The Excitation and the OH Band Rotation Temperatures of a Plasma Jet Light Source

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Methods of the measurement of the excitation and the rotation temperatures under a variety of discharge conditions were reported in detail. Two sorts of the discharge gases, which were Ar-N₂ and Ar, were compared. Effects of the desolvation of solution samples, the additions of KCl to the samples and the observed points of different heights etc. on the temperatures' changes were discussed. Lateral and radial distributions of the spectral line intensities were measured. These two distributions in the case of the excitation temperature had a same inclination which was flat in the center of the discharged plasma. But in the case of the OH band rotation temperature, the radial intensity distribution was ringlike in the outer side of the discharged plasma, and the temperature measurement was possible only in this area. The partial pressures of OH in the discharge gas were calculated. From thermochemical calculations, intensity changes of the OH band according to temperature changes were obtained and these coincide with the above results.

1. Introduction

The problem of the light sources is one of the most important, such as these of spectrometers and spectrophotometric measurements, in the field of the emission spectrochemical analysis. Recently, against usual light sources such as flame, arc and spark, which have been put to practical use, varieties of new light sources are developed and recommended.

To examine and to compare the performance of these new light sources, the temperature measurement is one of the direct and important beginnings. There are several methods of the temperature measurements, and in a same method, for example, in the measurement of the excitation temperature, regions of wavelengths and Ag values of spectrum lines, used in each report, are different for different reporters. Consequently, even a direct comparison of the results of its measurements is impossible.

In this report, two methods of the temperature measurements were investigated in detail, and a step forward of elucidation of the problem was intended. By a performance of a temperature measurement under a variety of conditions in the discharge of light sources, it is possible to study what nature of the light sources is expressed by a method of the temperature measurement, and it is also possible to speculate inductively what is the tempera-
ture which is measured by a definite method.

2. Measurement of the excitation temperature

Generally, spectral line intensity \( I \) of a wavelength \( \lambda \) is,

\[
I = N_n A_{nm} h \nu.
\]  

(1)

\( N_n \): number of atoms, excited on an excited state \( n \), in an emissive light source

\( A_{nm} \): transition probability of a transition \( n \rightarrow m \)

\( h \): Planck's constant

\( \nu \): frequency \( = c / \lambda \) (\( c \): velocity of light)

If \( g_n \) is a statistical weight of the excited state \( n \) and \( J \) is an inner quantum number,

\[
g = 2J + 1.
\]  

(2)

\( U(\nu) \): Sum over states or partition function of an excited state \( n \)

\( E_n \): excited energy of an excited state \( n \)

\( k \): Boltzmann's constant

\( T \): the excitation temperature, K

On the assumption that the thermal equilibrium exists and the Boltzmann's distribution is established in an emissive gas,

\[
N_n = N_0 \frac{g_n}{U(\nu)} \exp(-E_n/kT).
\]  

(3)

\( N_0 \): number of total atoms

From these formulas, \( \log \left( \frac{I_\lambda}{Ag} \right) = -5040 \frac{T}{E} + C_1 \cdot \)  

(4)

In a graph, values of \( \log(\frac{I_\lambda}{Ag}) \) are put on the ordinate, and values of energy of upper states, \( E(\text{eV}) \), on the axis of abscissa. When the points in the above graph are plotted about several spectral lines, a straight line is obtained. Inclination of this line corresponds to \( -5040T \). From this inclination, a temperature is obtained.

This method is the most popularized one in the study of the spectrochemical analysis, but

1. The results of measurements considerably differ with the values of \( Ag \).

2. The results of the two line method have a lot of errors. So, use of spectral lines as many as possible is desirable to increase the accuracy of the measurement.

