

PRESSURE-INDUCED INFRARED ABSORPTION SPECTRA OF
POLYATOMIC MOLECULES WITH A CENTER OF SYMMETRY
AND PRESSURE EFFECT OF PERTURBING GASES ON
THEIR SPECTRA*

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1 Introduction

Symmetrical molecules, whether they are diatomic (H_2), linear polyatomic (CO_2 and C_2H_2 , represented by point group $D_{\infty h}$, together) or plane polyatomic (C_2H_4 , point group V_h), possess no permanent dipole moment. However if during the vibrational motion of a molecule the charge distribution undergoes a periodic change, then we may say in general (though not always) the dipole moment changes periodically. For example, in the linear symmetric C_2H_2 molecule, during the totally symmetric linear vibrations ν_1 and ν_2 and the symmetric perpendicular vibration ν_4 , the dipole moments always remain zero as the displaced configurations of the nuclei have a center of symmetry, therefore these vibrations are infrared-inactive. On the other hand, for the other two vibrations ν_3 and ν_5 , dipole moments perpendicular to and in the molecular axis respectively arise because of the asymmetry of the displacement positions. Thus these vibrations are active for infrared. Namely, the symmetrical modes of molecular vibration are all normally inactive in infrared absorption but active in Raman displacement. Therefore, the appearance of a certain transition of polyatomic molecules with a center of symmetry such as C_2H_2 and C_2H_4 takes place either in the infrared or in the Raman spectrum, but never in both. There is a strict rule of mutual exclusion concerning with the selection rules of infrared and Raman Spectrum.

But this is no longer true when by a suitable physical means (liquefaction or compression) the average distance between the molecules is appreciably decreased. If a particular molecule comes within the field of the quadupole of another molecule, or if their electron shells overlap, the symmetric vibration of the absorbing molecule will be distorted in such a way as to induce a dipole moment which will persist for the period of the perturbing action with neighbouring molecules. In this state the induced dipole moment will give rise to a break-down of the selection rules and the appearance of forbidden transitions in the spectrum.

These predictions were fully confirmed in homopolar diatomic molecules by Welsh *et al.*¹⁾, who observed the forbidden infrared absorption bands of the compressed gaseous H_2 and N_2 at

* This paper is part of a dissertation submitted to the Graduate School of Kyoto University in partial fulfilment of the Degree of Doctor of Philosophy.

1) H. L. Welsh, M. F. Crawford, and J. L. Löcke, *Phys. Rev.*, **76**, 580 (1949)
M. F. Crawford, H. L. Welsh, J. C. F. MacDonald, and J. L. Locke, *ibid.*, **80**, 469 (1950)

the Raman vibrational frequencies of these gases (4155 and 2331 cm^{-1} , respectively). When they changed the pressures of the gases, they found that the absorption intensities are proportional to the square of the pressures, so they suggested that these absorptions were induced by intermolecular forces. Also such a dipole moment induced by pressure gave rise to transitions obeying the selection rules for Raman spectra, rather than for infrared.

On the other hand, there is another noteworthy spectral effect as the density increases, that is, "simultaneous vibrational transitions" which give rise to absorption bands corresponding to the sum of the individual frequencies of each pair of interacting molecules. This type of infrared absorption spectrum was found in mixtures of compressed gases; $\text{HCl} \sim \text{H}_2$ and $\text{CO}_2 \sim \text{N}_2$ by Vodar *et al.*²⁾ and Ketelaar *et al.*³⁾, respectively.

In the present investigation, the pressure-induced infrared absorption of totally symmetric vibration $\nu_2(\Sigma_g^+)$ at 1970 cm^{-1} of gaseous C_2H_2 has been investigated in the pure gas at the pressures up to 43 kg/cm^2 and in the mixtures containing the perturbing gases (N_2 , H_2 , and A) at the total pressures up to 120 kg/cm^2 . Then the correlation of induced effects with the molecular polarizabilities of the perturbing gases has been examined. Also, in the KBr optics the symmetric double degenerate perpendicular vibration $\nu_4(\Pi_g)$ at 612 cm^{-1} of C_2H_2 has been observed as a pressure-induced absorption in the infrared spectrum. For CO_2 the pressure-induced absorptions⁴⁾ of the totally symmetric vibration at 1388 cm^{-1} and the first overtone $2\nu_2$ at 1286 cm^{-1} , which are in Fermi resonance⁵⁾, have been studied at the total pressures up to 69 kg/cm^2 , and new absorptin bands observed in the liquid state at the pressures up to 74 kg/cm^2 .

Having sure information regarding the pressure-induced absorption, a plane molecule of point group V_h , C_2H_4 has been studied in every detail for pure C_2H_4 and mixtures containing the perturbing gases (N_2 , O_2 , H_2 , and A) up to the total pressures of 145 kg/cm^2 . Quantitative experimental results obtained on the pressure effect of the perturbing gases indicate that the origin of the induced dipole of the absorbing molecule is the reaction field of the polarizable perturbing gas molecules in its neighbourhood.

II Experimentals

A. Apparatus

The measurements of the spectra were carried out with a Perkin-Elmer Model 21 infrared spectrometer equipped with NaCl and LiF prisms and a Koken DS 301 spectrometer with NaCl and KBr prisms. The Nernst glower was used as the radiation source. The instruments were calibrated with polystyrene, water vapor, ammonia, and carbon dioxide bands. The calibration error should

2) J. Robin and B. Vodar, *Comptes rendus*, **240**, 956 (1955)

R. Coulon and Vu-Hai, *ibid.*, **245**, 2247 (1957)

3) J. Fahrenfort and J. A. A. Ketelaar, *J. Chem. Phys.*, **22**, 1631 (1954)

4) H. L. Welsh, M. F. Crawford, and J. L. Locke, *Phys. Rev.*, **76**, 580 (1949)

J. Fahrenfort, H. de Kluiver, and T. Babeliowsky, *J. Phys. et Radium*, **15**, 617 (1954)

5) E. Fermi, *Z. Physik*, **71**, 250 (1931)

be less than $\pm 3\text{cm}^{-1}$ from $400\sim 650\text{cm}^{-1}$, and $\pm 5\text{cm}^{-1}$ from $650\sim 3200\text{cm}^{-1}$.

