Study of the Effect of Pressure Splitting on the Mean Absorption Intensity using an NDIR Gas Analyzer

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(Received: December 15, 2005; Accepted for publication: April 11, 2006; Published on Web: October 2, 2006)

In the infrared region, an expression for the mean absorption intensity has been obtained using the Elsasser model based only on the assumption of pressure broadening. Around atmospheric pressure, however, a better interpretation of the empirical results has been found by introducing a new effect of splitting due to the pressure of the degenerate vibrational-rotational levels.

Keywords: Mean absorption intensity, Two-body impact theory, Pressure splitting of degenerate vibrational-rotational levels, Effect of pressure splitting, Equivalent effective pressure, Elsasser model, Pressure broadening

1 Introduction

The formulas for the mean absorption intensity have been derived[1–3] from the Elsasser model by assuming that the absorption coefficient lines have a Lorentzian shape based on the pressure broadening theory for nondegenerate energy levels by Van Vleck and Weisskopf[4] who based it on the adiabatic approximation (in general, the Lorentz line shape can also be deduced from the method of Green functions through the Born approximation in the theory of collisions[5, 6]). However, the transition theory by P. W. Anderson[4, 7], among degenerate rotational levels based on the two-body impact theory and on the sudden approximation, has brought about variations in the half widths of the respective absorption coefficient lines; it causes them to be not common to all the lines. Afterwards, therefore, in accordance with this result of his, the derived formulas have been revised and generalized[2].

The pressure effect on the vibrational-rotational levels will, basically considered, consist of the following three effects:(1) shift, (2) broadening of widths, and (3) splitting of the degenerate levels. A simple shift of (1) obviously exerts no influence on the mean absorption. Moreover, the splitting phenomenon of (3) may not also appear at low pressures from the two-body impact theory especially in the microwave region, so that only from the standpoint of the pressure broadening of (2), were the investigations and mathematical calculations carried out. At pressures near atmospheric, however, a deviation between experiment and calculation was seen to occur; namely, the introduced correction factor $D$, which was considered a constant, happened to vary from low to high pressures (0.16 and 0.07 for CO gas, and 0.52 and 0.36 for CO$_2$ gas)[1].

There are now to be initially considered as the important factors which cause degenerate rotational levels that split the $l$-doubling[4] produced by a Coriolis interaction[8] between vibrations and rotation of a molecule, the $\Lambda$-doubling[4, 9] produced by an interaction between the electronic and rotational motions in a molecule, Stark effects[10], Zeeman effects and so on. The former two, however, do not depend on the gas pressure surrounding the molecule due to their dependence merely on the intramolecular interactions. The latter two, which are due to macroscopic electromagnetic fields, may not take place when using electrically neutral gases.

During the course of deriving at high pressures the approximate theoretical formula if the validity of the effect of pressure splitting of (3) is to be recognized which the pressure causes in degenerate vibrational-rotational levels and which, in general, may not occur in the microwave region but may occur in the infrared, the previously derived formula shall be revised again by introducing a novel notion of equivalent effective pressure for the effect of pressure splitting and thereby a better agreement.
with the experiments will be determined.
(It should also be noted that as an important pressure effect other than the above three, there is also that of asymmetry, which is, however, considered to be of little consequence at pressures around atmospheric, and therefore is not taken into consideration, only that due to the splitting effect itself.)

2 Theoretical

2.1 Splitting of Degenerate Vibrational-rotational Levels

The rotational energy level of a linear molecule of the symmetry of point group C


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omeg, such as CO or CO2, has the degree of degeneracy 2J+1 where \( J \) is the rotational quantum number. As a result of some proper external perturbations, the degeneracy may be partially or totally removed. In this study, its perturbation is due to the collisions of foreign molecules surrounding an absorbing molecule.

For a degenerate state, the first approximation \( E^{(1)} \) of an eigenvalue is obtained[9] by solving the following secular equation in \( E^{(1)} \)

\[
|V_{n'n'} - E^{(1)}\delta_{n'n'}| = 0
\]

where \( n \) and \( n' \) are the number of states belonging to the given unperturbed eigenvalues. \( V_{n'n'} \) corresponds to \( (n|P|n') \) in Anderson’s theory[4, 7] where \( P \) is not the total pressure but the quantity related to an integral of the external intermolecular perturbation with regard to time.

