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Pressure Effect of the Nondispersive Infrared Gas Analyser

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Based on the Elsasser model, a formula for the mean absorption applicable to the pressure effect of the nondispersive infrared gas analyser has been derived. The formula is generalized by removing the assumption in the Elsasser model that the total absorption coefficient, the half width and the spectral distance are constant.

In previous papers,[1,2)] a formula was given for the mean absorption corresponding to the screening percent for the infrared ray due to the null balance shutter of the analyser as a function of the partial pressure of absorber p_a, the total pressure P and the cell length l. Many similar formulas, often empirical, have been reported,[3-6)] but it is difficult to determine the coefficients in the formulas either experimentally or theoretically. There are two theories concerning the derivation of the formulas: total absorption by Ladenburg and Reiche,[7)] and mean absorption by Elsasser.[8)] The Lorentz type absorption coefficient is assumed in both theories. However the method for approximate evaluation of the following integral,

$$\int\{1-\exp(-k(\nu)l)\}\mathrm{d}\nu$$

viz. total absorption, is different.

The Elsasser theory is based on the three assumptions that the following are constant: i) the total absorption coefficient α_m, ii) the half width of the line δ_m and the spectral distance of the vibrational rotational line d_m. When assumption i) was removed, it was possible to obtain a good quantitative comparison between the theory and experiment.[2)] In this paper, the formula is generalized by removing the remaining assumptions.

Apparatus

The apparatus and the principle of measurement have been reported.[2)]

Theoretical

Half Width of Absorption Lines. According to the classical kinetic theory of gases, the collision width of the line is given by[2)]

$$\delta=\frac{1}{4\pi}\sum_i N_i(D_{a,i})^2\left[[2\pi kT\left(\frac{1}{m_a}+\frac{1}{m_i}\right)\right]^{1/2} \tag{1}$$

where N_i is the number density of a molecule of the gas of ith type, $D_{a,i}$ the sum of the optical collision diameters of the absorbing molecule and the molecule of the ith type, m_a the mass of the absorbing molecule and m_i the mass of the ith type of molecule. For binary mixtures, Eq. 1 becomes

$$\delta=\frac{1}{4\pi}(2\pi kT)^{1/2}\left[N_a(D_{a,a})^2\left(\frac{2}{m_a}\right)^{1/2}\right.$$
$$\left.+N_b(D_{a,b})^2\left(\frac{m_a+m_b}{m_a m_b}\right)^{1/2}\right]. \tag{2}$$

It is not necessarily correct that the half width is common to all the lines according to Eqs. 1 and 2. It was found that each line differs slightly in half width.[9)] From quantum mechanics[10)] the half width of the line is not constant since the colliding molecules exert different interaction due to the intermolecular force on each vibrational rotational energy level of the absorbing molecule.

Taking the above situation into consideration, it is better to express Eq. 2 as follows.

$$\delta_m=\frac{1}{4\pi}(2\pi kT)^{1/2}\left[N_a(D_{a,a})^2_m\left(\frac{2}{m_a}\right)^{1/2}\right.$$
$$\left.+N_b(D_{a,b})^2_m\left(\frac{m_a+m_b}{m_a m_b}\right)^{1/2}\right]. \tag{3}$$

where the subscript m is the number of the line. $(D_{a,a})_m$ and $(D_{a,b})_m$ should be determined quantum mechanically. The first term of Eq. 3 explains the effect the collisions between absorbing molecules exert on the half width of the mth line, and the second the effect the collisions between the foreign and absorbing molecules exert on the mth line. Expressing N_i in term of partial pressure, Eq. 3 becomes

$$\delta_m=\frac{1}{4\pi}\left(\frac{2\pi}{kT}\right)^{1/2}[(C_{a,a})_m P_a+(C_{a,b})_m P_b]$$
$$=\frac{1}{4\pi}\left(\frac{2\pi}{kT}\right)^{1/2}(C_{a,a})_m\left[P_a+\frac{(C_{a,b})_m}{(C_{a,a})_m}P_b\right] \tag{4}$$

where

$$(C_{a,a})_m=(D_{a,a})^2_m(2/m_a)^{1/2}$$

and

$$(C_{a,b})_m=(D_{a,b})^2_m(m_a+m_b/m_a m_b)^{1/2} \tag{5}$$

Here the notation δ_{0m} is defined by

$$\delta_{0m}=\frac{1}{4\pi}\left(\frac{2\pi}{kT}\right)^{1/2}(C_{a,a})_m. \tag{6}$$