The special high pressure absorption cell was made of machined milled steel stock. A diagram of this cell is reproduced in Fig. 1. The windows of the same design of 28 mm in diameter and

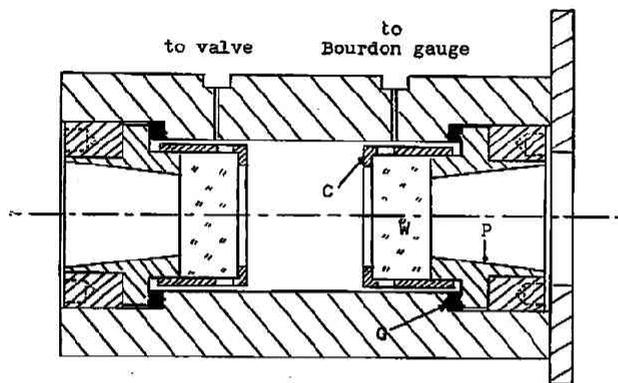


Fig. 1 The pressure proof optical window mounting to the absorption cell

W: window,
P: supporting plug,
C: steel cap,
G: Al gasket

20~22 mm in thickness, being cut from a large single crystal, were set in a symmetrical position on both sides of the absorption cell with about 2.4 cm internal path length. NaCl windows were used up to 200kg/cm^2 for the study of regions above 650cm^{-1} . Below this frequency, where the NaCl absorbs strongly, KBr windows were used up to 100kg/cm^2 . The optical windows, W with polished faces were cemented with Araldite Cement against the finely ground surface of the plug, P. The perforated steel cap, C, which was screwed outside the supporting plug, was also useful for holding the window in position when the cell was evacuated. After passing through the cell the radiation beam was focussed on the slit of the spectrometer. Pressures above one atm. were measured by Bourdon gauges reading to 100 and 200kg/cm^2 . The gauges used were calibrated locally on the dead-weight tester.

B. Preparation of Gases

The purification of gaseous C_2H_2 from calcium carbide and water was performed by the same method as described in the previous papers⁶⁾. The CO_2 and C_2H_4 gases used in this work were brought in liquid form into pressure bombs after purification by liquefying and distilling at liquid air temperature, and the perturbing gases used were available in commercial bombs.

C. Procedure

The absorption coefficients were determined as follows. With the cell evacuated, the radiation curve of the source was obtained over a spectral region including the expected absorption, and with the cell containing the absorbing gas at density ρ , the same region was scanned under the same instrumental conditions. The average of the recorder traces for each density was used to calculate $\frac{1}{l} \ln(T_0/T)$ as a function of frequency across the band, where T_0 and T are the signals transmitted at frequency ν on the two traces and l is the path length.

The Amagat densities of the gases under the experimental conditions for $PV=1$ at 1 atm.

6) R. Kiyama, S. Minomura, and K. Ozawa, *Proc. Japan Acad.*, **30**, 758 (1954)
S. Minomura, *Rev. Phys. Chem. Japan*, **24**, 49 (1955)

and 0°C were calculated by reference to the appropriate pressure~density isothermal for the gas. The *PVT* data necessary for the calculation of the isothermals were obtained from sources in the literatures which are listed in the reference as follows; C₂H₂⁷⁾, CO₂⁸⁾, C₂H₄⁹⁾, N₂¹⁰⁾, A¹¹⁾, O₂¹²⁾, and H₂¹³⁾. It was assumed for the gaseous mixtures that the density of each gas could be calculated from its partial pressure.

The mixing of gases at pressure takes place very slowly. It was found that significant concentration gradients existed over long periods of time in gases sealed in the absorption cell. In practice the spectral measurement was performed after waiting 1/2 hour after the mixing of gases ended. Also in the mixing of gases there was another difficulty which was the decrease of the base density of the absorbing molecule by back diffusion when the perturbing gas was being added. But this effect could be made negligibly small by employing a capillary pipe between the bomb and the cell.

III Experimental Results and Considerations

A. Induced Absorption of Acetylene

A great deal of work has been done on the Raman¹⁴⁾ and infrared^{15,16)} spectra of the acetylene molecule. The C₂H₂ molecule is linear and symmetrical and has five distinct fundamental vibrations which are shown in Fig. 2.

	ν_1	(3374 cm ⁻¹)	Σ_g^+	Species
	ν_2	(1974 cm ⁻¹)	Σ_g^+	Species
	ν_3	(3287 cm ⁻¹)	Σ_u^+	Species
	ν_4	(612 cm ⁻¹)	Π_g	Species
		twofold degenerate		
	ν_5	(729 cm ⁻¹)	Π_u	Species
		twofold degenerate		

Fig. 2 Actual form of the fundamental vibrations of C₂H₂.

The two totally symmetric (Σ_g^+) vibrations, ν_1 and ν_2 , and the twofold degenerate (Π_g) vib-

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- 7) R. Kiyama, T. Ikegami, and K. Inoue, *Rev. Phys. Chem. Japan*, **21**, 58 (1951)
 J. Sameshima, *Bull. Chem. Soc. Japan*, **1**, 41 (1926)
- 8) F. Din, *Thermodynamic Functions of Gases, Vol. 1*, (Butterworths, London, 1956) p. 102
- 9) A. Michels and Geldermans, *Physica*, **9**, 967 (1942)
- 10) J. Otto, A. Michels, and H. M. Wouters, *Phys. Zeits.*, **35**, 97 (1934)
- 11) A. Michels and H. Wijker, *Physica*, **15**, 627 (1949)
- 12) C. M. Meyers, *J. Res. N. B. S.*, **40**, 457 (1948)
- 13) H. W. Wooley, R. B. Scott, and F. G. Brickwedde, *ibid.*, **41**, 379 (1948)
- 14) C. M. Lewis and W. V. Houston, *Phys. Rev.*, **44**, 903 (1933)
- 15) E. E. Bell and H. H. Nielsen, *J. Chem. Phys.*, **18**, 1382 (1950)
- 16) R. Kiyama, S. Minomura, and K. Ozawa, *Proc. Japan Acad.*, **30**, 758 (1954)
 S. Minomura, *Rev. Phys. Chem. Japan*, **24**, 49 (1955); **26**, 9, 41 (1956)
 K. Ozawa, *ibid.*, **27**, 9 (1957)

ration, ν_4 , which do not occur as infrared bands even with a fairly long absorption path, are active only in the Raman effect; the remaining two vibrations, $\nu_3(\Sigma_g^+)$ and $\nu_5(\Pi_u)$, are active only in infrared absorption. This proves that C_2H_2 must have a center of symmetry. According to what has been said in the Introduction, the infrared spectrum of compressed C_2H_2 might be expected to show a number of new absorption bands, not present in the low pressure spectrum.

