Depolarization Rayleigh Scattering as a Means of Molecular Concentration Determination in Plasmas

R. F. G. Meulenbroeks, D. C. Schram, L. J. M. Jaegers, and M. C. M. van de Sanden
Department of Physics, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands
(Received 5 May 1992)

The difference in polarization for Rayleigh scattered radiation on spherically and nonspherically symmetric scattering objects has been used to obtain molecular species concentrations in plasmas of simple composition. Using a Rayleigh scattering diagnostic, the depolarized component of the scattered signal, proportional to the density of molecules in the plasma, was measured. This new method has been used to locally determine molecular species densities in pure nitrogen and pure hydrogen expanding plasmas. The results were used to obtain the dissociation degree of an expanding hydrogen plasma.

PACS numbers: 52.35.Nx, 52.70.Kz

The fundamental study of hydrogen kinetics in plasmas is of vital importance for the realization of hydrogen negative ion (H^-) or hydrogen neutral (H^0) sources. The latter are important for surface studies and surface modification, whereas H^- sources are crucial links in neutral beam injectors for fusion plasmas. In the process of negative ion production (and destruction) in hydrogen plasmas the H_2 molecular density, the hydrogen neutral density, as well as the shape of the electron energy distribution function are important parameters [1-3]. Furthermore, hydrogen plays a pertinent role in plasma deposition, as it is commonly added as an etching agent in order to improve the quality of the deposit. In order to understand the deposition mechanism, knowledge of hydrogen kinetics is essential as well.

In the search for enhancement of particle source strength (and, thus, deposition rates), expanding thermal plasmas have proven to be successful [1-6]. In this method, a cascaded arc produces an atomized and partially ionized particle beam which expands into a low-pressure background. Expanding cascaded arc plasmas in hydrogen are used successfully as H^0 neutral sources and may serve for volume production of H^- negative ions as well.

As the cascaded arc produces a hot (12000 K), thermal plasma, it can be considered as producing only atoms and atomic ions, e.g., H^0 and H^+ in the hydrogen case. In hydrogen, the study of the expansion out of the cascaded arc is severely hindered by anomalous recombination. This recombination, in which residual hydrogen molecules play a pertinent role, results in a low electron density and, consequently, little light emission. Also other expanding molecular plasmas (e.g., nitrogen) show this ionization loss, although to a lesser extent.

The mechanism responsible for this fast recombination in the first few centimeters of the expansion is charge exchange between atomic ions (H^+) and molecules (vibrationally excited H_2) and subsequent dissociative recombination of the formed molecular ion (H_2^+) [7]. The molecules necessary for this process are not produced in significant amounts by the arc and, thus, must be formed by association, most likely at the steel vessel walls. Together with a strong recirculation flow in the vessel, this wall association process will provide a reentry flow of (vibrationally excited) hydrogen molecules into the expansion.

Because of the little light emission, traditional plasma diagnostics, such as optical emission spectroscopy, cannot be used on this type of plasma. Furthermore, quantitative information on this anomalous recombination requires quantitative knowledge of the abundance of molecules in their electronic ground state, i.e., not readily observable by passive means. So, a *spatially resolved*, active molecular concentration measurement is essential for research on expanding hydrogen or nitrogen plasmas, and would be extremely useful in the study of other kinds of plasma particle sources (and in plasma etching and deposition research) as well.

A well-known active diagnostic such as Rayleigh scattering makes no distinction between atoms and molecules, except in polarization characteristics. The new method introduced here makes use of this fact to obtain molecular species densities in these relatively "dark" hydrogen and nitrogen plasmas.

Electromagnetic radiation can scatter off free electrons in a plasma in a process called Thomson scattering [8,9]. For scattering off bound electrons, the elastic process is the well-known Rayleigh scattering ($\Delta h\nu = 0$ for the scattered radiation), whereas the inelastic version ($\Delta h\nu \neq 0$) is known as Raman scattering.