In this report, eleven iron spectral lines as shown in Table I are used. In the previous

<table>
<thead>
<tr>
<th>Wavelength (Å)</th>
<th>( E_{\text{lower}} ) (K)</th>
<th>( E_{\text{upper}} ) (eV)</th>
<th>( \log \frac{Ag}{\lambda} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>3008.14</td>
<td>888</td>
<td>34122</td>
<td>4.88</td>
</tr>
<tr>
<td>3009.57</td>
<td>7388</td>
<td>40594</td>
<td>5.17</td>
</tr>
<tr>
<td>3017.63</td>
<td>888</td>
<td>34017</td>
<td>4.22</td>
</tr>
<tr>
<td>3024.03</td>
<td>888</td>
<td>33947</td>
<td>4.33</td>
</tr>
<tr>
<td>3030.15</td>
<td>19621</td>
<td>52613</td>
<td>6.52</td>
</tr>
<tr>
<td>3031.22</td>
<td>19788</td>
<td>52769</td>
<td>6.26</td>
</tr>
<tr>
<td>3059.09</td>
<td>416</td>
<td>33096</td>
<td>4.10</td>
</tr>
<tr>
<td>3083.74</td>
<td>7986</td>
<td>40405</td>
<td>5.01</td>
</tr>
<tr>
<td>3180.23</td>
<td>19757</td>
<td>51192</td>
<td>6.35</td>
</tr>
<tr>
<td>3225.79</td>
<td>19351</td>
<td>50342</td>
<td>6.24</td>
</tr>
<tr>
<td>3286.76</td>
<td>17550</td>
<td>47967</td>
<td>5.95</td>
</tr>
</tbody>
</table>

Table I: Energy levels and log ratios of \( Ag \) to wavelength of Fe I spectral lines for temperature measurements.

report, besides this lines' group, other two lines' groups, 3400~3600Å (6 lines) and 3700~4000Å (6 lines), were also used. But these latter two lines' groups are overlapped with band spectra in many cases. And, photographic plates have generally a reliable characteristic curve in the wave length region of 2500~3500Å. For these two reasons, the above latter two spectral lines' groups were not used in this study.

As the results of the measurements, plots of the points in the graph have always a definite tendency, shown in Fig. 1, and Fig. 2. The plot of the spectral line 3059.09Å (excitation potential 4.10 eV) is always higher than the straight line in the graph. The plots of 3009.57Å line (5.03 eV) and 3083.74Å line (5.01 eV) are always lower together. And, the plots of 3030.15Å line (6.52 eV) and 3031.22Å (6.54 eV) are always lower.

In the spectral lines used, it seems to be that, the plots of three lines, 3008.14Å (4.23 eV), 3017.63Å (4.22 eV) and 3024.03Å (4.21 eV), those make a group, and other three lines 3180.23Å (6.35 eV), 3225.79Å (6.24 eV) and 3286.76Å (5.95 eV) have the most reliable values. These spectral lines of two groups have all medium spectral intensities, which easily enter in the proper range of the photographic photometry.
In the photographic photometry, because of the narrow proper range of the line intensity, for a strong line such as 3059.09 Å, the density is frequently saturated. On the other hand, for too weak lines such as 3030.15 Å and 3031.22 Å, the photographic measurements get into trouble.

The results of the higher values of the plots of 3009 Å and 3083.74 Å lines are thought to be due to a reason that the $A_g$ values of these lines are questionable.

According to the above discussion, to do a temperature measurement by this atomic lines intensity method, it becomes necessary to draw the line in the graph by a fixed way as shown in Fig. 1 and Fig. 2. Especially, to compare the temperatures which are measured under various discharge conditions of a light source, a drawing of the straight line by a fixed way is indispensable. If a line is drawn indistinctly in the middle of the obtained spots without having regard to the two points, which are the propriety of $A_g$ values and the proper range of the photographic photometry, there will be a risk, that is, no meaningful result will be obtained.

3. Measurement of the OH band rotation temperature

Intensities of the OH band rotational lines, which are listed in Table II, were compared. The energy levels and the $A_g$ values associated with each line are also listed in the table.