For respective pressures from 2 to 43 kg/cm² at 20°C, the absorption contours of the pressure-induced ν_2 -band of C_2H_2 in the region from 1800~2100 cm⁻¹ are reproduced in Fig. 3. Each of

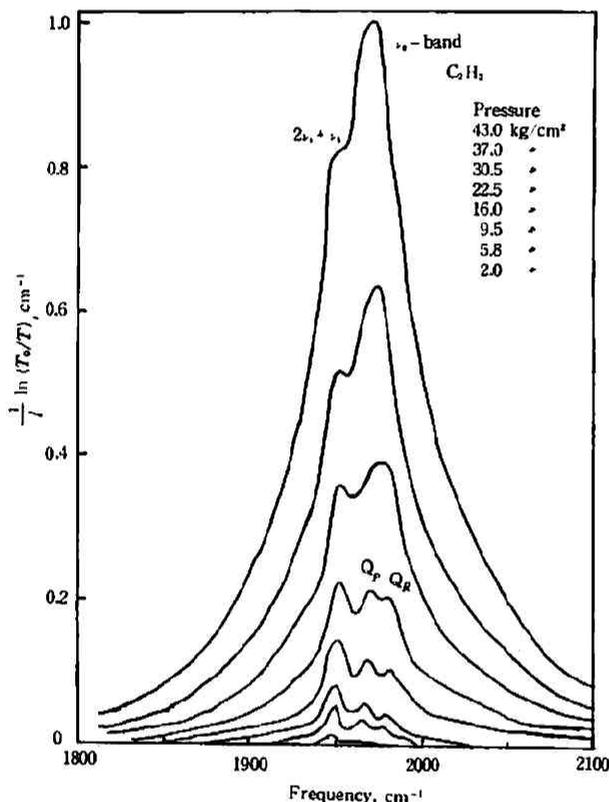


Fig. 3 The induced ν_2 -band of gaseous C_2H_2 at various pressures at 20°C

the spectra shows that the two main peaks of bands at around 1950 and 1970 cm⁻¹ remarkably increase as the pressure increases. The pressure-induced band should have O , Q , and S branches, corresponding to the Raman selection rule, $\Delta J=0, \pm 2$.

The recent investigation of the Raman spectrum on this region of C_2H_2 by Welsh *et al.*¹⁷⁾ has shown that the Raman spectrum of ν_2 -band consists of three branches, which can be attributed to O ($\Delta J=-2$; 1865~1952 cm⁻¹), Q ($\Delta J=0$; 1973 cm⁻¹), and S ($\Delta J=+2$; 1985~2084 cm⁻¹), and two "hot" bands, $\nu_2 + \nu_4^{l-1} - \nu_4^{l-1}$ (1960 cm⁻¹) and $\nu_2 + \nu_5^{l-1} - \nu_5^{l-1}$ (1941 cm⁻¹), which have as initial states the low lying twofold degenerate levels ν_4^{l-1} and ν_5^{l-1} , respectively. Furthermore in this region the infrared active band, $2\nu_4^{l=0} + \nu_5^{l=1}$ (Π_u) with very weak intensity has been ob-

17) T. Feldman, G. G. Shepherd, and H. L. Welsh, *Can. J. Phys.*, **34**, 1425 (1956)

served by Stitt¹⁸). The main peaks observed will therefore be interpreted as Q branch with two submaxima (Q_P and Q_R) and the "hot" bands superimposed upon the $2\nu_4^{l=0} + \nu_6^{l=1}$ band.

To ascertain the form of the dependence of the absorption coefficient on the density, the absorption coefficients of the band peaks for unit Amagat density of C_2H_2 , $\frac{1}{\rho l} \ln(T_0/T)$, are plotted against the density of C_2H_2 , in Fig. 4. The experimental evidences that the absorption

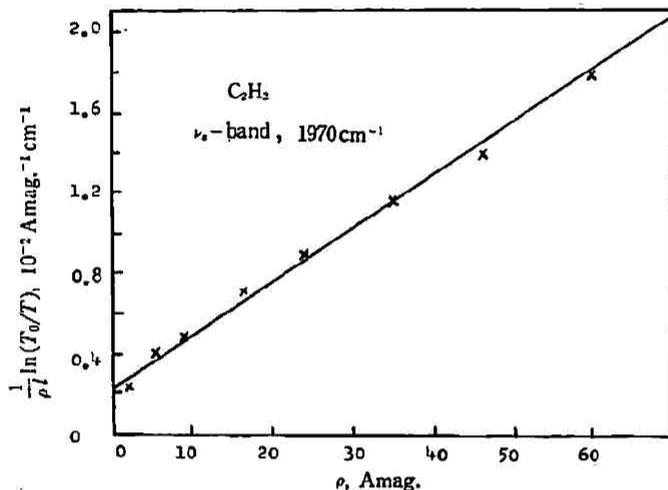


Fig. 4 The relation between the Amagat density of C_2H_2 and the absorption coefficient of ν_2 -band for unit Amagat density $\frac{1}{\rho l} \ln(T_0/T)$, Amag., cm^{-1}

intensities increase as the square of the density of absorbing molecule, are consistent with the hypothesis that the pressure-induced absorption is caused by the distortion of the charge distribution of the absorbing molecule during a close binary collision. The theoretical calculations of van Kranendonk *et al.*¹⁹) and Galatry²⁰) support this hypothesis.

The effect of the perturbing gases on the contour of the induced band is also very marked. A number of experiments with mixtures of C_2H_2 and non-absorbing perturbation gases such as N_2 , A, and H_2 were carried out to have more information regarding the nature of the molecular interaction and to investigate the hypothesis that the intermolecular forces during collision in which the absorbing molecules participate, are mainly due to the electrostatic fields²¹). To this purpose, the spectrum of C_2H_2 in the pure state, and afterwards the same spectrum after being pressurized by N_2 , A, and H_2 to the base density of C_2H_2 were measured. The results obtained are shown in Fig. 5 where the change of absorption intensity on addition of the perturbing gases up to the total pressure of 120 kg/cm² to the fixed pressure of C_2H_2 at 25 kg/cm² is observed in the region of ν_2 -band. The absorption of C_2H_2 in all cases has been found to be enhanced by the addition of perturbing gases. The effect is highest for N_2 . On the other hand, as the quantity of added perturbing gas is in-

18) F. Stitt, *J. Chem. Phys.*, **3**, 56 (1940)

19) J. van Kranendonk and R. Bird, *Phys. Rev.*, **82**, 964 (1951); *Physica*, **17**, 953, 968 (1951)

20) L. Galatry and B. Vodar, *Comptes rendus*, **240**, 1072 (1955); **242**, 1871 (1956)

21) E. U. Condon, *Phys. Rev.*, **41**, 759 (1932)

