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Nonequilibrium rovibrational energy distributions of hydrogen isotopologues in an expanding plasma jet

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State resolved densities of high rovibrationally excited hydrogen isotopologues H_2 , HD, and D_2 in the electronic ground state have been measured in a supersonically expanding plasma jet. The obtained state distributions differ substantially from thermal equilibrium. Moreover, the distributions are not the same for H_2 , HD, and D_2 indicating different formation and relaxation rates for each isotopologue. Mechanisms for this deviation from a Boltzmann distribution are given and compared to hydrogen reactions in other environments. The difference between the measured highest occupied rovibrational states in H_2 , HD, and D_2 is ascribed to an isotope effect in the dissociation process. © 2010 American Institute of Physics. [doi:10.1063/1.3352550]

I. INTRODUCTION

Hydrogen is the most abundant and simplest neutral molecule. Therefore, it is an often used subject in quantum mechanical models. Due to its vibrational (v) and rotational (J) energy levels in its electronic ground state $X^1\Sigma_g^+$, molecular hydrogen is important for the cooling of interstellar gas clouds, eventually resulting in the formation of stars and planets.^{1,2} While in the extremely cold regions of our cosmos, usually, only the lower energy levels of molecular hydrogen are occupied. In extremely hot regions, e.g., in an experimental fusion reactor, high rovibrationally excited states of hydrogen molecules have been found close to the reactor walls.^{3,4} Gas phase and surface reactions of atomic and molecular hydrogen also play a vital role in applications such as the deposition of ultrahard diamondlike films or microcrystalline silicon layers in thin film solar cell production, where hydrogen controls the crystallinity during the deposition process.^{5,6}

It has been shown that under low pressure conditions, surface association processes, e.g., on walls of a fusion reactor or the surface of interstellar dust grains, lead to high rovibrationally excited hydrogen molecules.^{7–9} These highly excited molecules transfer their internal energy to other molecules and atoms within the gas phase by inelastic collisions and chemical reactions. Cross sections depend strongly on the internal energy of the collision partners, thus the reaction dynamics is influenced by the internal energy and its distribution. Depending on the internal energy of the molecules, the corresponding rate coefficients can vary over several orders of magnitude.¹⁰ Therefore, understanding of the plasma chemistry requires a detailed knowledge of the internal energy distribution of molecules, which is very often deviating from thermal equilibrium, both in technological plasmas and in environments such as the interstellar medium.^{1,2,11}

An understanding of relaxation processes, leading to distributions in thermal equilibrium, requires detailed information about collision cross sections and the distribution of internal energy. However, even the simplest atom-molecule collision ($H+H_2$) and the simplest molecule-molecule collision (H_2+H_2) are still subjects of ongoing research (see e.g. Refs. 12 and 13). Research in this field is primarily driven by astrophysical demands and, due to the cold environment of interstellar space, cross sections of collisions with higher excited molecules ($v>2, J>10$) are mostly unknown. Moreover, state-to-state cross sections are mostly given with vibrational, but not with rotational resolution.¹¹

A direct spectroscopic measurement of the distribution of the internal energy of rovibrationally excited hydrogen molecules is difficult. Transitions between rovibrationally excited states within the electronic ground states of homonuclear H_2 and D_2 are dipole-forbidden, while the heteronuclear HD molecules have only a very weak dipole moment.¹⁴ Furthermore, emission spectroscopy yields only densities of the upper states, and ground state densities can only be derived indirectly from collisional-radiative models.³

We measured the distributions of the internal energy of H_2 , HD, and D_2 molecules in their electronic ground states by means of vacuum ultraviolet (VUV)-laser-induced fluorescence spectroscopy. The high rovibrationally excited molecules were formed in a plasma source and detected in a supersonically expanding hydrogen jet directly after leaving the plasma source.

II. EXPERIMENT

A direct measurement of $X^1\Sigma_g^+$ state densities by excitation to electronically excited states requires radiation with an energy in the order of 10 eV, which has to be tunable over an energy range of several electronvolts with a bandwidth narrow enough to resolve individual transitions ($\approx 10^{-5}$ eV). We use stimulated anti-Stokes (AS) Raman scattering in hydrogen to produce simultaneously ten laserlike beams in the VUV.^{15,16} Every beam is shifted up in energy with respect to

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FIG. 1. Scheme of the plasma source, a cascaded arc, and the plasma expansion. Rovibrationally excited molecules are detected at the position indicated with a cross.

