Vibrational population of hydrogen molecules excited by an RF discharge in an expanding thermal arc plasma as determined by emssion spectroscopy

Contrib. Plasma Phys. 35 (1995) 3, 195–202

Vibrational Population of Hydrogen Molecules Excited by an RF Discharge in an Expanding Thermal Arc Plasma as Determined by Emission Spectroscopy

D. K. Otorbaev, M. J. de Graaf, M. C. M. van de Sanden and D. C. Schram

Department of Physics, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands

Abstract

This work is devoted to the determination of the vibrational population of hydrogen molecules in the ground and excited electronic states from the analysis of visible spectra of the H_2 molecules excited by an RF discharge in an expanding thermal arc plasma. Comparison of the experimental results on relative electron-impact excitation cross sections for the transition $H_2(X^1\Sigma_g^+, v^0 = 0) \rightarrow H_2(d^3\Pi_u, v')$ with other experiments, and with calculations based on the Franck-Condon principle, shows good agreement. This means, that for plasma under investigation: 1) in the ground electronic state $H_2(X^1\Sigma_g^+)$, only the lowest vibrational level with $v^0 = 0$ is significantly populated, and 2) direct electron exictation of $H_2(d^3\Pi_u, v')$ state from the ground state $H_2(X^1\Sigma_g^+, v^0 = 0)$ dominates.

1 Introduction

Hydrogen plasmas have important applications in many areas of modern science and technology, in particular in surface modification techniques, such as deposition and etching, desorption of boundary layers of solids and liquids [1–3]. The kinetics of hydrogen vibrationally-excited molecules are of great interest in understanding the processes of H^- formation in volume and surface production negative ion sources [4]. In connection with these topics, a special interest arises in the development and characterisation of high intensity sources of reactive hydrogen radicals; vibrationally-excited molecules, atoms and ions.

A new cascaded arc expanding plasma source shows very promising perspectives in view of the use of these plasmas for ultrafast deposition of amorphous silicon, amorphous carbon, graphite and diamond thin film [5–7]. In the past, the fundamental of the pure argon expanding plasmas have been studied extensively. This research has resulted in a good understanding of expanding plasmas in pure argon [8, 9]. The next step towards the applications is the study of hydrogen plasmas, since the hydrogen is the permanent component in the deposition experiments [5–7], as well as in the schemes, where the expanding plasmas is used as a hydrogen negative and positive ion source [10].

Properties of vibrationally-excited hydrogen molecules is the subject of special interest for the characterization of expanding thermal plasma [11, 12]. De Graaf et al. [13] have shown that the main reason for the recombination of expanding flows of hydrogen-containing plasma is the charge transfer between a proton and a vibrationally-excited hydrogen molecule followed by the dissociative recombination of H_2^+. The bottleneck of above mechanism is presence in the expanding plasma flow of vibrationally-excited hydrogen molecules $H_2^{v \geq 4}$. In principle, such molecules can be produced either by the cascaded arc, or/and through the excitation processes in the expanding volume [12, 14]. For example, if

hydrogen molecules are formed on the metal walls of the arc or/and of the vessel they should be in vibrationally-excited states [15–17]. Since the detailed mechanism of production and destruction of H_2^v molecules in the expansion is not know yet, a new information about the total density of vibrationally-excited hydrogen molecules is crucial both for the fundamentals, and for the applications of expanding plasma sources.

In spite of importance of characterisation of H_2^v properties, the problem concerning the relation between the vibrational distributions of H_2 in ground and electronically excited states is far from complete solution. From the practical point of view such an investigation is essential for the determination of the vibrational distribution in the ground electronic states using molecular emission spectroscopy [18]. Such a method is in many cases to be preferred because of its inherent simplicity. The only alternatives are rather complicated methods of laser spectroscopy such as Coherent Anti-Stokes Raman Scattering (CARS) [19, 20], four-wave frequency mixing (FWFM) [21], Laser-Induced Fluorescence [22], or Resonance-Enhanced Multi-Photon Ionization (REMPI) [15]. The aim of the present paper is apply emission spectroscopy to measure the vibrational population of hydrogen molecules in the electronically excited state $H_2(d^3\Pi_u)$, and then to calculate the vibrational population of H_2 in the ground electronic state $H_2(X^1\Sigma_g^+)$ for an additional RF discharge excited expanding thermal arc hydrogen plasma.

