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A comparative study of rotational temperatures using diatomic OH, O_2 and N_2^+ molecular spectra emitted from atmospheric plasmas

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Abstract

From the application point of view, gas temperature is one of the most important parameters for atmospheric plasmas. Based on the fact that the gas temperature is closely related with the rotational temperature of an atmospheric plasma, a spectroscopic method of measuring the rotational temperature is described in this work by analyzing OH, O_2 and N_2^+ molecular spectra emitted from the atmospheric plasma in ambient air. The OH and N_2^+ molecular spectra are emitted because of the oxygen, hydrogen and nitrogen atoms existing in the ambient air. The O_2 diatomic molecular spectrum is emitted from the oxygen plasma that is frequently produced for atmospheric plasma applications. In order to utilize a spectrometer with modest spectral resolution, a synthetic diatomic molecular spectrum was compared with the experimentally obtained spectrum. The rotational temperatures determined by the above three different molecular spectra are in good agreement within 2.4% error. In the case of a plasma with low gas temperature, the temperature measured by a thermocouple was compared to verify the accuracy of the spectroscopic method, and the results show excellent agreement. From the study, it was found that an appropriate diatomic molecular species can be chosen to be used as a thermometer depending on experimental circumstances.

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Keywords: Atmospheric plasma; Rotational temperature; Diatomic molecular spectrum; Spectroscopy

1. Introduction

Atmospheric plasma sources have been studied for decades due to their many advantages, such as no necessity of expensive vacuum equipment, low cost and simple systems, and easy operation. Because of the advantages, many types of atmospheric plasma sources have been developed. For example, a microwave and radio frequency (RF) plasma torch, a dielectric barrier discharge (DBD), and an arc plasma torch are well known types of atmospheric plasma sources [1–3].

However, the atmospheric plasma has, in general, many different physical characteristics from

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the low-pressure counterpart due to its high-pressure environment, which imposes the importance of the plasma diagnostics. Because of the frequent collisions between electrons and neutrals at high pressure, the electrostatic Langmuir probe method that is widely used for measuring low pressure plasma parameters is generally less useful for plasmas produced at atmospheric pressure. Therefore, other diagnostic methods are needed and optical emission spectroscopy (OES) has been used as one of the alternative diagnostics because of its simplicity and non-intrusive nature.

Since many atmospheric plasma applications such as material processing, surface modification, and remediation of hazardous gases such as perfluorocarbon gas utilize the gas temperature effect of the plasma, accurate measurement of the gas temperature is very important to optimize the performance of the plasma treatment [4,5]. Doppler broadening measurement of spectral lines emitted from neutral particles is the most straightforward. However, in order to use the Doppler broadening method, a high-resolution spectrometer is required due to its very small broadening width. For example, the Doppler broadening width of a hydrogen atom at 3000 K is only approximately 0.018 nm. The second method is from the Boltzmann plot of diatomic molecular spectrum [6–10] based on the fact that the gas temperature is closely related with the rotational temperature of an atmospheric plasma. The gas temperature, which is defined as the kinetic temperature of heavy particles, can be obtained in equilibrium plasmas by measuring the rotational temperature of the diatomic molecular spectra and also in non-equilibrium plasmas at atmospheric pressure because the rotational-translational relaxation is sufficiently fast to equilibrate the rotational temperature and the gas temperature [11,12]. By the similar reason, a high resolution spectrometer is needed to obtain the well-resolved Boltzmann plot because several tens of molecular lines exist in the very short range of wavelength spectrum, for example, more than one hundred OH spectral lines in 5 nm range.

The third method is by comparing the experimentally-obtained molecular spectrum emitted from the plasma with the synthetic spectrum [11,13–15]. This method is useful especially with a spectrometer of modest spectral resolution. The generally-utilized spectra include OH, N_2^+ and O_2 lines. In most cases, the most suitable molecular spectrum is chosen among the above three depending on the experimental circumstances. In many works, just one molecular species was usually utilized to determine the rotational temperature [9,11,13–15]. Even in the cases with two molecular species such as OH and N_2^+, a comparative study of the rotational temperature was performed using only Boltzmann plot method [10]. In this work, however, all the above three diatomic molecular spectra emitted from the same plasma source were independently utilized to measure the rotational temperature. By comparing the measured values, the accuracy and usefulness of the three different spectra were investigated.

