Characterization of N_2 and N_2+H_2 plasmas using near infrared emission spectroscopy

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Abstract: Infrared (IR) emission spectroscopy measurements were performed in N_2 and N_2+H_2 microwave discharges at pressures ranging from 0.5 to 3 Torr. Although emission spectroscopy in the infrared region has rarely been investigated, this technique has nevertheless provided numerous key data. Different atomic and molecular transitions were detectable in the plasma. Numerical simulation of spectra to match experimental FTIR emission data allowed estimating plasma temperature in N_2 and N_2 +H_2 plasma.

Keywords: plasma diagnostics, infrared optical emission spectroscopy, plasma applications

1. Introduction

Plasma surface modification has become popular in biomedical applications. For instance, plasma technologies allow modifying the chemical structure of a shallow surface layer without changing the material bulk properties. The formation of surface amino (NH_2) groups on polymers is often privileged through the use of different nitrogen containing (N_2, N_2+H_2, NH_3) plasmas. These plasma treatments are usually optimised by extensive characterization of the modified surfaces using different surface characterisation methods. However optimising the experimental plasma parameters is inevitable in order to better control the surface modification processes.

Plasma diagnostic techniques, combined with the use of surface characterization methods may be applied for fundamental studies leading to the optimisation of plasma parameters. In this context, the knowledge of fundamental mechanisms of formation of activated species occurring in the plasma is a prerequisite for further process control.

UV-Visible optical emission spectroscopy is amongst the most popular methods and is well documented in the literature. However emission spectroscopy of plasmas in the infrared (IR) region has scarcely been studied despite bringing completely new information with respect to spectroscopic investigations performed in the UV-Visible region. In particular, near IR emission spectroscopy in N_2 and N_2+H_2 plasma allowed detecting features originating from the nitrogen first positive system as well as nitrogen and hydrogen atomic transitions which can be advantageously used for plasma diagnostics and kinetic analyses. In this work, the results of FTIR emission spectroscopy (800-2000 nm) of low pressure N_2 and N_2+H_2 microwave discharges are presented. In addition, the effect of adding H_2 in N_2 plasmas on the rotational temperatures of the plasma species was investigated by comparing the experimental and numerically simulated spectra.

2. Experimental set-up

The experimental set up is shown in **Fig. 1**.

The low pressure plasma reactor illustrated is described in detail elsewhere [1]. Briefly, the experiments were performed in a microwave reactor purchased from Plasmionique Inc. (Varennes, QC, Canada). The N_2 gas (99.998% purity) and H_2 gas (99.999%) used for the plasma characterisation were introduced in the discharge tube by means of mass

flow controllers. The remote plasma column was created in N_2 and N_2+H_2 gas at pressures ranging from 0.5 to 3 Torr. The microwave (2.45 GHz) power delivered to the resonnance cavity was 300 W.

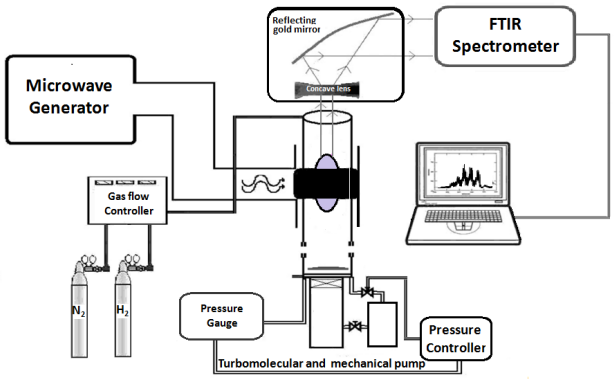

Figure 1. Experimental set-up for MW discharge and emission spectroscopy.

As aforementioned, the plasma characterisation was performed using IR emission spectroscopy. The near infrared spectra were recorded with a FTLA2000 FTIR (770-3300 nm) spectrometer purchased from ABB-Bomem (Québec, QC, Canada) at a resolution of 2 cm^{-1}. For infrared collection, the IR light exiting through a ZnSe feedthrough window, was expanded through a concave ZnSe lens then was redirected by a concave gold mirror into the FTIR's entrance port.

