The impacts of temperature on the absorption spectral lines of carbon monoxide

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Abstract. In order to study the change of temperature on the effects of carbon monoxide absorption spectral lines, first of all proceed from the principle of absorption spectra, using theoretical analysis method, and the transmission and absorption database of the high-resolution molecular educed the carbon monoxide absorption spectrum intensity of spectral lines, integrated widening line type function and absorption coefficient concerned with temperature, then we got the change curve between carbon monoxide absorption spectrum intensity of spectral lines, integrated widening line type function and absorption coefficient with temperature by the numerical simulation of MATLAB, and analyzed and discussed the relationship between the temperature and them. The results showed that the temperature on the effects of carbon monoxide absorption spectral lines, especially on an Integrated widening line type function is complex, and different laser frequencies will also affect the relationship of the line type function and the absorption coefficient change with temperature, which has important reference value for the absorption and measurement of carbon in practical application.

1. Introduction

At macro level, a temperature is one of factors, which affect the absorption coefficient of CO gas. However, the specific laws of the absorption coefficient of CO gas with temperature are seldom seen. In particular, the regular reports of the absorption spectra and comprehensive widening spectrum line type function with the impact of temperature are lacking. It is important to measure CO concentration in combustion furnace smelting with standard atmospheric [1]. In this paper, from the theory of absorption spectroscopy, by the use of the HITRAN molecular spectroscopy database, it is analyzed that the intensity of absorption spectrum line and widening line type function of spectrum line change with temperature, to obtain the dependent relation between absorption coefficient of spectrum line and temperature.

2. Theoretical basis

2.1. Absorption lines intensity
The absorption line intensity $S(T)$ indicates the absorption intensity of a certain frequency (cm$^2$ • (mol • cm$^{-2}$)$^{-1}$), it is a temperature-related function, and it is also affected by the type of molecular isotopes. The intensity of CO absorption line $S(T)$ can be queried by use of the high-resolution transmission molecular absorption database (HITRAN), or by the analysis software to calculate. But in practice,
order to get the intensity of the absorption line at any temperature, the formula (1) will be used to calculate the intensity [1, 2]:

\[
S(T) = S(T_0) \frac{Q(T)}{Q(T_0)} \exp\left(-\frac{h \nu_0}{kT}\right) \frac{1 - \exp\left(-\frac{h \nu_0}{kT_0}\right)}{1 - \exp\left(-\frac{h \nu_0}{kT_0}\right)}
\]

Where, \( T_0 \) is the reference temperature (K), \( S(T_0) \) is the intensity of the absorption spectrum gotten by the HITRAN database with the temperature \( T_0 \), \( Q \) is the total molecular partition function, \( E \) is lower energy transition state (cm\(^{-1}\)), \( h \) is Planck's constant, \( k \) is the Boltzmann constant, \( c \) is the speed of light. In this formula, the third item is the Boltzmann distribution, the fourth item is the excitation radiation. The total molecular partition function \( Q \) is relative to the molecular isotopic species. The molecule value of different isotopic partition function is different, its value can be query form the HITRAN molecular spectroscopy software, but in the HITRAN molecular database [3], the data provided with the temperature is not continuous, it is shown in table 1.

**Table 1.** The total internal partition function look-up table for \(^{12}\)C\(^{16}\)O.

| Temperature T/K | 296    | 297    | 298    | 299    | 300    | 301    |
|-----------------|--------|--------|--------|--------|--------|--------|
| Q(T)            | 107.1169 | 107.4785 | 107.8400 | 108.2016 | 108.5632 | 108.9249 |

Table 1 shows the total molecular partition function values of the isotope \(^{12}\)C\(^{16}\)O with the temperature range of 296K to 301K, it is seen by the table that the temperature can not query in decimal. So, the second subdivision interpolation method will be taken to calculate \( Q(T) \) as following:

\[
Q(T) = Q(T_i) \left(\frac{T - T_i}{T_i - T_1}\right) + Q(T_2) \left(\frac{T - T_1}{T_2 - T_1}\right) + Q(T_3) \left(\frac{T - T_2}{T_3 - T_2}\right)
\]

In the formula (2), the temperature \( T_i \) is between the temperature \( T_1 \) and \( T_2 \), \( T_1 < T_2 < T_3 \), \( Q(T_i) \) is the partition function of the temperature \( T_1 \), \( Q(T_2) \) is the molecular partition function of the temperature \( T_2 \), \( Q(T_3) \) is the molecular partition function of the temperature \( T_3 \).