2. Method

If an atmospheric plasma is produced in ambient air, the hydroxyl (OH) molecular band ($A^2\Sigma^+$, $v=0\rightarrow X^2\Pi$, $v'=0$, 306–310 nm) and the nitrogen monopositive ion N_2^+ first negative system ($B^2\Sigma_u^+$, $v=0\rightarrow X^2\Sigma_g^+$, $v'=0$, 388–392 nm) are observed in the emission spectrum due to water molecules in the air and nitrogen from the air composition, respectively. On the other hand, the O_2 diatomic molecular spectrum ($b^1\Sigma_g^+$, $v=0\rightarrow X^3\Sigma_g^-$, $v'=0$, 758–772 nm) is emitted from the plasma by adding a small fraction of O_2 gas or from the oxygen plasma that is frequently produced for various applications such as ozone generation.

The rotational temperature T_{rot} of a plasma can be obtained by comparing the afore-mentioned synthetic diatomic molecular spectrum with the measured one. The theoretical diatomic molecular spectrum intensity is given by [6,7]

$$I = D_0 k^4 S \exp\left(-\frac{E_r}{k_B T_{\mathrm{rot}}}\right) \quad (1)$$

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_r is the rotational energy level. D_0 and

E_r are expressed, respectively, as

$$D_0 = \frac{C(J' + J'' + 1)}{Q_r},$$

$$E_r = B_v hcJ'(J' + 1),$$

where C is a constant depending on the change of dipole moment and total number of molecules in the initial vibrational state, Q_r 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 [8]. Especially for N_2^+ molecular spectrum, even–odd alternation of intensity was considered, which is owing to the alternating statistical weights of the rotational levels in the upper and lower state [8]. The OH, N_2^+ and O_2 spectra were obtained from the data of Dieke and Crosswhite [7], Dick et al. [16], and Touzeau [9], respectively.

In order to compare the experimentally-obtained spectrum with the synthetic spectrum, the line broadening of the intensity profiles should be taken into account. Generally, the measured intensity profile is a convolution of the instrumental broadening caused by various spectroscopic instruments used in the experimental setup, the Doppler broadening due to the thermal motion of radiators in the plasma, and the Stark broadening due to the electric fields generated by charged particles surrounding the radiators. In most of the non-thermal atmospheric plasmas, the Doppler broadening is usually negligible because of the relatively low temperature nature of the plasma. As an example, if the instrumental broadening is in 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. (1) and the Gaussian function, and is expressed as

$$I = \frac{I_0}{\Delta_i \sqrt{\pi/2}} \exp\left(-\frac{2(\lambda - \lambda_0)^2}{\Delta_i^2} \right) \qquad (2)$$

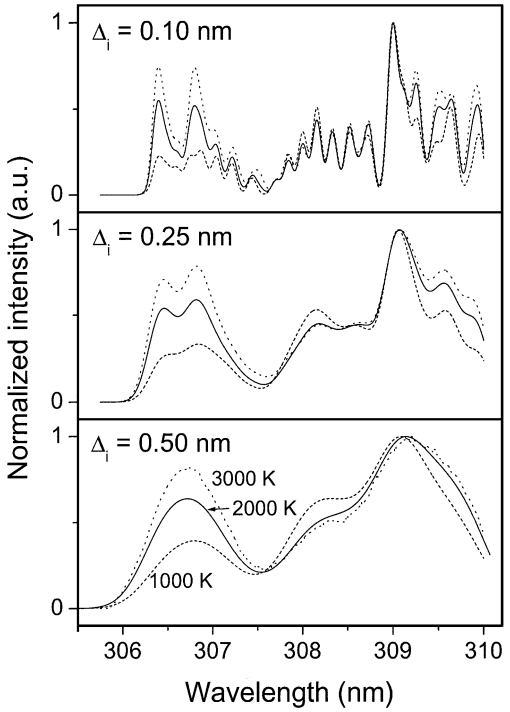

Fig. 1. Synthetic OH spectrum at various rotational temperature (1000, 2000, 3000 K) and instrumental broadening width, (a) $\Delta_i = 0.10$ nm, (b) $\Delta_i = 0.25$ nm, (c) $\Delta_i = 0.50$ nm.

where I_0 is the intensity obtained from Eq. (1) at the wavelength λ_0, and Δ_i is the full width at half maximum (FWHM) of the Gaussian-shaped instrumental broadening. Based on this, synthetic spectra of OH, N_2^+ and O_2 were obtained through the summation of each line intensity in the wavelength region of interest.