the pump beam by a multiple of the fundamental vibrational Raman shift of H_2 , i.e., 4155.22 cm^{-1} . All beams are focused simultaneously into the vacuum chamber, where they excite hydrogen molecules via Lyman transitions ($X\ ^1\Sigma_g^+ \rightarrow B\ ^1\Sigma_u^+$). The AS radiation has a bandwidth of 0.15 cm^{-1} and covers a spectral range from 115 to 165 nm, i.e., about 2/3 of the spectral range of the Lyman band system of molecular hydrogen. By tuning the frequency of the pump beam, all ten AS-beams are scanned simultaneously; this multiplex scheme drastically decreases the recording time of the Lyman spectra and allows for simultaneous measurement of many (v, J) states of the three isotopologues. The fluorescence radiation due to spontaneous emission of the excited hydrogen molecules is collected by a mirror and focused onto a photomultiplier tube (PMT).

Analysis of recorded spectra is performed using transition energies and probabilities of H_2 , HD, and D_2 Lyman lines provided by Abgrall and Roueff.^{17–19} A radiative model includes the excitation by AS beams and the de-excitation by spontaneous emission ($X\ ^1\Sigma_g^+ \leftrightarrow B\ ^1\Sigma_u^+$) leading to a system of rate equations, which has been solved analytically. A fluorescence yield is calculated for each possible excitation taking into account the excitation rate, spontaneous and stimulated emission probabilities, optical properties of the spectrometer, and saturation effects. Other influences such as cascading processes from higher excited levels can be neglected because the measurement has been performed in the nonactive part of the plasma jet. Moreover, the time resolution of the PMT (around 1 ns) is high enough to resolve the emission peak (around 10 ns long) and to subtract any possible background signal.

The minimal detectable hydrogen state density depends on the fluorescence yield and is around 10^{12} m^{-3} . This is, at least in the case of a hot hydrogen gas/plasma, low enough to detect rovibrationally excited hydrogen molecules with internal energies close to the dissociation limit at 4.5 eV internal energy. A lower limit for the detectable internal energy exists at 1 eV because the required radiation with wavelengths below 115 nm is blocked by the MgF_2 windows that are used to separate plasma chamber and VUV spectrometer.

Rovibrationally excited H_2 , HD, and D_2 molecules are produced in a wall-stabilized thermal arc plasma source^{20,21} operated with 7 kW of dc power. A 50:50 mixture of H_2 and D_2 gas enters the arc channel of 4 mm diameter and 4 cm length at a total flow rate of $1.25 \times 10^{21}\text{ s}^{-1}$ (Fig. 1). Within

the thermal plasma in the arc channel ($p \approx 9000\text{ Pa}$ and $T \approx 6000\text{ K}$), almost all hydrogen molecules are dissociated, while H and D atoms recombine within the gas phase and associate at the surface of the channel and nozzle walls to hydrogen molecules. Rovibrationally excited H_2 , HD, and D_2 molecules are leaving the plasma source through a straight nozzle (6-mm-long) with a 1:2:1 ratio of the total densities.¹⁹ Using this type of nozzle and a chamber background pressure of 100 Pa, there is no light emission from the plasma jet due to H_2 Fulcher band or H atom Balmer line series, but only the emission due to the excitation by the laser AS beams. The plasma expands supersonically into a vacuum chamber, which is kept at a pressure of 100 Pa. The densities of rovibrationally excited hydrogen molecules are measured 8 mm downstream in the center of the plasma jet, i.e., in the supersonic part of the plasma expansion. A shock front is formed about 12 mm downstream, where the expansion undergoes a transition to subsonic, diffusion dominated flow.

III. ROVIBRATIONAL DENSITY DISTRIBUTIONS OF H_2 , HD, AND D_2

In the measured spectral range from 60 000 to 85 000 cm^{-1} , 170 recorded lines have been identified as Lyman transitions of H_2 , 159 lines of HD and 65 lines of D_2 , respectively. From measured line intensities, hydrogen state densities have been calculated in this work using the radiative model. The resulting state distributions of rovibrationally excited H_2 , HD, and D_2 in the electronic ground state $X\ ^1\Sigma_g^+$ are shown in the Boltzmann plots in Fig. 2, where the state densities $n(v, J)$ divided by the statistical weight $g(v, J)$ are plotted over the total internal energy.