### 2.2. Comprehensive widen line type function

In general, CO gas is always appears in spectrum line broadening. When the gas is in pressure and temperature simultaneously, its spectrum line will is widened with homogeneous broadening and Doppler non-uniform broadening caused by collisions. Then the widening line type function is no longer a simple line type function, such as simple Lorenz or Gauss line type function [4, 5], but it is decided by both of them, that is Voigt line type function [6, 7], expressing as:

\[
f_v (\nu, \nu_0) = \int_{-\infty}^{\infty} f_G (\nu_0, \nu_0) f_L (\nu, \nu_0) d\nu_0
\]

In the formula (3), \( \nu_0 \) is atomic center frequency (cm\(^{-1}\)), \( \nu_0 \) is the center frequency of non-uniform broadening, \( f_G (\nu_0, \nu_0) \) is the line type function of Doppler broadening, \( f_L (\nu, \nu_0) \) is the line type function of collision broadening, their expressions are such as equation (4) and (5):
\[
f_G(v, v_0) = \frac{2}{\Delta v_G} \sqrt{\frac{\ln 2}{\pi}} \exp \left[-4\ln 2 \left(\frac{v - v_0}{\Delta v_G}\right)^2\right] 
\]

(4)

\[
\Delta v_G = 7.16 \times 10^{-7} \frac{T}{M} v_0
\]

(5)

\[
f_L(v, v_0) = \frac{\left(\frac{\Delta v_L}{2}\right)^2}{(v - v_0)^2 + \left(\frac{\Delta v_L}{2}\right)^2} \]

(6)

\[
\Delta v_L = 2\gamma_{air} \left(\frac{290}{T}\right)^n P
\]

(7)

In the equation (4) and (6), \(v\) is the frequency of the laser (cm\(^{-1}\)), \(M\) is the molar mass of CO molecules g.mol\(^{-1}\), \(\gamma_{air}\) is the air-broadening coefficients, \(n\) is the collision broadening index, \(P\) is the pressure of the CO.

In the equation (3), when \(\Delta v_L << \Delta v_G\), the homogeneous broadening caused by the collision is much smaller than the non-uniform broadening caused by the Doppler effect, the above-mentioned integral of equation (3) has the non-zero value near \(\nu \nu\) in only a small range. In this context, the function \(\tilde{f}_G(\nu_0, \nu_0)\) can be replaced with a constant \(\tilde{f}_G(\nu, \nu_0)\), therefore:

\[
\tilde{f}_V(v_0, \nu) = \tilde{f}_G(v_0, \nu_0) \int_{-\infty}^{\infty} f_L(v_{\nu_0}) dv = f_G(v, \nu_0)
\]

(8)

That is, the Voigt line type function is approximately equal to Gauss line type function when \(\Delta v_L << \Delta v_G\).

As the same, when \(\Delta v_L << \nu\), the non-uniform broadening caused by the Doppler effect is much smaller than the collision-induced homogeneous broadening, the spectral function is expressed as:

\[
\tilde{f}_V(v, \nu_0) = \tilde{f}_L(v, \nu_0)
\]

(9)

That is, the Voigt line type function is approximately equal to Lorenz line type function. From equations (7) and (9), it is known that the Lorenz line type function and the Gauss line type function are only the two extreme forms of the Voigt line type function. They are consistent with the physical models. For Voigt line type function, it can be solved numerically by look-up table or by polynomial to match the curve [8].

2.3. Absorption coefficient

The mathematical expression of the absorption coefficient is [9, 10]:

\[
a(v) = S(T) \tilde{f}_v(v_0, \nu_0)
\]

(10)

In the formula (10), \(S(T)\) is the intensity of molecular absorption spectrum lines, \(\tilde{f}_v(v_0, \nu_0)\) is the integrated broadening line type function of the absorption spectrum lines (cm\(^{-1}\)), the frequency \(v\) is \textit{the} frequency of the laser output (cm\(^{-1}\)). The absorption coefficient here is also named as the monochromatic absorption coefficient (cm\(^{-1}\).mol\(^{-1}\)) and it represents the absorption ability of the point of the frequency \(v\). After obtaining the absorption coefficient, the concentration of CO can be calculated by using differential absorption methods and so on.

3. Simulation analysis
In order to study the absorption coefficient changed with temperature, in the measurement gas chamber, an atmospheric pressure is set and the parameter values of the expression are shown in the table 2. Here is the wave number instead of the frequency. CO has been found that it has six isotopic molecules. In them, $^{12}\text{C}^{16}\text{O}$ is for 98.654 percent, so it is a main element.

Table 2. The value of each parameter for CO.

| Parameter      | Meaning                                      | Value       | Units           |
|----------------|----------------------------------------------|-------------|-----------------|
| $S(T_o)$       | Line intensity at $T_o=296\text{K}$          | 2.179e-23   | cm$\cdot$mol$^{-1}$ |
| $Q(T_o)$       | Total internal partition at $T_o=296\text{K}$ | 107.116880  | /               |
| $\gamma_{av}$  | Air-broadened half width at $296\text{K}$    | 0.0599      | cm$^{-1}$·atm$^{-1}$ |
| $n$            | Collision broadening index                    | 0.5         | /               |
| $E_l$          | Lower state energy                            | 107.6424    | cm$^{-1}$       |
| $T_g$          | Reference temperature (Room temperature)     | 296         | K               |
| $v_o$          | Wave number (absorption peak)                | 6369        | cm$^{-1}$       |
| $M$            | Molar Mass of CO                              | 28          | g·mol$^{-1}$    |
| $C$            | The speed of light                            | 2.99792458e+8 | m·s$^{-1}$     |
| $h$            | Planck constant                               | 6.626176e-34 | J·S            |
| $K$            | Boltzmann constant                            | 1.380662e-23 | J·K$^{-1}$     |

