Estimation of Line Width by Self-Absorption Measurement using Fourier Transform Infrared Spectrometry

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Synopsis

A simple method of estimating the width of a narrow spectral line with a low-resolution optical system has been proposed. The method consists of the measurement of an emission spectrum of a gaseous sample, and measurement of the amount of its attenuation caused by placing an absorption gas cell filled with the same chemical species as that emitted. If the line width of either emitting or absorption gas is known, the line width of the other can be obtained by calculation. Two sets of experiments were conducted on carbon monoxide (CO); (1) measurement of pressure broadening in the line widths of the absorption lines of CO by the use of narrow CO emission lines, (2) measurement of the line widths in the emission lines of CO by the use of a set of absorption lines of CO, whose widths are known. As a result, the translational temperature of the emission system was determined.

1. Introduction

At present most common infrared spectrometers have a resolution of about 0.3 cm⁻¹, and with such spectrometers the spectral line shape can be determined only when the line is as broad as 1 cm⁻¹. As far as the line width is concerned, however, this can be estimated by the use of a low-resolution optical instrument in the following manner: One first observes an apparent emission spectrum of a gaseous sample, A. Then an absorption cell which contains A is placed in the optical path, and the apparent percent transmission, t, is observed for each spectral line. Suppose that the line profiles of both emission and absorption lines are known. If, in addition, the true width of the emission line is known, then the
true width of the absorption line of A can be obtained from \( t \). If, on the other hand, the true width of the absorption line is known, the true width of the emission line of A can be derived from \( t \). We have found that this method has a practical significance, and hence some details will be given below with a few examples.

1.1 Case I. An examination of pressure broadening

We postulate here a case (case I) where the emission line of A is very narrow (0.002 cm\(^{-1}\), for example) and the absorption line is broad (0.1-0.01 cm\(^{-1}\), for example). Let us assume that the profile of the absorption line is given in the Lorentz function,

\[
L(\nu) = \frac{b_e}{2\pi[(\nu^2 + (b_e/2)^2)]} \tag{1}
\]

where \( \nu \) gives the abscissa scale (in cm\(^{-1}\)) measured from the line center (\( \nu = 0 \)), and \( b_e \) is the spectral line width (in cm\(^{-1}\)). In this case, the apparent percent transmission \( t \) at \( \nu = 0 \) should be equal to the true percent transmission \( T(\nu = 0) \), so that

\[
\log_{10} t = \log_{10} T(\nu = 0) = a \cdot L(\nu = 0) \cdot \frac{pl}{2.303} \tag{2}
\]

where \( a \) is the integrated absorption coefficient of the absorption line now in question, and \( a \cdot L(\nu = 0) \) is the absorption coefficient at \( \nu = 0 \). In equation (2), \( p \) is the partial pressure (in atm) of A, and \( l \) is the optical path length (cm) of the absorption cell. From equation (2),

\[
b_e = \frac{2apl}{2.303 \cdot (-\log_{10} t)} \tag{3}
\]

Thus, by examining \( t \) at a given total pressure \( P \), the width \( b_e \) of the absorption line can be determined. The \( b_e \) value should be a function of \( P \). The value of \( a \) for each absorption line can be obtained by allotting a share of the total integrated absorption coefficient, \( a_{\text{total}} \), to each line in proportion to the Boltzmann factor of the lower level times the weight \((J' + J'' + 1)\) of the transition.\(^{13}\)

1.2 Case II An examination of the Doppler width and translational temperature

We next postulate a case (case II) where both the emission and absorption lines of A are as narrow as 0.01 cm\(^{-1}\) in the order of magnitude. Let us assume that the profiles of the emission and absorption lines are both as given in the Gaussian functions,

\[
G_e(\nu) = \frac{2}{b_e \sqrt{\pi}} \exp \left[ -\frac{(2\nu)^2}{b_e^2} \right] \tag{5}
\]

and

\[
G(\nu) = \frac{2}{b_p \sqrt{\pi}} \exp \left[ -\frac{(2\nu)^2}{b_p^2} \right] \tag{6}
\]

respectively. In this case the apparent transmittance \( t \) is given

\[
t = \int_{-\infty}^{\infty} G_e(\nu) \cdot T(\nu) d\nu \tag{7}
\]

where

\[
T(\nu) = \exp \left[ -a p l G(\nu) \right] \tag{8}
\]

is the true transmittance and is expanded as

\[
T(\nu) = 1 - \kappa G(\nu) + \frac{1}{2!} (\kappa G(\nu))^2 + \cdots \tag{9}
\]