The detector used during each experiment was a thermoelectrically cooled Indium Arsenide (InAs) semiconductor diode which is sensitive in the range of 3000-14000 cm^{-1} (710-3300 nm). One hundred interferograms were routinely co-added and Fourier-transformed, thereby enabling to record spectra with an acceptable signal-to-noise ratio and reasonable acquisition time.

3. Results and discussion

3.1 Structure of the IR emission spectrum.

Typical infrared emission spectrum of the N_2 and N_2+H_2 microwave discharge is shown in **Fig. 2**. In the present study, the observed infrared N_2 spectra consisted mostly of N_2 first positive transitions. In addition, spectra recorded at low gas pressures $p \leq 1$ Torr allow visualizing various N I atomic transitions. In the illustrated spectrum, the infrared features are related to different vibrational transitions originating from the first positive system of nitrogen $N_2\left(B^3\prod_g \rightarrow A^3\sum_u^+\right)$. Moreover, as shown in **Fig. 2**, the N_2+H_2 plasma consisted mainly of N_2 first positive transitions.

Also of interest, emission spectroscopy in the IR region allows detecting nitrogen atomic transitions. Indeed, no intense atomic transition in the UV-Visible spectral region is detectable in the pressure and microwave power ranges selected for this study. However, atomic emission lines can be easily observed in the near-infrared. The most intense lines are highlighted by rectangles in **Fig. 2**. One of them located at 939.3, is assigned to ^2P-$^2D^o$ transitions. Other strong lines are observed at 1359 nm and 1343 nm and are due to [[^2P-$^2S^0$ (or $^2D^0$-^2P)]] and ^2P -^2S° atomic transitions, respectively. In N_2+H_2 plasmas, an intense hydrogen atomic transition is detectable at 1875 nm which is due to [4-3, Paschen α] transition while that observed at 1282 nm is assigned to [5-4 Paschen β] transition.

Figure 3 shows the pressure dependence of the aforementioned atomic transitions. These results indicate that the concentration of excited nitrogen and hydrogen atoms decreased with increasing gas pressure, coming in part from a decrease of electron temperature [2] and thus of electron excitation rate of atoms with gas pressure. Moreover, by increasing the pressure, ions undergo more frequent collisions. Therefore the ions do not acquire enough energy to dissociate the molecules during collisions.

3.2 Rotational temperature

The relative intensity of the N_2 rotational transitions measured in the spectra are generally described by a Boltzmann distribution, with the rotational temperature determined from these transitions being close to the gas temperature [3]. In principle, the rotational temperature of N_2 can be determined either by using different bands from the first negative or the second positive systems [4] through a Boltzmann plot, provided that the spectrometer resolution is high enough to separate the rotational structure of the bands, or by fitting numerical models to the band envelope when medium to low resolution spectrometers are used.