<table>
<thead>
<tr>
<th>Line designation</th>
<th>Wavelength (Å)</th>
<th>Energy level (Initial) cm$^{-1}$ eV</th>
<th>Relative transition probability $a_d(A_g)$ log$A_g$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_2$ 8</td>
<td>3068.277</td>
<td>33949.67 4.2091</td>
<td>28.8 1.4594</td>
</tr>
<tr>
<td>$R_2$ 7</td>
<td>3069.177</td>
<td>33650.38 4.1720</td>
<td>24.8 1.3945</td>
</tr>
<tr>
<td>$R_13$</td>
<td>3069.675</td>
<td>35911.59 4.4524</td>
<td>49.1 1.6911</td>
</tr>
<tr>
<td>$R_{14}$</td>
<td>3071.145</td>
<td>36393.24 4.5121</td>
<td>53.2 1.7259</td>
</tr>
<tr>
<td>$R_{15}$</td>
<td>3073.028</td>
<td>36902.90 4.5753</td>
<td>57.2 1.7574</td>
</tr>
<tr>
<td>$R_4$ 4</td>
<td>3074.369</td>
<td>32947.05 4.0848</td>
<td>12.8 1.1072</td>
</tr>
<tr>
<td>$R_5$ 3</td>
<td>3077.028</td>
<td>32778.49 4.0639</td>
<td>8.9 0.9494</td>
</tr>
</tbody>
</table>
A scanning of the band spectral lines with a microphotometer is shown in Fig. 3.

The background intensity of spectrum of the plasma jet light source used is rather low in the vicinity of the wave length region of the OH band. But, in the shorter wave length region, background corrections of three lines which are 3068.3 Å, 3069.2 Å and 3069.7 Å became difficult. According to the literature, the OH band has a structure which is sufficiently open to permit use of a reciprocal linear dispersion of 2.5 Å/mm.

The spectrograph used in this experiment, is 1.25 m Czerny-Turner spectrograph, JEOL Type 125B, which was equipped with 1200 line-per-mm grating, blazed for 3000 Å, giving a reciprocal linear dispersion of 6.2 Å/mm in the first order. This dispersion is insufficient to separate the above three lines.

Consequently, a graph of the photometric measurement as shown in Fig. 4 was obtained. That is, the plots of the four lines which are 3071.1 Å (4.51 eV), 3073.0 Å (4.58 eV), 3074.4 Å (4.09 eV) and 3077.0 Å (4.06 eV) are put on a straight line. But the plots of the other three lines come off occasionally from the straight line. Accordingly, the line must be drawn depending on the above reliable four lines.

Consequently, a graph of the photometric measurement as shown in Fig. 4 was obtained. That is, the plots of the four lines which are 3071.1 Å (4.51 eV), 3073.0 Å (4.58 eV), 3074.4 Å (4.09 eV) and 3077.0 Å (4.06 eV) are put on a straight line. But the plots of the other three lines come off occasionally from the straight line. Accordingly, the line must be drawn depending on the above reliable four lines.

In the both cases of the excitation temperature and the OH band rotation temperature, a plate calibration was performed by means of preliminary curve which was made by usual two step method using a step sector. Eastman Kodak SA–1 plates were developed for five minutes using D–19 developer at 20°C.

4. Precision of the measurements

Examples of precision of the temperature measurements under two discharge conditions, in which plasma jets were discharged at the electric currents of 38 A and 43 A, were shown in Table III. Solution samples were nebulized with an ultrasonic nebulizer and desolvated through a desolvation instrument. Metal iron was dissolved in 1:10 HCl solution so that

![Fig. 4. An example of the inclination of a line, drawn on the plots of OH band rotational lines which express the relation between log (I/Ag) and the upper excitation potential to measure an OH band rotation temperature.](image-url)
Table III. Reproducibility of temperature measurement, K.

