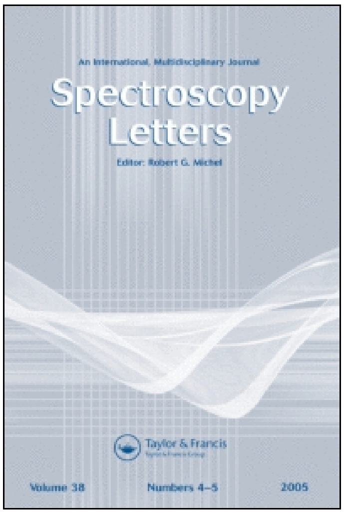

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Simplified Method for the Rotational Temperature Determination of Carbon Monoxide from Absorption Spectra Measured at High Resolution

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SIMPLIFIED METHOD FOR THE ROTATIONAL TEMPERATURE DETERMINATION OF CARBON MONOXIDE FROM ABSORPTION SPECTRA MEASURED AT HIGH RESOLUTION①

Key Words: Infrared; FTIR; Molecular Absorption Spectra; Temperature Measurements; Hot Gas

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Abstract

A fast and convenient method for determining the temperature of hot gas from their Fourier transform infrared absorption spectra was given on the bases of band fitting method. According to the half-width of spectral lines measured at different temperature, we studied the effect of the index of a particular line, m, on the half-width of spectral lines. Almost 27 rotation-vibration lines in the P- and/or R-branches of foundamental band of CO were used in this procedure. Quantitative evaluations of the gas temperature indicate that the temperature can be measured with an accuracy better than 2.7%. In addition, this formular is applied to other spectra reported in literature. Temperatures calculated by our method also have good results.

I. INTRODUCTION

The theory and technique for determining the hot gas temperature from their vibrational-rotational absorption of foundamental band have been well documented[1-4]. Generally, through the measurements of the frequency, the intensity and the half-width of spectra lines, quantification of temperature can then be obtained. But the incomplete knowledge of half-width of the absorption lines can complicate

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this procedure. Measurements on the half-width of spectral lines of carbon monoxide had been made by Hoover and Williams[5], Tubbs and Williams[6], Varanasi and Sarangi[7], and Nakazawa and Tanaka[8]. However, the differences among the results are considerable. And equations which describe the half-width of absorption lines have also been developed. Simple laws were deduced from Anderson—Taso—Curnutte theory[9-11]. Other quasi- or semi- theory[12-14] used to calculate the half-width of spectral lines exists also. But either from experimental measurements or from theoretical consideration, it seems that the half-width of spectral lines can't be easily obtained accurately and directly, especially at high temperature or/and at low spectra resolution.

Here, we will study the effect of temperature on half-width of spectral lines of carbon monoxide. For the use of CO as the experimental gas, there are four reasons. First, it has the lowest boiling point of all infrared active gases. Second, it can be produced in whatever flame. Third, it can describe the combustion efficiency of flame. Fourth, it itself is a kind of gas pollution which do harm to human's health. So we will discuss its spectra to present a fast and convenient method for determining gas temperature on the bases of band fitting method. In our experiment, the fine structure in the foundamental band of CO is scaned by high resolution (0.125 cm^{-1}) Fourier Transform Infrared Spectrometer. Almost more than 27 rotation-Vibration lines in the P- and/or R- branches of foundamental band of CO were scaned, respectively. Temperatures calculated by our method have good results and agree well with those calculated from other methods[2,15]. By the way, although this method is deduced from the values of CO, it should be applied to other hot gas, such as those in the flame combustion.

Ⅱ. THEORY

The intensity I_{ab} of absorption spectra lines may be given by

$$I_{ab} = B_{lu}U_{\Delta\nu}h\nu n_l - B_{ul}U_{\Delta\nu}h\nu n_u \qquad (1)$$

where B_{lu} is the Einstein transition probability of stimulated absorption, B_{ul} is the Einstein transition probability of stimulated emission, $U_{\Delta\nu}$ is radiation emittance; $U_{\Delta\nu}=I_o \cdot t$, n_l is the number of molecules in the lower energy state, n_u is the number of molecules in the upper energy state, h is Plank's constant, ν is the frequency of the lines.

