Quenching of atomic states in a low-pressure hydrogen glow discharge

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A laser perturbation method is used to determine the relaxation rates of levels $n = 3, 4, 5$ of atomic hydrogen as a function of pressure and current intensity in a glow discharge. Quenching is due to spontaneous emission of radiation towards lower levels and to inelastic collisions with H_2 molecules in the ground and quasimetastable states with thermally averaged cross sections of about 1.5×10^{-14} cm^2.

I. INTRODUCTION

Early studies on the dissociation of H_2 by electronic collisions[1-3] indicate that in the energy range of gas discharge plasma electrons ($E_e \sim 2$–10 eV), the dominant process responsible for the formation of hydrogen atoms, is the dissociation reaction

$$H_2(X^1\Sigma_g^+) + e^- \rightarrow H + H + e^- , \quad (1)$$

whose efficiency is greater than that of the secondary reaction

$$H_2(X^1\Sigma_g^+) + e^- \rightarrow H_2^+ + e^- + e^- \rightarrow H + H^+ + 2e^- . \quad (2)$$

Excitation (respectively, ionization) of these ground-state atoms is then ensured by electronic inelastic collisions. Under continuous electric excitation, a quasistationary equilibrium sets up in which excitation processes are on the whole balanced by radiative and collisional depopulating processes. These deexcitation processes may be in the case of atomic hydrogen: diffusion toward the walls of the discharge tube, emission or absorption of radiation, inelastic collisions with electrons, and inelastic collisions with heavy particles (i.e., H_2 molecules). Except for metastable states, diffusion does not contribute to the destruction of excited atomic states in low-pressure glow discharge.

II. EXPERIMENT

We have studied the quenching mechanisms of the $n = 3, 4, 5$ atomic hydrogen excited states in the positive column of a low-pressure glow discharge by a time resolved spectroscopic analysis of the population relaxations following a short resonant laser pulse pumping. The experimental apparatus is schematically shown on Fig. 1. It has been previously described in experiments dealing with radiative and collisional processes in a helium glow discharge.[4-6] A tunable dye laser excited by a pulsed nitrogen laser SOPRA (pulse width, 4 ns, spectral width 0.2 Å, energy/pulse ~10 μJ, repetition rate, 15 Hz) is used to induce a selective and short perturbation on the population of an atomic hydrogen state by resonant optical pumping.

Excited states are produced in a capillary glow discharge (inner diameter, 4 mm, length, 60 mm) After high-vacuum cleaning (10^{-6} Torr) the discharge is created under continuous electrical power supply with a constant flow of hydrogen high-purity gas (flow rate <1 l/h). Pressure P, measured with two Pirani probes, can be adjusted from 0.2 to 2 Torr and current intensity i from 5 to 40 mA. For each experimental situation (P, i) corresponding value of the electronic density n_e is measured by a high-frequency cavity perturbation method, and value of the mean electronic kinetic energy E_e is only estimated in the frame of glow discharge theory. In pressure and current ranges under study, we obtain, respectively, $5.10^9 < n_e$

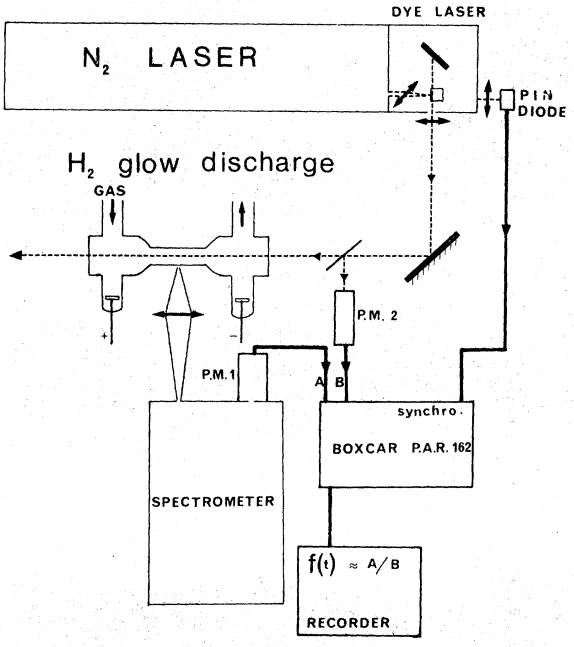

FIG. 1. Laser perturbation experimental setup.