Figs. 1–3 show examples of the synthetic spectra of OH, N_2^+ and O_2 molecular lines at various rotational temperature (1000 K, 2000 K, 3000 K) and instrumental broadening width (0.10 nm, 0.25 nm, 0.50 nm), respectively. Each spectrum is normalized with respect to the largest intensity in the selected region of wavelength for the sake of convenience. The rotational temperature is simply obtained by comparing the synthetic spectrum with the measured spectrum using the chi-square method.

This diagnostic technique may be limited to the maximum rotational temperature of approximately

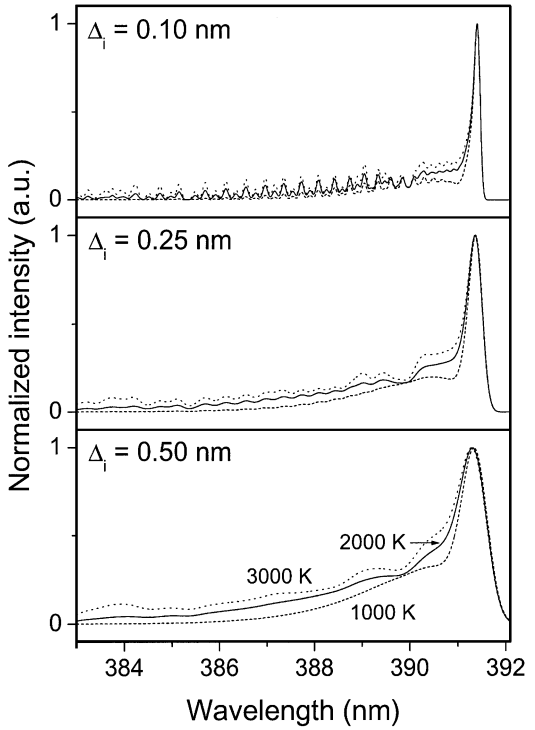

Fig. 2. Synthetic N_2^+ spectrum at various rotational temperature (1000, 2000, 3000 K) and instrumental broadening width, (a) $\Delta_i = 0.10$ nm, (b) $\Delta_i = 0.25$ nm, (c) $\Delta_i = 0.50$ nm.

10 000 K for N_2^+ and approximately 7000 K for OH and O_2. This is because the overall shape of the molecular spectrum becomes less sensitive to the temperature variation above this temperature value although the overall intensity level increases, indicating the temperature resolution becomes poor. In addition, at high rotational temperature, various atomic and other molecular lines that pollute the molecular spectrum of interest may appear to make the analysis difficult.

3. Experimental set-up

In this work, two different types of atmospheric plasma sources were used for the rotational temperature measurement as shown in Fig. 4. Depicted in Fig. 4a is a plasma source for low gas temperature, which consists of a 15 kV AC transformer, a biased electrode of 6 mm in diameter surrounded by a cylindrical dielectric tube for gas injection, and a grounded electrode of 40 mm in diameter. A 6 mm inner diameter nozzle was used to produce a stable atmospheric plasma. The distance between the two electrodes was 50 mm, and the distance from the end of the nozzle to the grounded electrode was 20 mm. Helium gas was provided at 6 ℓpm flow rate. To observe a measurable level of O_2 atmospheric molecular band from the plasma, O_2 gas was added to the helium gas at 4 ℓpm. In addition to the O_2 band, the OH molecular spectrum and N_2^+ first negative system were simultaneously observed. Another type of the atmospheric plasma source used for the experiment is a microwave plasma torch consisting of a 2.45 GHz microwave launcher, WR-284 waveguide components, and a field applicator (Fig. 4b). The forward and reflected powers were monitored by a directional coupler and a power detector. The reflected power was dumped into a water load through the