M. F. Crawford and I. R. Dagg, *ibid.*, **91**, 1569 (1953)

R. W. Terhune and C. W. Peters, *J. Molec. Spectr.*, **3**, 138 (1959)

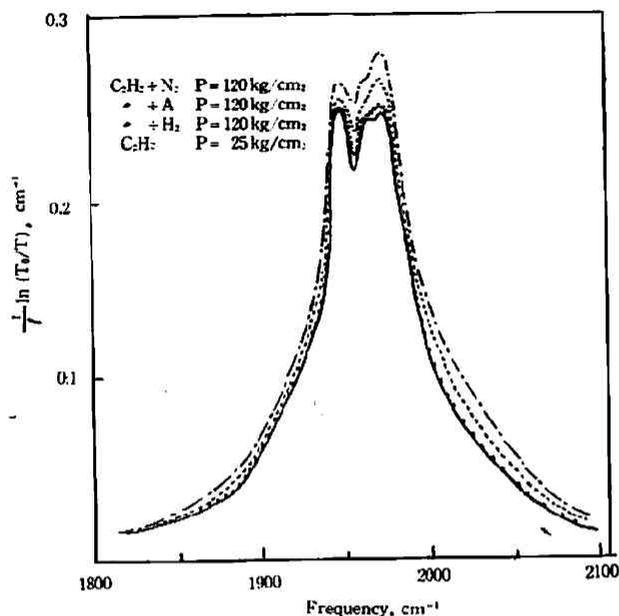


Fig. 5 The pressure effect of perturbation gases on the contour of the induced ν_2 -band of C_2H_2 .

creased, especially the higher frequency submaximum which will be referred to as the Q_R component, grows to higher intensity, while the influence on the Q_P component and the lower frequency peak at around 1950cm^{-1} is not so great. These phenomena with the addition of perturbing gases have a similarity to the induction of a Q_R branch in the induced band of H_2 as found by Welsh *et al.*²²⁾ and of a Q branch in the vibrational-rotational bands of HCl ²³⁾ and HBr ²⁴⁾ by Vodar *et al.*

Furthermore we may remark that the order of the magnitude of perturbing effect, $N_2 > A > H_2$, coincides with that of the polarizability of molecules. Namely, this fact is consistent with the assumption that the vibration dipole of the absorbing molecule is increased by the reaction field of the polarizable perturbing gases in its neighbourhood.

In the KBr prism region one could think that the symmetrical perpendicular vibration, ν_4 -band (Π_g ; 612cm^{-1}), which is normally forbidden in infrared, would be also expected to be observed in infrared absorption spectrum of compressed C_2H_2 . The absorption profiles of the pressure-induced ν_4 -band of C_2H_2 obtained by employing a cell with the KBr windows at pressures from 4 to 38kg/cm^2 at 20°C are reproduced in the region from $560\sim 640\text{cm}^{-1}$ in Fig. 6. Although the band at around 615cm^{-1} is superimposed on the lower frequency wing of a strong C_2H_2 absorption

22) D. A. Chisholm and H. L. Welsh, *Can. J. Phys.*, **32**, 291 (1954)

W. F. J. Hare and H. L. Welsh, *ibid.*, **36**, 88 (1958)

Z. J. Kiss, H. P. Gush, and H. L. Welsh, *ibid.*, **37**, 362 (1959)

23) R. Coulon, L. Galatry, B. Oksengorn, St. Robin, and B. Vodar, *J. Phys. et Radium*, **15**, 58, 641 (1954)

R. Coulon, B. Oksengorn, and B. Vodar, *Comptes rendus*, **239**, 964 (1954)

Vu-Hai and B. Vodar, *ibid.*, **248**, 2082 (1959)

24) R. Coulon and Vu-Hai, *ibid.*, **245**, 2247 (1957)

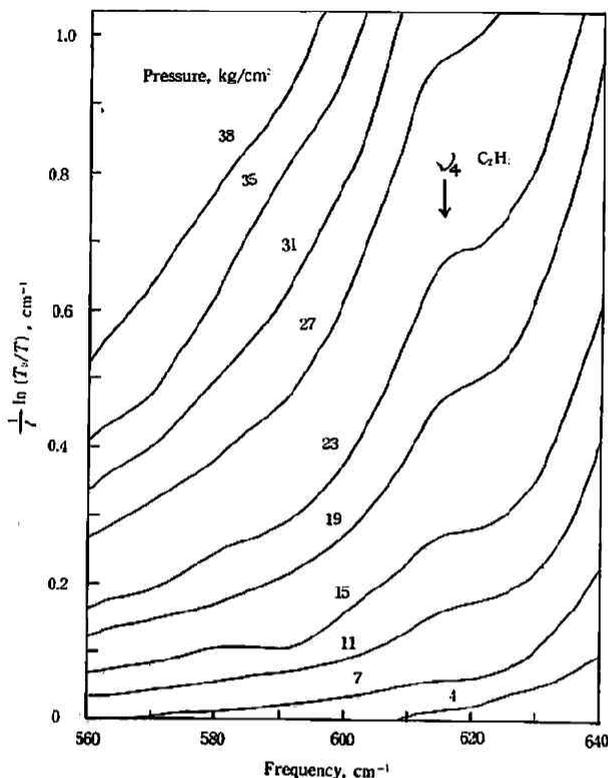


Fig. 6 The induced ν_4 -band of gaseous C_2H_2 at various pressures at $20^\circ C$

band $\nu_3(\Pi_u)$ having a maximum peak at 729cm^{-1} , the band at around 615cm^{-1} also definitely has an induced character, of which the intensity proved to be proportional to the square of the C_2H_2 density, and there are no other such bands of a measurable intensity expected in that region. Also furthermore the absorption feature is consistent with that reported for the ν_4^{1-1} Raman spectrum of C_2H_2 by Welsh *et al.*¹⁷⁾

On the other hand the ν_1 -band (Σ_g^+) expected to pressure-induce at 3374cm^{-1} could not be unfortunately detected in infrared because of the intense ν_3 -band (Σ_u^+) which is infra-active and superimpose upon the induced ν_1 -band in this frequency region.

B. Induced Absorption of Carbon Dioxide

Such a triatomic linear symmetrical molecule with point group $D_{\infty h}$ as CO_2 should have three fundamental vibrations, which may be represented in Fig. 7.

$\circ \rightarrow$	\bullet	$\leftarrow \circ$	ν_1	(1388 cm^{-1})	Σ_g^+	Species
\odot	\updownarrow	\odot	ν_2	(667 cm^{-1})	Π_u	Species
				twofold degenerate		
$\circ \rightarrow$	$\leftarrow \bullet$	$\rightarrow \circ$	ν_3	(2349 cm^{-1})	Σ_u^+	Species

Fig. 7 Actual form of the fundamental vibrations of CO_2

Already Welsh *et al.*⁴⁾ have for the first time suggested that the symmetrical vibrations of CO_2 should be possible in infrared, and they have observed them at pressures up to 25 atm. and furthermore Ketelaar *et al.*²⁵⁾ have observed the simultaneous transitions of CO_2 vibrations with vibrations of N_2 , O_2 , or H_2 in compressed mixtures of these gases.

In this work the pressure-induced absorption bands of CO_2 were investigated in expansion of the pressure range to 74 kg/cm^2 for pure gas and further with the change of state taking place in going from the dense gas to the liquid phase.