$<5.10^{10}$ cm^{-3} and $3<E_e<10$ eV. Gas temperature is measured by means of a thermocouple in contact with the discharge tube ($T_g \sim 320 \pm 5$°K) assuming an homogeneous distribution in the medium.

After spatial filtering, the pump laser beam transverses the discharge tube avoiding stray light diffusion. The fluorescence light emitted by a cross section of the positive column is observed in a perpendicular direction and is imaged by a fused silica lens ($f=180$ mm, magnification = 1) onto the slits of a 1.15 m SOPRA grating spectrometer (resolving power: 50 000) and then onto a RCA 72 65 photomultiplier tube (rise time: 2 ns). Time dependence of the output signal is analyzed by a Princeton Applied Research Boxcar averager (PAR 162) synchronized with the pulsed laser giving on both channels A and B (PAR 164) a time resolution of 5 ns. The fluorescence signal (channel A) is normalized to the pump laser intensity peak detected by an auxiliary photomultiplier (channel B), since the Boxcar averager allows the measurement of the ratio A/B of two signals. Great care is taken to prevent saturation of the electronic by the fluorescence light and to avoid laser saturation effects on the relaxation of excited state populations. Finally, each fluorescence relaxation curve corresponds to 1.5×10^4 laser shoots average.

III. MEASUREMENTS

A partial diagram of hydrogen atomic and molecular energy states is shown in Fig. 2. The relaxations of population variations $\Delta N_n(t)$ for the $n=3,4,5$ atomic states induced by laser optical pumping of the following transitions:

$n'=2 \rightarrow n=3$ (H_α line $\lambda = 6563$ Å, dye: $R6G+CVP$),

$n'=2 \rightarrow n=4$ (H_β line $\lambda = 4861$ Å, dye: $C30+7D4MC$),

$n'=2 \rightarrow n=5$ (H_γ line $\lambda = 4340$ Å, dye: $POPOP$),

have been studied for various discharge conditions, (P, i). For the three transitions, the laser spectral width exceeds the width of the lines emitted by the discharge so that the whole atomic velocity distribution is pumped. $\Delta N_n(t)$ relaxations are deduced from measurements of the time variations of the spectrally integrated resonance fluorescence light intensities $\Delta I_n^{\text{fluorescence}} \propto \Delta N_n(t)$. Typical experimental results for $P=0.35$ Torr and $i=30$ mA are shown in Fig. 3 for $n=3,4,5$. After the laser pulse has ceased, the level populations go back to their equilibrium values with a nearly exponential time dependence. In this laser-free relaxation mode, level population variations can be represented by the law

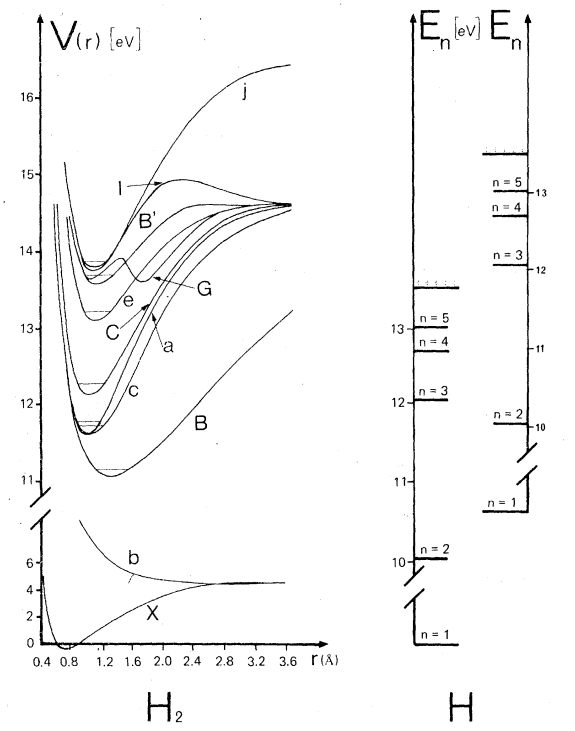

FIG. 2. Partial energy schemes of the H_2 molecule and H atom. The shifted and unshifted H energy diagrams correspond, respectively, to collisions with the quasimetastable and ground states of the H_2 molecule. (Data taken from Refs. 11 and 14).

