

Observation of Exceptionally High Vibrational Excitation of Hydrogen Molecules Formed by Wall Recombination

P. J. Eenshuistra, J. H. M. Bonnie, J. Los, and H. J. Hopman

*Association EURATOM-FOM, FOM Institute for Atomic and Molecular Physics,
NL-1098 SJ Amsterdam, The Netherlands*

(Received 8 September 1987)

Relative densities of H atoms and $H_2(v'')$ molecules in vibrational levels up to $v''=5$, effusing from a metal box containing heated tungsten filaments, were detected by a resonance-enhanced multiphoton ionization technique. The atom production is compatible with dissociation of molecules at the filament. The formation of $H_2(v'')$ is attributed to an Eley-Rideal-type reaction, in which a free atom recombines with an adsorbed atom at the cold wall, followed by desorption. Above 2800 K we observe an abrupt drop in the atom and the $H_2(v'')$ densities. It is ascribed to the effects of annealing on the filament surface.

PACS numbers: 79.20.Nc, 33.80.Rv, 52.50.Dg, 82.65.Yh

It is commonly accepted that in a hydrogen volume source the negative hydrogen ions (H^-) are formed by dissociative attachment of slow electrons to vibrationally excited molecules $H_2(v'')$ ¹⁻³ where v'' is the vibrational quantum number. The vibrational excitation is attributed to electron-impact excitation of molecules (in $v''=0$) by the fast primary electrons in the discharge.⁴ To gain information on these processes one is interested in the measurement of the distribution of vibrationally excited molecules.⁵ We have chosen resonance-enhanced multiphoton ionization (RMI)⁶ as the method to study the discharge in our volume source. RMI is a powerful method because it allows the efficient detection of (metastable) molecules in specific rotational and vibrational states,⁷ as well as atoms.

The present Letter is concerned with the discovery that with the filaments heated, but the discharge turned off, we have been able to detect vibrationally excited molecules with v'' up to 5. In a similar experiment, Hall *et al.*⁸ observed the formation of $H_2(v'')$ molecules with v'' up to 9, using dissociative attachment of slow electrons to $H_2(v'')$ as a detection technique. Therefore, two independent detection techniques have been used by now to establish the presence of vibrationally highly excited molecules in the gas effusing from a nearly closed box containing hydrogen gas and heated filaments. The vibrational excitation is attributed to recombinative desorption of hydrogen atoms on the cold walls of the discharge chamber. The atoms result from dissociation of molecules on the hot filaments. The main distinction between our work and that of Hall *et al.*⁸ is our ability to detect atoms in addition to molecules. This way we can demonstrate the very close relation that exists between those two types of particles.

Other experiments dedicated to a study of recombinative desorption of hydrogen⁹⁻¹¹ used permeation through the sample to obtain a wall covered by atomic hydrogen. In these cases only $v''=1$ has been detected. With use

of various wall materials, the population of $v''=1$ was found to be in excess of the value expected on basis of the wall temperature.

The discovery that walls catalyze the population of high vibrational states will bear on different fields like catalysis and plasma or interstellar chemistry, because reaction rates are known to increase an order of magnitude with each higher vibrational quantum number.¹² Moreover, it might modify ideas about plasma-wall interactions in a tokamak when the neutral gas transports energy in the form of vibrational excitation across the boundary into the plasma. In particular, it presents the intriguing question concerning which mechanism dominates the production of $H_2(v'')$ molecules in a real discharge, wall recombination or fast electron excitation.

In the following, we present measurements on both the $H_2(v'')$ and the H-atom densities as functions of the filament temperature from 1600 to 3000 K, and of the pressure from 0.3 to 2 Pa. We restrict ourselves to the highest levels detected, $v''=4$ and 5, because they allow an unambiguous interpretation.

A constant flow of hydrogen is admitted to the chamber of a magnetic-multipole-bucket ion source. The dimensions of the rectangular chamber are $14 \times 14 \times 19$ cm³. Three sets of two tungsten filaments each, each filament with diameter 1.5 mm and length ≈ 15 cm, are mounted on insulated water-cooled feedthroughs. The water-cooled walls are made of oxygen-free copper and covered by a grey nontransparent layer of tungsten, evaporated from the filaments. No further analysis of the wall was made. In the edge-cooled frontplate is cut an aperture of 10×2 mm² through which the gas effuses.