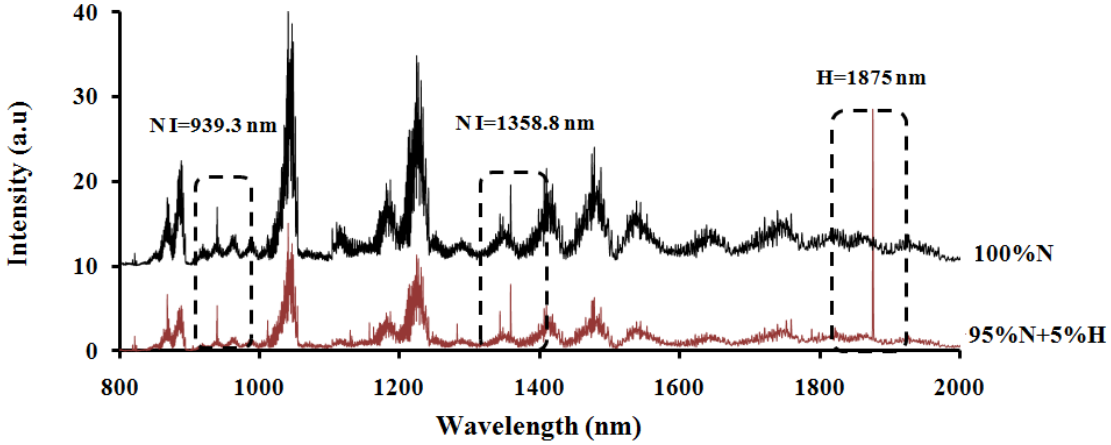

Figure 2. Nitrogen and Nitrogen-Hydrogen plasma emission spectrum in the 800-2000 nm range. Different atomic transitions are distinguished by rectangles (300W, 0.1 Torr, 10 sccm).

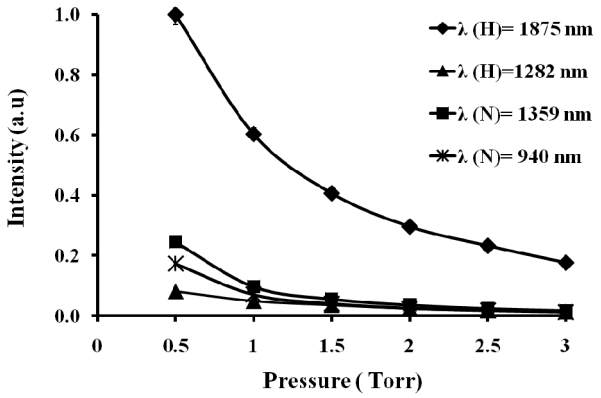

Figure 3. Variation of emission intensity of various atomic nitrogen and hydrogen transitions as a function of pressure. The data are recorded for input power =300 W. All of the results were normalised to the most intense transition at λ=1875 nm.

However, despite the intrinsisic characteristics of the 1st positive system that make it a more reliable tool for gas temperature estimation (low excitation threshold, long radiative lifetimes, higher predissociation level, and high emission intensity) its complex structure with 27 rotational branches has hampered the widespread use of it for gas temperature determination [3, 5].

Inspired by Biloiu *et al*. [3] the plasma gas temperature was evaluated by calculating and generating theoretical spectra closely matching the bands originating from 0-0 transition in the N_2 1st positive system which is observed in the range of 1025-1055 nm.

To that end, a synthetic spectrum which was automated in MATLAB™ [3] has been used. However, such a procedure requires the knowledge of the FTIR spectrometer response function which, in turn, has to be convolved with the calculated spectrum. Accordingly, the shape parameters of the 826 nm ArI line taken from the spectrum of an ArHg source was used, considering that the instrumental broadening could be modeled by a pseudo-Voigt function:

$$f(p,w) = p\frac{\sqrt{4\ln 2}}{\sqrt{\pi}w}\exp\left[-\frac{4\ln 2}{w^2}(\lambda-\lambda_0)^2\right]$$
$$+(1-p)\frac{2}{\pi}.\frac{w}{w^2+4(\lambda-\lambda_0)^2}$$

where p and 1−p are the relative magnitudes of the Gaussian and Lorentzian functions contributions, respectively, w is the full width at half maximum of the selected Ar line (FWHM), and λ_0 is the central wavelength. This allowed determining that p value was 0.5 while w was 0.2 nm for the experimental setup used in the present study.

It is worth mentioning that the p value has an error of ± 0.1. However, this has minimal effect on the temperature calculation as can be seen from the error bars on the curves presented in **Fig. 5**.

Figure 4 shows an example of a measured ro-vibrational N_2 spectrum along with the corresponding spectrum calculated using the aforementioned protocol.

