

УДК 533.9.01

EXPERIMENTAL AND NUMERICAL SIMULATION OF THE VIBRATIONAL DISTRIBUTION FUNCTION OF THE HYDROGEN MOLECULE IN THE GROUND STATE $X^1\Sigma_G^+$ IN GAS DISCHARGES¹⁾**Yu.A. LEBEDEV¹, V.A. SHAKHATOV¹, A. LACOSTE², S. BECHU²**¹ *Topchiev Institute of Petrochemical Synthesis RAS, Moscow*² *Centre de Recherche, Plasma – Matériaux – Nanostructures, Grenoble, France**E-mail: lebedev@ips.ac.ru***ЭКСПЕРИМЕНТАЛЬНОЕ И ЧИСЛЕННОЕ МОДЕЛИРОВАНИЕ КОЛЕБАТЕЛЬНОЙ ФУНКЦИИ РАСПРЕДЕЛЕНИЯ МОЛЕКУЛЫ ВОДОРОДА В ОСНОВНОМ СОСТОЯНИИ $X^1\Sigma_G^+$ В ГАЗОВЫХ РАЗРЯДАХ****Ю.А. ЛЕБЕДЕВ¹, В.А. ШАХАТОВ¹, А. ЛАКОСТЕ², С. БЕШУ²**¹ *Институт нефтехимического синтеза им. А.В. Топчиева РАН, г. Москва,*² *Исследовательский центр «Плазма-Материалы-Наноструктуры», г. Гренобль (Франция)***Summary**

The comparison of the vibrational distribution functions obtained by experimental techniques and numerical simulation in the different discharges was carried out. There are considered and discussed different sets of level – to – level rate coefficients at which a good agreement is observed between theory and experiment.

Key words: vibrational distribution function, hydrogen molecule, gas discharges.

Аннотация

Проведено сравнение колебательных функций распределения, полученных экспериментальными методами и путем численного моделирования для различных разрядов. Рассматриваются и обсуждаются различные наборы уровневых коэффициентов скоростей, для которых наблюдается хорошее согласие между теорией и экспериментом.

Ключевые слова: колебательная функция распределения, молекулы водорода, газовый разряд.

Introduction

Interest in the study of hydrogen low-temperature plasma (LTP) due to the development and optimization of discharge sources of intense ion beams of negative atomic hydrogen [1]. This work is a continuation of [2], and is devoted to the development of hydrogen collision-radiative model (CRM) considering the kinetics of hydrogen molecules in the singlet and triplet states. At this stage of the research focuses on the description of the vibrational kinetics of hydrogen molecules in the ground state $X^1\Sigma_g^+$ in a pulsed glow discharge (PGD) [3]. Set of level cross-sections and rate coefficients determined from the comparison of the calculated vibrational distribution function (VDF) with the measured VDF [4-8].

1. Collision-radiative model

CRM of hydrogen LTP consists of a database for the cross sections and rate coefficients of elementary particle processes in hydrogen; computational modules, which are designed to determine the electron energy distribution function (EEDF) and the concentration of particles in the excited states; a module for identifying and establishing a hierarchy of the kinetic processes.

¹⁾ This work was partly supported by RFBR (grant № 12-08-91052)

The initial data for calculations of the EEDF were measured gas pressure, the concentration of hydrogen atoms, electron density and temperature, the translational temperature, electric field [3–8]. Isotropic part of the EEDF is determined by solving the kinetic equation for the electrons in the binomial approximation. In [2], based on the analysis of a large set of experimental and calculated data created database of cross-sections of electron collisions with molecular hydrogen. In contrast to existing models, the increased number of elementary processes and excited states of hydrogen for use CRM in optical diagnostics of hydrogen plasma.

Identified: self-consistent set of cross-sections that should be used when calculating the EEDF, its moments and balance of electron energy in the hydrogen LTP; basic processes that determine the parameters of the electronic component in a wide range of the reduced electric field E/N .