The selection rule for the parallel vibration \( v_3 \) of the CO2 molecule at 2350 cm\(^{-1}\) is now \( \Delta J = \pm 1 \) and \( \Delta M = 0 \) at which the absorption may take place, where \( M \) is the magnetic quantum number. In the microwave region, the effect of its perturbation on the splitting of each rotational line may be generally considered to be almost similar, that is to say,

\[
V_{n'n'}^{(1)} = V_{n'n'}^{(0)}, \quad E_M^{(1)} = E_M^{(0)}
\]

where \( V_{n'n'}^{(1)}, E_M^{(1)} \), and \( V_{n'n'}^{(0)} \) and \( E_M^{(0)} \) refer to the upper and lower states, respectively. As a result, no splitting phenomenon may apparently occur in the observed spectrum (in particular, at low pressures). The spectrum in this study, however, belongs to the infrared region and therefore corresponds to the transitions between the vibrational-rotational states in which the lower state is the ground state of the vibration and the upper in the excited, so that the perturbation effect may vary between the two states and so probably, in general, the relation will hold i.e.

\[
|V_{n'n'}^{(1)}| > |V_{n'n'}^{(0)}|, \quad |E_M^{(1)}| > |E_M^{(0)}|
\]

Accordingly, the splitting phenomenon will produce in a transition between two degenerate vibrational-rotational levels, therefore in a degenerate absorption line, the following width of deviation (or shift)

\[
\text{Max}(E^{(1)}_M - E^{(0)}_M) - \text{Min}(E^{(1)}_M - E^{(0)}_M).
\]

When more than two overlapping degenerate lines of Lorentzian shape slightly shift in a mutual fashion, in general, the entire outline is not Lorentzian, but will be asymmetric as if distorted. However, by assuming that it may approximately keep a symmetric Lorentzian form because of a slight shift, the entire profile of the split degenerate lines, with the absolute intensity constant, that is, the integrated value of the line profile of overlapping absorption coefficients being kept invariable, will be considered to lower the height of its own peak and broaden. In fact, this is nearly the same phenomenon as that of the foreign gas broadening in which the unchanged integrated absolute intensity increases owing to the broadening of its own width the integrated absorption intensity, or in other words the mean absorption intensity according to Lambert-Beer’s law.

This splitting phenomenon due to collisions may be a comparatively trivial one at low pressures even in the infrared region, but it will be worth noticing that it gives rise to a significant effect on the mean absorption intensity at high pressures around atmospheric, where simultaneously the asymmetric effect[11] also due to the statistical types of theories[4] might happen to lead to an increase in the half width, but in the case of low absorbing gas pressures such an effect on the width may be regarded as quite slight.

2.2 Increase in the Half Width using the Splitting Effect due to Collisions

As the detailed circumstances concerning the splitting due to collisions of the respective degenerate rotational levels are unknown, the perturbation may be assumed according to the two-body impact theory to be proportional to the number of molecules per unit volume, that is, to the total pressure \( P \). In the case of the absorbing gas pressure \( p_a \ll P \), which is naturally that of foreign gas broadening, the following relation will hold from Eq.(4)

\[
\text{Max}(E^{(1)}_M - E^{(0)}_M) - \text{Min}(E^{(1)}_M - E^{(0)}_M) = \sigma_m P
\]

where \( P \) is the total pressure of the gas, \( m \) is the running number of the absorbing lines in the spectrum and \( \sigma_m \) is the proportional constant.

On the other hand, the peak height \( h_m(v_0) \) of the product \( k_m(v_0) \) of the absorption coefficient \( k_m(v_0) \) and path length \( l \) is such that for \( p_a \ll P \), where \( P \) is around atmospheric pressure,

\[
h_m(v_0) = \frac{(\alpha_m/\pi \delta_m)l}{(\alpha_{0m}/\pi \delta_{0m}P_e)l} \quad (\text{for} \quad p_a \ll P)
\]

\[
= \frac{(B\alpha_{0m}/\pi \delta_{0m}P)l}{(\alpha_{0m}/\pi \delta_{0m}P)}
\]

\[
(6)
\]
where \( \delta_m = \delta_{0m}P_c \), \( P_c \) is the effective pressure, \( \alpha_m = \int k_m(\nu)\,d\nu\approx \alpha_{0m}P_a \) and \( B \) is the self-broadening coefficient. From Eq.(6) \( h_m(\nu_0) \) is found to be proportional to \( w \) at a constant value of \( P \). In this case, even if \( p_a \) varies within a narrow range of low pressures, the half width is found to be unchanged, i.e.

\[
\delta_m = \frac{\delta_{0m}P_c}{\delta_{0m}P_c + \delta_{0m}(p_a + p_b)/B} = \frac{\delta_{0m}(p_a - 1/B + P/B)}{\delta_{0m}P/B = \text{const}}
\]  
(7)

where \( p_a \) is the partial pressure of the foreign gas and

\[
1 - 1/B = \begin{align*}
0.02 & \quad \text{for CO} + \text{N}_2 \quad (B = 1.02) \\
0.23 & \quad \text{for CO}_2 + \text{N}_2 \quad (B = 1.30)
\end{align*}
\]