δ_{0m} is the constant independent of pressure if the temperature is constant. Though it is not necessarily obvious that the ratio of $(D_{a,a})_m$ to $(D_{a,b})_m$ is constant, its ratio is assumed to be constant according to the method in the previous papers.[1,2)] Then the following relation can be assumed

$$\frac{(C_{a,a})_m}{(C_{a,b})_m}=\left(\frac{2m_b}{m_a+m_b}\right)^{1/2}\left\{\frac{(D_{a,a})_m}{(D_{a,b})_m}\right\}^2$$
$$=B(=const)$$

where B is the so-called self-broadening coefficient. As a result, the half width of the line can be expressed by

$$\delta_m=\delta_{0m}P_e \tag{7}$$

where P_e is the effective pressure defined by

$$P_e=p_a+(1/B)p_b. \tag{8}$$

The difference in the half width of each line is taken consideration by Eq. 7. Namely δ_m should be understood for δ of Eq. 2 to be extended. The theoretical expressions obtained in the previous papers,[1,2] however, must not be altered, except that $\delta_0\left(=\frac{1}{4\pi}\left(\frac{2\pi}{kT}\right)^{1/2}(C_{a,a})\right)$ in the definition of k_{0m} is simply replaced by δ_{0m} of Eq. 6.

Total Absorption Coefficient of the Line, α_m. The total absorption coefficient of the mth line is determined by means of the integral of the absorption coefficient which is ordinarily approximated by the following Lorentz type function in the infrared region.

$$k_m(\nu) = \frac{4\pi N_a}{3\hbar C}\nu_m|\mu_m|^2\frac{\delta_m}{(\nu-\nu_m)^2+\delta_m^2} \tag{9}$$

where μ_m is the matrix element of the dipole moment. The total absorption coefficient is, therefore,

$$\alpha_m = \int_0^\infty k_m(\nu)\mathrm{d}\nu = \int_0^\infty \frac{4\pi N_a}{3\hbar C}\nu_m|\mu_m|^2\frac{\delta_m}{(\nu-\nu_m)^2+\delta_m^2}\mathrm{d}\nu \tag{10}$$

It is evident that α_{0m} is proportional to the number density of absorber N_a. N_a is rewritten by the partial pressure p_a and we have

$$\alpha_m = \alpha_{0m}P_a. \tag{11}$$

α_{0m} is directly related to the Einstein transition probability except for the numerical constant.

By substituting $N_a=p_a/kT$ into Eq. 10, α_{0m} is expressed by the molecular constants as follows.

$$\alpha_{0m} = \frac{4\pi^2\nu_m|\mu_m|^2}{3\hbar ckT} \tag{12}$$

It was assumed that $\alpha_m=const$ in the Elsasser model. However, α_m is not constant in this paper.

Extension of the Definition of k_{0m} *and the Approximate Expression for the Parameter* t *Determinable from the True Slit Function.* If we denote the product of α_{0m} and δ_{0m} by l_{0m}

$$\alpha_{0m}\delta_{0m} \equiv l_{0m}, \tag{13}$$

it is determined from Eqs. 6 and 12 with use of the molecular constants as follows.

$$l_{0m} = \frac{1}{4\pi}\left(\frac{2\pi}{kT}\right)^{1/2}(D_{a,a})_m^2(2/m_a)^{1/2}\frac{4\pi^2\nu_m|\mu_m|^2}{3\hbar ckT} \tag{14}$$