2 Background

After the suggestion in Ref. [23], the method of determination of vibrational populations in the ground state of the N_2 molecule from the intensities of the electronic-vibrational (vibronic) emission bands of the second positive system of molecular nitrogen $N_2(C^3\Pi_u \rightarrow B^3\Pi_g$ transition) has been developed in [24, 25]. At low enough discharge pressure, when direct electron impact and radiative decay of the $N_2(C^3\Pi_u)$ prevail, the populations of vibrational levels in the ground electronic state $N_2(X^1\Sigma_g^+)$ can be calculated from the measured populations of excited electronic states. To that end the assumption was made in [23–25] that for direct electron impact, the relative excitation cross sections for transitions between various vibrational levels of the ground and excited electronic states are proportional to the Franck-Condon factors. This assumption has later been confirmed experimentally for molecular nitrogen [26]). The attempts to take into account a form of the electron energy distribution function $f(\varepsilon)$ in the calculation of excitation rates for different vibronic levels, have been made in [25–28], where either theoretical or experiment information on $f(\varepsilon)$ was used.

3 Experiment

The measurements of vibrational populations in the electronically excited state $H_2(d^3\Pi_u, v')$ (vibronic populations) have been carried out for pure hydrogen plasma of an expanding thermal arc. The apparatus consists of a thermal plasma (cascaded arc) mounted on a vacuum vessel (Fig. 1). The cascaded arc is used to produce a wall stabilized thermal plasma and can be operated over a wide range of pressures and currents. The discharge is drawn between three cathode tips and an anode plate. Thermal confinement of the plasma is realized by a stack of electrically insulated water cooled copper plates with 4 mm central bore. Pure hydrogen is fed through a mass controller into the cathode side where it is ionized. The plasma flows through the channel, accelerates and expands into a vessel at low pressure. Typical operation conditions for the cascaded arc are: discharge current – 35–55 A, voltage – 150–200 V, gas flow – 50–150 scc/s, pressure in the arc – 0.1–1 bar [11, 14]. The vacuum chamber has a length of 40 cm and a diameter of 40 cm. It is pumped by a chain of two roots blowers and a rotary pump; the pressure can be regulated between 0.25 and 13 mbar.

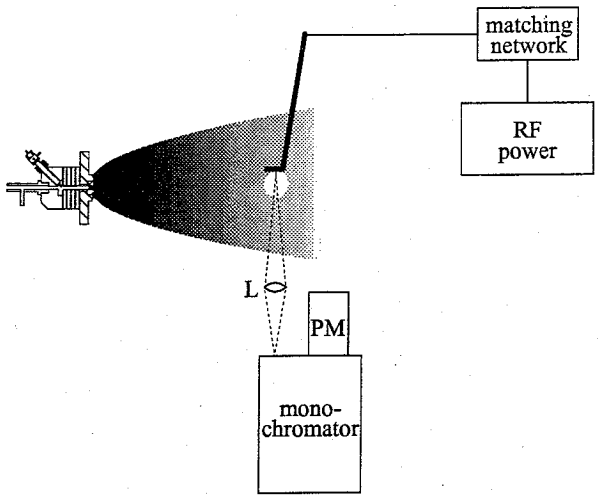

Figure 1. The experimental set up with the RF active probe.

