Application of Semi-automatic Program for Gas Temperature Measurement in Atmospheric Pressure Plasmas Using a Synthetic Diatomic Molecular Spectrum Method

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Abstract

Gas temperature is one of the most important parameters for atmospheric pressure plasma applications. Based on the fact that this parameter is closely related to the rotational temperature of diatomic molecules at atmospheric pressure, a spectroscopic method of measuring the rotational temperature was used by analyzing the OH, O₂, N₂⁺, CH, and CN molecular spectra, which are frequently observed in various atmospheric pressure plasmas. In this work, a semi-automatic program for the determination of the rotational temperature was developed, allowing the use of modest resolution monochromators, generally used in industries and laboratories. Different atmospheric pressure plasma sources were used for application to the various gas temperatures in the range of 400-2500 K. Different diatomic molecular spectra emitted under the same plasma condition showed almost the same gas temperature. Through a sensitivity study of the method, it was found that the diagnostic conditions, such as molecular species and optical resolution, should be carefully selected for more accurate measurements.

Keywords: Atmospheric-pressure plasma, Rotational temperature, Gas temperature, Diatomic molecular spectrum, Optical emission spectroscopy

I. Introduction

Atmospheric pressure plasma sources have recently received increased attention due to their many advantages. These advantages include the fact that they do not require expensive vacuum equipment and are low-cost and simple systems that are easy to operate. Because of these advantages, many types of atmospheric pressure plasma sources have been developed using various frequency range powers from direct current to microwave, or with a short pulse. For example, the microwave and radio frequency (RF) plasma torch, dielectric barrier discharge, arc plasma torch, and the atmospheric-pressure capacitively coupled plasma (CCP) jet are well known examples of atmospheric pressure plasma sources [1-5]. As atmospheric pressure plasmas have many applications, particularly for surface modification of thermally weak materials, such as fabrics, polymers, or glass plates for display industries, remediation of hazardous gases utilizes the gas temperature effect of the plasma; thus, accurate measurement and control of the gas temperature are very important to optimize the performance of the plasma treatment [6,7]. The gas temperature, which is defined as the kinetic temperature of heavy particles, can be obtained through spectroscopic methods, such as the Doppler broadening method and the Boltzmann plot method, in which optical emission spectroscopy has been generally used because of its simplicity and nonintrusive nature. The gas temperature measurement by the Doppler broadening of the spectral lines emitted from neutral particles is the most straightforward method, given by the following equation.

\[ \Delta \lambda / 2 = 7.16 \times 10^{-7} \lambda \sqrt{\frac{T_g}{M}}, \]  

where \( \Delta \lambda / 2 \) is the FWHM of Doppler broadening, \( M \) is the mass of neutrals, \( \lambda \) is the center wavelength, and \( T_g \) is the gas temperature [8]. However, to use the Doppler broadening method, a high-resolution spectrometer is required due to its very small
broadening width. For example, as seen in Fig. 1(a), the Doppler broadening width of a hydrogen atom at 3000 K is only approximately 0.018 nm.

The second method, the Boltzmann plot of diatomic molecular spectrum, is based on the fact that the gas temperature is closely related to the rotational temperature of an atmospheric pressure plasma [8-10]. The gas temperature can be obtained by measuring the rotational temperature of the diatomic molecular spectra in equilibrium plasmas, as well as in nonequilibrium plasmas at atmospheric pressure because the rotational-translational relaxation is sufficiently fast to equilibrate the rotational and the gas temperatures [11,12]. Figures 1(b) and 1(c) show a typical OH molecular spectra calculated with a given temperature and broadening value, and the Boltzmann plot diagram obtained by analyzing the intensity ratio according to each spectral line, respectively. Similarly, because several tens of molecular lines exist in the very short wavelength region, a high-resolution spectrometer is also required to obtain the well-resolved Boltzmann plot. In recent studies, therefore, an improved method using the synthetic spectrum has been used to overcome the limitation of resolution [11-14]. In this work, to achieve this, a semiautomatic program for the gas temperature measurement was developed using the synthetic spectrum method. In particular, three kinds of diatomic molecules (OH, N₂, and O₂), frequently observed in many atmospheric pressure plasmas due to their open-air operation, were selected. Furthermore, the CH and CN emission spectra, as sometimes observed by the addition of CH₄ gas to deposit carbon-based materials, were investigated [15,16]. By comparing the measured values, the accuracy and usefulness of the different spectra were examined. In section 2, theories regarding the Boltzmann plot and synthetic spectrum method are described, and numerical code is introduced. In section 3, we present the experimental results and the validity of the numerical code; the conclusion follows in section 4.