In Fig. 8 the pressure-induced absorption in CO_2 , which is forbidden at the normal state, at

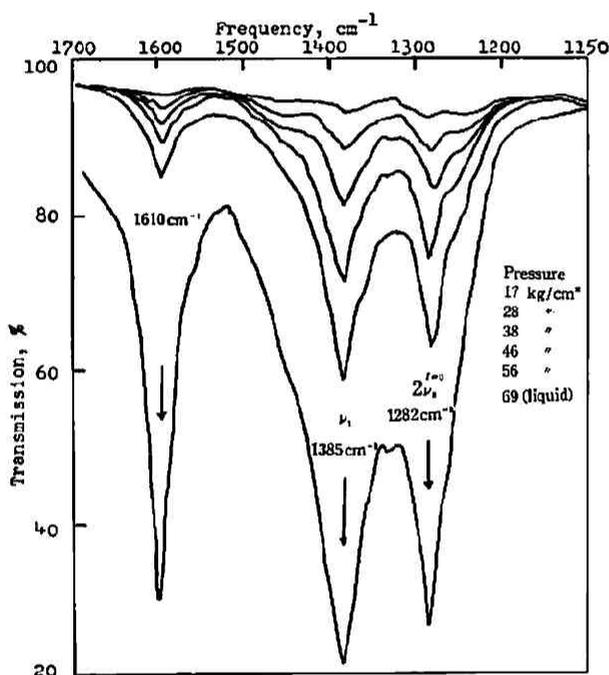


Fig. 8 The pressure-induced absorption spectra of compressed CO_2 in the region of the Raman doublet

pressures up to 69 kg/cm^2 at 20°C is shown in the frequency range of $1150\sim 1700\text{ cm}^{-1}$. The spectra indicate the maxima at 1282 ($2\nu_2^{1-0}$) and 1385 cm^{-1} (ν_1), which are infra-inactive at low pressure but Raman-active. The bands at 1385 and 1282 cm^{-1} are brought about in consequence of the Fermi resonance between the totally symmetric fundamental ν_1 and the first overtone of perpendicular band, $2\nu_2^{1-0}$. For these induced-bands the absorption intensity was proportional to the square of the density of CO_2 .

On the other hand, it was possible to obtain important information regarding the nature of the liquid and of the intermolecular forces from the measurement of the spectrum in going from the gaseous to the liquid state at high pressure. In Fig. 9 the observed absorption curves obtained by LiF prism for liquid CO_2 at pressures up to 74 kg/cm^2 at 20°C are reproduced in the frequency

25) J. A. A. Ketelaar and J. Farenfort, *Nuovo Cimento, Serie X* 2, 766 (1955), Supplemento
J. P. Colpa and J. A. A. Ketelaar, *Physica*, 24, 1035 (1958)

region from $1500\sim 2000\text{cm}^{-1}$. In the phase change from the gaseous to liquid state with compression the absorption spectrum may be changed by modifying the neighbouring molecules and the internal structures of the absorbing molecules, but this effect is usually difficult to interpret because of the complex nature of intermolecular forces.

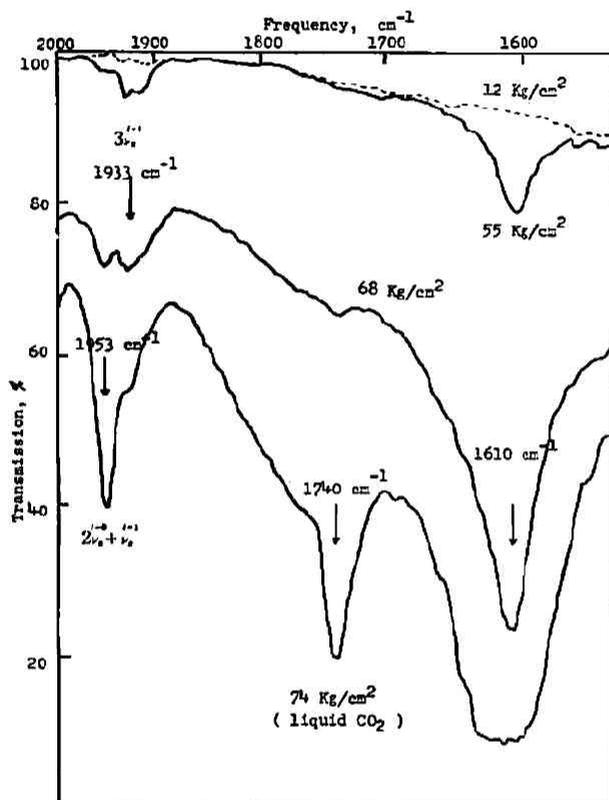


Fig. 9 The pressure-induced absorption of CO_2 in the gas and in the liquid at various pressures in the frequency region from $1500\sim 2000\text{cm}^{-1}$

From Fig. 9 the new bands having the maxima at 1933 , 1740 , and 1610cm^{-1} were observed. The band at 1933cm^{-1} can be interpreted as the Q branch of the $3\nu_2$ band, although the induced bands at 1933 , 1740 , and 1610cm^{-1} cannot be assigned to any forbidden combination of the bands already listed in Herzberg's Table²⁶⁾.

However if the intermolecular simultaneous vibrational transitions arising from collision complexes, as predicated by van Kranendonk¹⁹⁾, are permitted, these bands newly observed may readily be assigned as the combination of a transition in one molecule and a transition in the other. This intermolecular simultaneous vibrational transition in which one energy quantum is absorbed by a cluster of molecules within a short distance of one another, have to be distinguished from the intramolecular simultaneous transitions corresponding to combination frequencies of different vibrations within one molecule. Admitting this idea the induced new bands at 1933 , 1740 , and

26) G. Herzberg, *Infrared and Raman Spectra of Polyatomic Molecules* (D. van Nostrand Company, Inc., New York, 1945) p. 274

1610 cm^{-1} are interpreted as the $2\nu_2^{l=0} + \nu_2^{l=1}$, $\nu_2^{l=1} + (\nu_3 - 2\nu_2^{l=0})$ or $(\nu_3 - \nu_1) + (\nu_1 + \nu_2^{l=1} - 2\nu_2^{l=0})$, and $(\nu_3 - \nu_1) + (3\nu_2^{l=1} - \nu_2^{l=0})$ bands respectively, which may be calculated as follows:

$$\begin{array}{l} \left(\begin{array}{ccc} 0 & 0^{\circ} & 0 \longrightarrow 0 & 2^{\circ} & 0 \\ 0 & 0^{\circ} & 0 \longrightarrow 0 & 1^1 & 0 \end{array} \right) \quad \text{at } 1286 + 667 = 1953 \text{ cm}^{-1} \\ \left(\begin{array}{ccc} 0 & 2^{\circ} & 0 \longrightarrow 0 & 1^1 & 1 \\ 0 & 0^{\circ} & 0 \longrightarrow 0 & 1^1 & 0 \end{array} \right) \quad \text{at } 1064 + 667 = 1731 \text{ cm}^{-1} \\ \text{or} \quad \left(\begin{array}{ccc} 1 & 0^{\circ} & 0 \longrightarrow 0 & 0^{\circ} & 1 \\ 0 & 2^{\circ} & 0 \longrightarrow 1 & 1^1 & 0 \end{array} \right) \quad \text{at } 961 + 791 = 1752 \text{ cm}^{-1} \\ \text{and} \quad \left(\begin{array}{ccc} 1 & 0^{\circ} & 0 \longrightarrow 0 & 0^{\circ} & 1 \\ 0 & 2^{\circ} & 0 \longrightarrow 0 & 3^1 & 0 \end{array} \right) \quad \text{at } 961 + 648 = 1609 \text{ cm}^{-1}. \end{array}$$