If polarized incident radiation is scattered off free electrons, the 90° scattered Thomson signal either remains polarized (if the polarization vector of the incident radiation is perpendicular to the plane through the incident wave vector and the line of sight to the observer) or is absent (if the polarization vector lies in this plane). This is a consequence of the specific scattering geometry (e.g., [10]).

In the case of Rayleigh scattering, the situation is somewhat more complicated. In a simple classical approach of scattering [11], one can show that the 90° Rayleigh scattered radiation is fully polarized only if the scattering objects are spherically symmetric, e.g., in the case of ground-state atoms. In the case of nonspherically

symmetric molecules a small component of the scattered radiation is depolarized. According to this classical approach, the ratio of the depolarized (say, horizontal) and polarized (vertical) scattering components I_h/I_v for vertically plane polarized incident radiation and a medium of *linear* molecules is given by

$$\rho \equiv \frac{I_h}{I_v} = \frac{3\gamma^2}{45\alpha^2+4\gamma^2}, \quad (1)$$

where $\alpha = \frac{1}{3}(\alpha_\parallel + 2\alpha_\perp)$ is the average dipole polarizability ($\alpha_\parallel$ and $\alpha_\perp$ are the components of the polarizability tensor along the internuclear axis and perpendicular to it), and $\gamma = \alpha_\parallel - \alpha_\perp$ is the polarizability anisotropy. The components of the polarizability tensor are all frequency dependent [12].

In the quantum-mechanical treatment, Eq. (1) must be modified to include the effect of Raman scattering. The Raman peaks are very weak in intensity compared to the Rayleigh peak, but they are strongly depolarized. If only the central (Rayleigh) peak is considered, the depolarization ratio for this peak (ρ_{Rayl}) in the quantum-mechanical treatment is *4 times smaller* than the one calculated from Eq. (1) [12]. This, however, is an approximation, and it limits the accuracy of the method described here: This ρ_{Rayl} slightly depends on the rovibrational state of the scattering molecules. It can be shown that the total averaged ρ_{Rayl} changes about 10% for a temperature change (and, hence, a rovibrational redistribution) from 300 to 1400 K in the case of hydrogen. Theoretical values for the α's [12–14] can be inserted to obtain the Rayleigh peak depolarization ratios for 532 nm radiation and a temperature of 300 K: $\rho_{\mathrm{Rayl},H_2} = 2.3\times10^{-3}$; $\rho_{\mathrm{Rayl},N_2} = 2.69\times10^{-3}$. In the following, we will consider only the Rayleigh peak depolarization.

In the case of Rayleigh scattering on a plasma, depolarization may also be due to the presence of excited *atomic* states. In the cases discussed here, however, we may totally neglect this influence, as the number of excited states is very small compared to the number of molecules and ground-state atoms (typically smaller by a factor of 10^6–10^{10}).

Figure 1 shows the expanding cascaded arc plasma: a wall-stabilized, continuously operated cascaded arc produces a hot, thermal plasma (diam: 4 mm) at subatmospheric pressure (± 0.6–0.2 bar). This plasma is allowed to expand into a heavily pumped, low-pressure (p_{back} around 1–1000 Pa) background through a conically shaped nozzle, creating a supersonically expanding plasma jet. This plasma source is described in detail elsewhere [4,6]. The plasma conditions for the hydrogen measurements will be referred to as *condition 1*: $I_{\mathrm{arc}} = 37$ A, $V_{\mathrm{arc}} = 208$ V, H_2 flow=3.0 SLM, $p_{\mathrm{back}} = 715$ Pa. For the nitrogen case, *condition 2*: $I_{\mathrm{arc}} = 45$ A, $V_{\mathrm{arc}} = 160$ V, N_2 flow=3.5 SLM, $p_{\mathrm{back}} = 170$ Pa. (SLM stands for standard liters per minute.)