II. Experimental details

If an atmospheric pressure plasma is produced in ambient air, the hydroxyl (OH) molecular band (A²S¹⁺ - X²P, 309 nm) and the nitrogen monopositive ion (N₂⁺) first negative system (B²S₁⁺ - X²S₀⁺, 391.4 nm) are observed in the emission spectrum due to water molecules in the air and nitrogen from the air composition, respectively. Meanwhile, O₂ (b³Σ_u⁺ - X³Σ_g⁻, 759.4 nm), CH (A₂Δ - X²P, 431.4 nm), and CN (B²Σ⁺ - X²Σ⁺, 388.3 nm) are emitted from the plasma by the addition of a small fraction of O₂ and CH₄ gas for specific applications. The theoretical spectrum intensity corresponding to any rotational temperature (T_rot) can be calculated as follows [8-10]:

![Figure 1.](image-url)
\[ I = D_0 k^2 S \exp\left(-\frac{E_v}{k_B T_{\text{rot}}^*}\right), \]  
(2)

where \( k \) is the wavenumber, \( S \) is the oscillator strength, \( k_B \) is the Boltzmann constant, \( D_0 \) is a coefficient containing the rotational partition function, and \( E_v \) is the rotational energy level. \( D_0 \) and \( E_v \) are expressed respectively as:

\[ D_0 = \frac{C(J' + J'' + 1)}{Q}, \]  
(3)

\[ E_v = B_v h c J' (J' + 1), \]  
(4)

where \( C \) is a constant depending on the change of dipole moment and total number of molecules in the initial vibrational state, \( Q \) is the rotational partition function, \( J' \) and \( J'' \) are the upper and lower state, respectively, and \( B_v \) is a rotational constant in the state of the vibrational quantum number \( v \). All the constants can be replaced by adequate values for energy levels and transitions of each molecular spectrum based on the well-known data by Herzberg [10].

In particular, for the \( \text{N}_2^* \) molecular spectrum, even-odd alternation of the intensity was considered, owing to the alternating statistical weights of the rotational levels in the upper and lower states [10]. The theoretical \( \text{OH}, \text{N}_2^*, \text{O}_2, \text{CH}, \) and \( \text{CN} \) spectra were calculated based on the data of Dieke and Crosswhite [9], Dick [17], Touzeau [18], Luque [19], and Acquaviva [20], respectively. Eq. (2) shows an ideal rotational spectrum of diatomic molecules that does not consider the line broadening effect. To approach the realistic emission spectrum, the line broadening effects, such as instrumental broadening, Doppler broadening, and Stark broadening, must be considered. In most of the non-thermal atmospheric pressure plasmas, the Doppler broadening is usually negligible because of the relatively low gas temperature nature of the plasma [11-14]. As an example, if the instrumental broadening has Gaussian shape and is the dominant broadening source, which is the case of our experimental condition, the measured intensity profile would be the convolution of Eq. (2) and the Gaussian function, expressed as:

\[ I = \frac{I_0}{\Delta_i \sqrt{\pi/2}} \exp\left(-\frac{2(\lambda - \lambda_0)^2}{\Delta_i^2}\right), \]  
(5)

where \( I_0 \) is the intensity obtained from Eq. (2) at the wavelength \( \lambda_0 \) and \( \Delta_i \) is the width of the Gaussian-shaped instrumental broadening corresponding with the FWHM \( (= \Delta_i \sqrt{\ln 2}) \). Based on this, the synthetic spectra of the diatomic molecules were yielded through the summation of each line intensity in the wavelength region of interest. Figure 2 shows the typical synthetic spectra of diatomic molecules at 3000 K with instrumental broadening width of 0.1 nm.

The powerful advantage of the synthetic method is the possibility of a low-resolved spectrometer for the \( T_{\text{rot}} \) measurement. For this reason, we developed a semiautomatic program using the synthetic method for accurate gas temperature determination. The main process of the program is the comparison of an experimental emission spectrum with its corresponding synthetic spectrum, as calculated by Eq. (5) for given \( T_{\text{rot}} \) and instrumental broadening \( \Delta_i \) values. To determine the corresponding spectra, the spectrum of the smallest chi-square cross value with respect to the experimental emission spectrum must be considered as the best fit with it. Figure 3 describes the logic organization of
the semiautomatic program for $T_{\text{rot}}$ determination. The experimental molecular spectrum was imported and normalized by band head. After reading the experimental files, molecular types and an instrumental broadening value were selected. The instrumental broadening $\Delta_i$ of the optical setup can be easily obtained using a He-Ne laser and/or a mercury lamp. In the successive step, the synthetic spectra of a given molecule and the instrumental broadening were calculated and compared to find the best fit with the experimental spectrum.