<table>
<thead>
<tr>
<th>Observation condition</th>
<th>Sample, introduced</th>
<th>Height of observed point</th>
<th>Current, Exposure time, Excitation temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>remove</td>
<td>Fe 100 ppm</td>
<td>0.52 mm upper</td>
<td>37.9A, 4 sec. 5390 37.5A, 1.5 sec. 5210 38.2A, 2 sec. 4800</td>
</tr>
<tr>
<td>almost</td>
<td>KCl 2/10 mol</td>
<td>3.2 mm upper</td>
<td>5650 5520 5520 5570</td>
</tr>
<tr>
<td>H₂O</td>
<td></td>
<td>5.88 mm upper</td>
<td>5540 5510 5540 5514</td>
</tr>
</tbody>
</table>

The concentration becomes 100 ppm, and the emissions of these iron's spectral lines were used to measure the excitation temperature.

The plasma jet discharges were imaged on the slit of the spectrograph by the slit image method. As the results, the positions of the heights, 0 mm to 6.4 mm, come to the width of the spectrum in the spectrographic plate. The scanning with the microphotometer were done on three positions of the spectrum, which corresponded to the heights 0.52 mm, 3.2 mm and 5.88 mm in the plasma jets from the exit hole of the discharge of the cathode. These positions are those used for the practical spectrochemical analysis.

In the repeated experiments of the two discharge electric currents, results of three times' measurements agree with one another within a precision of ±100 degree.

In the case of the plasma jet light source used, the position of the point of the horizontal 3 mm cathode is effective remarkably on the discharge and the spectral line intensities, consequently, to the results of the temperature measurements. In the case, where the horizontal cathode projects too far out, shown as "a" in Fig. 5, the cathode hampers the ejection of the plasma jet, the spectral line intensities become weaker and the excitation temperatures are lowered. Values of the electric currents are enlarged and correspond to 27.0 A in the

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Fig. 5. Three positions of the extreme cathode top in the discharge hole.
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Table IV. Effect of position of the cathode point on its excitation temperature, K.

<table>
<thead>
<tr>
<th>Observation condition</th>
<th>Sample, introduced</th>
<th>Height of observed point</th>
<th>Current, Exposure time, Excitation temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>remove</td>
<td>Fe 500 ppm</td>
<td>0.52 mm upper</td>
<td>27.0A, 2 sec. 4590 25.8A, 2 sec. 4340 25.5A, 1.5 sec. 4070</td>
</tr>
<tr>
<td>almost</td>
<td></td>
<td>3.2 mm upper</td>
<td>4620 4600 4790</td>
</tr>
<tr>
<td>H₂O</td>
<td></td>
<td>5.88 mm upper</td>
<td>4600 4480</td>
</tr>
<tr>
<td>remove</td>
<td>Fe 500 ppm</td>
<td>0.52 mm upper</td>
<td>37.9A, 2 sec. 4810 36.6A, 1.5 sec. 4720</td>
</tr>
<tr>
<td>almost</td>
<td></td>
<td>3.2 mm upper</td>
<td>5010 4920</td>
</tr>
<tr>
<td>H₂O</td>
<td></td>
<td>5.88 mm upper</td>
<td>4920 4800</td>
</tr>
</tbody>
</table>
upper column and 37.9 A in the lower column in Table IV. When the cathode is put too back (Fig. 5, c), the ejection of the plasma jet becomes forcibly, the spectral line intensities become strong and the excitation temperatures are higher. The values of the electric currents become smaller. The 25.5 A of the upper column in Table IV corresponds to this case. In the case of the central position of the horizontal cathode (Fig. 5, b), values of the electric current and the excitation temperature are intermediate. The 25.8 A in the upper column and the 36.6 A in the lower column in Table IV correspond to the last case. Temperature difference in these cases amounts to 450 degree.

5. Results of the measurements

A feature of the plasma jet light source, used in this experiment, is that a variety of gases or mixtures of gases are usable as a discharge gas to eject many sorts of plasma jet.

5.1 The excitation temperature of Ar-N₂ plasma jet

When Ar 5 l/min. is used as a carrier gas, carrying the moisture of sample, and N₂ 2 l/min. is used as an additional gas, the excitation temperatures become as shown in Table V. Temperatures under the condition that almost all water vapor is removed by the operation of the desolvation instrument are shown in the upper column in Table V. In this case, water solution of 500 ppm Fe was used as a sample. In the middle column, excitation temperatures under the condition that all of water is transmitted to the light source by stopping the operation of the desolvation instrument are shown. By the existence of water vapor in the light source, differences of the temperatures become as follows.