We measured the filament temperature T_f for I_f up to 90 A (that is T_f up to 2700 K, uncertainty of ≈ 30 K) with an optical pyrometer. For larger I_f we estimated T_f (uncertainty 50–100 K) in the following way. Assuming that the filaments have a uniform temperature

profile, we calculated the specific resistivity from the measured current and voltage needed to heat the filaments. Then, we compared tabulated values of the specific resistivity¹³ with calculated ones to derive a temperature. The effective filament length was obtained by our fitting the estimated temperature to the one measured with the pyrometer for I_f below 90 A.

Outside the source chamber the beam of an excimer-pumped dye laser is focused approximately 5 mm in front of the aperture. An electric field of 1 MV/m accelerates the laser-produced ions into a lens system, which transports them to the detector. The 5-mJ, 15-nsec laser pulse is focused to a spot of $\approx 20 \mu\text{m}$ diam. A detailed description of the experiment and diagnostic is given in a separate paper.¹⁴

State-selective detection of hydrogen molecules and atoms is obtained by application of (3+1) RMI, i.e., a three-photon excitation, one-photon ionization scheme. Molecules with $v''=4$ and $v''=5$ were detected with the $C^1\Pi_u$ level with $v'=1$ and $v'=2$, respectively, as intermediate resonant state. The assignment is performed with use of the energy levels given by Dabrowski.¹⁵ To obtain information on the density of the $\text{H}_2(v''=4)$ molecules, denoted by $n(v''=4)$, we measured the amplitude of the ion signal associated with the strong $Q(J''=1)$ transition, where J'' is the rotational quantum number of the ground state, and Q denotes $\Delta J=0$. This amplitude is proportional to $n(v''=4)$, since we have no indication that the rotational temperature changes much with source parameters. To obtain the atom density, $n(\text{H})$, we used the same procedure. The atoms were excited from the $n=1$ ground state to the $n=2$ state ($\lambda=364.74$ nm). Each measuring point was obtained by our averaging at least 500 laser pulses, in order to eliminate statistical variations in the ionization signal. Note that this

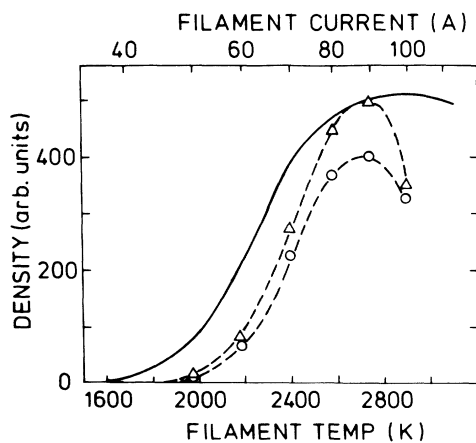


FIG. 1. Measured densities as a function of filament temperature: $n(\text{H})$, triangles; $n(v''=4)$, circles. The upper axis gives the corresponding filament current. The pressure is 1 Pa. The full drawn curve is an estimate of the atom density based on Eqs. (1) and (2). It gives values proportional to $P_a/\sqrt{T_f}$.

procedure does not lead to an absolute determination of the densities, because the three-photon excitation cross sections are not known. It allows us to determine the dependence of the densities on T_f and gas pressure.

First we describe the measurements of $n(\text{H})$, $n(v''=4)$, and $n(v''=5)$ at different gas pressures. After each change in pressure, the RMI signal at first shows a rapid change, and then continues to change slowly with a time constant of about 2 min until it reaches a steady state. Therefore the densities have been measured 10 min after changes in pressure. It is expected that they represent stationary conditions. The differences between the densities measured at increasing or at decreasing pressure are about 10%. The slow change in signal after pressure changes might be caused by diffusion of hydrogen from the surface into the bulk or from the bulk towards the surface. We observed that atoms and vibrationally excited molecules have the same almost linear pressure dependence.

Figure 1 gives the stationary densities $n(\text{H})$ and $n(v''=4)$ as function of filament temperature T_f , and at a pressure of 1 Pa. One set of two filaments was used. Measurements were done 10 min after a change in T_f . Differences between data obtained with increasing and decreasing T_f are of the order of 15%. Although $n(\text{H})$, $n(v''=4)$, and $n(v''=5)$ vary more than 1 order of magnitude when we change T_f from 1600 to 2900 K, their ratios $n(v''=4)/n(\text{H})$, derived from Fig. 2, and $n(v''=5)/n(\text{H})$ stayed almost constant within 30%. So the data indicate that, within the experimental uncertainty, we find the same dependence on T_f for $n(\text{H})$, $n(v''=4)$, and $n(v''=5)$.