3.1 The impacts of temperature to the intensity of absorption spectrum line

According to equation (1) and the reference temperature $T_o=296\text{K}$, the intensity of the spectrum line can be calculated under temperature $T$. Figure 1 shows the relative intensity of spectrum line at the different temperature:

![Figure 1](image)

**Figure 1.** The relationship between the intensity of absorption spectrum line and temperature $T$ at transition wave number 6369 cm$^{-1}$.

In figure 1, as the temperature is increased, the relative intensity of spectrum line is gradually reduced, due to $S(296)$ is a constant, so the corresponding intensity of absorption spectrum line $S(T)$ is gradually reduced.

3.2. The impacts of temperature on the integrated widening line type function

Selecting spectrum line 6369(cm$^{-1}$) as the center of CO absorption lines (absorption peak), it is corresponding to the 1.57um wavelength located to the optical fiber transmission window. When the
pressure in CO chamber is 1 atmospheric pressure, the comprehensive widening line type function is shown as figure 2.

![Figure 2](image2.png)

**Figure 2.** The relationship between comprehensive widening line type function and wave number at different temperature.

In Figure 2, using wave number as horizontal axis, the center absorption spectrum line is also 6369 (cm\(^{-1}\)), it can be seen that as the temperature increases, the peak value of widening line type function will increase. As the wave number off center position is far, the relative intensity of the absorption spectrum line will gradually decrease. The relative intensity value with high temperature will faster decrease than low temperature. With different temperature, the maximum value of relative intensity is located to the center position of the CO absorption spectrum line.

![Figure 3](image3.png)

**Figure 3.** The relationship between widening line type function and temperature at absorption peak of 6369cm\(^{-1}\).

Figure 3 reflects the relative intensity of peak nearby of the comprehensive widening line type function changes with the different temperature. As the temperature increases, the change trends of the comprehensive widening line type function have two directions. When the temperature is increasing from low temperature, the relative intensity value of the comprehensive widening line type function will increases, then when the temperature reaches high temperature, it finally increases to a saturation value. But to the wave number 6369(cm\(^{-1}\)) and 6369.07(cm\(^{-1}\)), at first, it increases with temperature, then, it reaches to saturation and decreases. Moreover to wave number 6369.035(cm\(^{-1}\)), at first, it increases with temperature, then, it reaches to saturation and begins decreasing and as temperature is gradually increases, it begins gradually increases. The relative intensity value of the comprehensive widening line type function is the greatest when the wave number is located to the central peak wave 6369 cm\(^{-1}\) peak.

3.3. The impacts of temperature on absorption coefficient

After obtaining the relative intensity of absorption lines and the relationship in which the comprehensive widening line type function changes with the temperature, the absorption coefficient
\( \alpha (\nu) \) can be described by equation (8). Figure 4 shows the relative absorption coefficient \( \frac{\alpha (\nu)}{\alpha (\nu_0)} \) changes with temperature. This \( \alpha (\nu) \) is the absorption coefficient of the peak \( \nu_0 = 6369.000 \text{cm}^{-1} \) when the temperature is 296K. From the analysis in the previous, the relationship of the comprehensive widening line type function with temperature is not same at different wave number, so selecting the central absorption peak of the CO absorption line to 6369 cm\(^{-1}\), the relation curves of absorption coefficient with temperature is shown as figure 4.

![Figure 4](image)

**Figure 4.** The relationship between the absorption coefficient and temperature at different laser wave number.

From Figure 4, as the temperature is increased, the absorption coefficient will decrease. And the absorption coefficient at low temperature is larger than high temperature. Meanwhile, the wave number is closer to the absorption peak, absorption coefficient is larger. In practice, it is best to make the laser frequency align the central peak frequency of absorption spectrum line to obtain a better measurement effect. And from the relationship of the absorption coefficient with the temperature, the intensity of absorption line has much more effect on the absorption coefficient than the comprehensive widening line type function.

### 4. Conclusion

The variation character of CO absorption spectral line with temperature can be analyzed by using the theory of absorption spectrum. The intensity of absorption lines and comprehensive widening line type function are the main the factors to determine spectral absorption coefficient, and the intensity of absorption lines makes a greater contribution to the spectral absorption coefficient than the comprehensive widening line type function. The change of temperature will give rise to the changes of the intensity of absorption spectrum line and comprehensive widening line type function, and then they will lead to change of absorption coefficient. In lower temperature and laser frequency closed to the central peak position of the absorption spectrum line, the absorption coefficient is the largest. It is good to measure absorption character of CO gas and its concentration.

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