Excitation of Balmer lines in low-current discharges of hydrogen and deuterium

Z. Stokic, M. M. F. R. Fraga,* J. Bozin,† V. Stojanović, Z. Lj. Petrović, and B. M. Jelenković
Institute of Physics, P. O. Box 57, 11000 Belgrade, Yugoslavia
(Received 21 November 1991)

Measurements have been made of electron-impact ionization and excitation of Balmer lines in low-current, steady-state discharges of hydrogen and deuterium. Results were obtained from spatial scans of H_α lines for E/N ranging from 250 Td to 10 kTd. Here E is the electric field, N is the gas density, and 1 Td $=10^{-21}$ V m^2. Ionization and excitation coefficients versus E/N are presented for E/N between 250 and 1800 Td, and Nd (where d denotes the gap length) between 2.3×10^{22} and 1.7×10^{21} m^{-2}. Excitation coefficients obtained for H_α and D_α are placed on an absolute scale using a standard tungsten lamp calibrated against the blackbody radiation standard. The ionization coefficients are compared with previous experimental and theoretical data, while the excitation coefficients are compared with the calculated values.

PACS number(s): 52.20.Fs, 52.25.Rv

I. INTRODUCTION

Studies of hydrogen discharges are of great importance since hydrogen is often used in the plasma processing of materials, e.g., the deposition and etching of semiconductors used in microelectronics [1]. The need to increase our knowledge of elementary collision processes involving electrons, atoms, and ions in discharges in H_2 and in mixtures of hydrogen and different hydrocarbons has recently increased because of the role of hydrogen in diamond deposition [2]. Studies of electron behavior in H_2 discharges at moderate and high E/N values are important for fusion research, particularly for studies of processes during the startup of tokamak devices [3].

Although the hydrogen discharge is of great interest from physical and technological points of view, we still lack some important information on the behavior of various particles, electrons, ions, and neutrals in H_2 discharges. The recent transient and steady-state spectroscopic data obtained in low-current [4] and in glow [5,6] hydrogen discharges were used to determine the onset of the effect of heavy particles on excitation with increasing E/N. These data, and compilation of the cross sections by Phelps [7], gave valuable information on the significance of the heavy particle excitation and ionization, on the type of energy distribution of atomic and molecular ions and neutrals, on the role that the cathode surface plays in providing the discharge with additional flux of fast particles going away from the cathode, and on the kinetics of electrons. The data have shown that collisions involving heavy particles are important even at $E/N=1000$ Td.

Knowledge of electron behavior in high electric field and low pressures, such as used in this experiment, is important because of the cathode fall region at the glow discharges. After crossing the region of high electric field of the cathode fall, electrons enter the negative glow where their collisions with H_2 are the main source of ions and radicals. The energy and the total flux of electrons entering the glow region determine the rate of subsequent processes that can lead to surface etching, deposition, etc. Therefore, data such as electron ionization and excitation rate coefficients at different and high E/N are essential for understanding the steady-state and transient behavior of glow discharges.

The electron motion was treated theoretically at low E/N using Boltzmann calculations [8–10] and at high E/N using Monte Carlo techniques [11]. Nonequilibrium kinetics of electrons was also studied by using the moment technique for the solution of the nonequilibrium Boltzmann equation [12,13]. While the cross sections for electron excitation of H_α have been measured by several authors and/or determined by using the swarm technique, there are significant discrepancies even in the low-energy region [14]. There have been numerous experimental determinations of swarm parameters at low E/N, including excitation coefficients [15], and only a few studies of excitation of Balmer emission at high E/N for hydrogen [4] and deuterium [16]. And there are no absolute measurements of excitation coefficients at high E/N for these gases.