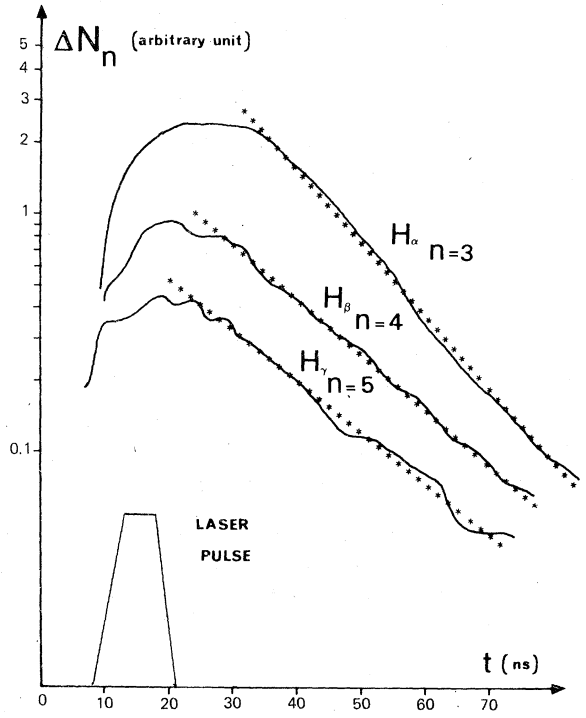

FIG. 3. Relaxation curves of the $n=3$, 4, 5, level population variations of H for $P=0.35$ Torr and $i=30$ mA.

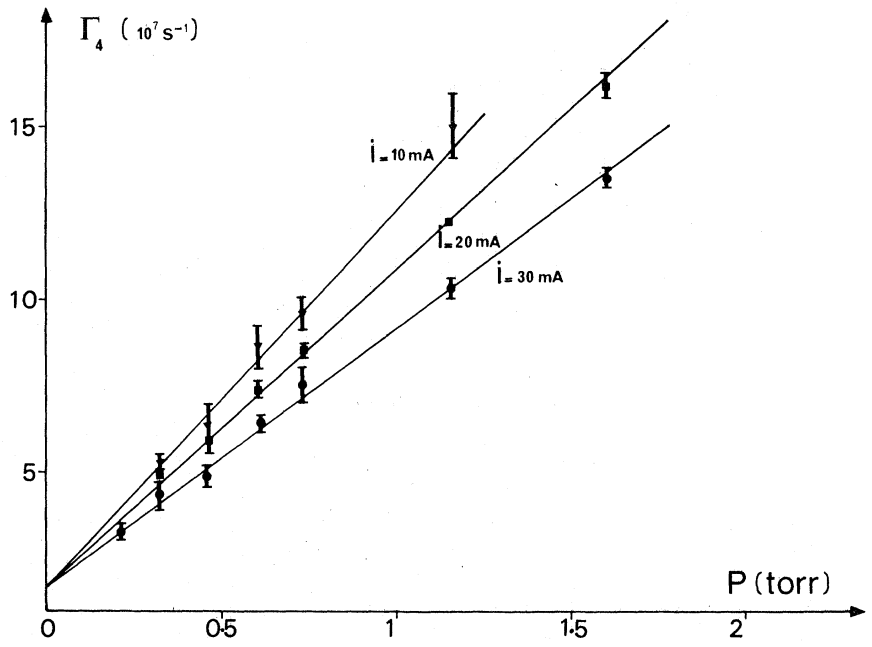

FIG. 4. Variations of the quenching rates $\Gamma_n(P, i)$ with P and i for $n=4$ H atomic state.

$$\Delta N_n(t) = \Delta N_n^{\circ} e^{-\Gamma_n(P,i)t} , \tag{3}$$

where $\Gamma_n(P, i)$ is the quenching rate of level n and depends on the discharge pressure and current intensity. As an example, the $\Gamma_n(P, i)$ experimental values deduced from the relaxation curves through Eq. (3) are shown on Fig. 4 as a function of the total pressure P in the discharge with i acting as a parameter for $n = 4$. From these curves, it follows with a rather good approximation that in the pressure and current ranges under study, $\Gamma_n(P, i)$ can be expressed in the form:

$$\Gamma_n(P, i) = A_n + B_n(i)P , \tag{4}$$

where A_n is a constant and $B_n(i)$ is a function of i alone.