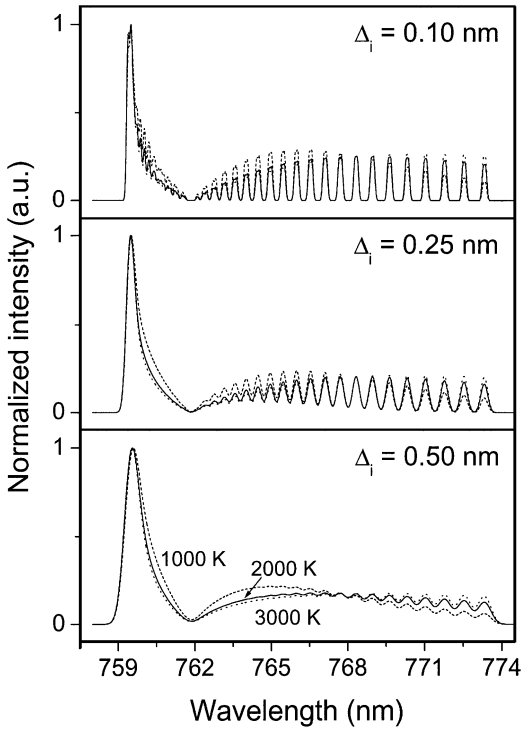

Fig. 3. Synthetic O_2 spectrum at various rotational temperature (1000, 2000, 3000 K) and instrumental broadening width, (a) $\Delta_i = 0.10$ nm, (b) $\Delta_I = 0.25$ nm, (c) $\Delta_i = 0.50$ nm.

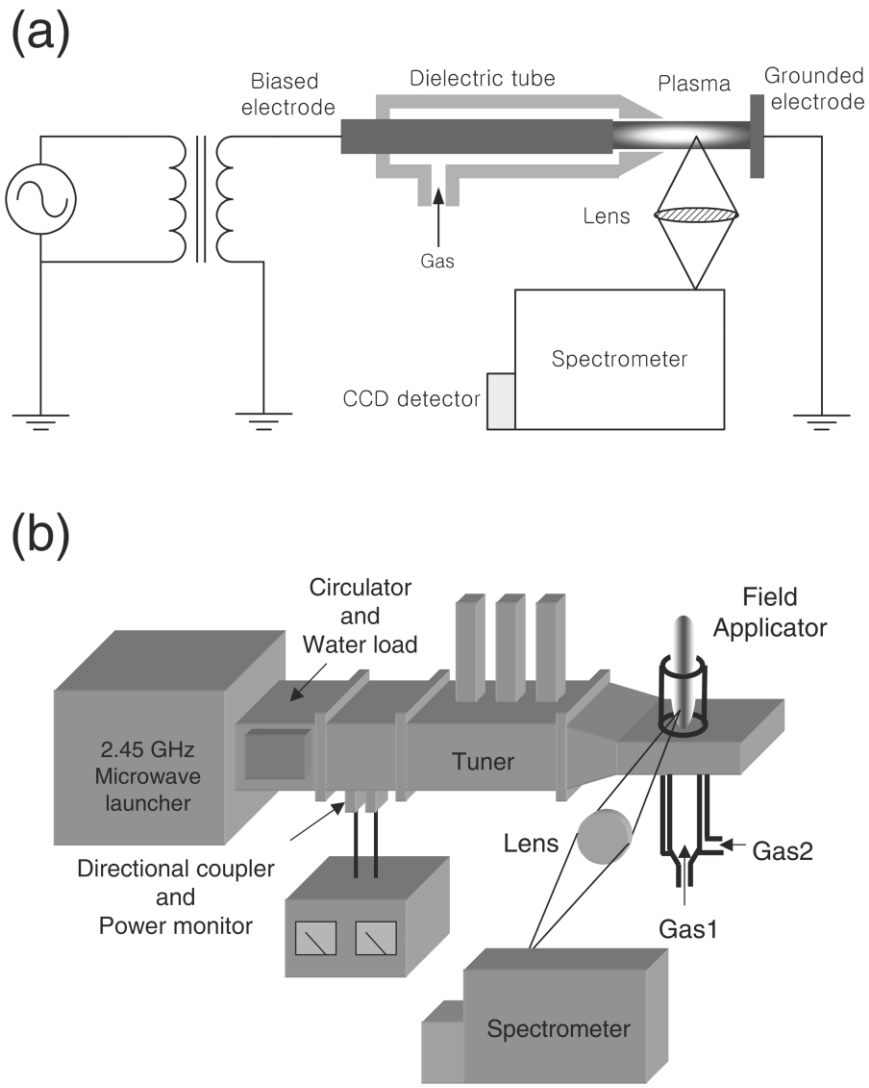

Fig. 4. Schematic view of the experimental setup for atmospheric plasma generation. (a) An AC plasma and (b) a microwave torch plasma for observing diatomic molecular spectra.

circulator. The WR-284 waveguide was tapered off to 80×10 mm to increase the electric field strength where the field applicator was located. A coaxial dielectric tube of 18 and 13 mm inner diameter was inserted vertically, perpendicular to the wide wall of the waveguide, and was served as the discharge tube.