Because the distribution of population among the rotational energy levels follows the Maxwell-Boltzman law

$$n_u = n_M \frac{g_u}{Z} e^{-E_u/(k\cdot T)} \qquad (2)$$

$$n_l = n_M \frac{g_l}{Z} e^{-E_l/(k\cdot T)} \qquad (3)$$

where n_M is the total number of molecules in the initial vibration state, E_u and E_l are the rotational energy of the upper and lower states respectively, g_u and g_l are the statistical weights of energies E_u and E_l respectively, Z is the rotational partition function, k is the Boltzmann constant and T is the absolute temperature.

Then substituting Eq. (2) and Eq. (3) into Eq. (1), we obtain for the intensity of an absorption line

$$I_{ab} = B_{lu} h\nu \frac{I_o \cdot L}{c} n_l \left(1 - \frac{g_l n_u}{g_u n_l}\right) \tag{4}$$

where I_o is the intensity of the incident radiation, L is the length of radiation, c is the velocity of light in vacuum.

Since $\frac{g_l n_u}{g_u n_l} << 1$, we have

$$I_{ab} = B_{lu} h\nu \frac{I_o \cdot L}{c} n_l \tag{5}$$

Besides that, we should consider another important factor which has the rather large influence on line intensities for many molecules especially in determining temperature from line intensity distribution. That is the vibration-rotation interaction in the vibration-rotation bands of diatomic molecules. This F factor for the various transition had be given by Herman and Wallis[16]

$$F(m) = 1 + C_1 m + C_2 m^2 \tag{6}$$

where constants C_1 and C_2 may be obtained from matrix element[17], m is the index of a particular line of R- and/or P- branches of foundamental band of CO, which equals $J+1$ and $-J$ for the R- and P- branches respectively, J is the rotational quantum number.

Thus from Eqs. (5) and (6), the line intensity can be represented by

$$I_{ab} = F(m) B_{lu} h\nu \frac{I_o \cdot L}{c} n_l \tag{7}$$

Taking logarithms, we obtain the relation between I_{ab} and $E(m)$

$$ln(I_{ab}(m)/(F(m)\nu(m)|m|)) \; a - E(m)/(k \cdot T) \tag{8}$$

Generally, a Lorentzian line shape is assumed for the absorption of infrared radiation. The line intensity is then given by

$$I_{ab}(m) = 7.234 \cdot A_{peak} \cdot \gamma(m) \tag{9}$$

where $\gamma(m)$ is the half-width at half-height of the spectral lines. Through measurements of A_{peak} and $\gamma(m)$ gas temperature can be estimated.

But in our experiment with temperature range from 290 to 462K there is something little differences towards the half-width at half-height. Although $\gamma(m)$ still has the tendency to decrease with the increase of $|m|$, this effect is very small. Actually it is more likely to become constant in these measurements (we will prove it later). If this assertion is an adequate one, Eq. (8) then become

$$ln(A_{peak}(m)/(F(m)\nu(m)|m|)) \; a - E(m)/(k \cdot T) \tag{10}$$

Therefore a plot of $ln(A_{peak}(m)/(F(m)\nu(m)|m|))$ against $E(m)$ should produce a straight line of slope $-1/(k \cdot T)$, from which the temperature could be calculated.