If the measurements are done "fast" (1 min at each measuring point, no stationary condition reached) we observe a hysteresis, especially when T_f rises above 2700 K. This is shown in Fig. 2 for $n(\text{H})$ and $n(v''=4)$. We remark that despite the large decrease of both $n(\text{H})$ and

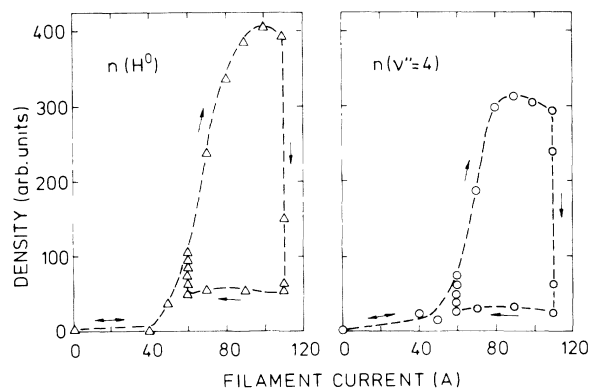


FIG. 2. Measurement of the densities $n(\text{H})$ and $n(v''=4)$, as functions of filament current under nonstationary conditions, demonstrating the strong hysteresis. Each measurement is taken 1 min after the previous one. The pressure is 1 Pa. The arrows give the direction in which the data are measured.

$n(v''=4)$ at filament temperatures above 2900 K, the ratio of these densities approximately stays constant.

The rotational temperatures T_r are determined from a Boltzmann plot containing the measured amplitudes of the $Q(J''=1)$, $Q(J''=2)$, and $Q(J''=3)$ transitions. For $v''=4$ we found a rotational temperature of ≈ 500 K (uncertainty 50 K) at pressures of 1 and 2 Pa. Note that this is much below the filament temperatures of 2900 K. This observation is consistent with the lack of observable excitation effects for $v'' > 0$ in the measurements of Hall *et al.*⁸

First we discuss the formation of atomic hydrogen and the scaling of $n(\text{H})$ with T_f . The only mechanism available for the production of atomic hydrogen in a cold chamber with hot filaments is dissociation of molecules on those filaments.^{16,17} Therefore, we look in more detail at the phenomena taking place at the filament surface. First we mention that on a hot filament the hydrogen coverage is very small. A simple rate equation for θ , the fraction of a monolayer of hydrogen atoms actually present on the filament surface, gives $\theta < 10^{-4}$. It means that molecules incident on the filament collide with a bare tungsten surface. Then, the flux of atoms $\phi(\text{H})$ leaving the filament is given by

$$\phi(\text{H}) = 2s_m P_a \phi(\text{H}_2), \quad (1)$$

where s_m is the sticking probability of molecular hydrogen, P_a is the atomization probability, and $\phi(\text{H}_2)$ is the flux of molecules towards the filaments. The right-hand side of Eq. (1) gives the flux of hydrogen molecules arriving at the surface, sticking there, and dissociating. The factor 2 accounts for the fact that each molecule dissociates into two atoms. Tamm and Schmidt¹⁸ give a sticking probability s_m for hydrogen molecules of 0.07 on a polycrystalline W surface at zero coverage and 300 K. The behavior of s_m at high temperatures is not known to us. Essentially the same value (0.06) is quoted by Rettner *et al.*¹⁹ for a single-crystal W(110) surface. The probability of atomization P_a of molecules which stick to a hot filament is calculated from an expression given by Brennan and Fletcher,¹⁶

$$P_a = \frac{1}{4} [(K_p/\gamma p)(K_p/\gamma p + 8)]^{1/2} - K_p/\gamma p. \quad (2)$$

Here, K_p denotes the equilibrium constant for the reaction $\text{H}_2 \leftrightarrow 2\text{H}$,²⁰ $\gamma = (T_f/T_g)^{1/2}$, in which T_g is the gas temperature, and p is the gas pressure. Equation (2) is valid for molecules which stick to and equilibrate with the filament surface.

At a filament temperature $T_f = 2500$ K, Eqs. (1) and (2) result in an atomic flux $\phi(\text{H}) = 4 \times 10^{17} \text{ s}^{-1} \text{ cm}^{-2}$. A flux is converted to a density by dividing it by $\sqrt{T_f}$. Therefore, plotting in Fig. 1 the calculated value of $P_a/\sqrt{T_f}$, we can compare the measurements with our simple estimate. We see that they show the same trend for $T_f < 2800$ K. Above ≈ 2800 K, some process interferes with the atomization, because $n(\text{H})$ decreases

strongly and abruptly; see Figs. 1 and 2.