In this work, we used different kinds of atmospheric pressure plasma sources, such as RF atmospheric pressure CCP [15] and atmospheric pressure microwave-induced plasma [13]. Detailed descriptions for the plasma source and configuration are in references [13,15]. The spectroscopic setup consisted of a Chromex 250 spectrometer with 1200 and 600 grooves/mm gratings and a convex lens of 6.3 cm focal length. The instrumental broadening of the detection setup was measured using a He-Ne laser and/or a mercury lamp.

III. Results and discussion

Figure 4 shows a comparison of the $T_{\text{rot}}$ determination between the synthetic spectrum and the experimental spectrum observed from RF atmospheric pressure CCP. Without CH$_4$ gas addition, the helium plasma in open air emitted a N$_2^+$ rotational spectrum, which showed a $T_{\text{rot}}$ of 455 K at 150 W. By adding CH$_4$, the CH and CN emission spectra were observed and showed $T_{\text{rot}}$ values of 450 and 430 K, respectively. For CN, the mismatch between the synthetic spectrum and the experimental spectrum mainly resulted from the vibrational spectrum of CN (1-1, 2-2) because only the (0-0) band of CN was used to determine $T_{\text{rot}}$ in this
work. For the atmospheric pressure microwave-induced plasma, the $T_{\text{rot}}$ of 2200 K was measured using the OH and O$_2$ molecular spectra at 550 W microwave power, as seen in Fig. 5. However, as argon and oxygen gases were used for the microwave-induced plasma generation, argon atomic lines were mixed with the O$_2$ molecular band; the atomic lines should be excluded in the comparison. In addition, the measured $T_{\text{rot}}$ showed a similar value to the gas temperature, which was obtained by a thermocouple around the 1000-K region [13]; hence, any diatomic molecular spectra as a thermometric particle could be selected to induce the gas temperature at atmospheric pressure.

Until the above results were obtained, the $T_{\text{rot}}$ in the range of 400–2500 K was investigated using the numerical code developed in this work. Considering the sensitivity of the method in various rotational temperatures and instrumental broadening widths, the $\chi^2$ values of the calculated spectra were checked in the wide range of $T_{\text{rot}}$ of 300–12000 K and $\Delta_i$ of 0.1–0.5 nm. The spectrum of 300 K was used as a reference for comparing with different rotational temperatures. Therefore, if the variation of a spectral pattern between successive rotational temperatures is noticeable, the $\chi^2$ value is large. This indicates that the large variation of $\chi^2$ would assure the distinguishable spectrum between temperatures. Figure 6 describes the $\chi^2$ values with respect to various $T_{\text{rot}}$ and $\Delta_i$ values for OH (top), O$_2$ (middle), and N$_2^+$ (bottom) molecular spectra. As shown by the results, except the OH case, as $\Delta_i$ increased, $\chi^2$ also increased. For the OH molecular spectra, however, as the value of $\Delta_i$ increased, the $\chi^2$ value decreased. This is because the shape of the OH spectrum became more simple; in particular, two groups in the range of 306–307 nm, which have relatively strong dependence on the $T_{\text{rot}}$, merged into one simple bell-shaped figure [11,13].

Another noticeable information from Fig. 6 is the temperature dependence of the spectra. The rotational spectra of the diatomic molecules are more suitable for low-gas temperature plasma. By increasing the temperature, the slope of $\chi^2$ variation saturated to a certain value at each $\Delta_i$ value, indicating that the plasma would be in the thermal equilibrium state.

**IV. Conclusions**

In this work, a rotational temperature measurement program was developed to measure the gas temperature of atmospheric pressure plasmas. The semiautomatic program analyzed OH, O$_2$, N$_2^+$, CH, and CN molecular spectra, which are frequently emitted from atmospheric pressure plasmas. According to the results applied to
different plasma sources, the method shows high accuracy of measurement in the range of 400–2500 K. From the simultaneous investigation of the different molecular spectra emitted from the same plasma source, almost the same value of the rotational temperature was obtained. Through the sensitivity study of the method at various rotational temperatures and instrumental broadening values, it was found that the molecular type, the rotational temperature region, and the optimum instrumental broadening value should be decided for high-accuracy measurements depending on the experimental environment.

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