In the work presented here we have studied the electron behavior at high E/N, between 250 Td and 10 kTd. The results of the measurements of excitation and ionization coefficients versus $E/N \leq 1800$ Td, are presented. The analysis is restricted to uniform electric fields, so that data can be compared with Boltzmann calculations. At the lower values of E/N, electrons quickly reach equilibrium with the gas and electric field. At higher ranges of E/N, electron behavior is a function of Nd. The electron energy and the rates for electron excitation and ionization change as the electron moves across the gap. The measured excitation coefficients and their comparisons with calculations are good tests of the applicability of different model calculations at different E/N and of the cross sections used in these calculations. Our experimental data on excitation and ionization coefficients are also of interest for studies of collisional quenching of excited states, the effect of electrons backscattered from the anode, and the significance of the nonequilibrium region near the anode [17].

II. EXPERIMENT

The experimental setup is shown in Fig. 1. The electron drift tube for high-voltage and low-current discharges, on the left-hand side of the Paschen minimum, has been described already [18]. It consists of two parallel-plate electrodes, 80 mm in diameter and at distance 36 mm, enclosed in a tightly fitted quartz tube. The cathode was made of stainless steel, and the anode of vacuum-grade, sintered graphite. The reason for choosing graphite is its much lower electron backscattering coefficient [19]. Experimental data were obtained at the *Nd* values and discharge voltages shown on the Pashen curves for H_2 and D_2 (Fig. 2). Such a simple design enabled us to run discharges at currents between 1 and 10μA, for which the discharge voltage is nearly independent of current, e.g., the space-charge distortion of the electric field can be neglected. The low-current diffuse discharge, for the discharge currents in our experiment, can be oscillatory at higher pressures [20], and those oscillations set the lower limit for E/N in the experiment. Outside the oscillation region the discharge was made stable by using a 0.5–1-MΩ resistor in series to the discharge gap. The discharge current was measured using an electrometer. The pressure was between 0.15 and 2 Torr and measured with the capacitance manometer.

The light emitted from the H_2 discharge was detected through two quartz windows on the vacuum chamber using two sets of photon-counting chains. Each chain consists of a collimator, i.e., sets of parallel slits separated by 20 mm, a monochromator, and a photomultiplier. One set was at a fixed position, detecting the light from the region 5 mm from the anode. The spatial resolution at full width at half maximum (FWHM) was 0.5 mm. This optical system was used to measure the absolute values of the excitation coefficients. The other optical system was placed on the table, moved by a stepper motor, and used to measure the spatial scans of Balmer lines, e.g., ionization coefficients. The spectral resolution of both systems was around 2 nm.

The absolute calibration of the quantum efficiency of the detection system, used for the measurements of the excitation coefficients, was done using a standard tungsten strip lamp which was calibrated against the radiation from the blackbody radiation standard. Only radiation emitted from the central portion of the filament was allowed to reach the detector. The quartz window was placed between lamp and detector during the calibration procedure. Calibration of the system for the wavelength region 550–800 nm was done with the lamp operating at two different temperatures, 1400 and 1700 K. The light intensity was measured with and without an interference filter and with different neutral density filters for two temperatures of the lamp, to reduce the signal and avoid the saturation of the detector. We made seven different measurements of the quantum efficiency and the different sets of data agree well, the maximum deviation from the mean value for wavelengths around 650 nm being 10%, which is the overall uncertainty of absolute calibration.

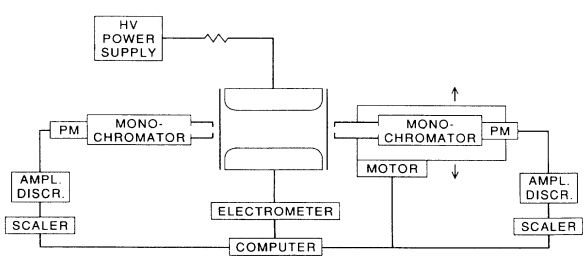

FIG. 1. Experimental setup; PM is the photomultiplier.