The sudden decrease cannot be ascribed to the burying of H atoms on the cold walls by tungsten atoms evaporated from the filaments. The flux of tungsten atoms $\phi(\text{W})$ at the filament surface due to evaporation¹³ at 2800 K is $3 \times 10^{14} \text{ s}^{-1} \text{ cm}^{-2}$, which is 1000 times lower than the value calculated for $\phi(\text{H})$. Other wall-related effects are just as unlikely. Therefore, the seat of this process should be at the filaments.

We attribute the drop in atom production to a change in filament surface structure. We suppose that above 2800 K some kind of annealing of the surface takes place. As a result of this annealing, the surface becomes dominated by (110) facets. Polizzotti and Ehrlich²¹ conclude from their data that physically adsorbed hydrogen does not serve as a precursor to chemisorption on the densely packed (110) plane.

We thus come to the following picture. A cold filament with a generally rough surface is gradually heated. On rough planes and on surface imperfections of (110) planes the molecules adsorb, attain equilibrium, and dissociate. This kind of atom production is described by Eq. (1), and fits the experimental data as seen in Fig. 1. Above 2800 K, surface imperfections reduce in number and the whole surface attains a (110) character. This process takes of the order of 2 min, and the production of hydrogen atoms decreases, as is verified by Fig. 2. When we let the filament cool down, the surface roughness is restored, a process that can be mediated for instance by segregation of impurities.²² Thus we go through the hysteresis cycle shown in Fig. 2.

In principle, $\text{H}_2(v'')$ can be produced in three ways: (1) production on hot filaments, (2) gas-phase recombination, and (3) recombination of atoms on walls. In the following discussion we will show that $\text{H}_2(v'')$ production is attributed to recombinative desorption of H atoms on the cold walls, one atom coming from the vacuum.

If the excitation took place on the filaments, one would expect an increase in vibrational temperature with T_f , that is a rapid increase in the ratio $n(v''=5)/n(v''=4)$. This contradicts our measurements which showed no change of $n(v''=5)/n(v''=4)$ with T_f . Near $T_f = 2800$ K, Figs. 1 and 2 show a saturation in the densities, which cannot be explained on basis of this assumption either. Therefore, two experimental facts are at variance with this idea, making it unlikely that the filaments are the source of vibrational excitation.

The rate coefficient for three-body gas-phase recombination of H atoms²³ predicts a negligibly small production of molecules. Besides, gas-phase recombination of H atoms would give a linear increase of $n(v'')/n(\text{H})$ with increasing $n(\text{H})$, which is not observed.

The fact that $\text{H}_2(v'')$ observed in this experiment can neither be formed by gas-phase recombination nor by formation at the filaments led us to the hypothesis that

$H_2(v'')$ is formed by recombination of two atoms on the wall. This view is supported by recent measurements of Hall *et al.*⁸ who observed molecules with $v''=1-9$ under similar conditions. In the following discussion we will demonstrate that in this type of wall recombination one of the two atoms must come from the vacuum in order to have enough excess energy to populate higher v'' levels.

At low atomic coverage θ_a of the cold wall, the atoms from the hot filament mainly arrive at unoccupied sites and stick. Then, θ_a scales as $n(H)$, and desorption is due to the recombination of two adsorbed atoms. Hence, one would expect that $n(v''=4)$ is proportional to θ_a^2 , and thus to $n(H)^2$. However, this behavior does not characterize the present experimental data. Moreover, if two atoms recombine on the cold wall, the available energy, being the difference of the dissociation energy and 2 times the binding energy, is just enough to populate $v''=1$.⁹

If we assume a high coverage, $\theta_a \approx 1$, $H_2(v'')$ is formed by recombination of a surface atom with one coming from the vacuum. This is an example of the so-called Eley-Rideal reaction (reviewed by Kasimo and Lundquist²⁴). Then, $n(v''=4)$ should scale as $n(H)$. This is indeed what we observe when varying pressure and I_f (Fig. 1). The available energy is the dissociation energy minus 1 times the binding energy. Depending on which value one takes for E_b ,^{9,16} we find an energy which is between 2 and 2.5 eV. This is sufficient to populate $v''=4$ and possible $v''=5$, in agreement with our measurements. Although the potential of a subsurface hydrogen is not known, recombination with an atom that is bound in an inner well provides the possibility for excitation of the desorbed molecules to vibrational levels $v'' > 5$ (see Fig. 2 in paper of Ref. 9). An alternative, although less likely, explanation for the observation of Hall *et al.*⁸ that even molecules up to $v''=9$ are emitted is the direct recombination of two atoms coming from the gas phase. This process though would give for a $v'' > 5$ a quadratic dependence of $n(v'')$ on $n(H)$. As we were not able to extend our measurements beyond $v''=5$, we unfortunately were not able to measure the relation between $n(v'' > 5)$ and $n(H)$. Of course, at $\theta_a \approx 1$ recombination of adsorbed atoms is still possible. But this process does not lead to $v'' > 1$, and does not modify measured scaling laws.