Secondly, it should be emphasized that the more flattened the absorption coefficient \( k_m(\nu) \) or \( k_m(\nu)/l \) is, the stronger the splitting effect appears and begins to significantly depend inversely on \( w \). Then it follows that

\[
\sigma_m = \sigma_{0m}(w)
\]  
(8)

Taking into consideration its effect, the half width \( \delta_m \) leads to

\[
\delta_m = \frac{\delta_{0m}P_c}{\delta_{0m}P_c + \sigma_{0m}(w)P} = \frac{\sigma_{0m}(w)P + \tau_m(w)P^2 + \nu_m(w)P^3 + \ldots}{\sigma_{0m}(w)P + \tau_m(w)P^2 + \nu_m(w)P^3 + \ldots}
\]  
(9)

where \( \delta_{0m}^0 \) is a pure half width due only to the pressure broadening and \( \sigma_{0m}(w)P \) is a supplementary half width related to the cross section for the foreign gas splitting, which is supposed to be given by

\[
S_m(w;P) = \sigma_{0m}(w)P + \tau_m(w)P^2 + \nu_m(w)P^3 + \ldots
\]  
(10)

where \( \sigma_{m}(w) \) is not exactly equal to \( \sigma_m(w) \), but \( \sigma_{m}(w) \leq \sigma_m(w) \). The half width of an absorption coefficient line profile accompanied by the splitting effect is more lowered in its determining position than that in the absence of the splitting effect since its peak position is lowered due to the splitting, and is increased more than the magnitude \( \sigma_{0m}P \) of the genuine splitting width so that the quadratic term of \( P \) and higher ones are added in Eq.(10), that is to say, the greater importance attached to that effect, the greater the \( P \) and the smaller the \( w \).

Because it is probably related to those higher terms of “prohibitive” difficulty in Anderson’s theory[7], the functional dependence of \( S_m(w;P) \) on \( w \) and \( P \) is too involved to be determined at present with accuracy, but it may be safely mentioned by analogy with the foreign gas broadening that, in general, the more flattened a spectral line is by making \( P \) large and \( w \) small, the larger the \( S_m(w;P) \) grows due to the splitting effect. On the contrary, the increasing of \( w \) under the constant value of total pressure in which \( \delta_{0m}^0P_c = \text{const} \) from Eq.(7) causes the peak height of the spectral line or \( k_m(\nu)/l \) to proportionally increase from Eq.(6), which leads the line to become sharper, because at the same time, it causes \( \sigma_{m}^0(w) \) or \( \tau_m(w) \) etc. therefore \( S_m(w;P) \) to rather rapidly decrease.

By the way the following approximation may hold

\[
\delta_{0m} = \delta_{0m}^0 + \sigma_{m}^0
\]  
(11)

where \( \sigma_{m}^0 \) is the value of \( \sigma_m \) for the pressure of \( P = p_a \) = 1 cmHg which is the slight width produced by the pure splitting effect and is supposed to be independent of \( l \) because of the sharpened line due to self-broadening at low pressure.

By using Eq.(11), Eq.(9) may be rewritten in the form

\[
\delta_m = \sum \left[ \frac{P_c + C(w;P)}{\delta_{0m}^0} \right] \]  
(12)

where \( s \) is the ratio of the width due to the pure pressure broadening to the total width of Eq.(11) and may be \( s \approx 1 \) since \( \sigma_{m}^0 \ll \delta_{0m} \). \( C(w;P) \) corresponds to an equivalent effective pressure (E.E.P.) which changes the magnitude of the splitting effect to a pressure value.

### 2.3 The Expression \( z \) for the Mean Absorption Intensity including the Splitting Effect around Atmospheric Pressure

The \( x \) for the mean absorption intensity around atmospheric pressure is such that

\[
x = \int_0^\infty l_v \left\{ 1 - \exp \left( -\sum k_m(\nu_l/l) \right) \right\} \left\{ 1 - \exp \left( -\sum k_m(\nu_l/l) \right) \right\} \, dv
\]

\[
= 1 - \exp \left[ \sum (1 - 1/l)^n \, \nu (2\pi/n!) \left( \delta_{0m}^0 + \nu_m(w) \right)^n \right]
\]

which was obtained[2] based solely on the pressure broadening theory, where \( k_m \) are the absorption coefficients of the condenser microphone detector.