For the expanding hydrogen plasma no molecular bands, but only Balmer lines of atomic hydrogen, originating from electron-ion recombination are seen in the visible emission spectrum of the plasma [11, 14]. This is due to the fact that the expanding plasma from a cascaded arc in hydrogen is a strongly recombining plasma with a low degree of ionization, cold electrons and absence of any electron excitation [11, 14, 29]. In order to observe visible emission spectra of other than atomic hydrogen species, it is necessary to heat additionally the electrons in the plasma. One of the options is to apply a radio-frequency (RF) heating to some local points of the plasma. In our experiments we used an RF excited probe. The RF power was 8–20 W and the frequency was 100–400 kHz. The RF radiation of the probe excited a small local part of the plasma volume with the characteristic dimensions of 2–6 mm. The so-called active probe is located at a distance of 25 cm from the nozzle of cascaded arc on the vessel's axis (Fig. 1). The RF excited active probe causes around the probe locally the emission of visible light. The emission spectrum contains a large number of spectral lines of atomic and molecular hydrogen, which are excited by the fast electrons of RF discharge. Fig. 2 illustrates the example of a hydrogen spectrum, excited by a RF probe in the range 590–630 nm.

With a monochromator and photomultiplier, the intensities of different rotational lines of several diagonal vibronic bands of the Fulcher system of molecular hydrogen $H_2(d^3\Pi_u, v', j' \rightarrow a^3\Sigma_g^+, v'', j''$ transition) [18, 30] are measured. From those measurements the populations of different rovibronic levels in the electronically excited state $H_2(d^3\Pi_u)$ are determined.

4 Results and Discussion

From the emission spectra of molecular hydrogen, using Boltzmann-like plots for relative molecular line intensities, the rotational temperature of excited molecules can be obtained [18, 30]. In case of direct electron excitation of the molecules, the rotational temperature of the excited states is directly coupled to that of the ground state. As in this type of discharge the rotational temperature in the ground state is close to the gas (translational) temperature [30], emission spectra can be used to measure the gas temperature T_0. As it shown previously [30] the way to determine the rotational temperature in the ground electronic state is to measure a rotational temperature for the

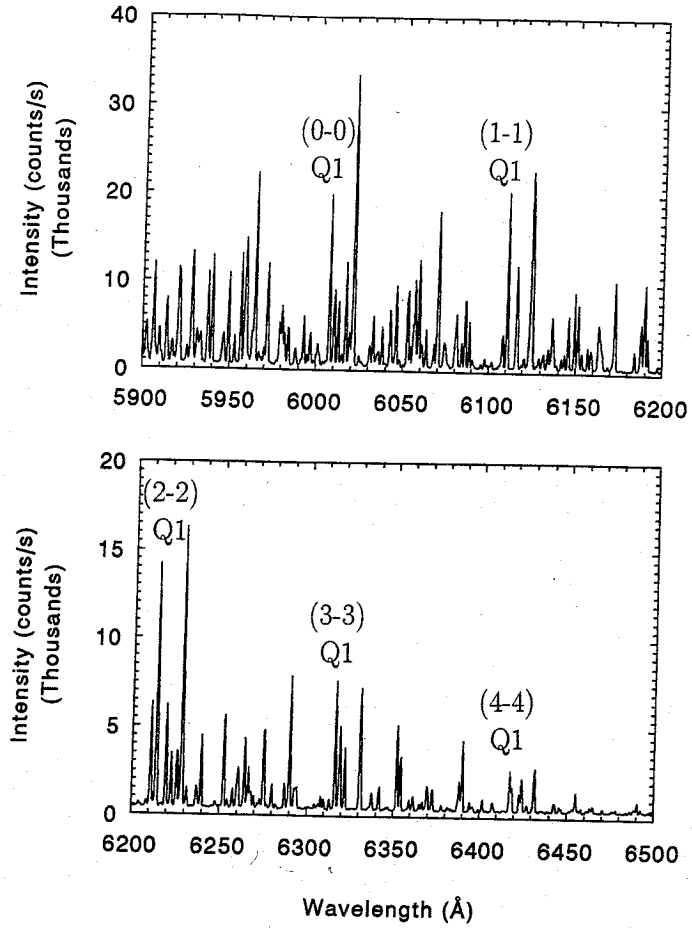

Figure 2. Experimental spectrum in the range of 590–630 nm, excited by a RF probe. The rotational lines Q1 of a various diagonal vibronic bands of Fulcher system of H_2 are indicated. Plasma parameters: gas flow rate 120 scc/s, arc current 37 A, applied to the active probe RF power 20 W.