The spectroscopic setup consisted of a Chromex 250is spectrometer with 1200 and 600 grooves/mm gratings and a convex lens of 5.3 cm focal length. The instrumental broadening of the detection setup was measured using a He–Ne laser and a mercury lamp. The measured line shape due to the instrumental broadening was well fitted to the Gaussian function, as shown in Fig. 5, of which the full-width-at-half-maximum (Δ_i) was 0.18 nm with the 1200 grooves/mm grating and 50 μm entrance slit width. Having the measured Δ_i, each

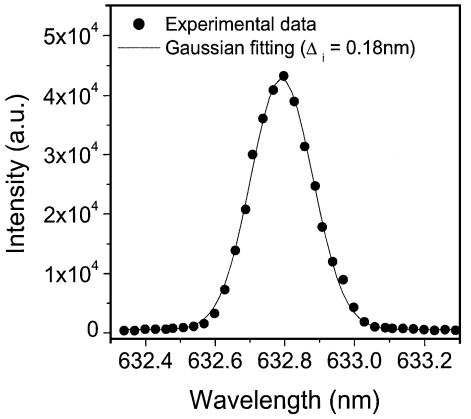

Fig. 5. The measured line shape of the 632.8 nm HeNe laser through the spectroscopic setup and its Gaussian fitting of the instrumental broadening. The full width at half maximum of the Gaussian peak was 0.18 nm using a 1200 grooves/mm grating and 50 μm entrance slit width.

synthetic spectrum (OH, N_2^+, O_2) was constructed based on Eqs. (1) and (2). Using the convex lens, the plasma under investigation was imaged onto a screen with the 1:1 image size and the local plasma emission was transported to the spectrometer entrance slit.

4. Results and discussions

Fig. 6 shows the comparison of the synthetic and the measured spectrum represented by a solid curve and open circles, respectively, obtained from the AC plasma illustrated in Fig. 4a. All the measurements were performed at 2 mm from the grounded electrode, and the instrumental broadening width Δ_i was 0.18 nm. As shown in the figure, excellent agreements are seen in the overall comparison between the synthetic and the measured spectra. The rotational temperatures derived from the OH, N_2^+ and O_2 spectrum are 930, 935 and 920 K, respectively, and the difference between the measured temperatures is less than 1.1%. The deviation of the experimental value from the synthetic spectrum above 309.4 nm for OH and above 770 nm for O_2 is thought to be due to the absence of the synthetic lines that correspond to the experimentally-observed lines.

One thing to note here is the presence of the large 388.8 nm helium neutral atomic line in the N_2^+ spectrum originated from the helium gas used for stable plasma generation. This atomic line was not included in the analysis for determining the rotational temperature. As shown in Fig. 6b, the experimental data and the synthetic spectrum agree well in the whole spectral range except (388.3–389.5) nm where the helium line exists. However, in order to double check how well the experimental data fit to the theoretically-obtained spectrum, the helium line was intentionally included in the N_2^+ synthetic spectrum with the 0.18 nm of Δ_i. A very nice agreement is seen in the wavelength range of (388.3–389.5) nm in Fig. 6b, indirectly demonstrating that the measured temperature and the instrumental broadening width are correct.