For solving the equation of electron transport the following processes were taken into account: elastic collisions of electrons with H_2 ; excitation and de-excitation of rotational levels J of hydrogen molecules (set of cross-sections includes transitions $J \rightarrow J+2$ and for levels $J = 2-11$); resonant excitation and de-excitation of vibrational levels $\nu = 1-14$ of the hydrogen ground state $X^1\Sigma_g^+$ (set of cross-sections includes includes both single-photon and multiphoton transitions $\nu \rightarrow \nu + \Delta\nu$, $\Delta\nu = 1-14$); excitation and de-excitation of 15 singlet electron excited states $2B^1\Sigma_u^+$, $2C^1\Pi_u$, $3B^1\Sigma_u^+$, $2D^1\Pi_u$, $4B'^1\Sigma_u^+$, $4D^1\Pi_u$, $2EF^1\Sigma_g^+$, $3I^1\Pi_g$, $3HH^1\Sigma_g^+$, $3GK^1\Sigma_g^+$, $3J^1\Delta_g$, $4P^1\Sigma_g^+$, $4O^1\Sigma_g^+$, $4R^1\Pi_g$, $4S^1\Delta_g$, and 11 triplet electron excited states $2c^3\Pi_u$, $2a^3\Sigma_g^+$, $3e^3\Sigma_u^+$, $3d^3\Pi_u$, $3h^3\Sigma_g^+$, $3g^3\Sigma_g^+$, $3i^3\Pi_g$, $4f^3\Sigma_u^+$, $4k^3\Pi_u$, $4r^3\Pi_g$, $4s^3\Delta_g$ with a resolution of the vibrational levels $\nu = 0-14$ of the ground electronic state; dissociative excitation of 15 singlet electron excited states $2B^1\Sigma_u^+$, $2C^1\Pi_u$, $3B^1\Sigma_u^+$, $2D^1\Pi_u$, $4B'^1\Sigma_u^+$, $4D^1\Pi_u$, $2EF^1\Sigma_g^+$, $3I^1\Pi_g$, $3HH^1\Sigma_g^+$, $3GK^1\Sigma_g^+$, $3J^1\Delta_g$, $4P^1\Sigma_g^+$, $4O^1\Sigma_g^+$, $4R^1\Pi_g$, $4S^1\Delta_g$ with a resolution of the vibrational levels $\nu = 0-14$ of the ground electronic state; dissociative excitation of 2 triplet states $2b^3\Sigma_u^+$ и $3e^3\Sigma_u^+$ with a resolution of the vibrational levels $\nu = 0-7$ and $\nu = 0-14$, respectively, of the ground state $X^1\Sigma_g^+$ of hydrogen; direct electron impact ionization of vibrational excited molecules of hydrogen H_2 ($X^1\Sigma_g^+$, $\nu = 0-14$); electron impact dissociative ionization of H_2 ($X^1\Sigma_g^+$, $\nu = 0-14$) through formation of the vibrational excited molecular ions in the stable $X^2\Sigma_g^+$ and unstable $B^2\Sigma_u^+$ states; electron capture H_2 ($X^1\Sigma_g^+$, $\nu = 0-14$) via formation of negative hydrogen molecular ion H_2^- .

In high-current atmospheric pressure PGD and in different discharges [3–8] a high degree of H_2 dissociation can be achieved. Along with the electron – molecule collisions a significant role in the kinetics of hydrogen LTP play electron – atomic collisions. Ref. [2] provides a review and analysis of the momentum transfer cross-sections for elastic scattering of electrons on the hydrogen atom (transport cross-sections) obtained in experiments and calculated. The transport cross-section was defined, which is recommended to use in the calculation of the EEDF.

To simplify the analysis of the kinetics of the vibrational levels of the hydrogen molecule in the ground electronic state in different discharges [3–8] processes of elastic and inelastic collisions of electrons with H are not considered in solving the equations for the EEDF and concentrations of excited particles. Atomic hydrogen kinetics of LTP is the subject of further research.

In solving the balance equations for the concentrations considered: vibration – excited hydrogen molecules in the ground electronic state H_2 ($X^1\Sigma_g^+$, ν) (15 vibrational levels up to the dissociation limit); hydrogen atoms in the ground state and the electrons e. Concentration of electrons in the calculations relied constant. For the conditions of atmospheric pressure hydrogen PGD it was equal to $N_e \approx 10^{15}$ [3]. To investigate the influence of hydrogen atoms in the ground state on the kinetics of H_2 ($X^1\Sigma_g^+$, ν) their concentration was varied in the calculations. In the calculations of the hydrogen molecule in PGD discharges [4–8] used the experimental values of the concentration of atomic hydrogen.

CRM for H_2 ($X^1\Sigma_g^+$, ν) kinetics consider the resonant excitation and de-excitation of vibrational levels of hydrogen ν by electron impact. Excitation of vibrational levels via singlet state of the hydrogen molecule will be considered at the next stage of research. Cross-section data necessary to determine the rate coefficients of vibrational excitation and de-excitation of hydrogen molecules included in the balance equations of vibrational kinetics discussed earlier in [2].

