansion, a beginning has been made to model the experimental results. In the model, hot H_2 gas flows from the arc channel into an infinitely large cold background. Two processes are taken into account: (1) inelastic collisions, in which energy is transferred between rotation and translation [R-T (rotational-translational) collisions], and (2) an overall loss in the population of the vibrational level under consideration. For the inelastic collisions only collisions in which $\Delta J = \pm 2$ are taken into account, since larger ΔJ steps are much less efficient.⁷ The model consists of a set of differential equations, or master equations, describing the density evolution of the first 20 rotational levels of $\text{H}_2(v=2)$. The system of master equations is defined as follows:

$$\begin{aligned} w(z) \frac{dn_0}{dz} &= N(n_2 k_{2,0} - n_0 k_{0,2}) - N n_0 k_{vib}, \\ w(z) \frac{dn_1}{dz} &= N(n_3 k_{3,1} - n_1 k_{1,3}) - N n_1 k_{vib}, \\ w(z) \frac{dn_J}{dz} &= N(n_{J+2} k_{J+2,J} + n_{J-2} k_{J-2,J} - n_J k_{J,J+2} \\ &\quad - n_J k_{J,J-2}) - N n_J k_{vib} \quad (2 \leq J \leq 17), \\ w(z) \frac{dn_{18}}{dz} &= N(n_{16} k_{16,18} - n_{18} k_{18,16}) - N n_{18} k_{vib}, \\ w(z) \frac{dn_{19}}{dz} &= N(n_{17} k_{17,19} - n_{19} k_{19,17}) - N n_{19} k_{vib}, \end{aligned} \quad (2)$$

where n_J are the densities of the rotational levels of $\text{H}_2(v=2)$ and $w(z)$ is the axial velocity as a function of the axial position z . This velocity is determined in the TALIF experiments described in Ref. 38. $k_{J,J'}$ is the rate for (de)excitation from rotational level J to level J' in R-T collisions. There have been several calculations to determine these R-T rates. In recent years several groups obtained similar results using semiclassical and quantum mechanical calculations.^{6,7} In this R-T model the rates from Flower and Roueff^{7,8} at 500 K have been used. For the $v=2$ they calculated the $\Delta J = -2$ deexcitation rates for $J=2$ to $J=10$ for both *ortho*- and *para*-hydrogen in collisions with $\text{H}_2(v=0, J=0)$. Up to the level $J=3$ the rates are about constant at a value of $\sim 4 \times 10^{-18} \text{ m}^3 \text{ s}^{-1}$. For the levels $J>3$ these reaction rates decrease exponentially with the $\Delta J = -2$ energy spacing between the levels down to $8.10 \times 10^{-20} \text{ m}^3 \text{ s}^{-1}$. The reaction rates for the rotational levels $J=11-19$ could be determined using an exponential extrapolation.

The main collision partners are assumed to be H_2 molecules in the ($v=0, J=0$) state with the total H_2 density N of $3.6 \times 10^{21} \text{ m}^{-3}$. The reasons for this assumption are as follows. First, the density of particles in the $\text{H}_2(v=0)$ state is much higher than the density of H atoms and the densities in other vibrational states (see Fig. 4), whereas the R-T rates are comparable for both H atoms and H_2 molecules as a collision partner. The contribution to the relaxation by the H atoms and $\text{H}_2(v>0)$ molecules is therefore neglected. And second, the R-T collision rate depends only very weakly on the rota-

FIG. 9. Comparison between experiment and model of the evolution of the rotational distribution of the $v=2$ in the plasma expansion at a background pressure of 20 Pa. The circles represent the experimental data at three positions in the plasma expansion. The lines represent the results from the model, where the experimental data at $z=20$ mm is taken as the initial condition for the model.

tional state of the collision partner.⁷ Therefore, all H_2 molecules are considered collision partner, with the R-T rates for collisions with the $\text{H}_2(v=0, J=0)$ level. So, the assumption of $\text{H}_2(v=0)$ molecules as the main collision partner seems valid.

An extra term $N n_J k_{vib}$ has been added to the rate equations of all the levels to account for the total loss in the $v=2$. This loss is assumed to be the vibrational depopulation of $v=2$, so mainly the V-V and V-T processes. The rate is assumed to be $k_{vib} = 2 \times 10^{-19} \text{ m}^3 \text{ s}^{-1}$ for all of the rotational levels. This value is about a factor of 5 higher than the value reported in literature,³ but fits our data better.

Starting from the measured rotational distribution of the $v=2$ at $z=20$ mm, the model is used to describe the evolution of the rotational distribution in the expansion. Therefore, the measured rotational distribution of the $v=2$ at $z=20$ mm is taken as the initial condition for the model. In Fig. 9 the distributions at $z=100$ and 400 mm, as predicted by the model, are compared with the measured distributions. At $z=100$ mm the model predicts only a very minor change, compared to the initial condition at $z=20$ mm, whereas measured distribution clearly shows a lower temperature for the lower rotational levels, and a decrease in the absolute density of the higher rotational levels. Despite its simplicity, the model seems to be able to predict the rotational distribution at $z=400$ mm of the lower J ($J<5$) quite well, but for the higher rotational levels the density decay is underestimated by the model. However, as in the measurements, the distribution of these higher levels is undisturbed, i.e., it looks to be frozen in the expansion. For the intermediate levels the model clearly shows the stagnation. The underestimation of the relaxation of the higher rotational levels probably arises from the assumption of only R-T collisions. This assumption is somewhat too coarse. Probably, other mechanisms, like rotational-rotational (R-R) and rotational-vibrational (R-V) play a non-negligible role. Due to the lack of reaction rates for the R-R and R-V processes, these processes have not been yet incorporated into the model.