As a final formula \( z \) for the mean absorption intensity including the effect of pressure splitting around atmospheric pressure, the following expression is obtained
from Eq.(12) and the x, 
\[
z = 1 - \exp \left[ -2\pi (g_{0m})_c \left\{ P_c + C(w, P) \right\} w \right. \\
+ \left. \left( 2\pi^2 / 2! \right) \left( g_{0m}^2 - g_{0m}^2 \right) \right] \\
\times \varepsilon^2 \left\{ P_c + C(w, P) \right\} w^2 - \left( 2\pi^3 / 3! \right) \\
\times \left( 3g_{0m}^3 - 3g_{0m}^2 g_{0m} + 2g_{0m}^3 \right) \\
\times \varepsilon^3 \left\{ P_c + C(w, P) \right\} w^3 + \cdots \right)
\] (15)
where
\[
d'_m = \alpha_m \delta_m / d_m^2, \quad i_{80m} = \sum_{m} d'_m / \sum_{m} d_m
\] (16)
and
\[
\varepsilon = \tan 2\beta'_m / 2\beta'_m[1], \quad \beta'_m = \pi \delta_m / d_m^2
\] (17)
where \(d_m^2\) are the widths of the rectangular forms by which the absorption lines are approximated for the detector. If \(p_c\) varies regardless of the splitting phenomenon, \(\varepsilon\) would be constant since \(\beta'_m = \text{const}\) from Eqs.(7) and (17). However, when there exists splitting, with the increasing \(p_c\), \(\varepsilon(p_c)\) might no longer be constant, and monotonously increase to 1, but is supposed to be constant \((\varepsilon \sim 1)\) within the experimental range.

Furthermore, Eq.(15) may be rewritten as
\[
\ln 1 / (1 - z) = 2\pi (k_{0m})_c \left\{ P_c + C(w, P) \right\} w / D_0 \\
- \left( (2\pi^2 / 2!) \right) \left( k_{0m}^0 \right) \left\{ P_c + C(w, P) \right\} w ^2 / D_0^2 \\
\times \left( k_{0m}^0 \right) \left\{ P_c + C(w, P) \right\} w ^3 / D_0^3 \\
\times \left( k_{0m}^0 \right) \left\{ P_c + C(w, P) \right\} w ^4 / D_0^4 + \cdots
\] (18)
where \(D_0\) is the constant correction factor determined at low pressures and
\[
k_{0m} = \left( \alpha_m \delta_m / d_m^2 \right) (t / 2)^2
\] (19)
where \(d_m\) is the interval of the vibrational-rotational absorption lines and \(t\) is the correction from the slit function of the infrared spectroscope used[2].

Eq.(18) is then
\[
\ln 1 / (1 - z) = 2\pi (j_{0m})_c (P_c w / D^2) \\
- \left( (2\pi^2 / 2!) \right) \left( j_{0m}^2 \right) (P_c w / D^2)^2 \\
+ \left( (2\pi^3 / 3!) \right) \left( j_{0m}^3 \right) (P_c w / D^2)^3 + \cdots
\]
\[
= \sum_{n=1} (-1)^{n-1} \left( (2\pi / n!) \right) \left( j_{0m}^n \right) (P_c w / D^2)^n
\] (20)
where
\[
\langle j_{0m} \rangle_c = \langle k_{0m} \rangle_c \\
\langle j_{0m}^2 \rangle_c = \langle k_{0m}^2 \rangle_c - \langle k_{0m} \rangle_c^2 \\
\langle j_{0m}^3 \rangle_c = \langle k_{0m}^3 \rangle_c - 3\langle k_{0m}^2 \rangle_c \langle k_{0m} \rangle_c + 2\langle k_{0m} \rangle_c^3
\] (21)
and assuming that \(\varepsilon \sim 1\) and \(s \sim 1\),
\[
D = D(w, P) = D_0 (\varepsilon S)^{-1/2} \left\{ 1 + C(w, P) / P_c \right\}^{-1/2}
\]
\[
\div D_0 \left\{ 1 + BC(w, P) / P_c \right\}^{-1/2}
\]
(22)
which gives
\[
C(w, P) = \left\{ (D_0 / D)^2 - 1 \right\} P / B.
\] (23)

2.4 The expression z at Low Pressures including Splitting Effect

From Eq.(12) and \(x\) viz. the mean absorption intensity for low pressures obtained[2] based only on the pressure broadening i.e.
\[
x = 2\pi (j_{0m})_c P_c w / D^2,
\]
the expression \(z\) at low pressures in the presence of the pressure splitting is given by
\[
z = 2\pi (j_{0m})_c P_c w / D^2 \left\{ P_c + C(w, P) \right\}^{1/2} 1 / 2.
\] (24)