IV. INTERPRETATION

Generally, in a low-pressure hydrogen-gas discharge, the quenching rate $\Gamma_n(P, i)$ of the atomic excited states may be expanded[7]

$$\Gamma_n(P, i) = \sum_{n' < n} A_{n'n} \Lambda_{n'n} + n_{H_2} \sum_{\nu} R_{n,\nu} + n_e \sum_{m} S_{nm} . \tag{5}$$

In this expression, $A_{n'n}$ and $\Lambda_{n'n}$ represent, respectively, the Einstein coefficient and the optical escape factor for the $n \rightarrow n'$ radiative transition, and $R_{n,\nu}$ [ν describing a molecular state ($\nu = \Omega, v, J$)] represents the rate for the reaction

$$H(n) + H_2 \rightarrow H + H_2^*(\nu) + \Delta E , \tag{6}$$

and S_{nm} is the excitation transfer rate from state n towards state m by electronic collisions

$$H(n) + e^- \rightarrow H(m) + e^- + \Delta E . \tag{7}$$

Finally, n_{H_2} and n_e are, respectively, the molecular and electronic population densities.

Under present experimental conditions, no induced atomic fluorescence was observed according to reaction (7) with $m > n$. On the other hand, transfers with $m < n$ were only detected for low pressure and current intensity and corresponded only to spontaneous radiative transitions from level n to m and not to reaction (7). These two experimental results clearly indicate that excitation transfer between $n = 3, 4, 5, 6$ atomic excited states of hydrogen by electronic collisions are negligibly small. This observation agrees well with calculated values[8] of the rates of reaction (7) and with recent experimental data.[9] Taking into account these results, Eq. (5) acquires the approximate form

$$\Gamma_n(P, i) \simeq \sum_{n' < n} A_{n'n} \Lambda_{n'n} + n_{H_2} \sum_{\nu} R_{n,\nu} . \tag{8}$$

Then, the observed variation of $\Gamma_n(P, i)$ with i can only be explained in terms of the variations of n_{H_2} with i, that is by the variation of the dissociation rate of H_2 with i in the discharge. Indeed, according to the dissociation process (1), the number density of H_2 molecules in the discharge $n_{H_2}(P, i)$ at total pressure P, gas temperature T_g, and current intensity i depends on the density and energy of electrons, so that one can write

$$n_{H_2}(P, i) = n_{H_2}^{\circ} f(n_e, E_e) , \tag{9}$$

TABLE I. Total radiative de-excitation rates of the $n=3$, 4, 5 levels of atomic hydrogen.

	$n=3$	$n=4$	$n=5$
$\sum_{n'<n} A_{n'n}\Lambda_{n'n}(s^{-1})$ (Thin plasma, Ref. 11)	9.98×10^7	3.02×10^7	1.153×10^7
$\sum_{n'<n} A_{n'n}\Lambda_{n'n}(s^{-1})$ (Thick plasma, Ref. 11)	4.41×10^7	1.74×10^7	0.743×10^7
$A_n(s^{-1})$ (This work)	$(4.42\pm0.05)\times10^7$	$(1.72\pm0.05)\times10^7$	$(0.90\pm0.05)\times10^7$

where $n^0_{H_2}$ is the molecular population density at total pressure P and gas temperature T_g without any dissociation (that is without electrical discharge $i=0$, $n_e=0$), and $f(n_e, E_e)$ is a function related to the dissociation rate of reaction (1) such that $f(n_e=0, E_e=0)=1$. A complete study of this dissociation rate will be published in a forthcoming paper,[10] but for the present work, one needs only to define $f(n_e, E_e)$ as the ratio of dissociated molecules at pressure P and current i. According to the relation $n^0_{H_2}=P/KT_g$, one gets: $n_{H_2}(P, i) = Pg(n_e, E_e)$ with $g(n_e, E_e)=f(n_e, E_e)/kT_g$, and Eq. (8) then becomes

$$\Gamma_n(P, i)=\sum_{n'<n} A_{n'n}\Lambda_{n'n}+Pg(n_e, E_e)\sum_{\nu} R_{n,\nu}\ . \quad (10)$$

By comparing Eq (4) and (10), one obtains

$$A_n=\sum_{n'<n} A_{n'n}\Lambda_{n'n},\quad B_n(i)=g(n_e, E_e)\sum_{\nu} R_{n,\nu}\ . \quad (11)$$

Here, A_n appears as the total radiative decay rate and $B_n(i)$ as the total collisional rate of level n.