Our model of hydrogen LTP differs from the models described in the literature that the process of excitation

and deactivation of $H_2(X^1\Sigma_g^+, \nu)$ by electron impact takes into account all kinds of single-photon and multiphoton transitions $X^1\Sigma_g^+, \nu \leftrightarrow X^1\Sigma_g^+, \nu'$ between vibrational levels (up to $\nu = 14$).

In describing the kinetics of gas-phase vibration – excited molecules following processes were taken into account: vibrational – translational (VT) exchange of energy and vibrational – vibrational (VV) exchange of energy between molecules; multiquantum vibrational – translational (VT) exchange of energy between molecules and atoms, which may be accompanied by chemical transformations; deactivation of $H_2(X^1\Sigma_g^+, \nu)$ on the wall of the discharge chamber.

2. Results and discussion

Figure 1 (a–d) shows the results of calculations performed by the CRM, developed in this work, and measurements [4–8] VDF of hydrogen molecules in the ground electronic state $X^1\Sigma_g^+$. The measured values of the vibrational temperature $T_\nu(X^1\Sigma_g^+)$ of the first level are in the range 1600–3800 K [4, 5], 1300–2390 K [6], 1450–2200 K [7] and 2300 K [8]. They are in satisfactory agreement with the results of calculation (1700–2760 K). It is important to emphasize that the CRM satisfactorily describes the concentration of $H_2(X^1\Sigma_g^+, \nu)$ on high vibrational levels (Figure 1a).

The best agreement between the calculated and measured VDF of hydrogen molecules and $T_\nu(X^1\Sigma_g^+)$ achieved for rate coefficients of VT and VV processes and the connection formulas given in [9]. It should be noted that the coefficient rates of multiphoton VT – exchange of energy between molecules and atoms, recommended in [10], seems to be overestimated by an order of magnitude.

The calculations revealed that EEDF in the hydrogen PGD ($E/N > 100$ Td, $T_e = 4$ eV, $N_e \approx 10^{15}$ cm $^{-3}$, $T_g = 310$ K), slightly differs from the Maxwellian EEDF. Maxwellian distribution with $T_e = 4$ eV was used to determine the rate coefficients of the processes of electron – molecule collisions.

Changing the kinetic scheme of stepwise excitation of vibrational levels of the hydrogen molecule by electron impact has little effect on the quasistationary VDF of hydrogen molecule. However, the relaxation time τ_{Ev} depends strongly on the number of processes in the kinetic scheme of CRM (the completeness of the kinetic scheme). Value τ_{Ev} is non-monotonic function of the number of processes.

Thus, to correctly describe the vibrational relaxation processes in a pulsed discharge and flow plasma chemical reactors, it is important to consider all possible transitions $\nu \leftrightarrow w$ between vibrational levels. The degree of completeness of the kinetic scheme of stepwise electron impact excitation of molecules plays an important role in describing the kinetics of $H_2(X^1\Sigma_g^+, \nu)$ in PGD.

Concentrations vs. time for all vibrational levels, except levels $\nu = 1 - 5$, are monotonic: the concentration of the vibrational level $\nu = 0$ decreases monotonically, while the concentrations of $\nu \geq 6$ vibrational levels increase monotonically with time as partial local thermodynamic equilibrium at $T_e = 4$ eV is achieved between the vibrational degrees of freedom of the hydrogen molecule and translational degrees freedom of electrons. The concentrations of levels $\nu = 1 - 5$ at the initial stage of vibrational relaxation increases, reaching maximum value the residence time of the molecules in PGD $\tau_D \approx 5 \cdot 10^{-6}$ s, and then slowly decrease.

Thus, a closed system, which includes the vibrational degrees of freedom of the hydrogen molecule and the translational degrees of freedom of electrons at times $\tau_D \leq 10^{-4}$ s, monotonically tends to partial local thermodynamic equilibrium between the degrees of freedom. This suggests that for correct description of the temporal evolution of the system is necessary to use approach of level-to-level (generalized, vibrational) kinetics.

Adding single-photon vibrational – translational – energy exchange between hydrogen molecules in the kinetic scheme leads to a noticeable change in the kinetics of the populations $H_2(X^1\Sigma_g^+, \nu \geq 9)$ at $\tau_D \geq 10^{-8} - 10^{-7}$ s. Processes of VT -energy exchange between hydrogen molecules cause an imbalance for a group of high vibrational levels $\nu \geq 9$. Found difference is due to high values of rate coefficients of the single-photon vibrational – translational VT -energy exchange between hydrogen molecules compared to the rate coefficients corresponding to electron collisions of the first and second kind with $H_2(X^1\Sigma_g^+, \nu \geq 9)$.