By leaving only the linear term in Eq.(14) in which \(\sigma_m\) is replaced by \(\sigma_m^0\) because of the low pressures, Eq.(24) becomes
\[
z = 2\pi (j_{0m}^0) P_c w / D_0 \left\{ P_c + \sigma_m^0 \delta_m \right\}^{1/2} 1 / 2
\]
\[
\div 2\pi (j_{0m}^0) P_c w / D_0 \left\{ P_c + \sigma_m^0 \delta_m \right\}^{1/2} 1 / 2.
\] (25)

Here, the relation \(\sigma_m^0 \ll \delta_m^0\) is used. Then the following approximate expression may hold
\[
z = 2\pi (j_{0m}^0) P_c w / D_0 \left\{ P_c + \sigma_m^0 \delta_m \right\}^{1/2} 1 / 2
\]
\[
\div 2\pi (j_{0m}^0) P_c w / D_0 \left\{ P_c + \sigma_m^0 \delta_m \right\}^{1/2} 1 / 2.
\] (26)
In particular, in the case of the self-broadening where \(p_b = 0\), the following holds
\[
z = 2\pi (j_{0m}^0) P_c w / D_0 \left\{ P_c + \sigma_m^0 \delta_m \right\}^{1/2} 1 / 2.
\] (27)
Eqs.(26) and (27) are apparently the same expressions as those without the splitting effect, which can be assumed to be negligible at low pressures.
2.5 The Expression y for the Mean Absorption Intensity

Based on the above considerations, the expression y for the mean absorption intensity around atmospheric pressure is obtained by adding the effect of pressure splitting to the pressure broadening as follows:

\[ y = \sum_{m} \int_{0}^{\infty} \left[ 1 - \exp(-k_{m}(v)/l) \right] dv / \sum_{m} d_{m} \]

\[ = 1 - \exp \left[ -2\pi(g_{0m}) \left\{ P_{e} + C(w, P) \right\} w \right. \\
\left. + \left( (2\pi)^{2} / 2 ! \right) \left\{ (g_{0m})^{2} - (g_{0m})^{2} \right\} \left\{ P_{e} + C(w, P) \right\} w^{2} \right. \\
\left. - \left( (2\pi)^{3} / 3 ! \right) \left\{ (g_{0m})^{3} - 3(g_{0m})^{2} \right\} \left\{ g_{0m} \right\} \right. \\
\left. + 2(g_{0m})^{3} \left\{ P_{e} + C(w, P) \right\} w^{3} + \ldots \right] \\
\[ = 1 - \exp \left[ \sum_{n=1}^{\infty} \frac{(-1)^{n-1} \left( (2\pi)^{n} / n ! \right) \left( g_{0m}^{2} \right)^{n} / n ! }{P_{e} + C(w, P)} \right] \]

(28)

where \( g_{0m} = \delta \Omega_{m} / d_{m} \)

and for low pressures, by the way,

\[ y = 2^{1/2} \left( g_{0m} \right)^{1/2} \left( P_{e}^{1/2} \right)^{1/2} \]

(29)

which is approximately the same expression as that without the splitting effect.

3 Results

3.1 Comparison between Experiment and Formula for the CO Molecule

The CO molecule has an absorption band at 2150cm\(^{-1}\). The precisely calculated data[2] which have been redone are given below (the experiments were all carried out at room temperature),

\[ \langle k_{0m}^{1/2} \rangle_{av} = 4.62 \times 10^{-4} \text{ cm}^{-1/2} \text{ cmHg}^{-1} \]

\[ \langle k_{0m}^{2} \rangle_{av} = 3.60 \times 10^{-7} \text{ cm}^{-1} \text{ cmHg}^{-2} \]

\[ \langle k_{0m}^{3} \rangle_{av} = 1.32 \times 10^{-11} \text{ cm}^{-2} \text{ cmHg}^{-4} \]

\[ \langle k_{0m}^{4} \rangle_{av} \sim 10^{-20} \text{ cm}^{-3} \text{ cmHg}^{-6} \]

(30)

From the solid line in Figure 1[3]

\[ \langle k_{0m}^{2} \rangle_{av} / D_{0} = 3.10 \times 10^{-3} \]

therefore,

\[ D_{0} = 0.149 \]

(31)

is obtained. From Eqs.(30) and (20) in the case of the foreign gas broadening for CO+N\(_{2}\), the following expression is represented

\[ \ln 1/(1-z) = 2.26 \times 10^{-6} P_{e} w / D(w, P)^{2} \]

\[ - 2.21 \times 10^{-13} \left\{ P_{e} w / D(w, P)^{2} \right\}^{2} \]

(32a)

\[ \mp 2.26 \times 10^{-6} P_{e} w / D(w, P)^{2} \]

\[ \mp 2.26 \times 10^{-6} P_{e} w / (BD(w, P)^{2}) \]

(32b)

in which the quadratic and higher terms except the first may be neglected, because they make almost no contribution. Table 1 shows the calculated values of \( D \) and \( C \) from Figure 2 [3] in which the solid line is perfectly superimposed and closely approximated by Eq.(32b). As expected in Figure 5, with the increasing \( w \), \( D(w, P) \) is found to increase from less than the value of \( D_{0} \) almost monotonously and asymptotically toward \( D_{0} \).