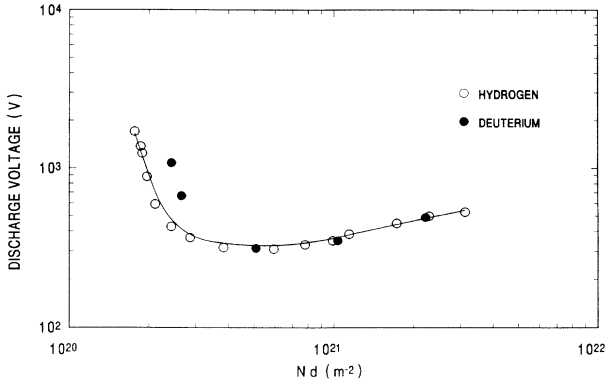

FIG. 2. Discharge voltage vs *Nd*, where *N* is the gas density and *d* is the distance between electrodes (Paschen curves) for hydrogen and deuterium. The results are for the graphite cathode and the stainless-steel anode.

III. RESULTS AND DISCUSSIONS

In this section we present the results of our measurements of ionization and excitation coefficients for Balmer α lines of hydrogen and deuterium. We compare our experimental results with previously published and unpublished data.

A. Spatial scans and ionization coefficients

Emission intensities of H_α normalized to the discharge current as a function of the position from cathode to anode at three different E/N values are shown in Fig. 3. Drastic changes in the spatial variation as E/N changes can be noticed. At $E/N < 2$ kTd the optical signal increases exponentially with distance; the distance from the cathode at which the signal starts to behave like this is increasing as E/N increases. This is due to the fact that an electron has to travel larger distances before it reaches equilibrium with the electric field and gas, and excitation in heavy-particle collisions becomes more and more significant. At E/N near 2 kTd and *Nd* values of 2.5×10^{20} m^{-2}, the exponential growth can be identified only at a short distance from the anode. It is between 1 and 2 kTd that equilibrium behavior of electrons exists together with heavy-particle excitation in a certain portion of the gap. The exponential dependence of the optical signal is evidence of a spatially independent electron ionization coefficient and exponential growth of the elec-

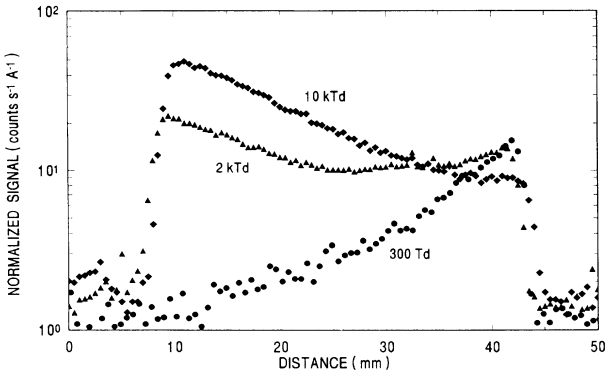

FIG. 3. Spatial variation of Balmer α radiation normalized to discharge current at 300 Td, 2 kTd, and 10 kTd.

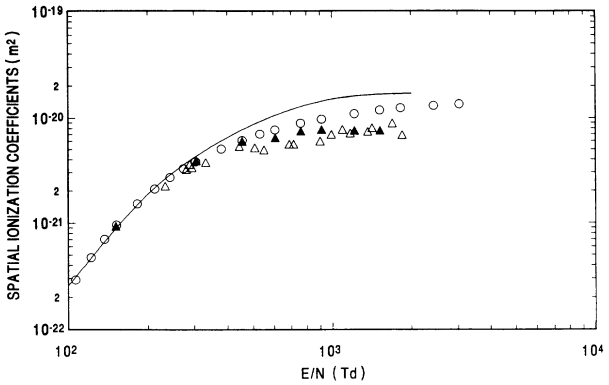

FIG. 4. Spatial ionization coefficients for hydrogen vs E/N: solid curve, Boltzmann calculations [8]; open circles, Rose [23]; solid triangles, Folkard and Haydon [24]; open triangles, present results.

tron current density.