-270°, -150°, -400°, -780°
-230°, -220°, -230°, -440°
-370°, -210°, -150°, -470°

Temperature difference in these cases amounts to 450 degree.

The lowerings of the temperatures, which correspond to 200°~800° appear, and they are more remarkable in the case of larger electric current and higher temperature.

When 2/10 mol KCl is dissolved together with 100 ppm iron in the solution sample, the excitation temperatures rise extensively as shown in the lower column in Table V. Comparing to the case of the upper column, where KCl is not added, differences of temperatures become as follows.

+300°, +550°, +580°, +300°
+380°, +500°, +490°, +500°
+320°, +460°, +360°, +180°

Rises of the excitation temperature, corresponds to 300°~600°, are obtained. According

<table>
<thead>
<tr>
<th>Effect of water vapor</th>
<th>Sample, introduced</th>
<th>Height of observed point</th>
<th>Current, Exposure time, Excitation temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>remove</td>
<td>Fe</td>
<td>0.52 mm upper</td>
<td>15.8A, 3 sec. 25.8A, 2 sec. 37.9A, 2 sec. 44.2A, 2 sec.</td>
</tr>
<tr>
<td>almost remove</td>
<td>500 ppm</td>
<td>3.2 mm upper</td>
<td>4540 4620 4810 5350</td>
</tr>
<tr>
<td>H₂O</td>
<td></td>
<td>5.88 mm upper</td>
<td>4260 4600 4720 5040</td>
</tr>
<tr>
<td>do not remove</td>
<td>Fe</td>
<td>0.52 mm upper</td>
<td>15.2A, 3 sec. 25.0A, 2 sec. 36.0A, 2 sec. 43.0A, 2 sec.</td>
</tr>
<tr>
<td>remove</td>
<td>500 ppm</td>
<td>3.2 mm upper</td>
<td>4270 4470 4410 4570</td>
</tr>
<tr>
<td>H₂O</td>
<td></td>
<td>5.88 mm upper</td>
<td>4030 4380 4490 4600</td>
</tr>
<tr>
<td>remove</td>
<td>Fe 100 ppm</td>
<td>0.52 mm upper</td>
<td>16.0A, 6 sec. 25.5A, 4 sec. 37.2A, 4 sec. 43.3A, 3 sec.</td>
</tr>
<tr>
<td>almost remove</td>
<td>KCl</td>
<td>3.2 mm upper</td>
<td>4840 5170 5390 5650</td>
</tr>
<tr>
<td>H₂O</td>
<td>2/10 mol</td>
<td>5.88 mm upper</td>
<td>4640 5100 5210 5540</td>
</tr>
</tbody>
</table>

5.2 The excitation temperature of Ar plasma jet

When Argon 5 l/min. is used as a carrier gas, carrying the moisture of sample, and Air 2 l/min. is used as an additional gas, the excitation temperatures become as shown in Table VI. Temperatures under the condition that almost all water vapor is removed by the operation of the desolvation instrument are shown in the upper column in Table VI. In this case, water solution of 500 ppm Fe was used as a sample. In the middle column, excitation temperatures under the condition that all of water is transmitted to the light source by stopping the operation of the desolvation instrument are shown. By the existence of water vapor in the light source, differences of the temperatures become as follows.
to these, several times’ increase of the spectral line intensities will be supposed in the case of Hg I 2536.6 Å line and Cd I 2287.0 Å line. And 10 to 30 times increase will be supposed in the case of Zn 2138.6 Å line. The rises of the temperatures in these case are more remarkable in the discharge of the intermediate electric currents.

5.2 The excitation temperature of Ar plasma jet

Using Ar gas as a carrier without addition of N₂ gas, an Ar plasma jet was discharged. In this case, the excitation temperatures are clearly lower compared to that of the Ar-N₂ plasma jet. That is, values shown in the upper column in Table VI become lower compared to that in the upper column in Table V as follows.