The experimental values of the total radiative transition rates A_n are compared to accepted values: $\sum_{n'<n} A_{n'n}\Lambda_{n'n}$ (Table I) for an optically thin plasma: $\Lambda_{n'n}=1$, and for a plasma with reabsorption in the resonance lines: $\Lambda_{n'n}=1$, $n'\neq1$, and $\Lambda_{1n}=0$. The $A_{n'n}$ are taken from Ref. 11. Comparison shows that in the pressure range $0.1<P<3$ Torr the $n=3\rightarrow n'=1$, L_β, and $n=4\rightarrow n'=1$, L_γ, lines are completely trapped, whereas for $n=5$, an escape of radiation in the L_δ line of about 40% explains the relative discrepancy with the thick plasma case. A similar effect (escape of resonance radiation) has been studied previously in a He glow discharge.[5]

The collisional rates for reaction (6) are deduced from expression (10) after extrapolation of the experimental quenching rate $\Gamma_n(P, i)$ to zero current intensity. In these conditions, $g(n_e=0, E_e=0)=1/kT_g$ so that $B_n(0)=\sum_\nu R_{n,\nu}/kT_g$. Details of this extrapolation procedure will be reported in Ref. 10. $B_n(0)$ values and corresponding collisional thermally averaged cross sections $\bar{\sigma}^n_{H\text{-}H_2}\sim1.5\times10^{-14}$ cm^2, are given in Table II and indicate that quenching of excited H atoms by H_2 molecules is a powerful process fulfilling the quasiresonant condition $\Delta E/kT_g\simeq0$. The $\bar{\sigma}^n_{H\text{-}H_2}$ values are compared in Table II to recent results obtained by Lewis and Williams[12] who measured cross sections of the quenching collisions $H(n=3, 4, 5)$ with ground state H_2 after excitation and dissociation of the molecular gas by a 40-keV electron beam. For the three states an important disagreement is observed. In order to give an explanation of this discrepancy, we have looked for the molecular states (Ω, v, J) for which

TABLE II. Collisional de-excitation rates $B_n(0)$ and thermally averaged collisional cross sections $\bar{\sigma}^n_{H\text{-}H_2}$ for the $n=3, 4, 5$ levels of atomic hydrogen.

	$n=3$	$n=4$	$n=5$
$B_n(0)(s^{-1}\ \text{Torr}^{-1})$	$(15.0\pm0.2)\times10^7$	$(14.2\pm0.4)\times10^7$	$(14.5\pm0.5)\times10^7$
$\bar{\sigma}^n_{H\text{-}H_2}$(Å^2) (This work)	156 ±3	145 ±4	146 ±5
$\bar{\sigma}^n_{H\text{-}H_2}$(Å^2) (Ref. 12)	76 ±3	32 ±3	8.9±0.7

the following reactions:

$$H(n)+H_2[X^1\Sigma_g^+(0,J)]\rightarrow H(n'=1)+H_2(\Omega,v,J)+\Delta E\ , \tag{12}$$

are propable, as they fulfill the condition $\Delta E \ll kT_g$ and obey the usual optical selection rules. Energy values of H_2 and H states have been taken from Refs. 11, 13, and 14. Then, following Ref. 12, we have $\bar{\sigma}^n_{H\text{-}H_2} \propto \sum_{\nu,\nu'} A_{n1} q_{\nu\nu'} g_\nu$ with A_{n1} the Einstein coefficient for the $n\rightarrow 1$ transition, $q_{\nu,\nu'}$ the Franck-Condon factor for the electronic transition $\nu(X^1\Sigma_g^+, v=0, J)\rightarrow \nu'(\Omega', v', J')$, and g_ν the fraction of H_2 molecules in the state ν. Summation is performed on all states ν, ν' (typically three or four states) satisfying reaction (12). With the Franck-Condon factors given in Ref. 15, we obtain the following ratio: $\bar{\sigma}^3_{H\rightarrow H_2}/\bar{\sigma}^4_{H\rightarrow H_2}/\bar{\sigma}^5_{H\rightarrow H_2} = 1/0.2/0.02$. Experimentally, this ratio was found to be 1/0.9/0.9. Results of Ref. 12 are on the other hand in better agreement with this elementary model. In Ref 12, H_2 molecules were mainly in the ground state $X^1\Sigma_g^+(0,J)$ so that only reactions (12) contributed to atomic excited-state quenching as assumed in the model. But in our experiment, a part of H_2 molecules is also in electronic excited states. This part is generally small compared to the ground-state population, except for the quasimetastable group of states $c^3\pi_u$ and $a^3\Sigma_g^+$ which then may intervene as supplementary collisional deexcitation channels of atomic states[16]

$$H(n)+H_2\begin{pmatrix} c^3\ \pi_u \\ a^3\ \Sigma_g^+ \end{pmatrix}\rightarrow H(n'=2)+H_2(\Omega', v', J)+\Delta E\ . \tag{13}$$