Inclusion of the vibrational – vibrational VV -energy exchange between hydrogen molecules in the kinetic scheme leads to the enrichment of the populations at high vibrational levels $\nu \geq 9$ at $\tau_D \geq 10^{-7}$ s, as compared with those obtained without taking them into account. Competing of electron collisions of the

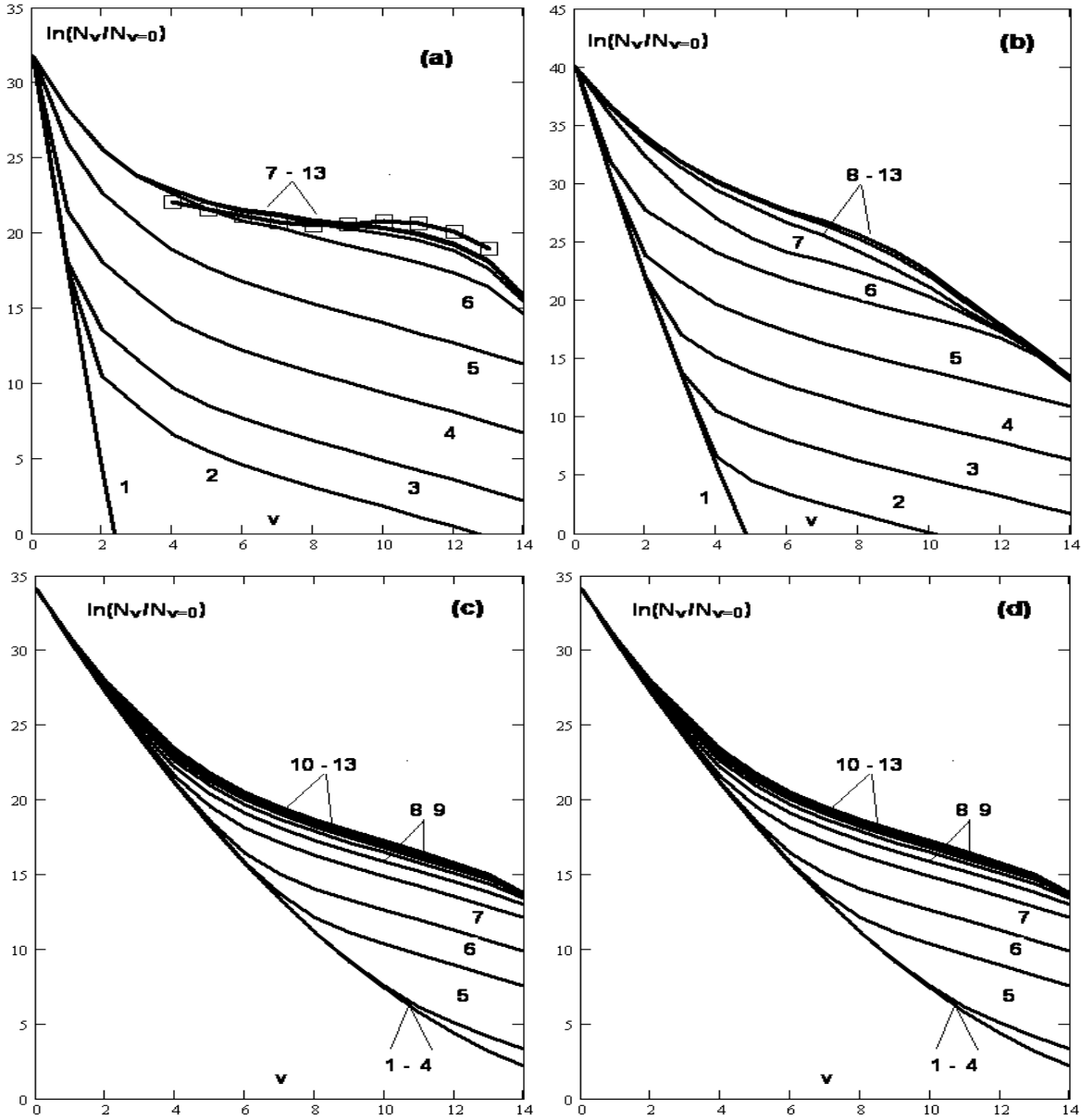


Fig. 1: Results of calculations (solid lines) and experiments (symbols) of hydrogen molecules VDF at different time (τ_D , s): (a) $1 - 10^{-19}$, $2 - 5 \cdot 10^{-10}$, $3 - 10^{-8}$, $4 - 10^{-6}$, $5 - 10^{-4}$, $6 - 10^{-2}$, $7-13$ from 0.1 to 0.15 [4, 5], $T_\nu(X^1\Sigma_g^+) = 1700$ K; (b) $1 - 10^{-19}$, $2 - 10^{-13}$, $3 - 10^{-11}$, $4 - 10^{-9}$, $5 - 10^{-7}$, $6 - 10^{-6}$, $7 - 3 \cdot 10^{-3}$, $8-13$ from $5 \cdot 10^{-3}$ to 0.4 [6], $T_\nu(X^1\Sigma_g^+) = 1800$ K; (c) $1-4$ from 10^{-19} to 10^{-9} , $5 - 10^{-7}$, $6 - 10^{-6}$, $7 - 10^{-5}$, $8 - 3 \cdot 10^{-5}$, $9 - 6 \cdot 10^{-5}$, $10-13$ from $9 \cdot 10^{-5}$ to $2 \cdot 10^{-4}$ [7], $T_\nu(X^1\Sigma_g^+) = 1680$ K; (d) $1-4$ from 10^{-19} to 10^{-9} , $5 - 10^{-7}$, $6 - 10^{-6}$, $7 - 10^{-5}$, $8 - 3 \cdot 10^{-5}$, $9 - 6 \cdot 10^{-5}$, $10-13$ from $92 \cdot 10^{-5}$ to $22 \cdot 10^{-4}$ [8], $T_\nu(X^1\Sigma_g^+) = 2760$ K.

first and second kind with $H_2(X^1\Sigma_g^+, \nu)$, and the single-photon VT - and VV -energy exchange between hydrogen molecules leads to disruption of partial local thermodynamic equilibrium between the vibrational degrees of freedom of the hydrogen molecule and translational degrees of freedom of the electrons.

The key points in the modeling of vibrational kinetics of the hydrogen molecule in the PGD are the concentration of atomic hydrogen in the ground electronic state in the plasma and the values of level

multiphoton VT – the exchange of energy between molecules and hydrogen atoms.