The authors wish to thank Dr. R. Hall (Université P. et M. Curie, France), Dr. J. Peterson (SRI International, California), Dr. A. van Veen (Interuniversitair Reactor Instituut, Delft, The Netherlands), and Dr. A. W. Kleyn and Dr. W. C. Sinke (FOM-Instituut voor Atoom- en Molekulfysica) for stimulating discussions,

and P. Dijkstra for his technical assistant. This work is part of the research program of the association agreement EURATOM and the Stichting voor Fundamenteel Onderzoek der Materie with financial support from the Nederlandse Organisatie voor Zuiver Wetenschappelijk Onderzoek and EURATOM.

-
- ¹M. Bacal, Phys. Scr. **T2/2**, 467 (1982).
 - ²J. R. Hiskes and A. M. Karo, J. Appl. Phys. **56**, 1927 (1984).
 - ³C. Gorse, M. Capitelli, J. Bretagne, and M. Bacal, Chem. Phys. **93**, 1 (1985).
 - ⁴J. R. Hiskes, Comments At. Mol. Phys. **19**, 59 (1987).
 - ⁵M. Pealat, J.-P.E. Taran, M. Bacal, and F. Hillion, J. Chem. Phys. **82**, 4943 (1985).
 - ⁶E. E. Marinero, C. T. Rettner, and R. N. Zare, Phys. Rev. Lett. **48**, 1323 (1982).
 - ⁷J. H. M. Bonnie, P. J. Eenshuistra, and H. J. Hopman, Phys. Rev. Lett. **57**, 3265 (1986).
 - ⁸R. I. Hall, I. Čadež, M. Landau, F. Pichou, and C. Scherman, preceding Letter [Phys. Rev. Lett. **60**, 337 (1987)].
 - ⁹G. Comsa and R. David, Surf. Sci. **177**, 77 (1982), and Surf. Sci. Rep. **5**, 145 (1985).
 - ¹⁰G. D. Kubiak, G. O. Sitz, and R. N. Zare, J. Chem. Phys. **83**, 2538 (1985).
 - ¹¹H. Zacharias and R. David, Chem. Phys. Lett. **115**, 205 (1985).
 - ¹²M. Allan and S. F. Wong, Phys. Rev. Lett. **41**, 1791 (1978).
 - ¹³Robert C. Weast, *Handbook of Chemistry and Physics* (CRC Press, Boca Raton, FL, 1982), 63 ed., p. E384.
 - ¹⁴J. H. M. Bonnie, E. H. A. Granneman, and H. J. Hopman, Rev. Sci. Instrum. **58**, 1354 (1987).
 - ¹⁵I. Dabrowski, Can. J. Phys. **62**, 1639 (1984).
 - ¹⁶D. Brennan and P. C. Fletcher, Proc. Roy. Soc. London A **250**, 389 (1959).
 - ¹⁷E. L. Cochran, V. A. Bowers, and F. J. Adrian, J. Chem. Phys. **57**, 2384 (1972).
 - ¹⁸P. W. Tamm and L. D. Schmidt, J. Chem. Phys. **55**, 4253 (1971), and **51**, 5352 (1969).
 - ¹⁹C. T. Rettner, L. A. DeLouise, J. P. Cowin, and D. J. Auerbach, Faraday Discuss. Chem. Soc. **80**, 127 (1985).
 - ²⁰*The Fluid State*, edited by J. S. Rowlingson, The International Encyclopedia of Physical Chemistry and Chemical Physics (Pergamon, New York, 1963), Topic 10, Vol. 5, p.85.
 - ²¹R. S. Polizzotti and G. Ehrlich, J. Chem. Phys. **71**, 259 (1979).
 - ²²R. W. Joyner, J. Rickman, and M. W. Roberts, Surf. Sci. **39**, 445 (1973).
 - ²³R. E. Roberts, R. B. Bernstein, and C. F. Curtis, J. Chem. Phys. **50**, 5163 (1969).
 - ²⁴B. Kasimo and B. I. Lundquist, Comments At. Mol. Phys. **14**, 229 (1984).