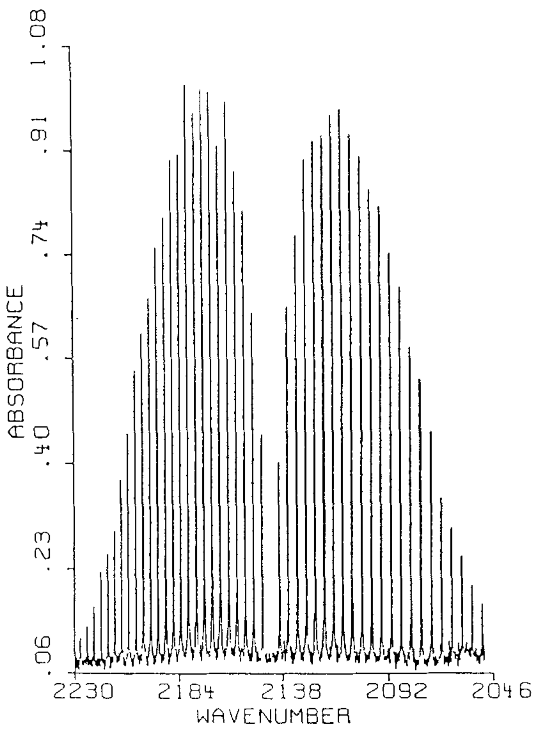

Fig. 1 CO absorption spectrum at 290K

Ⅲ. EXPERIMENTAL

The infrared spectra were recorded on a Nicolet 170RX Remote Source FT-IR Spectrometer. This instrumental configuration had been previously described in detail[18]. In order to get a high signal-to-noise ratio, all spectra are 512 scans signal-averaged. For these studies, the gas cell which can be heated by ring electronic heater was designed. It was made of pyrex glass with KBr windows. Absorption spectra of gaseous CO samples were collected in a 10 cm long, and 3.3 cm diameter gas cell with the mercury thermometer. But it should be mentioned here, in order to avoid temperature gradients along the optical pathlength, long periods of time should be spent to get the cell in thermal equilibrium. So that no significant changes in temperature could happen.

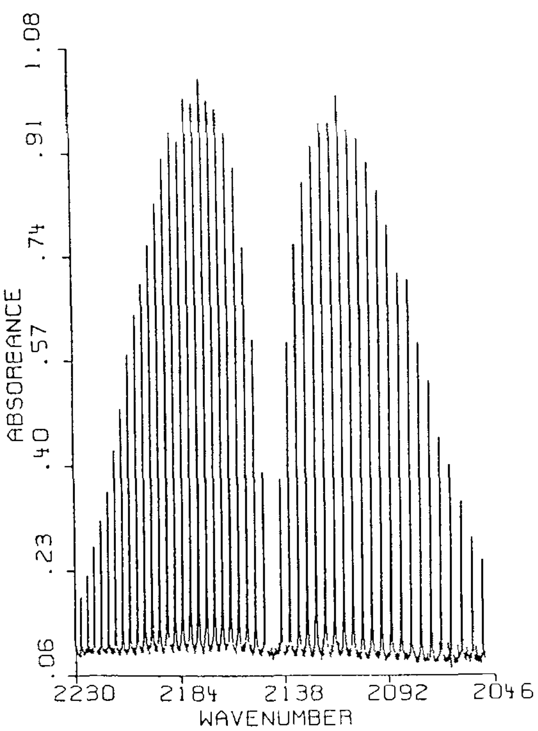

Fig. 2 CO absorption spectrum at 359K

The carbon monoxied used in this experiment was taken from cylinder, whose purity is 99.9%. The CO pressure introduced into the cell at room temperature was 25 mmHg.