$H_2(d^3\Pi_u^-)$ state and to relate this to the ground state rotational temperature. The excited state rotational temperature can be determined from the best line fit in a Boltzmann plot, $\ln(I_{j'j''}/\nu_{j'j''}^4 S_{j'j''})$ (here $I_{j'j''}$ are the rotational spectral line intensities, $\nu_{j'j''}$ are the rotational line wavenumbers, $S_{j'j''}$ are the Hönl-London factors) versus the rotational energy. Fig. 3 shows, as an example, the Boltzmann plot of a (0-0) rotational band of the Fulcher system of molecular hydrogen $H_2(d^3\Pi_u, v' = 0, j' \rightarrow a^3\Sigma_g^+, v'' = 0, j'')$ for three different pressures in the vessel. For the experimental conditions considered the rotational temperature of hydrogen molecules in the ground electronic state, which is equal to the gas temperature [30], is between 1200 and 1400 K. It is easy to calculate, that for such temperature a thermal excitation of hydrogen molecules to excited vibrational levels $v^0 > 0$ is very small. Furthermore, relative concentration of thermally excited molecules $H_2(v^0 > 0)$ will not be larger than 2% of the full concentration of H_2 molecules.

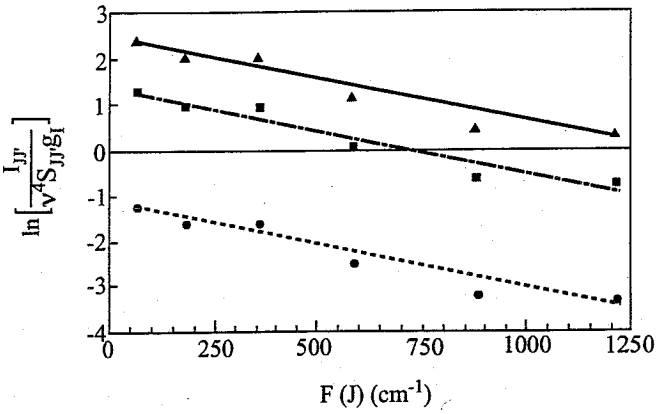

Figure 3. Boltzmann plot of the first six lines of Q-branch in the (0-0) rotational band of the Fulcher system of molecular hydrogen $H_2(d^3\Pi_u, v' = 0, j \rightarrow a^3\Sigma_g^+, v'' = 0, j'')$ for three different pressures in the vessel: ● — $p = 1$ mbar, ■ — $p = 6.5$ mbar, ▲ — $p = 13$ mbar. Plasma parameters are the same as in Fig. 2.

Tab. 1 illustrates the Franck-Condon factors for transitions between ground and high lying states of molecular hydrogen [31], relative electron-impact excitation cross sections of the Fulcher band of H_2, which have been obtained from both experiments in gas discharge plasma [28], and with crossed electron and molecular beam technique [32—34]. Our experimental results are shown in a last column of Tab. 1. The data presented are proportional to the molecular excitation rate for the reaction $H_2(X^1\Sigma_g^+, v^0) + e \rightarrow H_2(d^3\Pi_u, v') + e$. The results were calculated from the experimentally derived relative population densities of vibronic states of $H_2(d^3\Pi_u, v')$, with taking into consideration the relative probabilities for the radiative decay: $H_2(d^3\Pi_u, v' \rightarrow a^3\Sigma_g^+, v'')$ [35]. The relative population densities of the vibronic states have been measured and remained the same for the following experimental conditions: hydrogen flow rate 80—120 scc/s, background pressure $p = 1.3$ mbar cascaded arc current $I = 37$ A; applied to the active probe RF power is varied in the range of 10—20 W.