At $E/N > 2$ kTd the H_α emission near the cathode is dominant and, as can be seen from Fig. 3, at 10 kTd it far exceeds the electron excitation at the anode. Recently, significant work has been done to explain the origin of the strong cathode signal [4]. Petrović *et al.* [4] have presented a new mechanism for producing H_α in the cathode vicinity in which the heavy-particle excitations and the cathode surface play a crucial role. As for electron behavior at the anode at very high E/N, different models [12,13] and experiments [21] agree that the electron energy distribution can be approximated by that of the energetic electron beam(s) generated at the cathode and passing the gap with very few collisions. The experimental analysis of the behavior of electrons is difficult because of heavy-particle excitation and the strong presence of backscattered electrons from the anode and their wide energy distribution [19,22].

For E/N lower than 2 kTd the signal can be approximated by a single exponential function, from a point in the gap to the anode position. This, together with the good agreement between the observed exponential growth of H_α emission and the growth expected from previously published results for the ionization coefficients, can be regarded as evidence of electrons being in equilibrium at the anode and of the negligible effect of backscattered electrons.

The spatial ionization coefficients as a function of E/N, for $E/N < 1800$ Td, were derived from the exponential growth of H_α intensity and are shown in Fig. 4. Present results are indicated by open triangles; the solid curve shows the Boltzmann calculations of Buckmann and Phelps [8]. The same comparison was made with two sets of previous experimental measurements by Rose [23], given by open circles, and by Folkard and Haydon [24], shown by solid triangles. In both of these experiments the measurements of ionization coefficients were made at voltages below breakdown, by measuring the discharge current while changing the electrode separation and voltage proportionally (thus keeping E/N constant). The results of calculations [8] and the measurements of Rose [23] are considerably higher than ours at higher E/N. Similar findings at higher E/N, that spectroscopic data give lower ionization coefficients than current data, have been reported for nitrogen [25] and argon [26]. Our measurements are in better agreement with the data of Folkard and Haydon [24]. These authors have shown that the previous concept [23] of nonequilibrium distance from the cathode d_0, where electron multiplication is zero, and the equilibrium region for $z > d_0$ is unsatisfactory at high E/N. From the slope of the Gosseries plots (plots that relate the reciprocals of currents at two different electrode separations), they have found values of ionization coefficients. From the point of departure from linearity of Gosseries plots, they have determined the nonequilibrium distance from the cathode d_0', where ionization coefficients are changing with position. An examination of the plots shows that for $E/N < 750$ Td, d_0' is well defined and that Nd_0' is much smaller than the maximum Nd_s at which the breakdown will occur. Above 750 Td, d_0' is increasing rapidly; the ionization coefficients are then functions of the electrode separation and cannot be obtained from simple analysis of current measurements using the equilibrium current growth equation for $d > d_0$. The agreement between our results and those from Ref. [24] suggests that two different analyses can lead to the same results if particular care has been taken in the treatment of current data. The fair agreement between different types of measurements is an indication that the effect of backscattered electrons from the anode onto the ionization in the anode vicinity can be neglected for $E/N < 2$ kTd.

The uncertainty of our data is $\pm 7\%$, which is inferior to the technique applied by Folkard and Haydon. Yet our technique is much easier to implement, and can be applied even in the case of nonequilibrium, provided that the emission lines which are not excited by heavy particles are used [25] and the electron distribution function is known. Under these circumstances effective electron multiplication can be obtained and used to verify the ionization cross sections at energies which are usually not probed by swarm techniques, i.e., above 20 eV.

B. Excitation coefficients

The spatial excitation coefficient for a certain excited state is defined as a ratio of the rate coefficient to the convective drift velocity. It can be regarded as the number of excitation events per unit distance in the field direction per electron leaving the cathode, normalized to gas density. The experimental procedure for measuring the excitation coefficients has been discussed in detail [27]. The Balmer α excitation coefficients α/N at each E/N were determined by using the continuity equation in which the excitation by ions and neutrals was neglected:

$$\alpha/N=\frac{n^*e(A^*+Nk_q)}{j_e(z)N}\ , \tag{1}$$

where n^* is the density of excited H atoms with $n=3$, A^* is the radiative transition probability of the $n=3$ state, $j_e(z)$ is the local electron current density, z is the distance from the cathode, and k_q is the rate coefficient for the collisional quenching of the excited state $n=3$. The factor R that relates the emitted light and the measured steady-state signal at the position z is

$$R=Q(\lambda)A_B n^*\int_V\frac{\Omega(V)}{4\pi}dV\ , \tag{2}$$

where Ω is the solid angle subtended by the detector of the discharge volume dV; $Q(\lambda)$ is the quantum efficiency of the detection system, e.g., the number of counted pulses per each photon emitted at wavelength λ; V is the volume of the discharge from which the radiation can be detected; and A_B is the transition probability for the transition between states with $n=3$ and 2.

Finally, using Eqs. (1) and (2) the relation between excitation coefficients and measured optical signal and local current density is

$$\frac{\alpha}{N}=\frac{eR(z)}{Q(\lambda)Nj(z)\int_V\frac{\Omega(\nu)}{4\pi}d\nu}\frac{A^*}{A_B}\left[1+\frac{N}{N_0}\right]\ , \tag{3}$$

where $N_0=A^*/k_q$ is a quenching density, i.e., the density at which half of the excited states are collisionally quenched.

The current density at the position where light was detected, i.e., 5 mm from the anode, was calculated from the measured steady-state discharge current and our measured ionization coefficients (see Fig. 4). Here we have assumed that the discharge current is equal to the electron current at the anode.

The quantum efficiency of the optical system and solid angle of the detector were found to be 2.6×10^{-3} and 2.3×10^{-5} srad, respectively. The branching ratio $A^*/A_B=2.2$ was obtained from the published transition probabilities [28]. From the values of the transition probabilities [30] it can be seen that the Balmer emissions are mainly determined by the transitions from (ns) and (nd) states to lower p states, while (np) states predominantly decay into the ground state. Therefore, Balmer radiation is contributing through cascades to Lyman radiation, but the contribution of cascades to Balmer emission is negligible.

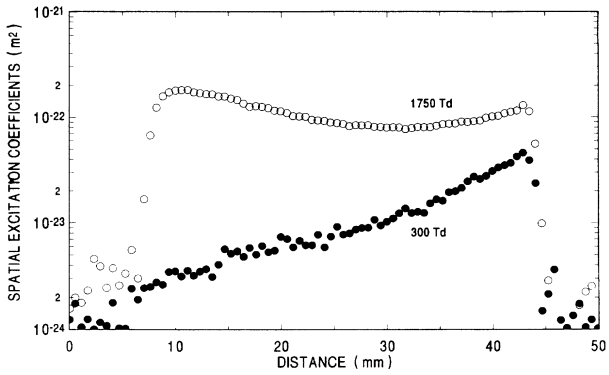

FIG. 5. Spatial excitation coefficients for 300 and 1750 Td.

There are several published rate coefficients [29] for collisional quenching of H_α with a large spread of results. The excitation coefficients shown in Figs. 5 and 6 were obtained using quenching rate coefficients from Lewis and Williams [29], who measured $A^*/k_q=N_0$ and reported the value of 4.3×10^{22} m^{-3}. The spatial scans of the Balmer α radiation of Fig. 3 can be placed on the absolute scale of the excitation coefficients by normalizing the extrapolated optical signal at the anode to previous measurements or calculations of electron excitation coefficients for H_α. This is another way of calibrating the detector, e.g., of obtaining the ratio $A^*/(\Omega/4\pi)Q(\lambda)VA_B$ in Eq. (3). The results are shown in Fig. 5, where we first converted the anode signal per unit current, at 300 Td, to the calculated excitation coefficient at the same E/N [8], and then used the same conversion factor to place the spatial variation of H_α at 1750 Td on the absolute scale.