IV. RESULTS AND DISCUSSION

1. High-resolution CO absorption spectra

Absorption spectra of CO measured at 0.125 cm^{-1} spectral resolution are shown in Figs. 1—4 at temperature 290, 359, 429 and 462K, respectively. It can be seen that the spectra had an excellent signal-to-noise ratio and the peaks for all spectral lines are very well resolved. But with increasing temperature the signal-to-noise ratio reduced and certain undesired absorption lines for temperature calculations ap-

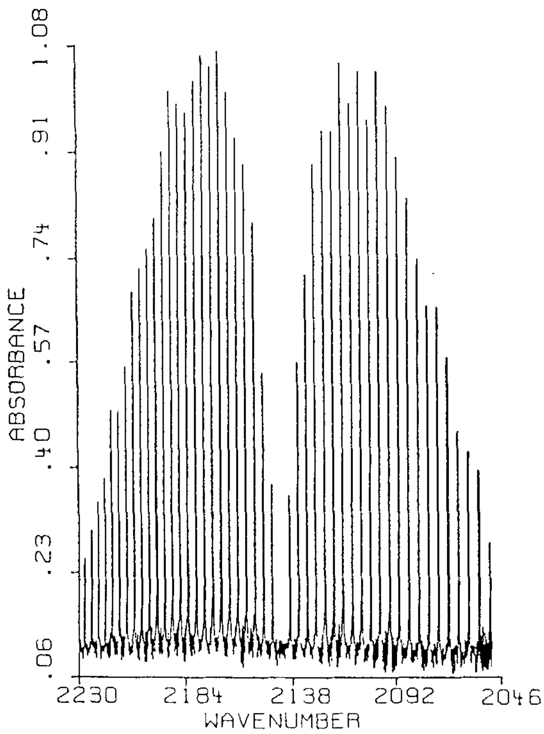

Fig. 3 CO absorption spectrum at 429K

pear. Part of the reasons lies in the second-order transition. Certainly, these lines must be excluded so as to yield correct calculated temperature. It should also be mentioned here, with the purpose of getting high quality spectra, the backgrouds should be removed from each sample spectra.

2. Variation of half-width of spectral lines at a certain temperature

Generally, the halfwidth of spectral lines $\gamma(m)$ at a certain temperature, T, can be calculated from known values $\gamma^{\circ}(m)$ at standard temperature ,T_0, and pressure , P_0

$$\gamma(m) = \gamma^{\circ}(\frac{P}{P_0})(\frac{T_0}{T})^N \tag{11}$$

where N is the temperature exponent.

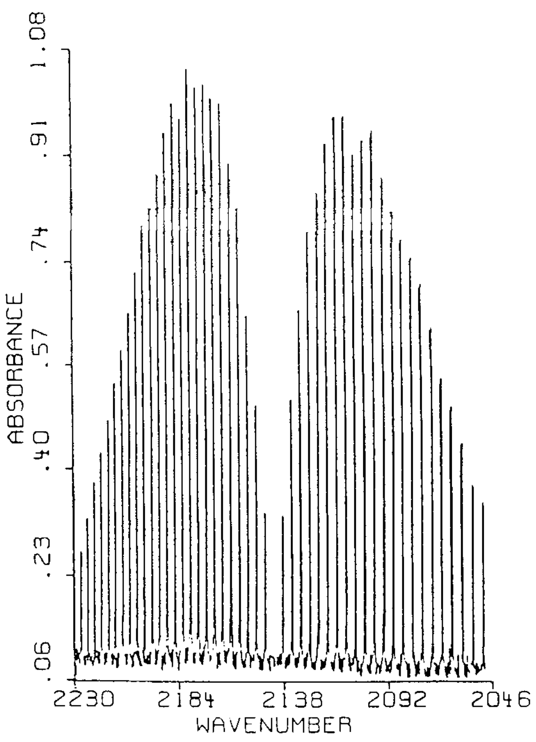

Fig. 4 CO absorption spectrum at 462K

γ^{0} can often derive from the measured linewidth at 300K, which Nakazawa and Varghese[8] had reported their measured values. Then the needed values $\gamma(m)$ at other temperatures can be obtained. And works on the measurements of half-width of spectral lines at lower temperatures was also been done by Nakazawa and Tanaka[8]. But they didn't give out the values of half-width of spectral lines at temperatures no more than 300K. In our experiment, a series of half-width of spectra lines for temperature 290, 359, 429 and 462K were measured and studied. The typical plots of $\gamma(m)$ for P- and/or R- branches of 1—0 band of CO against m are shown in Figs. 5—8, respectively. It seems that the variation of half-width of spectral lines with line index m is not obvious and more likely to become horizontal. Therefore in the practical calculations, we consider $\gamma(m)$ remains constant.