The combined Thomson-Rayleigh setup is sketched in Fig. 2 and consists of a high-power frequency-doubled Nd:YAG laser (wavelength 532 nm) with the beam imaged onto the plasma by a lens and two mirrors. The laser dump is placed far outside the vessel to reduce the stray light. The 90° scattered radiation is imaged onto a polychromator entrance slit. The signal passes an image intensifier and is sampled by a photodiode array. The po-

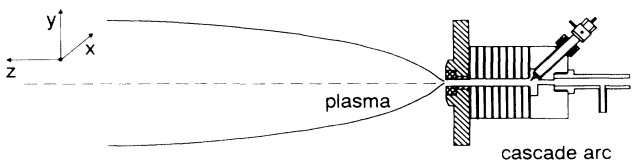

FIG. 1. The expanding cascaded arc experiment. A thermal plasma at atmospheric pressure is created in a cascaded arc, consisting of three cathodes, a number of electrically isolated copper plates, and an anode plate. All these parts are water cooled. The plasma expands into a low-pressure region, creating a supersonically expanding plasma jet.

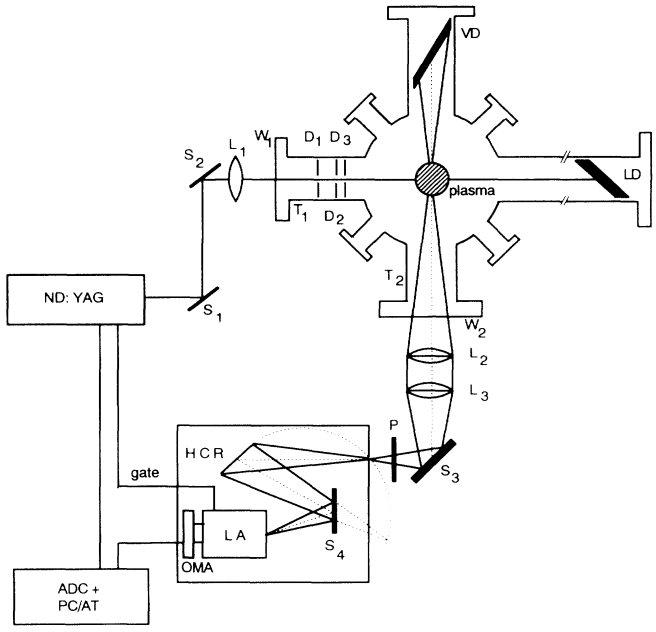

FIG. 2. The Thomson-Rayleigh scattering setup. Frequency-doubled Nd:YAG radiation is focused into the plasma by a system of two dichroic mirrors (S_1 and S_2) and a lens (L_1). The stray light level is reduced by placing the laser dump (LD) far away (i.e., 2 m), and by installing several diaphragms D_1–D_3. The scattered radiation is transmitted through an optical system consisting of lenses (L_2 and L_3) and a mirror (S_3). The dispersive element is a hollow concave grating (HCR), after which detection takes place by an image intensified optical multichannel analyzer (OMA). The gating of the light amplifier (LA) as well as the data processing is handled by a personal computer. The polarizer (P) is placed in front of the entrance slit of the polychromator.

larizer is placed in front of the polychromator entrance slit. The apparatus has been used very successfully in determining electron temperatures, electron densities, and neutral densities, locally and with high accuracy [8].

Measuring a plasma depolarization signal is cumbersome, since the signal is very weak. Three things must be carefully calibrated: (a) the stray light from the laser radiation; (b) the fact that the polarizer is nonideal and will thus show a ("parasitic") signal even if it is perpendicular to the polarization of a plane-polarized incident beam; and (c) the true depolarization signal for a known amount of gas in the vessel at room temperature.

(a) The vessel stray light is taken into account by measuring, without plasma, at a very low ($\ll 1$ Pa) pressure. This vessel stray light measurement is subtracted from the subsequent Rayleigh measurement. Actually, the stray light level is very low, and this makes possible the detection of the weak depolarization signal.