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3.2 Comparison between Experiment and Formula for the CO₂ Molecule

CO₂ has absorption bands at 2350cm⁻¹ and 3700cm⁻¹ in this study. The re-calculated values are given below, at 2350cm⁻¹

\[ \langle k_{0m}^{1/2} \rangle_{av} = 5.87 \times 10^{-3} \text{cm}^{-1/2} \text{cmHg}^{-1} \]
\[ \langle k_{0m} \rangle_{av} = 4.80 \times 10^{-5} \text{cm}^{-1} \text{cmHg}^{-2} \]
\[ \langle k_{0m}^{2} \rangle_{av} = 3.79 \times 10^{-9} \text{cm}^{-2} \text{cmHg}^{-4} \quad (33) \]

and at 3700cm⁻¹

\[ \langle k_{0m}^{1/2} \rangle_{av} = 1.07 \times 10^{-3} \text{cm}^{-1/2} \text{cmHg}^{-1} \]
\[ \langle k_{0m} \rangle_{av} = 1.33 \times 10^{-6} \text{cm}^{-1} \text{cmHg}^{-2} \quad (34) \]

where \( \langle k_{0m}^{2} \rangle_{av} \) is very small compared to \( \langle k_{0m}^{2} \rangle_{av} \) and is neglected.

Moreover, the following average values from Eqs.(33) and (34) are given below,

\[ \langle j_{0m}^{1/2} \rangle_{av} = \left( \langle k_{0m}^{1/2} \rangle_{av} + r \langle k_{0m}^{1/2} \rangle_{av} \right) / (1 + r) \]
\[ = 4.22 \times 10^{-3} \text{cm}^{-1/2} \text{cmHg}^{-1} \]
\[ \langle j_{0m} \rangle_{av} = \left( \langle k_{0m} \rangle_{av} + r \langle k_{0m} \rangle_{av} \right) / (1 + r) \]
\[ = 3.61 \times 10^{-5} \text{cm}^{-1} \text{cmHg}^{-2} \]
\[ \langle j_{0m}^{2} \rangle_{av} = \left( \langle k_{0m}^{2} \rangle_{av} + r \langle k_{0m}^{2} \rangle_{av} \right) / (1 + r) \]
\[ = 2.49 \times 10^{-9} \text{cm}^{-2} \text{cmHg}^{-4} \quad (35) \]
\[ \langle j_{0m} \rangle_{av} = \langle j_{0m} \rangle_{av} \]
\[ = 3.61 \times 10^{-5} \text{cm}^{-1} \text{cmHg}^{-2} \]
\[ \langle j_{0m}^{2} \rangle_{av} = \langle j_{0m} \rangle_{av} - \langle j_{0m} \rangle_{av} \]
\[ = 1.19 \times 10^{-9} \text{cm}^{-2} \text{cmHg}^{-4} \quad (36) \]

where \( r (= 0.524 \text{ at } 900^\circ \text{K}) \) is the ratio of the intensity \( I_i \) of the infrared rays from the source between the regions of both bands[1].

From Figure 3[3]

\[ \langle j_{0m}^{1/2} \rangle_{av} / D_0 = 8.00 \times 10^{-3} \]

therefore

\[ D_0 = 0.528. \quad (37) \]

In the case of the foreign gas broadening for CO₂+N₂, Eqs.(36) and (20) give to a second approximation

\[ \ln 1/(1 - z) = 2.27 \times 10^{-4} P_{w} / D(w, P)^2 \]
\[ - 2.35 \times 10^{-8} \left\{ P_{w} / (BD(w, P)^2) \right\}^2 \quad (38a) \]
\[ \approx 2.27 \times 10^{-4} P_{w} / (BD(w, P)^2) \]
\[ - 2.35 \times 10^{-8} \left\{ P_{w} / (BD(w, P)^2) \right\}^2 \quad (38b) \]

where the cubic and higher terms have been dropped for the same reason as in the case of CO.

Table 2 shows the values of \( D \) and \( C \) obtained from Figure 4[1] in which the empirical line is assumed to be perfectly fitted by Eq.(38b). As has been already pointed out, in Figure 6 CO₂ is found to produce a similar inclination as that of CO. A comparison between the two molecule’s values of the equivalent effective pressure (E.E.P.) viz. \( C(w, P) \) suggests that with the increasing \( w \), the splitting effect tends to go rapidly toward the end in CO₂, but continues in CO to slowly and gradually decrease, which will imply that CO is slower than CO₂ in getting to some extent a sharpened line.