Absolute values of the excitation coefficients for H_α and D_α versus E/N, obtained after the quantum efficiency and geometry of the experiment used in Eq. (3) were independently determined, are shown in Fig. 6. The results for hydrogen are shown as solid circles, while the deuterium data are represented by open triangles. The Boltzmann calculations of the excitation coefficients for

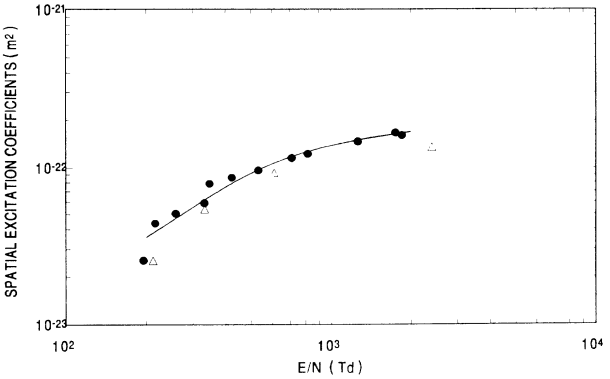

FIG. 6. Spatial excitation coefficients vs E/N for hydrogen (solid circles) and deuterium (open triangles). The solid line represents the results of Boltzmann calculations [8].

hydrogen [8] are shown with a solid line. The agreement between experiment and calculations is good except for the lowest value of E/N, where experimental results are much lower than theoretical results. A possible reason for these discrepancies might be the occurrence of small current oscillations [20] at pressures over 2 Torr, which may lead to an error in current readings. The excitation coefficients for deuterium were obtained using the same quenching density as for hydrogen. We have used the same values for the ionization coefficients, since it was shown that they are not different for the two gases at high E/N [23]; we also used the same procedure for determining the current at 5 mm from the anode as we did for hydrogen. The results are close but systematically lower for deuterium than for hydrogen in the E/N region investigated, similar to Boltzmann calculations of α/N for D_α [9] for $E/N < 650$ Td.

The procedure described for obtaining excitation coefficients at high E/N has been questioned by Blevin and co-workers [17,30]. Two issues have been raised: the nonequilibrium close to the anode which makes it difficult to connect the measurement of the electron flux at the anode and the flux away from the anode, and the additional ionization due to backscattering electrons which also affects the determination of local electron density. While these arguments are fully justified in general, we have shown that for the specific conditions of our experiment they do not affect our results. Blevin and coworkers showed that ionization frequency is independent of the position close to the metallic boundary for N_2 at 800 Td. Thus exponential growth of the electron flux can be extrapolated to the anode [18]. There were no such studies performed for hydrogen. From the sufficiently accurate approximation of the exponential growth to the anode, we may conclude that for the range of E/N for which the coefficients were determined, the width of the nonequilibrium anode region is small. Low energies of electrons being in equilibrium at the anode are an additional argument that the effect of backscattered electrons is small.

IV. SUMMARY

We have shown that optical data can be used for determinations of electron ionization and excitation coefficients. Spatial scans of optical emission can provide interesting and useful information on the behavior of electrons and heavy particles in gas discharges. The optical signals can be placed on the absolute scale of the excitation coefficients, and then used as a test of different models and theories of the ionization and excitation of the electron and heavy particles. When combined, for example, with Monte Carlo calculations of the spatial excitation rate coefficients, the data that we have presented can reveal important processes involving electron backscattering from different anode materials, excitation and ionization by ions and neutrals, reflection of heavy particles from the cathode, and formation of fast neutral particles—all very relevant and important processes for glow discharges, with a developed cathode sheath.

Spatial scans of H_α have shown the exponential growth of emission versus distance toward the anode, from some point in the gap, and if $E/N < 2000$ Td. The ionization coefficients obtained from such data agree well with the data of Folkard and Haydon [24]. Above 2 kTd and $Nd < 2.7 \times 10^{20}$ m^2, excitation by heavy particles becomes dominant and then the study of electron kinetics is no longer possible. Our measurements of the optical emission at high but uniform electric field are certainly less complex than the studies of high current discharge and therefore modeling the spatial scans of H_α is a first step toward better understanding of electron and heavy-particle kinetics in glow discharges. Our excitation coefficients of H_α for $250 < E/N < 1800$ Td agree well with the calculated values [9].