FIG. 10. Axial density dependence of the $J=3$ levels of H₂ $v=2, 4$, and 6 in the plasma expansion. The background pressure was 20 Pa.

V. VIBRATIONAL DISTRIBUTION

The behavior of the vibrational distribution is illustrated in Fig. 10, where the axial dependence of the densities of the $J=3$ levels of the $v=2, 4$, and 6 vibrational states are plotted. The densities of these levels behave relatively almost identically. This means that the shape of the vibrational distribution is practically independent of the position in the plasma. So the vibrational relaxation is very slow. This is even clearer in Fig. 11, where the vibrational distribution up to $v=6$ is shown at various positions in the plasma expansion at a background pressure of 20 Pa. The total densities are calculated as follows. Using the rotational populations of $v=2$ and $v=3$, a mean relative population $\bar{P}_J$ is determined for all the rotational levels, extrapolating for the highest rotational levels, that were not measured. For example, $\bar{P}_{J=1} = \frac{1}{2}[(n_{v=2,J=1}/N_{v=2}) + (n_{v=3,J=1}/N_{v=3})]$. The total density in a vibrational level is now calculated by the following formula:

$$N_v = \left\langle \frac{n_{v,J}}{\bar{P}_J} \right\rangle_{J_{\text{meas}}}, \quad (3)$$

FIG. 11. The vibrational distribution at several positions along the jet center of a hydrogen expansion at a background pressure of 20 Pa. Also shown is the total plasma density, which was determined using a Rayleigh scattering experiment.

where $n_{v,J}$ is the density in level (v,J) and $\langle \rangle_{J_{\text{meas}}}$ means averaging of the total vibrational populations calculated from each of the measured rotational levels of vibration v . For the $v=2$ the total number of measured rotational states was 12, for the $v=3$ it was 9, for the $v=1$ it was 5, for the $v=4$ it was 2, for $v=5$ it was 1, and for $v=6$ it was 2. Since for the $v=1$ only high rotational levels ($J=8, 12, 13$, and 17) were measured, and the relative populations of these levels is very low ($< 10^{-3}$), the relative uncertainty is large. It is estimated to be a factor of 3. The error in the density of the other levels is less than 40%.

The vibrational distribution is approximately thermal at an apparent vibrational temperature of 2600 K (at an axial position of 50 mm). In the course of the expansion, this temperature decreases slightly to a value of 2100 K at 400 mm. So, as already predicted from Fig. 10, the shape of the vibrational distribution remains almost unchanged throughout the complete expansion. There are simply not enough collisions for the relaxation of the vibrational levels. This is again related to the energy gap to the next vibrational level, which is very large, in the order of 3000 cm^{-1} . The vibrational energy spacing decreases towards higher vibrational levels, which could explain the slightly increasing depopulation.

A slight deviation from a thermal distribution can be observed for the levels $v > 2$. These levels are overpopulated compared to a distribution determined by the first three levels. This overpopulation could be explained by the production of H₂^{rv} via surface recombination of H atoms via an Eley-Rideal reaction at the metal surfaces surrounding the plasma, e.g., the nozzle.

VI. CONCLUSIONS

The m-LIF method in the vacuum-UV range is a well-suited diagnostic method to locally study H₂ molecules in almost all of the rovibrationally excited states. Moreover, due to the multiplexed nature of the m-LIF method, these levels can be measured relatively fast, compared to the regular LIF method. The low detection limit has enabled the detailed study of rovibrationally excited hydrogen with a very large dynamic range.

We have shown that there is a very significant rotational excitation in the hydrogen plasma. Due to the large energy spacings in the hydrogen level system, rovibrational relaxation is very slow. In going from the high temperature upstream region to the low temperature downstream region, the molecules undergo several hundred collisions. However, only the low rotational levels ($J \leq 5$) in the vibrationally excited states relax to a distribution that can be described by a Boltzmann distribution with a temperature of about 400 K, i.e., the ambient temperature, while the shape of the distribution of the high rotational levels ($J \geq 9$) seems to be frozen in the expansion. Even after several hundred collisions the shape of the distribution is still best described by a Boltzmann distribution with a temperature close to the up-stream region. The effect of the frozen shape of the distribution is even stronger for the vibrational population, leading to an

apparent vibrational temperature of more than 2000 K throughout the whole expansion.

Despite its simplicity, the presented model is able to predict the behavior of the low rotational levels relatively well. It also shows the frozen relative distribution of the higher rotational levels, but underestimates the density decay of those levels. To solve this, other reaction mechanisms, such as R-R or R-V, may have to be considered.

The data presented in this paper can serve as a test case for theoretical models describing rotational and vibrational relaxation phenomena in hydrogen.

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