On the other hand, t is approximately connected with the maximum extinction E_m as follows.[2]

$$E_m = t(\alpha_m\delta_m l)^{1/2}/a \tag{15}$$

where a is the slit width in cm^{-1} and l the cell length. For the simple component of the absorbing gas, Eq. 15 becomes

$$E_m = t(\alpha_{0m}\delta_{0m}l)^{1/2}P_a/a. \tag{16}$$

From Eqs. 13 and 16, we have

$$t = \frac{aE_m}{(l_{0m}l)^{1/2}P_a} \tag{17}$$

Here the quantity k_{0m} should be defined by

$$k_{0m} = E_m^2/\{4(d_m/a)^2P_a^2l\} \tag{18}$$

which can be evaluated from the maximum intensity of the absorption spectrum corresponding to the conditions of measurement. d_m is the spectral distance of the mth line. k_{0m} was defined with use of the mean spectral distance instead of d_m.[1,2] From Eqs. 17 and 18, the parameter t can be determined by the following approximate relation.

$$t = 2d_m\sqrt{\frac{k_{0m}}{l_{0m}}}. \tag{19}$$

Theoretical Extension of the Mean Absorption to the Molecules with Two Absorption Regions. The mean absorption of the molecules with a single absorption region should be extended to the molecules with weak bands such as the combination or the overtone band other than the fundamental one. In this case, the intensity of the infrared source I_ν and the mean spectral distance differ between both band regions. The expression for the mean absorption to be evaluated is as follows.

$$x = \frac{\sum_{m=1}^{n}\int_{u'}^{v'}I_f\{1-\exp(-k_m(\nu)l)\}\mathrm{d}\nu+\sum_{m'=1}^{n'}\int_{u''}^{v''}I_c\{1-\exp(-k_{m'}(\nu)l)\}\mathrm{d}\nu}{I_fnd'+I_cn'd''} \tag{20}$$

x corresponds to the screening percent of the incident light due to the null balance shutter of the infrared gas analyser. v', u', v'' and u'' are $\nu_m+d'/2$, $\nu_m-d'/2$, $\nu_{m'}+d''/2$ and $\nu_{m'}-d''/2$. d' and d'' are the widths of rectangles in each region by which the shape of absorption lines of the condenser microphone detector is approximated. By putting $I_c/I_f=r$ (the ratio of the intensity of the infrared source in both regions) and $n=n'$, the following expression is obtained for the high pressure near atmospheric pressure.

$$x = \frac{\sum_{n=0}^{\infty}(-P_ew)^n/n!\cdot\{\langle(k_{0m}/D^2)^n\rangle_{av}+r'\langle(k_{0m'}/D'^2)^n\rangle_{av}\}}{1+r'} \tag{21}$$

where

$$1/D = (2/t)\cdot(d/d'),\quad 1/D' = (2/t)\cdot(d/d''),$$
$$r' = rd''/d' \quad\text{and}\quad w=p_al. \tag{22}$$

k_{0m} and $k_{0m'}$ are determined with use of the mean spectral distance d over both regions.

$$k_{0m} = E_m^2/\{4(d/a)^2p_al\}$$

and

$$k_{0m'} = E_{m'}^2/\{4(d/a)^2p_al\}.$$

$\langle\ \rangle_{av}$ denotes the normal average over m or m'.

When $d'=d''$, Eq. 20 is simplified as follows for the low pressure,

$$x = 2\left(\frac{\langle k_{0m}^{1/2}\rangle_{av}+r\langle k_{0m'}^{1/2}\rangle_{av}}{(1+r)D}\right)P_e^{1/2}w^{1/2} \tag{23}$$

and for the high pressure in the exponential form,

$$x = 1 - \exp\left[-(2\pi/D^2)\cdot\left(\frac{\langle k_{0m}\rangle_{av}+r\langle k_{0m'}\rangle_{av}}{1+r}\right)P_ew\right.$$
$$+\frac{(2\pi/D^2)^2}{2!}\left\{\left(\frac{\langle k_{0m}^2\rangle_{av}+r\langle k_{0m'}^2\rangle_{av}}{1+r}\right)\right.$$