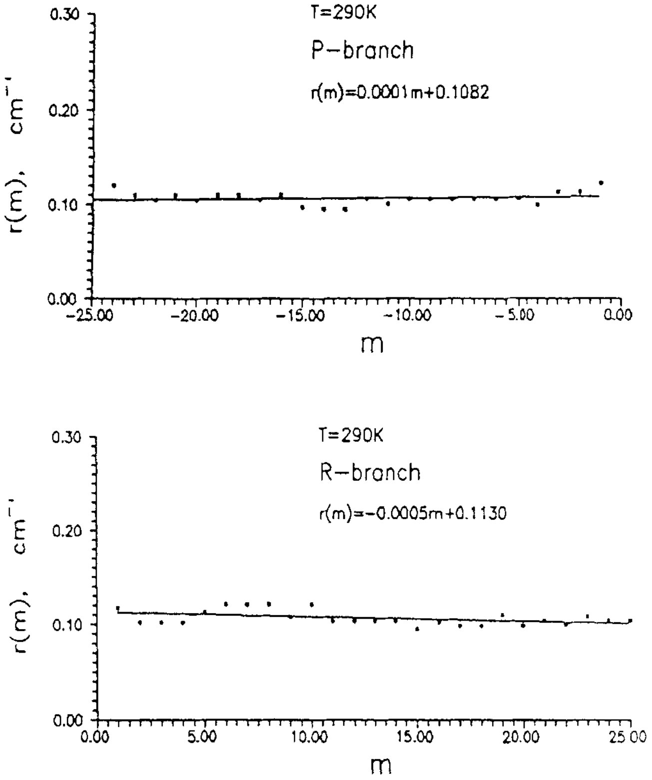

Fig. 5 The observed half-width of spectral lines ,$\gamma(m)$, in the foundamental band plotted versus the index of spctral lines ,m, at 290K

3. Temperature Calculatoins

For calculating temperature, almost 27 lines in the spectra region 2147 to 2221 cm^{-1}(R- branch $m=27$) and/or 2139 to 2059 cm^{-1}(P- branch $m=27$) of fine structure of foundamental band of CO were used in linear least-squares regression technique. But attention should be payed because this linear behavior can be got only after correction for photometric errors and line broadening. So it is necessary to establish a criterior for line acceptability before the temperature calculations. The calculating temperatures from Eq. (10) are listed in Table 1.