The calculated frequencies show a very good correspondence with the observed values given above. From the value for the disturbed rotational energy of CO_2 at the critical point, van Dranen²⁷⁾ has recently given the opinion that a liquid in equilibrium with its vapor is bound in its own characteristic volume, *e. g.*, a cluster of CO_2 molecules. Namely the occurrence of the intermolecular simultaneous transitions is an induction, pointing to the lattice vibrations in a quasicrystalline structure of the dense liquid.

C. Induced Absorption of Ethylene

The ethylene molecule with the plane symmetrical form (point group V_h) has twelve normal vibrations. The fact that there are no bands which are observed in the Raman as well as the infrared spectrum of C_2H_4 , indicates that the molecule has a center of symmetry.

However there are some outstanding problems in the vibrational assignment on the Raman spectrum of C_2H_4 . In a recent study on the Raman spectrum of C_2H_4 by Welsh *et al.*²⁸⁾ the ν_6 (B_{1g}) has not been observed in the gas state, while the band was observed in the liquid by Rank *et al.*²⁹⁾ at 1236 cm^{-1} , corresponding to the position for ν_6 calculated by Crawford *et al.*³⁰⁾ from infrared data. On the other hand the $2\nu_{10}$ (A_g) is indicated by the value 1606 cm^{-1} by Welsh *et al.* although observed at 1656 cm^{-1} by Rank *et al.* However we should expect to observe the $2\nu_{10}$ at the higher frequency than the ν_2 (1623 cm^{-1}) by the Fermi resonance between the intense ν_2 and the $2\nu_{10}$, if permitting a small positive anharmonicity so that $2\nu_{10}$ is not 1620 cm^{-1} ($=2 \times 810$), but small value greater than 1623 cm^{-1} .

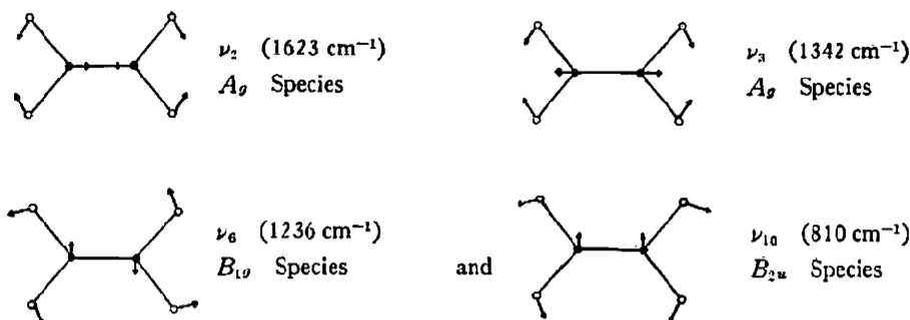
Thus it is also interesting to investigate the pressure-induced infrared absorptions of C_2H_4 at pressure appearing in the infrared spectrum as the result of a break-down of selection rules in the compressed state. The analogous experiments with C_2H_2 and CO_2 were made on C_2H_4 at pressures up to 70 kg/cm^2 in the region of the NaCl prism. The following vibration modes, which are the $2\nu_{10}$, ν_2 , ν_3 , and ν_6 , expected from the symmetric property of the molecule, are observed as the pressure-induced infrared absorption bands. The modes of vibration observed may be represented by the following schematic forms:

27) J. van Dranen, *J. Chem. Phys.*, **21**, 1404 (1953)

28) T. Feldman, J. Romanko, and H. L. Welsh, *Can. J. Phys.*, **34**, 737 (1956)

29) D. H. Rank, F. R. Shull, and D. W. E. Axford, *J. Chem. Phys.*, **18**, 116 (1950)

30) R. L. Arnett and B. L. Crawford, Jr., *ibid.*, **18**, 118 (1950)



but in which the last mode is the fundamental vibration mode of $2\nu_{10}$ (A_g) listed at 1656 cm^{-1} or 1606 cm^{-1} in Fermi resonance with ν_2 .

In Fig. 10 the infrared absorption spectrum at pressure 20 kg/cm^2 of C_2H_4 is reproduced in comparison with that at 1 kg/cm^2 . The induced bands are clearly observed at around 1640 cm^{-1} owing to pressure-induced vibrations of the $2\nu_{10}$ and ν_2 , and at around 1300 cm^{-1} by representing the anomalous increase of the absorption which would be due to the ν_3 and ν_6 band. If the values, 1623 and 1656 cm^{-1} , proposed by Rank *et al.* for ν_2 and $2\nu_{10}$ respectively are accepted, the pressure-induced band observed at 1640 cm^{-1} may be interpreted as the result overlapped by both ν_2 and $2\nu_{10}$.

In Fig. 11 the quantity, $\frac{1}{\rho l} \int \ln(T_0/T) d\nu$ was plotted against ρ of C_2H_4 at pressures up to 70 kg/cm^2 to ascertain the dependence of the integrated absorption intensity on the density. Thus the quadratic absorption coefficient, $\kappa = \int \epsilon(\nu) d\nu = \frac{8\pi^3 N_{12} \nu}{3hc} \left| \int \psi_1 \psi_2 \mu \psi_1' \psi_2' d\tau \right|^2$ with $2.1 \times 10^{-2}\text{ cm}^{-1}/\text{cm Amag}^2$ for 1640 cm^{-1} band was obtained from the slope of the linearity. Herein $\left| \int \psi_1 \psi_2 \mu \psi_1' \psi_2' d\tau \right|$ is the matrix element of the induced electric dipole moment of the collision pair, and N_{12} is the number of collision pairs per cm^3 .

Furthermore the pressure effects of the perturbing gases upon the induced bands of C_2H_4 have been investigated by the addition of such a non-absorbing gas as N_2 , A , O_2 , and H_2 to a fixed pressure of C_2H_4 . In the perturbing gases, N_2 , O_2 , and H_2 , being diatomic, hence have a quadrupole moment and different masses and diameter, while A being monatomic, has no quadrupole moment. As an example the measurements for the mixtures up to the total pressure of 145 kg/cm^2 to the base pressure at 20 kg/cm^2 of C_2H_4 are also shown in Fig. 10 where the changes of absorption intensity on addition of perturbing gases are observed only in the region of Raman active and infra-inactive bands of C_2H_4 . Only the quadratic dependence of densities for the pressure-induced bands in mixtures with the perturbing gas permits us to distinguish the pressure-induced transitions from the weak bands of infra-active transitions.