$$
-\left(\frac{\langle k_{0m}\rangle_{\rm av}+r\langle k_{0m'}\rangle_{\rm av}}{1+r}\right)^{2}\Bigg\}(P_{\rm e}w)^{2}
-\frac{(2\pi/D^{2})^{3}}{3!}\Bigg\{\left(\frac{\langle k_{0m}^{3}\rangle_{\rm av}+r\langle k_{0m'}^{3}\rangle_{\rm av}}{1+r}\right)
-3\left(\frac{\langle k_{0m}^{2}\rangle_{\rm av}+r\langle k_{0m'}^{2}\rangle_{\rm av}}{1+r}\right)\cdot\left(\frac{\langle k_{0m}\rangle_{\rm av}+r\langle k_{0m'}\rangle_{\rm av}}{1+r}\right)
+2\left(\frac{\langle k_{0m}\rangle_{\rm av}+r\langle k_{0m'}\rangle_{\rm av}}{1+r}\right)^{3}\Bigg\}(P_{\rm e}w)^{3}+\cdots\cdots\Bigg]. \tag{24}
$$

Eqs. 23 and 24 explain the mean absorption of the molecules with two absorption regions, and are reduced to the expressions for the single absorption region if r approaches 0.

Extension to the Case in which the Assumption that the Spectral Distance is Constant is Removed. The present study is based on the Elsasser model. However the spectral distance is actually assumed to vary quadratically according to the number of the line m. Taking this situation into consideration, a more precise expression for the mean absorption is obtained as follows.[2)]

$$
y=\frac{\sum_{m=1}^{n}\int_{u}^{v}\{1-\exp(-k_m(\nu)l)\}{\rm d}\nu}{\sum_{m} d_m} \tag{25}
$$

where v is $\nu_m+d_m/2$, and u is $\nu_m-d_m/2$. With use of the extended mean fractional transmission

$$
T_m=\frac{1}{d_m}\int_{u}^{v}\exp\left\{-\frac{(\alpha_m/\pi)\delta_m}{(\nu-\nu_m)^2+\delta_m^2}l\right\}{\rm d}\nu, \tag{26}
$$

y is given by

$$
y=1-\frac{\sum_{m} T_m d_m}{\sum_{m} d_m} = 1-\langle T_m\rangle \tag{27}
$$

where $\langle T_m\rangle$ should be interpreted as $\sum T_m d_m/\sum d_m$. For the region of low pressure, T_m is

$$
T_m = 1-2(\alpha_m\delta_m l)^{1/2}/d_m \tag{28}
$$

and then

$$
y=2\cdot\frac{\sum(\alpha_m\delta_m l)^{1/2}}{\sum d_m} = 2\cdot\frac{\sum(\alpha_m\delta_m l/d^2)^{1/2}}{n}. \tag{29}
$$

Thus y is reduced to the normal average. On the other hand, we have for the region of high pressure

$$
y=1-\frac{\sum\exp(-2\pi\alpha_m\delta_m l/d_m^2)\cdot d_m}{\sum d_m} = \frac{\sum\{(2\pi\alpha_m\delta_m l/d_m^2)-(2\pi\alpha_m\delta_m l/d_m^2)^2/2+\cdots\}}{\sum d_m} \tag{30}
$$

Thus the value of y can be obtained when the following expressions are calculated

$\sum(\alpha_m\delta_m/d_m^2)/\sum d_m$, $\sum(\alpha_m\delta_m/d_m^2)^2 d_m/\sum d_m$, *etc.*

For the sake of convenience, g_{0m} is defined by

$$
g_{0m}\equiv\frac{\alpha_{0m}\delta_{0m}}{\delta_m^2} \tag{31}
$$

g_{0m} is a constant characteristic of each line. g_{0m} is connected with k_{0m} of Eq. 18 by the relation

$$
g_{0m}=(2/t)^2 k_{0m}.
$$

With use of g_{0m}, Eq. 30 becomes

$$
y=1-\exp\Bigg\{-2\pi\langle g_{0m}\rangle P_{\rm e}w + \frac{(2\pi)^2}{2!}(\langle g_{0m}^2\rangle-\langle g_{0m}\rangle^2)(P_{\rm e}w)^2 - \frac{(2\pi)^3}{3!}(\langle g_{0m}^3\rangle-3\langle g_{0m}^2\rangle\langle g_{0m}\rangle+2\langle g_{0m}\rangle^3)(P_{\rm e}\omega)^3+\cdots\Bigg\} \tag{33}
$$

where

$$
\langle g_{0m}^n\rangle=\frac{\sum g_{0m}^n d_m}{\sum d_m}. \tag{34}
$$

Eq. 33 was obtained without the three assumptions in the Elsasser model.