The two effects of splitting \( S_{m}(p_a, P) \) at \( p_a=1 \text{cmHg and } P=70 \text{cmHg} \) were then compared. The ratio of the E.E.P. of CO to that of CO₂ is 147/48.0=3.06 and the ratio of \( S_{m} \) is about 0.37[1] so that from Eq.(14) the ratio of the values of \( S_{m}(1, 70) \) is calculated to be 0.37×3.06=1.13. Eventually, such a situation will be possible, if at \( w=1 \text{cm} \cdot \text{cmHg}, \) the magnitude of the splitting effect of CO is evaluated as 1.13 times larger than that of CO.
depends on \( w \) and wider difference between them (Table 3). It should be first noticed that the discrepancy should not depend so much on \( l \) since such a deviation is not observed for CO. This suggests that \( C(w, P) \) may no longer be approximated by a function solely of \( w \) and \( P \); namely, there is no excluding the possibility that \( C(w, P) \) might depend not only on \( w \) and \( P \), but also on \( p_a \).

It cannot be explicitly determined as one of the problems of how much influence on the derived formulas is the approximation by the rectangular shapes with a width of \( \Delta_w \) and a height of a unit concerning the absorption lines of the condenser microphone detector, but such a mechanical influence will be included almost all in the derived formulas.

In the following section, the influence of the modified Bessel function of order zero \( I_0 \) omitted in the Elsasser model was estimated to be 2.2–2.3% at most since \( I_0(0.3)=1.0226, \cos \theta \sqrt{m} \geq 1, \) \( \alpha \leq 1 \) so that \( I_0 \) will be correctly neglected within the experimental error. Next \( \epsilon \) will fall off from 1 with the decreasing \( w \), which may lead from Eq. (22) to an augmentation of the value of \( D \) the contrary to the empirical facts, so that in conclusion \( \epsilon \) may be regarded as const (~ 1) and to have no influence on \( D \).

The empirical values slightly deviated from the experimental curve of \( \text{CO}_2 \) near \( w=9 \) in Figure 4 indicate that the discrepancy should not depend so much on \( l \) as on \( p_a \), since such a deviation is not observed for CO. This suggests that \( C(w, P) \) may no longer be approximated by a function solely of \( w \) and \( P \); namely, there is no excluding the possibility that \( C(w, P) \) might depend not only on \( w \) and \( P \), but also on \( p_a \).

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The empirical values slightly deviated from the experimental curve of \( \text{CO}_2 \) near \( w=9 \) in Figure 4 indicate that the discrepancy should not depend so much on \( l \) as

### Table 2. CO\(_2\) + N\(_2\) system at total pressure \( P = 70 \text{ cmHg} \)

<table>
<thead>
<tr>
<th>( w ) (cm-cmHg)</th>
<th>( D(w, 70) )</th>
<th>( C(w, 70) ) (cmHg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>0.345</td>
<td>72.8</td>
</tr>
<tr>
<td>1</td>
<td>0.383</td>
<td>48.0</td>
</tr>
<tr>
<td>2</td>
<td>0.423</td>
<td>30.0</td>
</tr>
<tr>
<td>3</td>
<td>0.433</td>
<td>26.2</td>
</tr>
<tr>
<td>5</td>
<td>0.460</td>
<td>17.1</td>
</tr>
<tr>
<td>8</td>
<td>0.495</td>
<td>7.42</td>
</tr>
<tr>
<td>10</td>
<td>0.510</td>
<td>3.87</td>
</tr>
</tbody>
</table>

### Table 3. Comparison of E.E.P. and \( \bar{S}_m(w, P) \) between CO and \( \text{CO}_2 \), \( P = 70 \text{ cmHg} \)

<table>
<thead>
<tr>
<th>( w ) (cm-cmHg)</th>
<th>Ratio of E.E.P. (CO/CO(_2))</th>
<th>Ratio of ( \bar{S}_m ) (CO/CO(_2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3.06</td>
<td>1.13</td>
</tr>
<tr>
<td>2</td>
<td>4.57</td>
<td>1.69</td>
</tr>
<tr>
<td>5</td>
<td>6.96</td>
<td>2.58</td>
</tr>
<tr>
<td>10</td>
<td>21.6</td>
<td>8.00</td>
</tr>
</tbody>
</table>

CO\(_2\). The increase in \( w \) thereafter gives rise to a wider and wider difference between them (Table 3).