It is seen from the Tab. 1 that our experimental results agree satisfactorily with those determined ealier, both experimentally, and theoretically on the basis of the Franck-Condon principle. It means that for the experimental conditions: 1) only the vibrational level $v^0 = 0$ in the ground electronic state $H_2(X^1\Sigma_g^+)$ is significantly populated, and 2) direct electron excitation of $H_2(d^3\Pi_u, v')$ state from the ground state $H_2(X^1\Sigma_g^+, v^0 = 0)$ is the main channel of molecular electronic excitation. If only one of the mentioned conditions is violated, than we should have another vibrational population in $H_2(d^3\Pi_u, v')$ state. We should mention here that accuracy of the method is not high enough to provide information about the

Table 1
Franck-Condon factors and relative electron-impact excitation cross sections for the transitions $H_2(X^1\Sigma_g^+, v^0 = 0) \rightarrow H_2(d^3\Pi_u, v')$

v'	[31]	[28]	[32]	[33]	[34]	this work
0	0.58	0.66	0.57	0.68	0.52	0.55
1	0.97	0.88	0.86	1.09	0.91	0.82
2	1.00	1.00	1.00	1.00	1.00	1.00
3	0.82	0.77	0.78	0.86	0.96	0.71
4	0.60	0.35	—	—	0.37	0.33

distribution over the vibrational quantum states of H_2. However, the results of Tab. 1 show that the vibrational temperature is rather small.

It must be emphasized that the only parameter, which is unknown in the case of our experiments it is the electron energy distribution function $f(\varepsilon)$. A quantitative analysis of the influence of $f(\varepsilon)$ on the interpretation of the experimental data is very difficult in general, because in weakly ionized hydrogen plasmas the electron energy distribution function is non-Maxwellian (see, for example [36–38]. In order to take into account the actual form of $f(\varepsilon)$ in the interpretation of experimental data in the same manner as has been done in [28] we calculated the rate constants for electron-impact excitation of different vibronic levels ($v' = 0-4$) of the $H_2(d^3\Pi_u)$ state both with the experimental values of $f(\varepsilon)$ [36–38], and with a Maxwellian electron energy distribution function with mean energies of $\bar{\varepsilon} = 3-5$ eV. It is found that the relative rate constants for electron-impact excitation of various vibronic levels $H_2(d^3\Pi_u, v' = 0-3)$ are within 30% the same. This fact is evidently connected with the fact that near the excitation thresholds of the considered vibronic levels (E = 13.9–15.0 eV), the electron energy distribution functions have Maxwell-like forms (see also Ref. [39]). Thus for the data, presented in Tab. 1, we used a Maxwell's approximation of $f(\varepsilon)$. Note that 3–5 eV is not the electron temperature of the actual expanding plasma, but the T_e of the plasma generated by the active probe. The basic idea is that we use this RF produced plasma to excite the "passive actual plasma" without seriously disturbing the rovibrational distribution.

One of the important conclusions of the present study is that for our experimental condition the dominant part of hydrogen molecules $H_2(X^1\Sigma_g^+, v^0)$ are in the ground vibrational level. This fact also indicates that the RF discharge does not influence the vibrational population of H_2 in the expanding plasma beam. A comparison of our results with other experimental data on the vibrational distribution of hydrogen molecules in gas discharge plasmas learns, that in [15, 19] the nonequilibrium populations of excited vibrational levels have been found, especially for the high lying vibrational states. However, the conclusion in Ref. [28] was the same as in our case.

One can suppose, that those differences are connected with the presence of atomic hydrogen in the plasmas. The purpose of the first group of investigations [15, 19, 21] is the generation of nonequilibrium concentrations of vibrationally excited hydrogen molecules and, as a consequence, the production of negative ions. Corresponding experimental conditions were choosen favorable for those purposes: low pressure, large current, low gas temperature, presence of a fast electrons, significant ionization degree, and as small as possible concentration of atomic hydrogen. On the other hand the conditions of current experimens and of Ref. [28] (hollow cathode and capillary arc discharge at pressures $p \simeq 1$ Torr have been studied) are favorable for the generation of hydrogen atoms. Critical point in the above discussion is that the hydrogen atoms have much larger rate coefficients for vibrational quenching of H_2^v ($V - T$ relaxation) in comparison with hydrogen molecules. Those differences at the gas temperatures $T_0 = 1200-1400$ K reach two orders of magnitude) [40]. That fact and also significant differences in the pressures might be as one of the explanations of the differences between the results of various authors on vibrational distribution of hydrogen molecules in low-temperature plasmas.