-720°, -470°, -350°, -960°
-740°, -590°, -600°, -810°
—, -540°, -780°, -950°

Also, in the case of the Ar plasma jet, when all of water is transmitted to the light source by stopping the operation of the desolvation instrument, 200° to 600° lowerings of the temperatures, compared to the results of the upper column in Table VI appear as shown in the middle column in the same table. The lowerings of the temperatures owing to the existence of water vapor in the light sources in the case of the Ar plasma jet are equal to that in the case of the Ar-N₂ plasma jet.

When 2/10 mol KCl is dissolved together with 100 ppm iron in the solution, the temperatures of the light sources are higher, as shown in the lower column in Table VI compared to that in the upper column in the same table.

-120°, +60°, +90°, +60°
-170°, -70°, +260°, +150°
—, +150°, +330°, +160°

But the rises of the temperatures are not so much as that in the same case of the Ar-N₂ plasma jet.

5.3 The OH band rotation temperature

The OH band rotation temperatures of the Ar-N₂ plasma jet are shown in Table VII. Temperature differences according to the heights of observed points from the top of the discharge hole are not viewed, these are opposed to the results in the case of the excitation temperatures of the same plasma jet in Table V. And, differences of the OH band rotation temperature by the addition of 2/10 mol KCl to the sample are plus or minus, and have no fixed inclination.

The OH band rotation temperatures of the Ar plasma jet are shown in Table VIII. In these cases, temperature differences according to the heights of observed points from the discharge hole are small, and have also no inclination by the addition of 2/10 mol KCl to

<table>
<thead>
<tr>
<th>Effect of water vapor</th>
<th>Sample, introduced</th>
<th>Height of observed point</th>
<th>Current, Exposure time, Excitation temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>remove almost H₂O</td>
<td>Fe 500 ppm</td>
<td>0.52 mm upper</td>
<td>17.6A, 4 sec. 28.2A, 3 sec. 41.0A, 3 sec. 49.0A, 3 sec.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.2 mm upper</td>
<td>3820 4150 4280 4390</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5.88 mm upper</td>
<td>3520 4010 4120 4230</td>
</tr>
<tr>
<td>do not remove H₂O</td>
<td>Fe 500 ppm</td>
<td>0.52 mm upper</td>
<td>16.0A, 15 sec. 26.3A, 10 sec. 37.9A, 6 sec. 44.3A, 5 sec.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.2 mm upper</td>
<td>3250 3770 4080 4070</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5.88 mm upper</td>
<td>3220 3430 3660 3740</td>
</tr>
<tr>
<td>remove almost H₂O</td>
<td>Fe 100 ppm</td>
<td>0.52 mm upper</td>
<td>17.9A, 15 sec. 28.7A, 10 sec. 41.6A, 10 sec. 49.5A, 4 sec.</td>
</tr>
<tr>
<td></td>
<td>KCl 2/10 mol</td>
<td>3.2 mm upper</td>
<td>3700 4210 4370 4450</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5.88 mm upper</td>
<td>3350 3940 4380 4380</td>
</tr>
<tr>
<td></td>
<td></td>
<td>—</td>
<td>— 3650 3990 4060</td>
</tr>
</tbody>
</table>
the sample. The only differences between the values of the upper column in Table VIII, which are the results in the case in which water vapor is not removed, and those of the second column in the same table, which are the results in the case in which almost all water vapor is removed by the desolvation instrument, are viewed.

The differences are $+610^\circ, +10^\circ, +260^\circ, +60^\circ$

$+440^\circ, +90^\circ, +100^\circ, +100^\circ$

$- , +420^\circ, +70^\circ, +380^\circ$

Temperature differences of $\sim 600^\circ$ appear. Namely, the cases in which the water vapor is removed show clearly higher temperatures.