In this expression \( \kappa \) means

\[
\kappa = ap l \tag{10}
\]

where \( a \) is the integrated absorption coefficients of the absorption line, \( p \) is the partial pressure of the absorption gas, and \( l \) is the optical path length of the absorption cell. Combining Equations (7), (8), (9), and (10) leads to the result

\[
t = t_0 + t_1 + t_2 + \cdots + t_n + \cdots \tag{11}
\]

in which

\[
t_0 = 1, \tag{11a}
\]

\[
t_1 = -\kappa \int_{-\infty}^{\infty} G_e(\nu) \cdot G(\nu) d\nu = \frac{-2\kappa}{\sqrt{\pi} \sqrt{b_e^2 + b_p^2}} \tag{11b}
\]

\[
t_n = \frac{(-1)^n \cdot 2^n \cdot k^n}{n!b_e^{n-1}(\sqrt{\pi})^n \sqrt{n!b_e^2 + b_p^2}} \tag{11c}
\]
If \(a, p, l\) and \(b_D\) of the absorbing gas sample are all known, the \(b_{De}\) value of the emitting gas can be obtained by Equation (11) the observed value of \(t\). This would be valuable, because from \(b_{De}\) one can calculate the translational temperature \(T_e\) of the emitting gas by the relation,

\[
b_{De} = \frac{2\nu}{c} \left[ \frac{2kT_e}{m} \right]^{1/2}
\]

where \(k\) is the Boltzmann constant, \(m\) the mass of the molecule, \(c\) the light velocity, and \(\nu\) the wavenumber at the center of the emission lines now in question (no \((\ln 2)^{1/2}\) factor is needed here; \(b_{De}\) is the full width at \(1/e\) height but not half width at half height which is discussed by Townes and Schawlow\(^2\), for example).

2. Experimental and Method

2.1 Emission and absorption system

Fig. 1 shows our experimental apparatus for the self-absorption method. \(N_2\) gas was produced through a microwave discharge cavity operated at 2405 MHz, and was into a global reaction vessel (i.d., 15 cm, coated with gold) into which \(CO\) was simultaneously introduced through a nozzle. The infrared emission from the light source is applied to excited vibrational carbon monooxide infrared emission. Thus, an infrared emission of \(CO\) gas was caused by an energy transfer from vibrationally excited \(N_2\) (denoted as \(N_2^*\)) to \(CO\).

The emission was observed through a KBr window with a Digilab FTS-14 Fourier Transform Infrared Spectrometer (FTIR). A cylinder absorption-cell 10 cm long with windows was placed in the optical path. Sample pressure was measured with a Pirani gauge (Daia Vac. Co. Ltd.) and a mercury manometer.

2.2 Treatment of Data

In Fig. 2, the method of obtaining transmittance \(t\) of each line of \(CO\) is illustrated. Suppose that we are going to estimate the width \(b_e\) of each absorption line in the fundamental \(v=1\rightleftharpoons 0\) band of \(CO\) placed in \(N_2\) gas of 10 torr (i.e., \(P_{N_2}=10\) torr). The total pressure of the gas in the emission cell was kept as low as 0.5 torr or so, so that the pressure broadening of the emitting \(CO\) is negligibly small in comparison with that of absorbing \(CO\). In the absorption cell, 0.06 torr of \(CO\) and 10 torr of \(N_2\) are filled at 300 K. Thus, a \(CO\) emission spectrum attenuated by the self-absorption is now recorded as shown in Fig. 2(a). When the absorption cell is evacuated, the total emission (without attenuation) is recorded as shown in Fig. 2(d). In these spectra, not only the emission lines of the \(v=1\rightleftharpoons 0\) band but also the emission lines of the hot band \((v=2\rightleftharpoons 1)\) are apparently recognized. Although the hot band lines are disturbing, they are removed in the following way. The absorption cell was filled with 11.5 torr of \(CO\). The filled gas should absorb all the emission lines of the fundamental \((v=1\rightleftharpoons 0)\) band almost completely, but it dose not absorb the lines of the hot \((v=2\rightleftharpoons 1)\) band at all. The result of such a selective absorption is shown in Fig. 2(b); this is practically a pure \(v=2\rightleftharpoons 1\) component involved in the original emission spectrum. This is subtracted from the spectrum (a) and from the spectrum (d) by the use of the on-line computer. The results are shown in Fig. 2(c) and (e), respectively. These spectra ((c) and (e)) involve only the emission lines of the fundamental band \((v=1\rightleftharpoons 0)\). The transmittance \(t\) of each line is given by the peak-intensity ratio \((c)/(e)\) of each line. Actual work of obtaining the \(t\) values was made on plotter outputs with much greater abscissa.
Self-Absorption Measurement using FTIR

Fig. 2. Infrared emission spectra of CO gas. Each curve shown here is a reproduction of the plotter out-put of a Digilab FTS-14 Infrared Spectrometer, with an emission system and an absorption cell, that are shown in Fig. 1. (a) Emission system: 0.035 torr CO+0.34 torr N₂, absorption cell: 0.06 torr CO+10 torr N₂, at 300 K. (b) Emission cell: 0.035 torr CO+0.34 torr N₂, absorption cell: 11.5 torr CO, at 300 K. (c) Spectrum calculated with the on-line computer: (a)×0.954−(b). (d) Emission cell: 0.035 torr CO+0.34 torr N₂, absorption cell: vacuum. (e) Spectrum calculated with the on-line computer: (d)×0.875−(b). Each of the curves (a), (b), and (d) were recorded under the following conditions: number of scans=500, resolution=1 (This means that the maximum path difference examined in the interferograms is 1.036 cm).