Tables given in Ref. 13 indicate that for every level n, at least 20 deexcitation channels with $\Delta E < \frac{1}{4}kT_g$ exist. On the other hand, measurement by absorption of a cw dye laser beam at 5947.3 Å of the population density of the $a^3\Sigma_g^+(v=0, J=2)$ state leads to an estimate of the total population of quasimetastable states of about 5% of the total molecular population depending on the discharge conditions (P, i). We thus can expect to obtain an important population transfer of the atomic system towards the molecule according to reaction (13) which can explain the discrepancy with the results of Ref. 12. This has been experimentally verified for the $n=3$ level of H in the particular transfer reaction

$$H(n=3)+H_2[a^3\Sigma_g^+(v=0,J=4)]$$
$$\rightarrow H(n=2)+H_2(e^3\Sigma_u^+ v=2, J=5)-\tfrac{1}{15}kT_g\ . \tag{14}$$

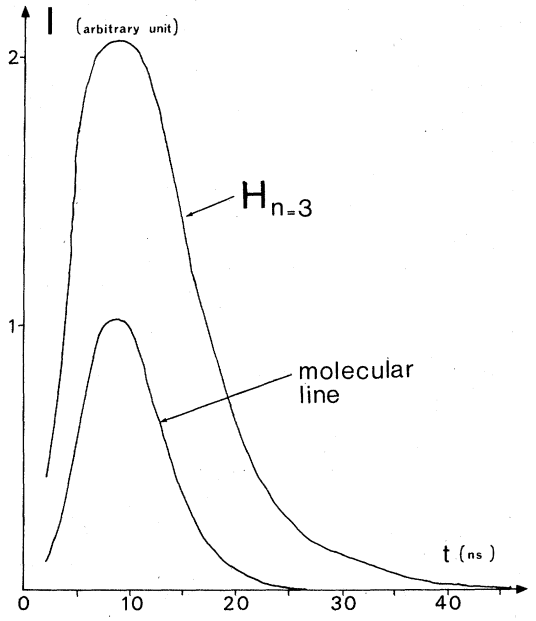

FIG. 5. Time resolved light intensities of the resonance atomic fluorescence (H_α) and collision induced molecular fluorescence (molecular line) according to the excitation transfer reaction (14).

Pumping the $n=3$ atomic level with the pulsed dye laser ($\lambda_a = 6563$ Å) we observed at the same time an increase of the induced fluorescence light starting from the $e^3\Sigma_u^+(v=2, J=5)$ state of $H_2(\lambda_m = 6568\ \text{Å} \neq \lambda_a)$. Result of the time resolved transfer experiment is shown on Fig. 5 in relative intensity scale, and exhibits clearly the efficiency of the quenching of H atomic states by metastable molecular states, since a great number of reactions similar to the one studied are allowed. The relaxation times of the atomic and molecular states deduced from Fig. 5 are of the same order of magnitude, which indicates that the two level populations are strongly coupled through collisions.

V. CONCLUSION

One thus can ascribe the quenching of atomic H states in a glow discharge to collisions with H_2 molecules in ground and quasimetastable states. Thermally averaged cross sections of 1.5×10^{-14} cm^2 indicate the great efficiency of the mechanisms which strongly connect atomic and molecular states. This coupling through atom-molecule excitation transfers may be for the main part responsible for the anomalies observed in the measurements of molecular rotational temperatures and atomic excitation temperatures in H_2 glow

discharges. The transfer process tends to depopulate atomic excited states for the benefit of excited molecular states, leading to an apparent increase of H_2 rotational temperature and an apparent decrease of H excitation energy. This is precisely the case of the discharge under study where $T_{rot}^{H_2} \sim 450$ °K, $T_{gas} \sim 320$ °K and $T_{exc}^{H} \sim 0.1$ eV, $E_e \sim 5$ eV.

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