Acknowledgements

This work was made possible by the Netherlands Technology Foundation (FOM/STW). D. K. OTORBAEV acknowledges support from the Eindhoven University of Technology. The work of M. C. M. VAN DE SANDEN was supported by the Royal Netherlands Academy of Arts and Sciences. The authors wish to thank M. J. F. VAN DE SANDE for his technical assistance.

References

[1] BACHMANN, P. K., COLLINS, A. T., and SEAL, M. (ed), Diamond 1992 Proc. III Int. Conference on the New Diamond Science and Technology, Elsevier, Amsterdam, 1992.

[2] GRABOWSKI, K. S., BARNETT, S. A., and ROSSNAGEL, S. M. (ed), Materials Modification by Energetic Atoms and Ions, Materials Research Society Symposium Proceedings, MRS, Pittsburgh (1992) **268**.

[3] THOMPSON, M. J. HAMAKAWA, Y, and LECOMBER, P. G. (ed), Amorphous Silicon Technology, Materials Research Society Symposium Proceeding MRS, Pittsburgh (1992) **258**.

[4] ALESSI, J. G., and HERSHCOVITCH, A. (ed). Production and Neutralization of Negative Ions and Beams AIP Conference Proceedings, AIP, New York (1994) **387**.

[5] WILBERS, A. T. M., MEEUSEN, G. J., HAVERLAG, M., KROESEN, G. M. W., and SCHRAM, D. C, Thin Solid Films **204** (1991) 59.

[6] BUURON, A. J. M., BEULENS, J. J., MEEUSEN, G. J., VAN DE SANDEN, M. C. M., and SCHRAM, D. C., J. Appl. Polymer Sci. **54** (1994) 115.

[7] BACHMANN, P. K., BEULENS, J. J., KROESEN, G. M. W., LYDTIN, H., SCHRAM, D. C., and WICHERT, D. U., Surf. Modif. Technol. **3** (1989) 69.

[8] VAN DE SANDEN, M. C. M., DE REGT, J. M., and SCHRAM, D. C., Phys. Rev. E. **47** (1993) 2792; VAN DE SANDEN, M. C. M., DE REGT, J. M., and SCHRAM, D. C., Plasma Sources Sci. Technol. **3** (1994) 501; VAN DE SANDEN, M. C. M., VAN DE BERCKEN, R. and SCHRAM, D. C., Plasma Sources Sci. Technol. **3** (1994) 511.

[9] MEULENBROEKS, R. F. G., VAN DER HEIJDEN, P. A. A., VAN DE SANDEN, M. C. M., and SCHRAM, D. C., J. Appl. Phys. **75** (1994) 2775.

[10] VAN DE SANDEN, M. C. M., ZHOU QING, OTORBAEV, D. K., DE GRAAF, M. J., WEVERS, J. C. A., and SCHRAM, D. C., Proc. V European Workshop on the Production and Application of Light Negative Ions, Dublin, Dublin City University (1994) 41.

[11] DE GRAAF, M. J., OTORBAEV, D. K., ZHOU QING, SEVERENS, R., and SCHRAM, D. C., IV European Workshop on Production and Applications of Light Negative Ions, Belfast (1991) Conf. Proc. p. 73.

[12] OTORBAEV, D. K., VAN DE SANDEN, M. C. M., and Schram, D. C., Plasma Sources Sci. Technol. **4** (1995) 293.

[13] DE GRAAF, M. J., SEVERENS, R., DAHIYA, R. P., VAN DE SANDEN, M. C. M., and SCHRAM, D. C., Phys. Rev. E. **48** (1993) 2098.

[14] DE GRAAF, M. J., Ph. D. thesis, Eindhoven University of Technology, The Netherlands (1994).

[15] EENSHUISTRA, P. J., BONNIE, J. H. M., LOS, J., and HOPMAN H. J., Phys. Rev. Lett. **60** (1988) 341.