(b) The parasitic depolarization signal was measured by performing Rayleigh scattering measurements on pure argon gas in the vessel. Argon produces no depolarization by itself, so all "depolarization" measured is due to the polarizer itself. To be able to correct for this effect, the polarized and depolarized signals were measured for different argon pressures: The ratio $I_h/I_v \equiv \rho_{\text{parasitic}}$ turned out to be constant and equal to $(6.0 \pm 0.6) \times 10^{-4}$. Each depolarization measurement will therefore consist of a measurement of the vertical and horizontal signals. The amount of parasitic depolarization can then be calculated from the vertical signal and $\rho_{\text{parasitic}}$.

(c) The calibration was performed by measuring the polarized (sample time 240 s) and depolarized (sample time 1800 s) scattering components for known amounts of hydrogen or nitrogen in the vessel at room temperature. For a pressure of 1300 Pa, hydrogen gave a "clean" depolarized signal of 1500 counts, whereas nitrogen gave 3134 counts. The errors in these numbers, resulting from Poisson noise and the subtraction of the parasitic depolarization signal, are around 15%. The measured values of the ρ's, then, are $\rho_{\text{Rayl},H_2} = (2.2 \pm 0.3) \times 10^{-3}$ and $\rho_{\text{Rayl},N_2} = (2.7 \pm 0.3) \times 10^{-3}$, in good agreement with the theoretical values. At room temperature, the particle densities in the calibration are 3.1×10^{23} m^{-3}. This yields the calibration factors to obtain molecular densities in the plasma, provided the ρ_{Rayl}'s do not change too much due to the higher temperature in the plasma.

The measurements were carried out locally (detection volume ≈ 0.25 mm^3) at different distances from the expansion nozzle: at $z = 15$ mm for condition 1, and at $z = 20$ mm and $z = 150$ mm for condition 2. As a result of the dissociation and the higher temperature in the plasma (and the resulting low molecular density at the same pressure), depolarization signals are weaker than in the calibration: 160 ± 50 counts for 1800 s measuring time for condition 1. With the calibration as described in (c), the hydrogen molecular density was calculated to be $(3 \pm 1) \times 10^{22}$ m^{-3}. An additional result can be obtained if we assume pressure equilibrium at this position and calculate the total plasma density with the gas temperature equal to the rotational temperature, measured in a similar experiment [15]: $T_{\text{rot}} \approx 1400$ K. The total density is, then, equal to about 5.2×10^{22} m^{-3}, resulting in a $[H]/[H_2]$ concentration ratio for the plasma at this point of 0.7 ± 0.3. This is an essential result, as a plasma of this type is used as a H^0 particle source.

The results for the nitrogen plasma (condition 2) are given in Fig. 3. In this case, a radial scan was performed at both $z = 20$ mm and $z = 150$ mm (axial and radial scans can be made easily in this experiment by moving the plasma and keeping the diagnostics fixed). The number density of molecules clearly increases at the edges of the plasma.

We conclude the following.

The difference in polarization characteristics of Rayleigh scattering on atoms and molecules can be used to determine the concentration of the molecules in plasmas (or gases) containing only one depolarizing molecular component, such as the plasmas mentioned, where molecules other than H_2 and N_2 are not present in significant amounts.

Every high-quality Thomson-Rayleigh diagnostic with an effective stray light reduction can be adapted for this kind of measurement by the simple insertion of a polarizer and proper calibration.

The accuracy of the method is limited by the fact that the temperature influence on ρ_{Rayl} is neglected, and by the weakness of the effect, which even with long sampling times results in noisy signals. The detection limit is around 10^{21} m^{-3}. Eventually, turning the polarization vector of the incident laser radiation by 90° to make it lie in the plane of incident radiation and line of sight will