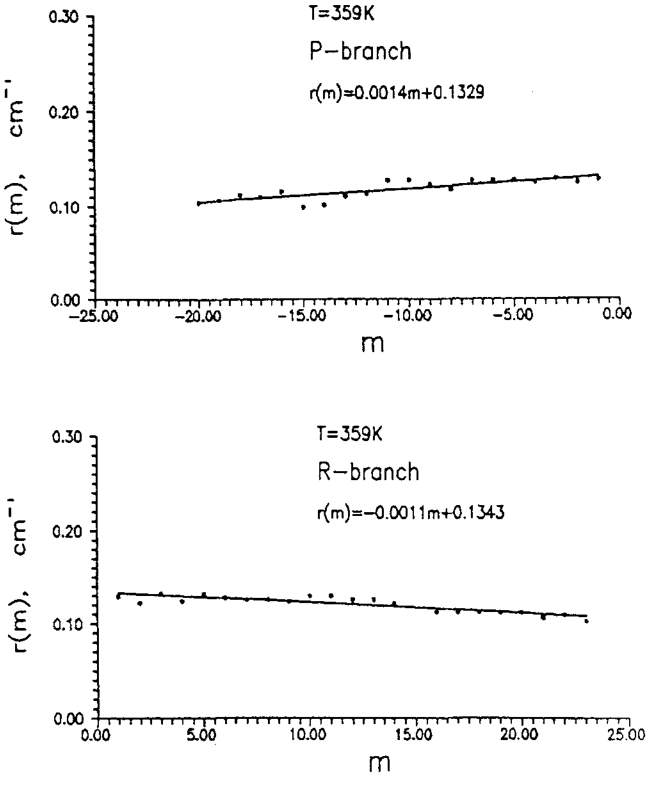

Fig. 6 The observed half-width of spectral lines ,$\gamma(m)$, in the foundamental band plotted versus the index of spctral lines ,m, at 359K

Good agreements between $T_{act.}$ and $T_{cal.}$ are observed both from R- and P-branches. The temperature calculations had an accuracy of 2.7% or better. As compared to other methods accuracies[3,20], this value is sufficient enough. A possible reason of it may be the use of very high resolution instrument, which makes the smallest spetral distortion.

4. Comparision with other methods

In order to examine the validity of present theory, other methods[2,15] of temperature determination from the infrared absorption line intensity in the fine struc-

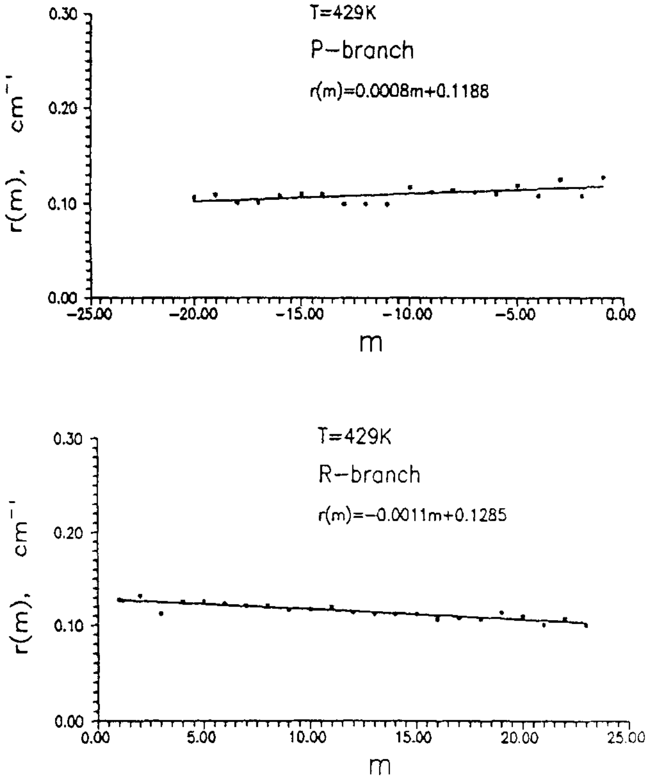

Fig. 7 The observed half-width of spectral lines ,$\gamma(m)$, in the foundamental band plotted versus the index of spctral lines ,m, at 429K

ture of rotation-vibration band of molecules were performed. Because at the ambient temperature line width data can obtained very accurately, comparisions were made under this condition. The results are listed in Table 2.

Clearly, among the three methods, since Anderson and Griffiths considered the effect of temperature on line width, it has the best values with the accuracy of 0.03%. But temperatures calculated from this work also have good results. Although it didn't reach that accuracy as the others, its accuracy is sufficient enough for practical applications.