The distributions differ from a Boltzmann distribution, i.e., the rotational states are not populated according to thermal equilibrium. This is more clear in Fig. 3, where only the rotational state densities for the vibrational state $v=6$ are shown, normalized to the density of the first rotational state $J=0$ of H_2 , HD, and D_2 , respectively. While the lower rotational states $J < 7$ follow a temperature $T_{\text{low } J}$ of several hundred Kelvin, the higher rotational states $J \geq 8$ are distributed according to a rotational temperature $T_{\text{high } J}$ of several thousand Kelvin. The temperatures have been derived from linear regression fits applied to the lower rotational state densities and higher rotational state densities, respectively, for each vibrational state v of H_2 , HD, and D_2 . However, it should be mentioned that the term “temperature” is not strictly defined in cases where the states are not populated according to thermal equilibrium. Therefore, we use it as a measure of the rotational distribution in certain rotational states (“low J ” and “high J ”). These derived temperatures are summarized in Table I.

As shown in Fig. 2, the shape of the rotational distributions are similar in all detected vibrational states v in case of H_2 and D_2 , while for HD the non-Boltzmann character of the rotational distribution is increasing with increasing vibrational states. HD is different from H_2 and D_2 in two ways: in contrast to H_2 and D_2 molecules, which are already in the feed gas, all HD molecules have to be newly formed in the

FIG. 2. State distributions of rovibrationally excited H₂ (top), HD (middle), and D₂ (bottom) molecules detected in the supersonic part of a hydrogen plasma jet at 8 mm downstream from the exit of the plasma source. Densities n per statistic weight g are plotted over the total internal energy of the molecules. The small vertical lines in the upper part of the figures indicate detected rotational levels J within several vibrational levels v .

plasma source. Moreover, HD has a small dipole moment resulting in different selection rules for radiative and collisional transitions, leading to different excitation and relaxation processes.

Although the detection limit is around 10^{12} m^{-3} , H₂ molecules with internal energies of up to 4 eV were detected, which is only 0.5 eV lower than the dissociation limit. At the kinetic conditions inside the plasma jet (some 1000 K or 0.1 eV), these highly excited molecules are effectively dissociated, leading to anomalously high H and D atom densities.²² The highest internal energy found for HD is lower (around 3.5 eV), indicating an isotope effect on the dissociation rates (as suggested in Ref. 10 and references therein). The distribution of D₂ molecules could be detected for internal energies up to 3 eV, where D₂ densities reach the detection limit of the setup.

FIG. 3. Rotational distributions for vibrational state $v=6$ of H₂, HD, and D₂ normalized to the density of the first rotational state $J=0$. The numbers indicate the rotational levels J .

IV. EXCITATION OF MOLECULAR HYDROGEN

Similar nonequilibrium distributions were found for H₂ in other kinds of gas discharges,^{15,23–25} but also for H₂ in the interstellar medium.^{1,2,11} However, despite the similarity in distributions, the proposed mechanisms leading to non-Boltzmann state distributions are very different. Lower rotational states of H₂ are, in interstellar media as well as in gas discharges, commonly believed to be populated according to the kinetic gas temperature of the medium.¹⁵ The kinetic temperature at the detection point within the plasma expansion, i.e., $z=8$ mm behind the nozzle exit of the plasma source, has been determined from the line widths of detected lines and was found to be very similar: 1600 ± 100 K in case of H₂, 1650 ± 100 K for HD, and 1800 ± 200 K for D₂, respectively. It is well known that the kinetic temperature is fast decaying within the supersonic expansion,²¹ implying even higher kinetic temperatures at earlier positions in the expansion and within the plasma source. This is interesting because the lower rotational states of H₂, HD, and D₂ are populated according to temperatures three times lower than the kinetic temperature, while the higher rotational states are populated according to higher temperatures (3000–4000 K). It indicates that thermalization within the plasma gas phase is far from complete even for low J states, at least for the detected vibrational states $v=2–8$.

Higher rotational states resemble a higher temperature, which has to be due to an additional pumping process. For interstellar media, this pumping is assumed to be due to surface association on dust grains, where the desorbing H₂ molecules have an additional internal energy up to 4.5 eV.^{1,2,8} This is in contrast to gas discharges, for which pumping is commonly assumed to be due to electron collisions, either by

TABLE I. Parameters $T_{\text{low } J}$ and $T_{\text{high } J}$ for H₂, HD, and D₂ molecules derived from distributions shown in Fig. 2.