[16] HALL, R. I., CADEZ, I., LANDAU, M., PICHOU, F., and SCHERMANN, C., Phys. Rev. Lett. **60** (1988) 337.

[17] JACKSON, B., and PERSSON, M. J., Chem. Phys. **96** (1992) 2378.

[18] LELEVKIN, V. M., OTORBAEV, D. K., and SCHRAM, D. C., Physics of Non-Equilibrium Plasmas, Elsevier, Amsterdam (1992).

[19] PEALAT, M., TARAN, J. P.-E., BACAL, M., and HILLION, F., J. Chem. Phys. **82** (1985) 4943.

[20] ASANOV, B. U., OCHKIN, V. N., SAVINOV, S. YU. SOBOLEV, N. N., and TSKHAI, S. N., Sov. Phys. Lebedev Institute Reports **9** (1986) 26.

[21] STUTZIN, G. C. YOUNG, A. T., SCHLACHTER, A. S., LEUNG, K. N., and KUNKEL, W. B., Chem. Phys. Lett. **155** (1989) 475.

[22] BUTTENHOFF, T. J., CARLETON, K. L., CHUANG, M. C., and MOORE, C. B. J., Chem. Soc. Faraday Trans. **85** (198) 2.

[23] BLEEKRODE, R., IEEE J. Quant. Electr. **5** (1969) 57.

[24] NOVGORODOV, M. Z., OCHKIN, V. N., and SOBOLEV, N. N., Sov. Phys. Tech. Phys. **40** (1970) 1268.

[25] MNATSAKANYAN, A. C., and PODLUBNY, L. I., Sov. Phys. Tech. Phys. **41** (1971) 2121.

[26] POLYAKOVA, G. N., ERKO, V. F., ZATS, A. V., and FOGEL, Y. M., Problems of Space Physics **8** (1973) 81.

[27] KOSORUCHKINA, A. D., XV ICPIG, MINSK (1981) Conf. Abstracts, p. 727.

[28] LAVROV, B. P., and PROSIKHIN, V. P., Opt. Spectrosc. **58** (1985) 524.

[29] MEULENBROEKS, R. F. G., VAN BECK, A. J., VAN HELVOORT, A. J. G., VAN DE SANDEN, M. C. M., and SCHRAM, D. C., Phys. Rev. E. **49** (1994) 4397.

[30] OTORBAEV, D. K., OCHKIN, V. N., RUBIN, P. L., SAVINOV, S. YU., SOBOLEV, N. N., and TSKHAI S. N., in: SOBOLEV, N. N. (Ed.), Electron Excited Molecules in Nonequilibrium Plasma, Nova Science Publishers, New York (1989).
[31] SPINDLER, R. J., J. Quant. Spectrosc. Radiative Transfer **9** (1969) 627.
[32] MÖHLMANN, G. R., and DE HEER, F. J., Chem. Phys. Lett. **43** (1976) 240.
[33] BALTAYAN, P., and NEDELEC, O. J., Quant. Spectrosc. Radiative Transfer **16** (1976) 207.
[34] BOGDANOVA, I. P., EFREMOVA, G. V., LAVROV, B. P., OSTROVSKY, V. N., USTIMOV, V. I., YAKOVLEVA, V. I., Opt. Spectrosc. **50** (1981) 121.
[35] SPINDLER, R. J., J. Quant. Spectrosc. Radiative Transfer **9** (1969) 597.
[36] KAGAN, YU. M., and MITROFANOV, N. K., Sov. Phys. Tech. Phys. **41** (1971) 2065.
[37] ABROYAN, M. A., DEMIDOV, V. I., KAGAN, YU. M., KOLOKOLOV, N. B., and LAVROV, B. P., Opt. Spectrosc. **39** (1975) 21.
[38] AMEMIYA, H., J. Phys. D. **23** (1990) 999.
[39] LOUREIRO, J., Phys. Rev. E. **47** (1993) 1262.
[40] GORSE, C., CAPITELLI, M., BACAL, M., BRETAGNE, J., and LAGANA, A., Chem. Phys. **117** (1987) 177.

Reveived December 8, 1994;
revised manuscript received February 20, 1995