6. Radial emission and temperature distributions

As shown in Fig. 6, the plasma jet cross section is divided into four circular zones which succeed at equal intervals of $J (= R/4)$. The emission per unit volume per unit solid angle is taken to be constant within a zone; it assumes the values $J_1$, $J_2$, $J_3$ and $J_4$ for the four zones. The total emission in the $y$ direction from the four sections parallel to the $y$ axis is $I_1 J_1$, $I_2 J_2$, $I_3 J_3$ and $I_4 J_4$.

In the practical measurements, four points of 0.5 mm ($I_1$), 1.5 mm ($I_2$), 2.5 mm ($I_3$) and 3.5 mm ($I_4$) from the center of the plasma jet.
are observed one after another by the photographic photometry.

There are differences of the degree of brightness of the spectral lines according to the measuring points and exposure times of the photographic photometry must be changed with every measuring point to do the photographic photometry in the optimum range of the spectral lines' intensities. That is, the intensities of a spectral line at each measuring point, \(I_1, I_2, I_3\) and \(I_4\) are corrected by the exposure times, and relative intensities are obtained. An example of lateral intensity change in an iron spectral line along x axis is shown as a line \(I_1-I_2-I_3-I_4\) in Fig. 7. After the Abel inversion according to the literature, a radial intensity change \(J_1-J_2-J_3-J_4\) of the same iron spectral line is obtained and shown in the same figure.

Opposed to the case of the iron spectral line, intensity distribution of the spectral line in the OH band is stronger in the outer side of the plasma jet as shown in Fig. 8. When the Abel inversion is done, emission intensities of the lines disappear in the central portions. The emission of the OH band spectrum is distributed as a ring in the outer side of the plasma jet discharge.

Lateral and radial distributions of the temperatures are obtained as shown in Fig. 9. For the lateral temperatures, those of \(I_1-I_4\), which are corrected by the exposure times, are used, and in the case of the radial temperature distributions, the radial spectral intensities \(J_1-J_4\) after the Abel inversion are used. In the case of the excitation temperature, lateral...
and radial intensity distributions are same in the inclination along x axis. Only some what rises of temperatures are observed after the Abel inversion. Opposed to this case of the excitation temperatures, the OH band rotation temperature can be measured in only the outer side of the plasma jet. In the latter case, a clear difference of the distribution between the lateral and the radial temperatures are viewed.

7. Calculation of the spectral line intensity in the OH band

As shown in the other report, when the water vapor is removed through a dry ice trap, using a desolvation instrument, the amount of the water vapor which is carried to the discharge is 2 mg/l. Namely, the amount of the water vapor in the carrier gas Ar is 10 mg/5 l. With the additional gas N₂ 2 l/min., water vapor of 10 mg/7 l is carried to the discharge per every minute in this experiment.

Under the normal state, H₂O 18 g corresponds to 22.4 l and the amount of water vapour, carried through to the discharge, becomes 22.4 l×10 mg/18 g per 7 l/min.=1.244×10⁻² l per 7 l/min. Accordingly, the partial pressure P of the water vapor becomes 1.244×10⁻² l÷7 l=0.178×10⁻² (Atm).

Then,
\[ \frac{P_0 P_{H}}{P_{OH}} = \exp \left[ -\frac{1}{RT} (\Delta F_1 + \Delta F_2 + \Delta F_3) \right] = K \quad (5) \]
\[ P_0 + P_H + P_{OH} = P \quad (\text{constant}) \quad (6) \]
\[ \frac{P_0}{P_H + P_{OH}} = \frac{1}{2} \quad (7) \]

In these,
\[ \text{Free energy} \]
\[ O \overset{H_2}{\rightarrow} \frac{1}{2} O_2 \quad \Delta F_1 \]
\[ H \overset{H_2}{\rightarrow} \frac{1}{2} H_2 \quad \Delta F_2 \]
\[ \text{OH} \overset{3}{\rightarrow} \frac{1}{2} (H_2 + O_2) \quad \Delta F_3 \]

\[ \frac{P_0}{\sqrt{P_{OH}}} = \exp \left( -\frac{\Delta F_1}{RT} \right) \]
\[ \frac{P_H}{\sqrt{P_{H_2}}} = \exp \left( -\frac{\Delta F_2}{RT} \right) \]
\[ \frac{P_{OH}}{\sqrt{P_{OH}} \sqrt{P_{H_2}}} = \exp \left( -\frac{\Delta F_3}{RT} \right) \]