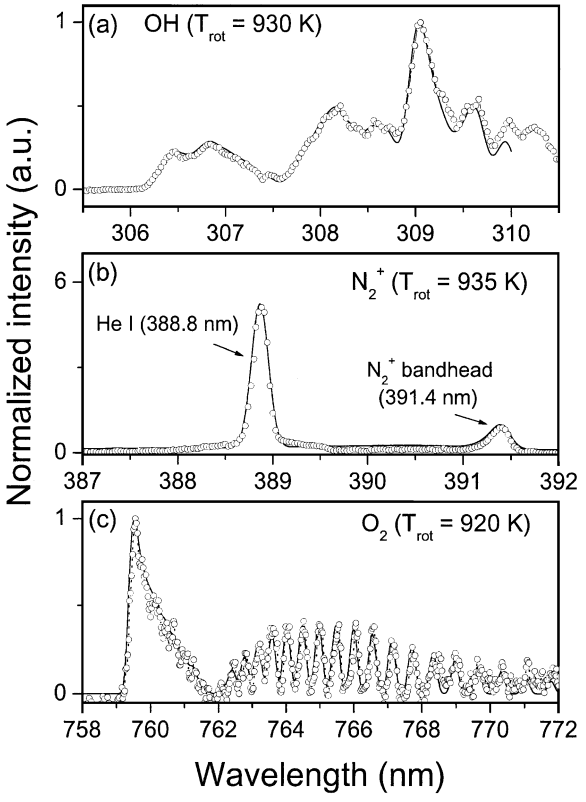

Fig. 6. Comparison of the measured spectrum (–○–) with the synthetic OH, N_2^+ and O_2 spectra (—), yielding a rotational temperature of 930, 935, 920 K, respectively.

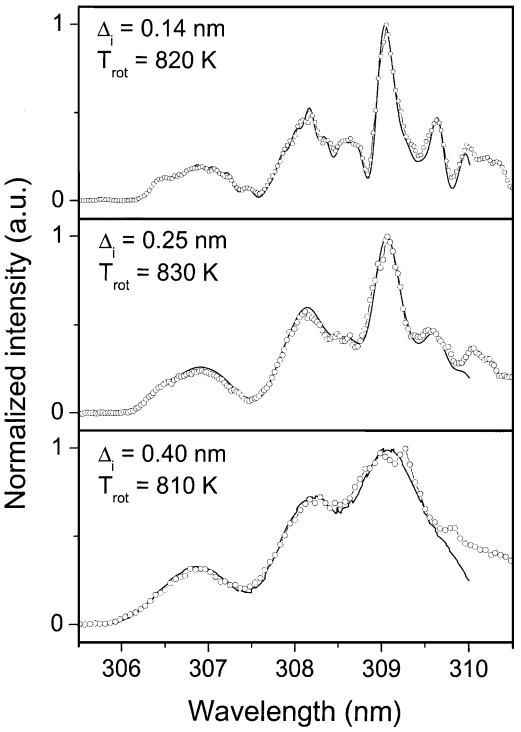

Fig. 7. Rotational temperature obtained by the OH spectrum from the same plasma measured at various instrumental broadening widths. At $\Delta_I = 0.14$, 0.25, 0.40 nm, the difference is only approximately 20 K in 820 K, which indicates that the accuracy of the diagnostic method is quite insensitive to the spectral resolution.

On the other hand, the same experiment was repeated at different spectral resolution to find out the accuracy of the temperature measurement depending on instrumental broadening. The Δ_i of the instrumental broadening was varied by changing the grating with different groove density and the entrance slit width of the spectrometer. Fig. 7 shows the rotational temperature obtained by the OH spectrum from the same plasma measured at various instrumental broadening widths. At $\Delta_i =$ 0.14, 0.25, 0.40 nm, the difference is only 20 K in 820 K, which is approximately 2.4%, The result indicates that the accuracy of this diagnostic technique is quite insensitive to the spectral resolution of the experimental setup, which is one of the merits of this method.

For checking the temperature obtained in this way, a measurement of the gas temperature using a thermocouple was attempted simultaneously with the spectroscopic method under the same plasma condition for comparison. Since the thermocouple used for the experiment had a maximum measurement range of 1500 K, it was applicable to the AC plasma described in Fig. 4a. The experimental data were acquired at all 5 mm intervals from the end of the nozzle to the grounded electrode at the radial center of the cylindrical geometry. The axial temperature profile measured by the OH spectrum and the thermocouple is shown in Fig. 8, where an excellent agreement is seen between the two diagnostic methods. As moving away from the nozzle, the gas temperature linearly increases because of the secondary electron emission from the grounded electrode.