Molecule	$T_{\text{low } J}$ (K)	$T_{\text{high } J}$ (K)
H ₂	700 ± 100	3800 ± 200
HD	500 ± 100	3400 ± 200
D ₂	300 ± 100	3000 ± 200

FIG. 4. Rotational distribution of HD($v=4$) measured at five different axial positions within the plasma jet.

electrons of low energy (≈ 1 eV) direct to higher rovibrational states within the $X^1\Sigma_g^+$ state (e-V process), or by electrons of higher energy (≈ 10 eV) via an excitation to the electronic excited states (E-V). The situation is different in the plasma source and in the plasma expansion used in this work, where the electron densities are not high enough and the temperatures are too low (<1 eV) for excitation of molecular hydrogen via E-V processes. Although an electron energy of about 1 eV is high enough for e-V excitation to lower (v, J) states, the high rotational excitation ($J > 20$) found in this work cannot be explained by e-V processes due to a lack of a sufficient numbers of collisions.

Since the energy distribution of hydrogen at the end of the arc channel is thermal with high temperatures of several thousand Kelvin, an excitation process via surface association of H atoms at the copper walls of arc channel and nozzle has been proposed for H_2 ,^{16,21} which leads to H_2 in high v and J states.⁷⁻⁹ As visible in Figs. 2 and 3, the distributions are not the same for H_2 , HD, and D_2 . Both the lower and the higher part of the rotational distributions follow different temperatures indicating different formation and relaxation rates for each isotopologue. Taking into account that the kinetic temperatures are very similar for H_2 , HD, and D_2 , we assume that gas phase collisions are not responsible for the difference in rotational distribution, but the difference in surface association rates for the different isotopologues.

V. RELAXATION OF MOLECULAR HYDROGEN

The relaxation of the internal energy of rovibrationally excited hydrogen molecules in a plasma jet originates from surface collisions in the nozzle²¹ or from collisions in the gas phase of the plasma jet itself at larger distances from the source.²⁶ In the latter case, the redistribution of the internal energy is due to molecule-molecule collisions, since atom, electron, and ion densities are orders of magnitude lower than that of the neutrals. The same effect has been measured for rotational states in vibrational state $v=4$ of HD molecules (Fig. 4). Compared to previous results on H_2 ,²⁶ the relaxation of rotational states of HD is increasing with rotational states J and becomes almost constant for $J \geq 8$.

With a simple model²⁶ including cross sections calculated by Flower and Roueff,²⁷ the relaxation of a H_2 gas at

FIG. 5. Simulation of the redistribution of the internal energy of molecular hydrogen by collisions with $H_2(0,0)$.

5500 K and 6000 Pa via collisions of H_2 molecules with ground state $H_2(0,0)$ has been calculated (Fig. 5). This kind of relaxation leads to a non-Boltzmann shape of the distribution, as those shown in Fig. 2, but the necessary time of 4×10^{-4} s is a factor of 100 higher than the available time within the jet between nozzle exit and the detection location. A more realistic modeling of the relaxation of internal energies would include state-to-state molecular collisions of H_2 , HD, and D_2 , but relevant cross sections have not been published in detail for high rovibrational states for any of the hydrogen isotopologues.^{11,13,27} However, the high densities of hydrogen molecules in highly excited rovibrational states in connection with the enhanced rate coefficients of gas phase¹⁰ and surface⁹ reactions for these states emphasize the vital role of excited hydrogen molecules, both in neutral gas and plasma. Another possible extension of the model are molecule-atom collisions, which cannot be neglected at close distances towards the plasma source, since high dissociation degrees have been measured using this type of nozzle.^{16,21} Another influence on the densities of high rovibrationally excited H_2 molecules could be the presence of low energetic electrons, which leads to dissociative attachment of excited molecules.¹⁰

VI. CONCLUSIONS

The distribution of the internal energy of H_2 , HD, and D_2 molecules has been measured in a plasma jet driven by a 50:50 mixture of H_2 and D_2 gas. A high amount of the H_2 , HD, and D_2 molecules are high rovibrationally excited due to surface association processes within the plasma source. The distributions are not according to thermal equilibrium and vary for each isotopologue, indicating different production and relaxation rates. The distribution of the rotational energy shows a similar shape for H_2 , HD, and D_2 and can be described by a low temperature of several hundred Kelvin for low lying rotational states, while higher rotational states follow a temperature of several thousand Kelvin. The relaxation of the internal energy within the plasma jet due to molecule-molecule collisions has been modeled. The resulting time scale is too long if only collisions with ground state molecules are included. This result shows that molecule-molecule collisions of highly excited hydrogen isotopo-

logues have to be included to model the relaxation. However, information on state resolved cross section data for these collisions is missing.

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