From the above formulas,
\[ P_H = \frac{1}{3} (2P - P_{OH}) \quad (8) \]
\[ P_0 = \frac{1}{3} (P - 2P_{OH}) \quad (9) \]
\[ P_{OH} = \frac{1}{4} [(5 + 9K)^2 - \sqrt{(5 + 9K)^2 + 16P}] \quad [\text{Atm}] \quad (10) \]

According to the literature,\(^7\)

<table>
<thead>
<tr>
<th>T</th>
<th>K</th>
</tr>
</thead>
<tbody>
<tr>
<td>3000 K</td>
<td>2.115×10⁻³</td>
</tr>
<tr>
<td>4000 K</td>
<td>1.389</td>
</tr>
<tr>
<td>5000 K</td>
<td>2.180×10</td>
</tr>
</tbody>
</table>

Using these values,

At 3000 K \( P_{OH} = 6.875 \times 10^{-4} \)
\( P_H = 9.58 \times 10^{-4} \)
\( P_0 = 1.35 \times 10^{-4} \)

At 4000 K \( P_{OH} = 2.035 \times 10^{-4} \)
\( P_H = 1.12 \times 10^{-3} \)
\( P_0 = 4.58 \times 10^{-4} \)

At 5000 K \( P_{OH} = 1.77 \times 10^{-5} \)
\( P_H = 1.18 \times 10^{-3} \)
\( P_0 = 5.82 \times 10^{-3} \)

On the other hand,
then,
\[
\log \left( \frac{I_i}{A_i} \right) = -\frac{5040}{T} E + C \quad (11)
\]

If the excitation potential of the OH band is 4.2 eV, with considering the above partial pressures of the OH band, the intensity of the OH band changes as follows,
\[
\frac{I_{3000K}}{I_{4000K}} = 1.532 \\
\frac{I_{3000K}}{I_{5000K}} = 13.75 \\
\frac{I_{4000K}}{I_{5000K}} = 13.79
\]

According to these results, the intensity of the OH band becomes suddenly weak, when the temperature rises from 4000 K to 5000 K. These results of the calculation coincide with that of the radial distribution measurements of the OH band in the plasma jet light source.

8. Conclusions

1. In the graph, in which the values of \( \log I - \log A_g \) are plotted, the plots of the every spectral lines have its own special drifts. And so, it is necessary to draw the inclined straight line by a definite way. This is true in the both cases of the excitation and the OH band rotation temperature.
   2. Generally, the excitation temperatures of the Ar-N\(_2\) plasma jet are 500° ~ 950° higher than that of the Ar plasma jet.
   3. The degrees of the rises of the excitation temperatures by the removal of water vapor using a desolvation instrument are the same in the both cases of the Ar-N\(_2\) and the Ar plasma jet.
   4. The degrees of the rises in the excitation temperatures by the addition of KCl to the sample solution are higher in the case of the Ar-N\(_2\) plasma jet than those in the case of the Ar plasma jet.
   5. No change in the OH band rotation temperature was observed for the different observed points with the heights from the discharge cathode hole, for the different discharge gases of Ar-N\(_2\) and Ar, and for the addition of KCl to the sample solution opposed to that in the cases of the excitation temperatures.

6. The radial intensity distribution of an iron spectral line which was used to measure the excitation temperature was flat in the center area of the discharged plasma. On the other hand, that of the OH band was distributed ringlike in the outer side of the discharge.

7. The radial excitation temperature has a same distribution as the lateral one. But in the case of the OH band rotation temperature, the temperature measurement was possible only in the outer side of the discharge.

From the above results (6) and (7), it is concluded that the discussion of an establishment of the thermal equilibrium from the measurements of the excitation and the OH band rotation temperatures is impossible.

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