ACKNOWLEDGMENTS

We are very grateful to A. V. Phelps for many helpful suggestions and discussions. We thank the Joint Institute for Laboratory Astrophysics (JILA) of the University of Colorado and the National Institute of Standards and Technology for loaning us valuable equipment. This work was supported in part by the Scientific Fund of Serbia, the Yugoslav-USA Fund for Scientific and Technological Cooperation under research Contract Nos. NIST JF 924 and 926, and the International Atomic Energy Agency under Contract No. 5950/RB. One of us (M. F.) acknowledges the financial support of INIC (Instituto Nacionale de Investigacao Cientifica) and one of us (B. J.) thanks the JILA faculty and staff for their hospitality during his visit.

*Permanent address: Physics Department, University of Coimbra, 3000 Comibra, Portugal.

†Also at Faculty of Physics, University of Belgrade, 11000 Belgrade, Yugoslavia.

[1] K. Pickering, P. Southworth, C. Wort, A. Parsons, and D. J. Pedder, J. Vac. Sci. Technol. A **8**, 1503 (1990); S. J. Pearton and W. S. Hobson, J. Appl. Phys. **66**, 5018 (1989); T. R. Hayes, M. A. Dreisbach, P. M. Thomas, W. C. Dautremont-Smith, and L. A. Heimbrook, J. Vac. Sci. Technol. B **7**, 1130 (1989); B. Tomčik, S. Radovanov, Z. Lj. Petrović, and B. M. Jenenković, in Proceedings of the Eighth International Symposium on Plasma Chemistry, Tokyo, 1987 (unpublished), p. 1726.

[2] T. Kokubo, F. Tochikubo, and T. Makabe, J. Phys. D **22**, 1281 (1989); A. Pastol and Y. Catherine, *ibid.* **23**, 799 (1990); J. Wagner, C. Wild, F. Pohl, and P. Koidl, Appl. Phys. Lett. **48**, 106 (1986).

[3] A. Buffa, G. Malesani, and G. F. Nalesso, Phys. Rev. A **3**, 955 (1971); L. P. Kubarev, S. A. Uryupin, and L. M. Fisher, Fiz. Plazmy **6**, 187 (1980) [Sov. J. Plasma Phys. **6**, 106 (1980)]; T. Fujiwara, T. Shimada, and K. Sugita, J. Phys. D **16**, 1217 (1983).

[4] Z. Petrović (unpublished); Z. Lj. Petrović, B. M. Jelenković, and A. V. Phelps, Phys. Rev. Lett. **68**, 325 (1992); B.

M. Jelenković, Z. Lj. Petrović, and A. V. Phelps (unpublished); Z. Lj. Petrović and A. V. Phelps, Proceedings of the First International Seminar on Reactive Plasmas, Nagoya, Japan, 1991, edited by T. Goto (unpublished), p. 351.

[5] C. Barbeau and J. Jolly, J. Phys. D **23**, 1168 (1990).

[6] S. B. Vrhovac, S. B. Radovanov, S. A. Bzenić, Z. Lj. Petrović, and B. M. Jelenković, Chem. Phys. **153**, 233 (1991); S. A. Bzenić, S. B. Radovanov, S. B. Vrhovac, Z. B. Velikić, and B. M. Jelenković, Chem. Phys. Lett. **189**, 108 (1991) and references therein.

[7] A. V. Phelps, J. Chem. Phys. Ref. Data **19**, 653 (1990).

[8] S. J. Buckmann and A. V. Phelps, J. Chem. Phys. **82**, 4999 (1985).

[9] A. V. Phelps (unpublished).

[10] H. Brunet and P. Vincent, J. Appl. Phys. **50**, 4700 (1979).

[11] S. R. Hunter, Aust. J. Phys. **30**, 83 (1977); M. Hayashi, J. Phys. D **13**, 2275 (1988); B. Jelenković, V. Stojanović, Z. Stokić, and Z. Lj. Petrović, in Proceeding of the International Symposium on Plasma Chemistry, Bochum, 1991, (unpublished), p. 12.