The anomalous enhancement of absorption at around 1550 cm^{-1} was observed in the mixture of C_2H_4 and O_2 in which the Raman band of O_2 at 1555 cm^{-1} is induced in the compressed state and overlapped by the induced bands of C_2H_4 in this frequency region. It is necessary to subtract

Pressure-induced Infrared Absorption Spectra of Polyatomic Molecules

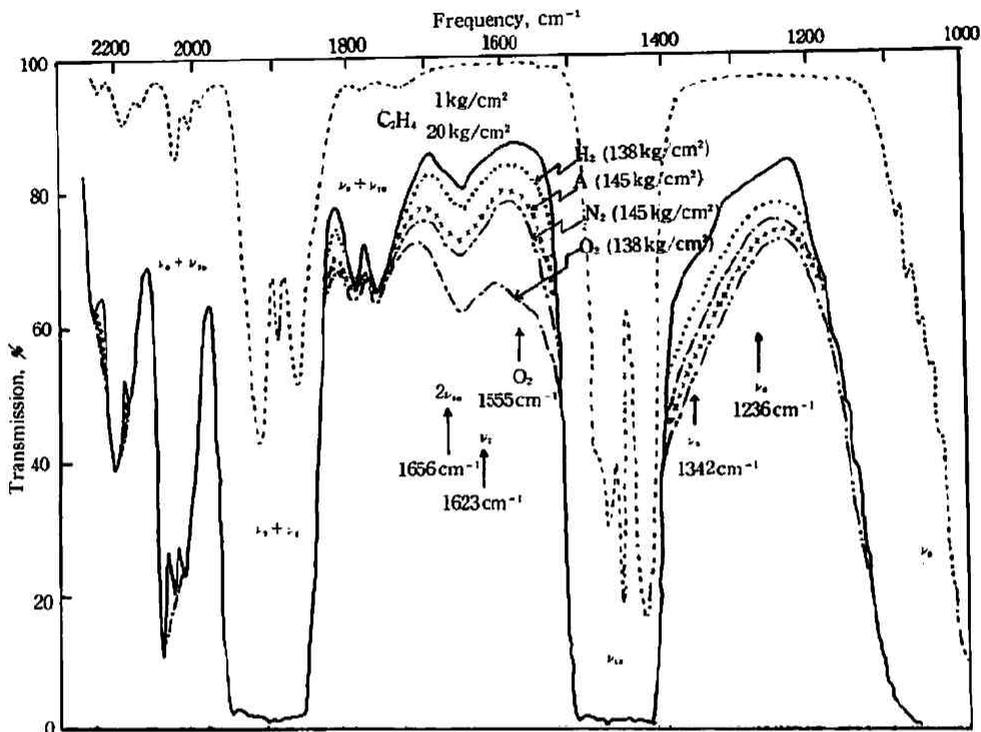


Fig. 10 Transmission curves of compressed C_2H_4 in the region from $1000\sim 2300\text{ cm}^{-1}$ showing the induced bands at $1236, 1342, 1623,$ and 1656 cm^{-1} , and the influence of addition of the perturbing gases on the C_2H_4 absorption in the same region

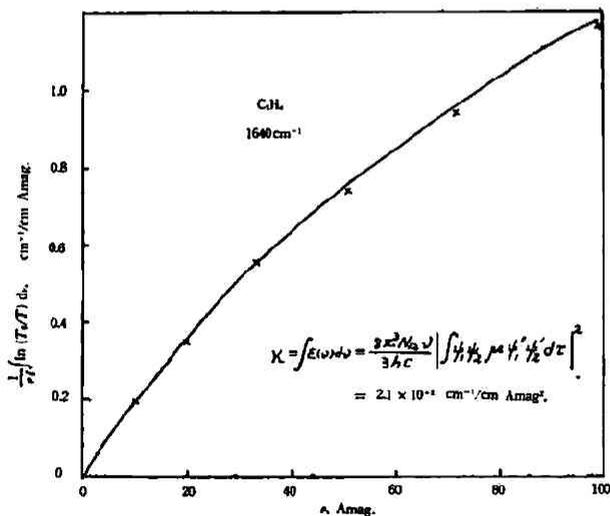


Fig. 11 The integrated absorption coefficients of the 1640 cm^{-1} band for unit Amagat density of C_2H_4 , as a function of density

from the total intensity of mixed gas the induced intensity due to O₂~O₂ collision in order to quantitatively estimate the pressure effect of the perturbing gases. As shown in Fig. 12, the

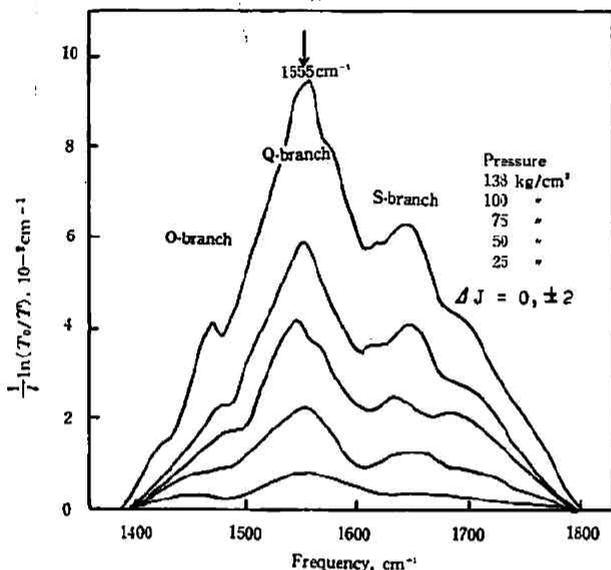


Fig. 12 The induced infrared absorption of compressed O₂

pressure-induced absorption of compressed O₂ which has three branches of O, P, and Q obeying the Raman selection rule, ΔJ=0, ±2, were observed at 1555cm⁻¹ as infra-active band and coincided with the data of Welsh *et al.*³¹⁾.

Assuming that the induced bands in compressed gases are due to binary collision pairs and that the ordinary Lambert-Beer law applies in the case of the mixture, we may write

$$T_m = T_0 \exp(-(\alpha_A \rho_A^2 + \alpha_M \rho_A \rho_P) l) \dots \dots \dots (1)$$

or

$$\epsilon_m(\nu) = \frac{1}{l} \ln \frac{T_0}{T_m} = \alpha_A \rho_A^2 + \alpha_M \rho_A \rho_P \dots \dots \dots (2)$$

For the integrated absorption, we have

$$\int \epsilon_m(\nu) d\nu = \kappa_A \rho_A^2 + \kappa_M \rho_A \rho_P \dots \dots \dots (3)$$

or

$$\frac{1}{\rho_A^2 l} \int \ln(T_0/T) d\nu = \kappa_A + \kappa_M \rho_P / \rho_A \dots \dots \dots (4)$$

where κ_A and κ_M are the quadratic integrated absorption coefficients, defined by κ_A = ∫ α_A dν and κ_M = ∫ α_M dν, due to absorbing molecule~absorbing molecule and absorbing molecule ~ perturbing molecule collisions respectively.