It has been established that the kinetics and the relaxation time of the hydrogen molecule VDF depends on those parameters. With increasing content of atomic hydrogen α_H from $5 \cdot 10^{-4} \%$ to $5 \cdot 10^{-1} \%$ transient period is reduced from $4 \cdot 10^{-7}$ to $\approx 10^{-7}$ s. Monotonic decrease in $H_2(X^1\Sigma_g^+, \nu)$ concentration with increasing number of the vibrational level is replaced by a dependence which has a maximum population level $\nu = 11$ (fig. 1a).

3. Conclusion

Thus, this study investigated the imbalance between the internal degrees of freedom of the hydrogen molecule in the ground electronic state and translational degrees of freedom of the molecules. The formation of the distribution function of the vibrational levels of the hydrogen molecule in the ground electronic state was studied. The database of the measured and calculated rate coefficients of vibrational – translational (VT) and vibrational – vibrational (VV) energy exchange between molecules and atoms in the ground state, the measured EEDF and VDF hydrogen molecules in the ground electronic state (vibrational temperatures), electron density and temperature, the translational temperature, the electric field intensity. Defined set of level-to-level rate coefficients for which the agreement is reached between the calculated VDF of hydrogen molecule with the measured VDF [4–8].

REFERENCES

1. Bechu S., Soum-Glaude A., Bes A., Lacoste A., Svarnas P. // *Physics of Plasmas*. – 2013. – V. 20. – P. 101601.
2. Shakhatov V.A., Lebedev Yu.A. // *High Temperature*. – 2011. – V. 49. – P. 265.
3. Amirov P.X., Asinovskii E.I., Markovec V.V. // *High Temperature*. – 1984. – V. 22. – P. 1002.
4. Mosbach T., Katsch H.-M., Dobelev H.F. // *Physical Review Letters*. – 2000. – V. 85. – P. 3420.
5. Mosbach T. // *Plasma Sources Sci. Technol.* – 2005. – V. 14. – P. 610.
6. Shirley J.A., Hall R.J. // *J. Chem. Physics*. – 1977. – V. 67. – P. 2419.
7. Pealat M., Taran J.-P.E., Bacal M., Hillion F. // *J. Chem. Phys.* – 1985. – V. 82. – P. 4943.
8. Scott C.D., Farhat S., Giquel A., Hassouni K., Lefebvre M. // *J. Thermophysics and Heat Transfer*. – 1996. – V. 10. – P. 426.
9. Billing G.D. // *Chem. Phys.* – 1977. – V. 20. – P. 35.
10. Gorse C., Capitelli M., Bacal M., Bretagne J., Lagana A. // *Chem. Physics*. – 1987. – V. 117. – P. 177