[12] K. G. Muller, Z. Phys. **169**, 432 (1962).

[13] A. V. Phelps, B. Jelenković, and L. C. Pitchford, Phys. Rev. A **36**, 5327 (1987).

[14] M. A. Morrison, R. W. Crompton, B. C. Saha, and Z. Lj. Petrović, Aust. J. Phys. **40**, 239 (1987); D. A. Vroom and F. J. de Heer, J. Chem. Phys. **50**, 580 (1969); M. A. Khakoo and S. Trajmar, Phys. Rev. A **34**, 146 (1986).

[15] S. J. B. Corrigan and A. von Engel, Proc. R. Soc. London Ser. A **245**, 335 (1958); K. J. Nygaard, in Proc. VI ICPIG, Paris, 1964 (unpublished), p. 191; K. J. Nygaard, Appl. Sci. Res. B **12**, 91 (1964); J. Appl. Phys. **36**, 743 (1965).

[16] B. Jelenković and A. Phelps, in *Swarm Studies and Inelastic Electron-Molecular Collisions,* edited by L. C. Pitchford, B. V. McKoy, A. Chutjian, and S. Trajmar (Springer-Verlag, New York, 1985), p. 113.

[17] L. J. Kelly and H. A. Blevin, in Proceedings of the XIXth International Conference on Phenomena in Ionized Gases, Belgrade, 1989 (unpublished), edited by J. Labat, p. 892; and (unpublished).

[18] V. Stojanović, J. Bozin, Z. Lj. Petrović, and B. M. Jelenković, Phys. Rev. A **42**, 4983 (1990).

[19] E. J. Sternglass, Phys. Rev. **95**, 345 (1954).

[20] Z. Lj. Petrović and A. V. Phelps, in Proceedings of the Symposium on Physics of Ionized Gases, Dubrovnik, 1990, edited by D. Veza (unpublished), p. 255.

[21] S. Vrhovac, S. Radovanov, Z. Lj. Petrović, and B. Jelenković, J. Phys. D **25**, 217 (1992).

[22] E. H. Darlington and V. E. Cosslett, J. Phys. D **5**, 1969 (1972); R. L. Verma, *ibid.* **10**, 1167 (1977); M. E. Woods and B. J. Hopkins, Surf. Sci. **162**, 928 (1985).

[23] D. J. Rose, Phys. Rev. **104**, 273 (1958).

[24] M. A. Folkard and S. C. Haydon, Aust. J. Phys. **24**, 519 (1971); **24**, 527 (1971).

[25] B. Jelenković and A. V. Phelps, Phys. Rev. A **36**, 5310 (1987).

[26] A. V. Phelps and B. Jelenković, Phys. Rev. A **38**, 2975 (1988).

[27] A. Lawton and A. V. Phelps, J. Chem. Phys. **69**, 1055 (1978).

[28] W. L. Wiese, M. W. Smith, and B. M. Glennon, Nat. Stand. Ref. Data Ser. Natl. Bur. Stand. I, 2 (1966).

[29] J. W. L. Lewis and W. D. Williams, J. Quant. Spectrosc. Radiat. Transfer **16**, 939 (1976); M. L. Burshtein, B. P. Lavrov, and V. N. Yakovlev, Opt. Spektrosk. **62**, 1233 (1987) [Opt. Spectrosc. (USSR) **62**, 729 (1987)]; A. Catherinot, B. Dubreuil, and M. Gand, Phys. Rev. A **18**, 1097 (1978); J. Bittner, K. Kohse-Hoinghaus, U. Meler, and Th. Just, Chem. Phys. Lett. **143**, 571 (1988).

[30] H. Blevin, L. J. Kelley, and M. J. Brennan (private communication); see also J. J. Kelly, M. J. Brennan, and A. B. Wedding, Aust. J. Phys. **42**, 365 (1989).