The temperature measurement technique by the diatomic molecular spectra was also applied to an atmospheric microwave torch plasma [14] of higher rotational temperature to ensure that the diagnostic method can be applied to a different plasma environment. In this plasma source depicted in Fig. 4b, argon and oxygen gases were introduced separately through the coaxial dielectric tube at the same flow rate of 4 ℓpm. The top side of the tube was open to the ambient air. The OH and

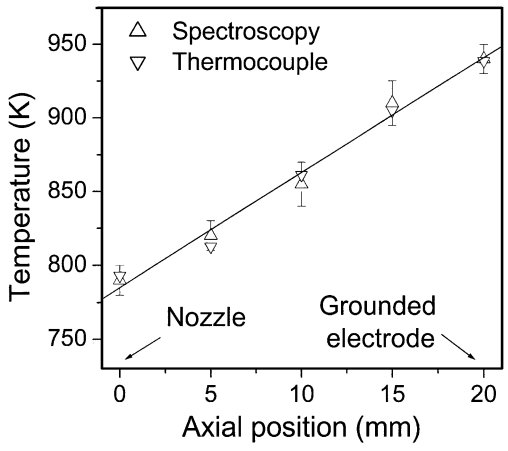

Fig. 8. Axial profile of the temperature measured by the spectral analysis (–△–) and by a thermocouple (–▽–) from the atmospheric plasma shown in Fig. 4a.

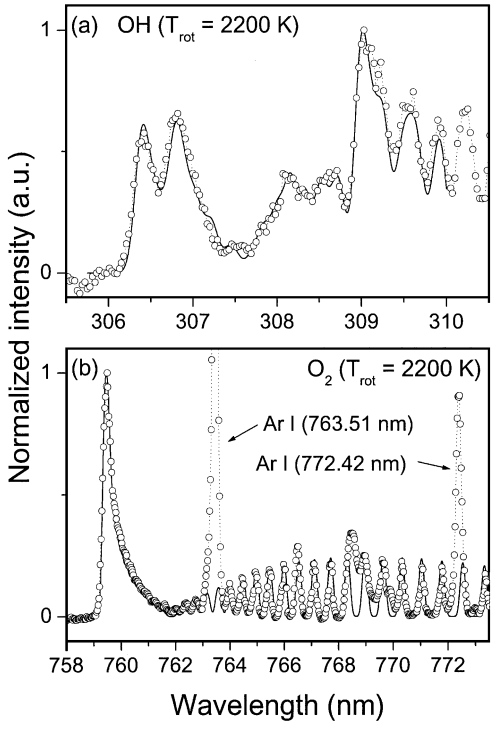

Fig. 9. Rotational temperature measured at the atmospheric microwave torch plasma by using the OH and O_2 molecular spectra. It shows the same temperature value of 2200 K. The synthetic spectrum and the experimental data are denoted by (—) and (–○–), respectively. $\Delta_i = 0.15$ nm.

O_2 molecular spectra were observed at 5 cm from the end of the tube. However, no quantitative measurement of the N_2^+ spectrum was made since the signal to noise ratio was very poor in this case. This may be due to the shielding of the oxygen gas flowing between the inner and the outer tube, which reduced the contact of the plasma to the ambient air. Using the OH and O_2 molecular spectra, the rotational temperature was obtained to be the same value of 2200 K as shown in Fig. 9. In the O_2 spectrum, argon atomic lines were also observed because of the argon feeding gas. These argon lines were not taken into account for determining the temperature as noted previously. From the results, it was confirmed that the rotational temperature of an atmospheric plasma can be obtained with high accuracy by using the diatomic molecular emission spectrum for various plasma sources.

5. Conclusions

The Boltzmann plot method and the Doppler broadening method for measuring the rotational or gas temperature of atmospheric plasmas require spectrometers with relatively high spectral resolution. However, the rotational temperature was obtained in this work by comparing the synthetic and the experimental spectra of the OH, N_2^+ and O_2 diatomic molecular emission spectra using a spectrometer with modest resolution. According to the results from the two different plasma sources with different plasma parameters, the three molecular spectra produced the almost same value of the rotational temperature within 2.4% error. At the low temperature AC plasma, the spectroscopically-obtained rotational temperature was compared with the gas temperature measured by a thermocouple, where an excellent agreement was seen. Dependence of the accuracy on the instrumental broadening width or the spectral resolution was investigated, and it turned out to be not significant in $\Delta_i = (0.14–0.40)$ nm range. On the other hand, this measurement technique was also applied to a microwave-induced atmospheric torch plasma, where the OH and O_2 spectra produced the same temperature value. From the results, it was confirmed that the rotational temperature of atmospheric plasmas can be obtained with high accuracy by using any of the diatomic OH, N_2^+, O_2 molecular emission spectra depending on the experimental environment. This diagnostic method will be especially useful for plasmas with rotational temperature higher than the measurement range of a thermocouple or for plasmas with limited access.