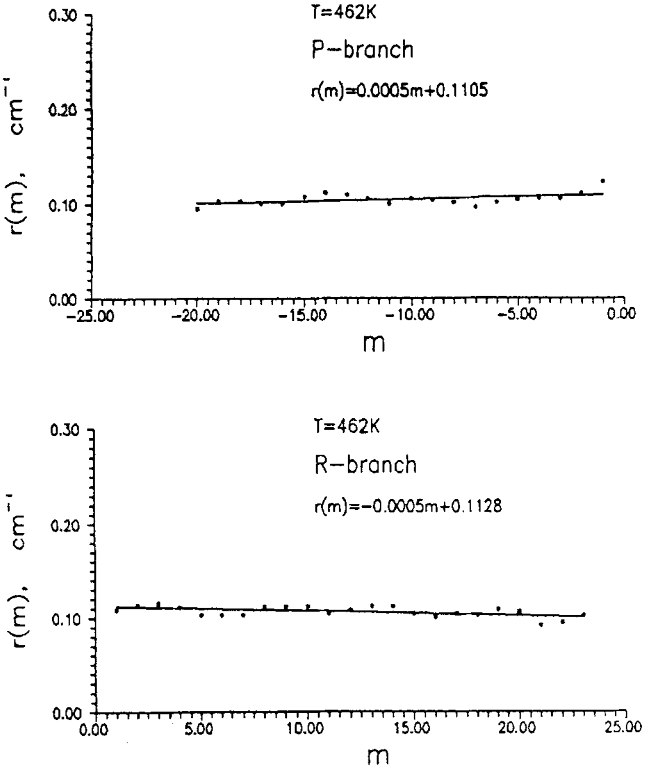

Fig. 8 The observed half-width of spectral lines ,$\gamma(m)$, in the foundamental band plotted versus the index of spctral lines ,m, at 462K

Table 1. Comparison of calculated and actual CO temperatures for the temperature-controlled gas cell used in these experiments over the range 290 to 462K

$T_{act.}$ (K)	R—branch		P—branch	
	$T_{cal.}$ (K)	error (K)	$T_{cal.}$ (K)	error (K)
462	465	−3	464	−2
429	432	−3	432	−3
377	388	−11	381	−4
359	364	−5	362	−3

$T_{act.}$ is the temperature measured by a mercury thermometer
$T_{cal.}$ is the calculating temperature
error is $T_{act.} - T_{cal.}$

Table 2. Comparisons of temperature

	$T_{act.}$ (K)	T_R (K)	T_P (K)	$\overline{T}$ (K)	$T_{act.} - \overline{T}$ (K)	$T_R - T_P$ (K)	Precision (%)
This work	290. 2	290. 2	290. 7	290. 5	−0. 3	−0. 5	0. 10%
Anderson(2)	290. 2	290. 2	289. 9	290. 1	0. 1	0. 3	0. 03%
Junde Wang(6)	290. 2	290. 5	290. 4	290. 5	−0. 3	0. 1	0. 10%

where $T_{act.}$ is the temperature measured by a mercury thermometer

T_R is the calculating temperature of R-branch

T_P is the calculating temperature of P-branck

$\overline{T}$ is the average calculating temperature

Precision is the persentage of difference

Table 3. Compare results obtained by this method with other methods

Furnace set point (K)	773	1073	1273
Temperatures reported by Medvecz[3] (K)	746	1048	1251
This work (K)	744	1050	1277

Towards the higher temperatures, the validity of the present theory can also be verified. In this procedure we used the spectra given by Medvecz et al[3]. In order to reduce the errors, each figure was enlarged previously. Then the values needed for every rotational lines in Eq. (10) can be obtained. In our calculations, 30 lines of P-branch of CO vibrational-rotational absorption spectra in reference[3] were used, respectively. A comparison of data by using this method is shown is Table 3.

It's evident that present theory is as good as Medvecz.[3]

V. CONCLUSIONS

Calculations of rotational temperature of CO have an accuracy better than 2. 7% according to the use of Eq. (10). Since the aim of this paper is to present a concise, easily measuring and calculating method, Eq. (10) alleviates the need for empirical half-width of spectral lines measurements, when comparing with other methods mentioned above. Thus it allows for simply measured procedures and easy calculations of gas temperature. Therefore, this theory of temperature calculations is valuable.

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