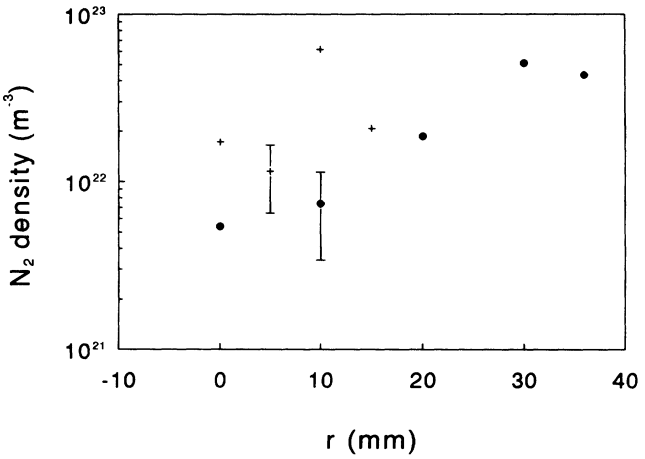

FIG. 3. Results of molecular concentration measurements on an expanding nitrogen plasma jet. Radial scans (r, distance from the center of the plasma jet) were made for two axial positions: $z = 20$ mm (+) and $z = 150$ mm (●).

reduce the noise level because in this case only the depolarized radiation is observed.

The measurements clearly indicate that in the hydrogen case, the density of molecules close to the expansion nozzle is unexpectedly high. This fact can be explained only in terms of wall association in combination with a recirculation flow, as was indicated above. In the case of nitrogen, a similar process may occur, as the number density of molecules increases to the edges of the plasma. In both cases, this information is essential to understand the fast ionization loss in the expansion.

This new application of a widely known phenomenon, depolarization of Rayleigh scattered radiation, can give spatially resolved information about the density of ground-state molecules, information which is difficult to obtain by other means. This knowledge can be essential for research on particle sources and plasma etching or deposition.

We would like to thank A. C. M. van Helvoort, M. J. F. van de Sande, A. B. M. Hüsken, and H. M. M. de Jong for their help and skillful technical assistance during the measurements.

[1] M. Bacal and G. W. Hamilton, Phys. Rev. Lett. **42**, 1538 (1979).

[2] J. R. Hiskes and A. M. Karo, J. Appl. Phys. **56**, 1927 (1984).

[3] M. B. Hopkins and K. N. Mellon, Phys. Rev. Lett. **67**, 449 (1991).

[4] P. K. Bachmann, J. J. Beulens, G. M. W. Kroesen, H. Lydtin, D. C. Schram, and D. U. Wiechert, Surf. Modif. Technol. **3**, 69 (1989).

[5] J. J. Beulens, A. J. M. Buuron, L. A. Bisschops, A. B. M. Hüsken, G. M. W. Kroesen, G. J. Meeusen, C. J. Timmermans, A. T. M. Wilbers, and D. C. Schram, J. Phys. (Paris), Colloq. **51**, C5-361 (1990).

[6] A. T. M. Wilbers, G. J. Meeusen, M. Haverlag, G. M. W. Kroesen, and D. C. Schram, Thin Solid Films **204**, 59 (1991).

[7] M. J. de Graaf, R. P. Dahiya, F. J. de Hoog, M. J. F. van de Sande, and D. C. Schram, J. Phys. (Paris), Colloq. **51**, C5-387 (1990).

[8] M. C. M. van de Sanden, J. M. de Regt, G. M. Janssen, J. A. M. van der Mullen, B. van der Sijde, and D. C. Schram, Rev. Sci. Instrum. (to be published).

[9] J. Sheffield, *Plasma Scattering of Electromagnetic Radiation* (Academic, New York, 1975).

[10] E. Hecht and A. Zajac, *Optics* (Addison-Wesley, Reading, MA, 1974).

[11] R. L. Rowell G. M. Aval, and J. J. Barrett, J. Chem. Phys. **54**, 1960 (1971).

[12] A. L. Ford and J. C. Browne, Phys. Rev. A **7**, 418 (1973).

[13] J. Rychlewski, Mol. Phys. **41**, 833 (1980).

[14] U. Hohm and K. Kerl, Mol. Phys. **69**, 803 (1990).

[15] M. J. de Graaf, D. K. Otorbaev, M. C. M. van de Sanden, and D. C. Schram (to be published).