Acknowledgments

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References

[1] M. Moisan, J. Hubert, J. Margot, G. Sauvé, Z. Zakrzewski, in: C.M. Ferreira, M. Moisan (Eds.), Microwave Discharge: Fundamentals and Applications, Chap. 1, Plenum, New York, 1992.

[2] J. Park, I. Henins, H.W. Hermann, G.S. Selwyn, Gas breakdown in an atmospheric pressure radio-frequency capacitive plasma source, J. Appl. Phys. 89 (2001) 15–19.

[3] C. Hibert, I. Gaurand, O. Motret, J.M. Pouvesle, [OH(X)] measurements by resonant absorption spectroscopy in a pulsed dielectric barrier discharge, J. Appl. Phys. 85 (1999) 7070–7075.

[4] P.P. Woskov, D.Y. Rhee, P. Thomas, D.R. Cohn, J.E. Surma, C.H. Titus, Microwave plasma continuous emissions monitor for trace-metals in furnace exhaust, Rev. Sci. Instrum. 67 (1996) 3700–3707.

[5] K. Pochner, W. Neff, R. Lebert, Atmospheric pressure gas discharges for surface treatment, Surf. Coat. Technol. 74 (1995) 394–398.

[6] P.W.J.M. Boumans, Inductively Coupled Plasma Emission Spectroscopy Part 2, John Wiley & Sons, New York, Chichester, Brisbane, Toronto, Singapore, 1987, Chap. 10.

[7] G.H. Dieke, H.M. Crosswhite, The ultraviolet bands of OH, J. Quant. Spectrosc. Radiat. Transfer. 2 (1962) 97–199.

[8] G. Herzberg, Molecular Spectra and Molecular Structure: 1. Spectra of Diatomic Molecules, 2nd edition, D. Van Nostrand Company, Princeton, New Jersey, Toronto, New York, London, 1964.

[9] M. Touzeau, M. Vialle, A. Zellagui, G. Gousset, M. Lefebvre, M. Pealat, Spectroscopic temperature measurements in oxygen discharges, J. Phys. D: Appl. Phys. 24 (1991) 41–47.

[10] J.M. Workman, P.A. Fleitz, H.B. Fannin, J.A. Caruso, C.J. Seliskar, A comparative study of rotational temperatures in a microwave plasma: OH radical vs. N_2^+, Appl. Spectroscopy 42 (1988) 96–100.

[11] S. Pellerin, J.M. Cormier, F. Richard, K. Musiol, J. Chapelle, A Spectroscopic diagnostic method using UV OH band spectrum, J. Phys. D: Appl. Phys. 29 (1996) 726–739.

[12] A. Czernichowski, Temperature evaluation from the partially resolved 391 nm N_2^+ band, J. Phy. D: Appl. Phys. 20 (1987) 559–564.

[13] C. de Izarra, UV OH spectrum used as a molecular pyrometer, J. Phys. D; Appl. Phys. 33 (2000) 1697–1704.

[14] S.Y. Moon, W. Choe, H.S. Uhm, Y.S. Hwang, J.J. Choi, Characteristics of an atmospheric microwave-induced plasma generated in ambient air by an argon discharge excited in an open-ended dielectric discharge tube, Phys. Plasmas 9 (2002) 4045–4051.

[15] O. Motret, C. Hibert, S. Pellerin, J.M. Pouvesle, Rotational temperature measurements in atmospheric pulsed dielectric barrier discharge-gas temperature and molecular fraction effects, J. Phys. D: Appl. Phys. 33 (2000) 1493–1498.

[16] K.A. Dick, W. Benesch, H.M. Crosswhite, S.G. Tilford, R.A. Gottscho, R.W. Field, High resolution spectra of bands of the first negative group of ionized molecular nitrogen (N_2^+ 1NG: $B^2\Sigma_u^+ \rightarrow X^2\Sigma_g^+$), J. Mol. Spectrosc. 69 (1978) 95–108.