### Figure 5. CO+N\(_2\). Dependence of \( D \) on \( w \) at total pressure \( P=70\text{cmHg} \)

![Figure 5](http://www.sccj.net/publications/JCCJ/225)

### Figure 6. CO\(_2\)+N\(_2\). Dependence of \( D \) on \( w \) at total pressure \( P=70\text{cmHg} \)

![Figure 6](http://www.sccj.net/publications/JCCJ/225)
the 2.7μ (3700cm⁻¹) band of the combination and over- 
tone, closer investigations will be necessary since it con-
ists of the nonlinear phenomenon of complexity due to the 
anharmonicity of vibration.

As for N₂O, NO, CH₄ gases and so on, the former 
two, which belong to the point group C₂v and the third 
one T₄, analogous analysis will be expected to hold true 
according to Eq.(20).

Finally, as a matter of course, the above investigations 
will also apply to atmospheric pressure or a little higher, 
which may be considered, however, to bring on a some-
what greater effect of splitting than that at 70cmHg so 
that the cubic term of (Pw) in Eq.(38) might not need to 
be omitted. For the purpose of reference, the results of 
the calculations are represented below,

\[
\langle k_{0m}^3 \rangle_{av} = 1.83 \times 10^{-13} \text{cm}^{-3} \text{cmHg}^{-6}
\]

\[
\langle j_{0m}^3 \rangle_{av} = \left( \langle k_{0m}^3 \rangle_{av} + r\langle k_{0m}^2 \rangle_{av} \right) / (1 + r)
\]

\[
= 1.20 \times 10^{-11} \text{cm}^{-3} \text{cmHg}^{-6}
\]

\[
\langle j_{0m}^3 \rangle_{c} = \langle j_{0m}^3 \rangle_{av} - 3\langle j_{0m}^2 \rangle_{av}\langle j_{0m} \rangle_{av} + 2\langle j_{0m} \rangle_{av}^3
\]

\[
= -5.6 \times 10^{-11} \text{cm}^{-3} \text{cmHg}^{-6}
\]

and as with the cubic term in Eq.(38a), though with a 
somewhat poorer accuracy,

\[-2.3 \times 10^{-12} (P_w/D(w, P^2)) \]

is obtained with a negative sign.

In the case of CO, the \(\langle k_{0m}^3 \rangle_{av}\) is too small to evaluate 
in Eq.(32) the cubic term or the higher ones, but in this 
connection, the quartic one of CO₂ is obtained as follows:

\[
\langle k_{0m}^4 \rangle_{av} = 1.00 \times 10^{-10} \text{cm}^{-4} \text{cmHg}^{-8}
\]

\[
\langle j_{0m}^4 \rangle_{av} = \left( \langle k_{0m}^4 \rangle_{av} + r\langle k_{0m}^3 \rangle_{av} \right) / (1 + r)
\]

\[
= 6.56 \times 10^{-11} \text{cm}^{-4} \text{cmHg}^{-8}
\]

\[
\langle j_{0m}^4 \rangle_{c} = \langle j_{0m}^4 \rangle_{av} - 3\langle j_{0m}^3 \rangle_{av}^2 - 4\langle j_{0m} \rangle_{av}^4 + 12\langle j_{0m}^2 \rangle_{av}\langle j_{0m} \rangle_{av}^2
\]

\[
+ 6\langle j_{0m} \rangle_{av}^4
\]

\[
= 5.87 \times 10^{-11} \text{cm}^{-4} \text{cmHg}^{-8}
\]

and

\[-3.80 \times 10^{-18} (P_w/D(w, P^2))^4.
\]

For higher pressures than those around atmospheric, the 
spectral lines become more flattened and more over-
lapped with the lines of the neighboring levels (and then \(\varepsilon \)
may no longer be regarded as const ). The basic assump-
tion of the two-body impact theory cannot hold good due 
to the appearance of many-body impacts, say, the fre-
cquency of three-body impacts, which is related directly 
to the half width, is no longer proportional to the pres-
sure but to its square. At the same time, the Lorentz line 
shape obtained from the pressure broadening theory may 
no longer be assumed to be correct because of the appear-
ance of the asymmetry of lines due to the statistical types 
of theories , so that other different considerations will be 
needed.

5 Conclusion

An expression for the mean absorption intensity around 
atmospheric pressure has been obtained by adding to the 
pressure broadening a new effect of pressure splitting of 
the degenerate vibrational-rotational levels using a novel 
notion of the equivalent effective pressure \(C(w, P)\). Here-
after, detailed investigations of the pressure splitting and 
its effect are desired.

References

[6] J. M. Ziman, Elements of Advanced Quantum The-
[13] G. Herzberg, Infrared and Raman Spectra of Poly-