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Determination of the neutral gas temperature of nitrogen-containing low-pressure plasmas using a two-temperature model

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Abstract

The neutral gas temperature, which is an important process parameter in low-pressure plasmas, is often determined by evaluating the shape of rotational spectra of appropriate molecules. However, the observed population of the rotational levels is determined by the excitation mechanisms and the rotational level population of the electronic states from which the upper electronic state of the chosen molecule band is populated. We used the first negative system of the nitrogen molecule ion for temperature determination in different low-pressure discharges. We will show that the spectra can be fitted best assuming that they are composed of two contributions representing two populations of the nitrogen molecule ion with distinctly different rotational temperatures. Thus, at least two excitation channels of the upper electronic state have to be considered which, in our opinion, are the electron impact on the ground state neutral nitrogen molecule connected with ionization and excitation (rotational level distribution remains essentially unchanged and reflects the gas temperature) and the impact of nitrogen molecules in high vibrational states on the ground-state nitrogen molecule ion (connected with rotational excitation, rotational temperature much higher than the gas temperature). Considering this, more reliable results are obtained compared to the conventional method where a single Boltzmann distribution of the rotational levels is assumed. Here, often, too high temperatures (up to several 100 K) are determined.

Keywords: Two-temperature model; Neutral gas temperature; Low-pressure plasmas; Optical emission spectroscopy; Rotational spectra

1. Introduction

The neutral gas temperature is an important process parameter in low-pressure discharges because chemical reactions may be thermally driven and the neutral gas may contribute to the thermal substrate load. The neutral gas temperature is often determined by evaluating the shape of rotational spectra of molecules. The rotational spectra of a great variety of molecules have been measured: H_2 [1], H_3^+ [2], C_2 [3], Bi_2 [4], CN [5], BH [6], CH [7], NH [7], SiH [8], SiO [9], OH [10], AuO [11], NO [12], and O_2 [13]. But one of the probably most used is the nitrogen molecule and its ion. A lot of spectroscopic methods can be used for the determination of the rotational level distribution of a certain electronic and vibronic state, among them optical emission spectroscopy (OES), laser-induced fluorescence, Raman scattering [14] or coherent anti-Stokes Raman scattering [1], Fourier-transformed infrared spectroscopy [4] and resonance-enhanced multiphoton ionization [15].

Only if thermalisation can take place during the lifetime of the excited molecule, the rotational level population reflects the neutral gas temperature. This is either the case for high pressures owing to the high collision rates (even if the lifetime is significantly reduced due to collisions) [10,16] or for metastable molecule states such as the $N_2(A^3\Sigma_u^+)$ [17] having very long lifetimes. In contrast, in low-pressure plasmas, the light emission usually takes place before the thermal-

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isation of the rotational level population of the electronically excited state. In this case, the observed population of the rotational levels is determined by the excitation mechanisms and the rotational level population of the electronic states from which the upper electronic state is populated. For a correct determination of the gas temperature, all excitation channels have to be considered [18,19]. This fact is frequently neglected in the literature, where only direct population by electron impact is considered [20] or the rotational level distribution of the excited molecule is simply assumed to be a Boltzmann distribution according to the gas temperature [21]. Often, too high rotational temperatures are determined (for example, [22]) which do not reflect the neutral gas temperature at all. In order to explain the rotational level distribution observed by measuring an emission band, difficult models have been suggested which take into consideration the temporal dependence of the rotational relaxation of the excited molecule [19]. A much simpler model, the two-temperature model, has been suggested in [23,24] for the 0–0 band of the first negative system (FNS0-0) of the N_2^+, considering two excitation channels of the $N_2^+(B^2\Sigma_u^+)$ state. One excitation channel results in a rotational level distribution according to the neutral gas temperature. The second excitation channel is connected with rotational excitation, and thus, the rotational temperature of generated molecules is much higher than the gas temperature.

2. Experimental set-up

2.1. Investigated types of discharges

Nitrogen-containing plasmas of different types of low-pressure discharges were investigated: magnetron discharges operated in dc, rf and pulsed mode as well as a glow discharge.

For the dc and rf (13.56 MHz) magnetron discharges a PLS570 assembly (Balzers Ltd.) equipped with a turbo-molecular pump was used. A water-cooled circular magnetron source with a boron target 100 mm in diameter was installed. The target–substrate distance was 10 cm and pure nitrogen was used as working gas with a gas flow of 100 sccm controlled by a mass flow controller (MKS Instruments). The pressure was adjusted by a throttle valve and measured using a baratron gauge. A schematic drawing of the assembly can be found in [25]. OES spectra were recorded at a distance of 10 mm from the target for both the rf and dc magnetron discharge. For each type of discharge, the discharge power was varied (rf discharge between 50 and 500 W, dc discharge between 50 and 300 W) at a pressure of 0.2 Pa and the pressure was varied at constant discharge power (rf discharge between 0.2 and 1.5 Pa at 500 W, dc discharge between 0.2 and 2.0 Pa at 200 W).

For the pulsed magnetron sputter discharge, a PLS500P assembly (Balzers Ltd.) was used. The water-cooled magnetron source was equipped with a 100-mm Mg target and driven by a 5-kW pulsed power supply (Pinnacle plus, Advanced Energy, Inc.). The target–substrate distance was 80 mm. The gas flow rates of Ar, O_2 and N_2 were 50 sccm, 10 sccm and 10 sccm, respectively, and were adjusted by mass flow controllers (MKS Instruments). The total pressure was again controlled by the throttle valve position. OES spectra were recorded 15 mm from the target. The discharge power was varied (between 100 and 700 W) at a pressure of 0.4 Pa and the pressure was varied (between 0.1 and 2.0 Pa) at a constant discharge power of 500 W. The frequency and the duty cycle were kept constant at 200 kHz and 60%, respectively.

For the DC glow discharge, a self-made vacuum equipment with a parallel-plate electrode configuration (electrodes diameter 90 mm, distance 60 mm) was used. Both the powered cathode and the grounded anode were made of titanium. The discharge was operated at a constant pressure of 150 Pa and constant current of 80 mA. The total gas flow rate was 100 sccm and the Ar/N_2 ratio was adjusted by setting the flow rates of each gas. OES spectra were recorded in the negative glow 4 mm from the cathode. The Ar/N_2 ratio was varied (between 0:100 and 95:5) at constant total pressure. The discharge voltage necessary for an operation at 80 mA depends on the gas composition (see Fig. 2(a)).

For the selected pressure ranges, the mean free path of the nitrogen molecules is well below the dimensions of the used vacuum chambers so that thermal equilibration of the gas can be assumed. Stability of the discharges was assured during the recording of the spectra.

2.2. Recording of the spectra

OES spectra were recorded using a spectrometer HR 460S (Jobin Yvon) with a focal length of 460 mm and a LN_2 cooled CCD detector. The grating with 2400 groves/mm yielded a spectral resolution of about 0.05 nm. The relative spectral sensitivity was constant in the recorded wavelength range [26]. Light emission from the plasma was collected by a glass fibre. The angle for light collection was limited to about 1.5° by a small tube of ceramics. This tube was positioned parallel to the surface of the powered electrode (magnetron or cathode) at the above given distances from the electrode. The integration time to record a spectrum was between less than 1 s and several 10 s depending on the plasma light emission intensity.

2.3. Fitting of the spectra

A tutorial discussion on rotational spectra in general can be found in [27]. We have chosen the 0–0 transition of the first negative system (FNS0-0) of the N_2^+ for the