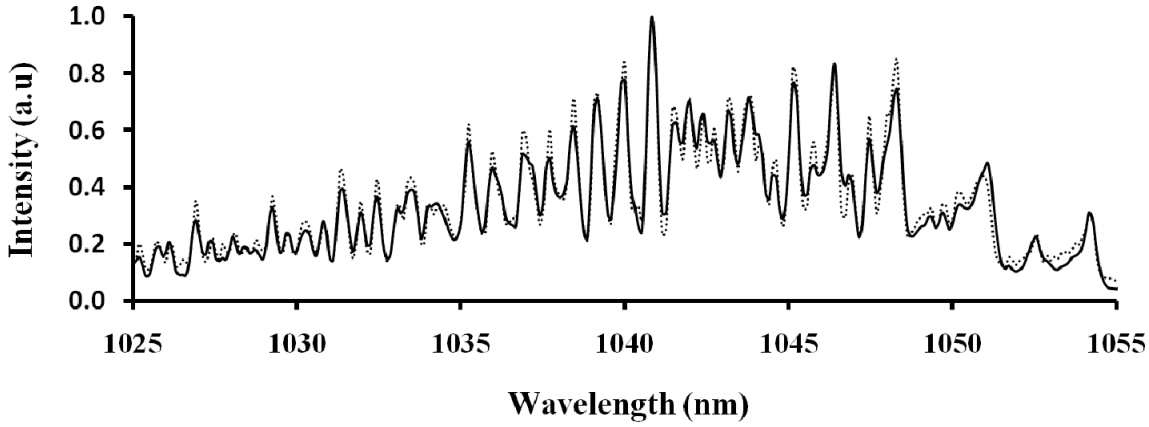

Figure 4. Experimental spectrum (solid line) and corresponding numerically generated (dotted line) spectrum of the 0-0 band for the best fit gas temperature. In this example, the evaluated rotational temperature (Tr) was 1009 K.

As can be seen, an excellent match between the calculated and experimental spectra was obtained, with a confidence level better than 95%.

This method was thereafter used to characterize the pressure-dependence of the rotational temperature in N_2 and N_2+H_2 plasmas generated at powers of 300 W. As seen in **Fig. 5**, T_r increased with pressure and power due to the more frequent collisions occurring between the plasma species which lead to a decrease in electron temperature and ion temperature with concomitant increase of gas temperature.

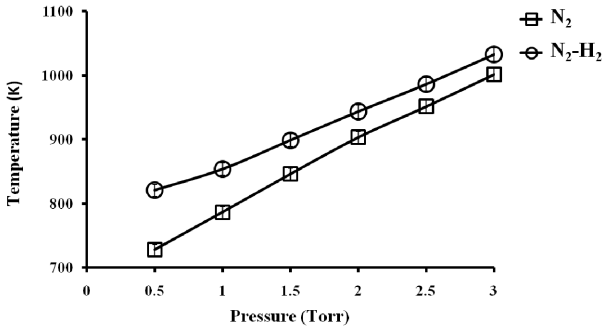

Figure 5. Rotational temperature as a function of pressure for N_2 and N_2 (95%) +H_2 (5%) plasma in 300W power.

The present results clearly highlighted that emission spectroscopy in the near IR region provides different information compared to UV-Visible emission spectroscopy. As an example, the numerical simulation of the spectrum of the 0-0 transition of the nitrogen first positive system allows calculating rotational temperatures [2].

4. Summary

Optical emission spectroscopy in the near IR spectral region was used for the diagnostic of low pressure N_2 and N_2+H_2 microwave discharges currently used for modifying the surface of biomedical polymers. The experimental infrared spectra consisted mostly of N_2 1st positive system transitions and N and H atomic transitions. Rotational temperatures were accurately measured by fitting the N_2 1st positive system spectra recorded from plasmas generated at 0.5 to 3 Torr of N_2 and N_2+H_2 with powers of 300 W. Under these conditions, the N_2+H_2 rotational temperatures increased as compared to N_2 rotational temperature in similar pressure conditions.

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