Application to the Infrared Gas Analyser. The above method can immediately be applied to the infrared gas analyser. The shape of the spectral lines of the condenser microphone detector is approximated by the rectangular lines with unit height and the width $d_m{}'$, which is not necessarily constant. The following expression corresponds to the absorption intensity of the sample gas in the nondispersive infrared gas analyser, and is of the same form as that of mean absorption.

$$
x=\frac{\int_0^\infty I_\nu\{1-\exp(-\sum_{m=1}^{n}k_m(\nu)l)\}\{1-\exp(-\sum_{m=1}^{n}k'_m(\nu)l')\}{\rm d}\nu}{\int_0^\infty I_\nu\{1-\exp(-\sum_{m=1}^{n}k_m{}'(\nu)l')\}{\rm d}\nu}. \tag{35}
$$

According to the above approximation, x is reduced to Eq. 25 if d_m is regarded as $d_m{}'$. x becomes

$$
x=2\langle g_{0m}'^{\,1/2}\rangle P_{\rm e}{}^{1/2}w^{1/2} \tag{36}
$$

for low pressure, and

$$
x=1-\exp\{-2\pi\langle g'_{0m}\rangle P_{\rm e}w + \frac{(2\pi)^2}{2!}(\langle g_{0m}'^{\,2}\rangle-\langle g'_{0m}\rangle^2)(P_{\rm e}w)^2\} - \frac{(2\pi)^3}{3!}(\langle g_{0m}'^{\,3}\rangle-3\langle g_{0m}'^{\,2}\rangle\langle g'_{0m}\rangle+2\langle g'_{0m}\rangle^3)(P_{\rm e}w)^3+\cdots\Bigg\} \tag{37}
$$

for high pressure, where

$$
g'_{0m}=\frac{\alpha_{0m}\delta_{0m}}{d_m'^{\,2}} \quad\text{and}\quad \langle g_{0m}'^{\,n}\rangle=\frac{\sum g_{0m}'^{\,n}d'_m}{\sum d'_m}. \tag{38}
$$

Usually g'_{0m} can not be calculated if the value of d'_m is not known. However, g'_{0m} can be calculated if $d'_m/d_m=const.$ If we put $(d'_m/d_m)\cdot(t/2)=D$, x agrees with the results[2)] which are obtained when r approaches 0 in Eqs. 23 and 24.

When $d_m{}'/d_m$ is not constant, x can not be expressed with use of the correction factor D because of the following relation

$$
\langle g_{0m}'^{\,n}\rangle=\frac{\sum g_{0m}'^{\,n}d'_m}{\sum d'_m}=\frac{\sum g_{0m}^n(d_m/d'_m)^{2n}d'_m}{\sum d'_m} \neq\frac{D2^n\sum k_{0m}^n d'_m}{\sum d'_m}. \tag{39}
$$

It is possible to extend Eqs. 36 and 37 to the cases of molecules with more than two absorption regions if $\langle g'_{0m}{}^n\rangle$ is regarded as

$$\langle g_{0m}'^{\,n}\rangle = \frac{\sum g_{0m}'^{\,n} d_m' + r\sum g_{0m'}''^{\,n} d_{m'}'' + \cdots}{\sum d_m' + r\sum d_{m'}'' + \cdots} \tag{40}$$

where

$$g_{0m'}'' = \frac{\alpha_{0m'}\delta_{0m'}}{d_{0m'}''^{\,2}}. \tag{41}$$

Conclusion

It was found that the original expressions2) hold good even if the assumption that δ_0 is constant is removed. However k_{0m} $(=\alpha_{0m}\,\delta_0/d^2)$ should be regarded as $\alpha_{0m}\delta_{0m}/d^2$. The ambiguous parameter t2) was approximately determined in the explicit form with use of the molecular constants. It is concluded that the molecules with more than two absorption regions have the same pressure dependence as the molecules with a single absorption region. A more general formula was obtained for the mean absorption with use of the constant g_{0m} without the three assumptions in the Elsasser model. It can be concluded that in general x can not be expressed with use of a correction factor D.

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