Fig. 3. The width $b_c$ of the absorption line of CO (partial pressure 0.05 torr) at 300 K plotted against the line number $m$.

Left: $N_2$ is added as a foreign gas up to the pressure, $P_{N_2}$.
Right: Ar is added as a foreign gas up to the pressure $P_{Ar}$. $m$ is defined as follows: $m=f''$ for P branch lines (△), and $m=f''+1$ for R branch lines (○), where $f''$ is the rotational quantum number of the lower level in each transition.
scale than the scale used in Fig. 2. The line width $b_c$ of each line can now be obtained by Equation (3) from the $t$ value of each line. Here it was assumed that $a_{\text{total}}=238.9 \text{ cm}^{-2} \text{ atm}^{-1}$; this is an average of six values given by the previous investigators $^3$-$^8$.

3. Results and Discussions

3.1 An example of case I (The pressure broadening of CO)

The $b_c$ values thus determined of the CO absorption lines are shown in Fig. 3 and 4. The $b_c$ has been found to be a linear function of the total pressure $P$ in the absorption cell. In addition, the pressure broadening caused by a given pressure of $N_2$ has been found to be appreciably greater than that caused by the sample pressure of Ar. The $b_c$ value of the CO line has also been found to depend upon the $J$ values (rotational quantum numbers) of the initial and final states of each transition. As shown in Fig. 5, the $b_c$ values found in our present study are in agreement with what were given by previous investigators $^9$-$^{11}$. This fact may indicate the validity of our proposed method.

3.2 An example of case II (Translational temperature of a CO sample)

The absorption cell was filled by 0.045 torr CO and kept at 300 K. Here, each absorption line was assumed to have a Doppler width for 300 K, i.e., $b_D=0.00604 \text{ cm}^{-1}$. The partial pressure of CO in the emission cell was kept at 0.035 torr and that of $N_2$ at 0.35 torr. We attempted to estimate the $b_{De}$ of the emission line and the translational temperature $T_e$ of CO in the emission cell. We have observed, on the one hand, the transmittance $t$ of each line of CO, and on the other hand calculated $t$ for various $\kappa$ and for various $T_e$. The results are compared in Fig. 6. As may be judged from the figure, the translational temperature $T_e$ of CO in the emission cell is $380 \pm 40$ K. The Doppler width $b_{De}$ of these lines is estimated to be $0.0068 \pm 0.0004 \text{ cm}^{-1}$ (see Fig. 7).

In a transient state, the translational temperature $T_e$ of a system is not necessarily equal to the rotational temperature $T_r$. The rotational temperature $T_r$ of CO in the same emission cell can be determined precisely from the intensity distribution of the rotational lines. As may be judged from the intensity versus $J(J+1)$ plot (Fig. 8), $T_r=373$ K. Thus, in our present examination, no difference between $T_e$ and $T_r$ has happened to be detected.

A sample result showing the effect of re-
Fig. 6. Calculated transmittance $t$ plotted against $\kappa$ (given by Equation (11)) for a system in which the absorption cell contains 0.035 torr of CO and 0.35 torr of N$_2$ at various $T_e$ (=100-1700 K). (O, △), actually observed $t$ values, where O for the R branch and △ for the P branch lines.

Fig. 7. The width $b_{De}$ of the emission line of CO produced by a system of 0.035 torr of CO and 0.35 torr of N$_2$ plotted against the line number $m$. The translational temperature $T_e$ calculated by Eq. (12) is also given here. $m$ is defined as follows: $m$ = $J''$ for P branch lines and $m$ = $J''$+1 for R branch lines, where $J''$ is the rotational quantum number of the lower level of each transition.

Fig. 8. Peak intensity, divided by $J' + J'' + 1$, of the emission line in the fundamental band $v = 1 \rightarrow 0$ of CO plotted against $J'(J' + 1)$ for a system obtained by N$_2$+CO$\rightarrow$N$_2$+CO$^*$. Partial pressure of CO is 0.035 torr and that of N$_2$ 0.35 torr. $J'$ and $J''$ are the rotational quantum numbers respectively of the upper and lower levels of each transition.

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References