The variations of the integrated absorption coefficients are shown by the graph in Fig. 13, in which $\frac{1}{\rho_A^2 l} \int \ln(T_0/T) d\nu$, (cm⁻¹ per cm per Amagat³), are plotted as a function of the density

31) M. F. Crawford, H. L. Welsh, and J. L. Locke, *Phys. Rev.*, **75**, 1607 (1949)

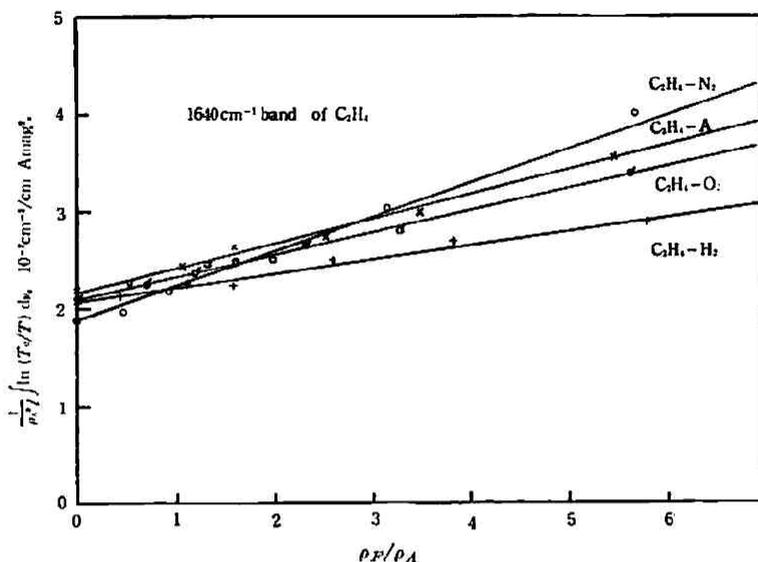


Fig. 13 The integrated absorption coefficient of 1640 cm^{-1} band of C_2H_4 mixtures containing the perturbing gases as a function of ρ_F/ρ_A

ratios, ρ_F/ρ_A , of the perturbing gases to the absorbing gas. The points on each graph appear to fall in a straight line over the whole range of density ratios confirming the Eq. (4). The values of κ_A and κ_M , as determined from intercepts and slopes of the straight lines in Fig. 13, are given in the Table.

Table The quadratic absorption coefficients of the 1640 cm^{-1} band of C_2H_4 for mixtures containing the perturbing gases

perturbing. gas	quadratic absorption coefficients ($\text{cm}^{-1}/\text{cm Amag}^2$)		κ_A/κ_M	molecular polarizability tensor (cc/mol)
	κ_A	κ_M		
N_2	1.9×10^{-2}	0.34×10^{-2}	5.6	1.70×10^{-25}
A	2.2×10^{-2}	0.25×10^{-2}	8.8	1.62×10^{-25}
O_2	2.1×10^{-2}	0.23×10^{-2}	9.2	1.56×10^{-25}
H_2	2.1×10^{-2}	0.14×10^{-2}	15.0	0.80×10^{-25}

Great accuracy cannot be claimed for the values of κ_A and κ_M since they are based in most cases on limited experimental data, and since the determination of κ_A in particular requires an extrapolation to zero density ratio. Nevertheless, the values of κ_A which indicate the quadratic absorption coefficient of C_2H_4 due to $\text{C}_2\text{H}_3 \sim \text{C}_2\text{H}_4$ binary collisions, are of the same order of magnitude. Thus, the integrated absorption coefficient for the 1640 cm^{-1} band of C_2H_4 , κ_A , can be determined as about $2.1 \times 10^{-2}\text{ cm}^{-1}$ per cm path length per Amag^2 of C_2H_4 , which is identical with the value obtained from Fig. 11. The ratio of the absorption coefficients κ_A and κ_M can be understood as showing the proportion of the effectiveness of a $\text{C}_2\text{H}_4 \sim \text{C}_2\text{H}_4$ to a $\text{C}_2\text{H}_4 \sim$ perturbing gas collision. These ratios are also given in the fourth column in the Table. From the data, it is known that the absorption coefficient of the 1640 cm^{-1} band due to $\text{C}_2\text{H}_4 \sim \text{C}_2\text{H}_4$ collisions is about 5.6 times as

large as the coefficient due to $C_2H_4 \sim N_2$ collisions. Furthermore the order of the magnitude of κ_M , $N_2 > A > O_2 > H_2$ is consistent with that of the molecular polarizability tensors of the perturbing gases listed the last column of the Table.

There is little doubt that the major factor responsible for the induced intensity of the absorbing molecule caused by collisions of heterogeneous molecules is the reaction field of the polarizable perturbing molecules in the neighbourhood, not the induction caused by the electric field given by the quadrupole moments of the perturbing molecules, known as the Mizushima effect³²⁾, since the effectiveness of A possessing no quadrupole moment in enhancing the induced absorption of the $C_2H_4 \sim A$ mixture is significantly observed.

IV Discussions

As is proved in the preceding chapter, the pressure-induced infrared absorption bands of polyatomic molecules with a center of symmetry have been successfully interpreted as arising from the dipole moment induced by the intermolecular forces in a cluster of interacting molecules. These pressure-induced effects observed in H_2 were interpreted theoretically by van Kranendonk^{19, 33)}, who showed that the induced bands are caused by three different mechanisms: (1) the overlap force due to the short range of the intermolecular forces, (2) the polarization of the absorbing molecule by the field of the quadrupole moment of the surrounding molecules (so-called Mizushima effect), (3) the polarization of the surrounding molecules by the quadrupole moment field of the absorbing molecule.

As is known from the experimental results, only the binary interactions called collision complex are of importance at moderate pressures up to a few hundred atmospheres. Thus the number of collisions per cm^3 per second is proportional to N^2 , if N is the number of molecules per cm^3 , and hence to the square of the density of the gas or to the product of the densities of both components in mixtures.

In order to explain the induced effect observed in the mixture of compressed gases by addition of the perturbing gas to the absorbing one, assuming that A is a centre-symmetrical absorbing molecule with the normal co-ordinate corresponding to one of the symmetrical vibrations, ν_A , and B is a gas of the same kind or a non-absorbed perturbing gas such as N_2 , then the induced dipole moment of the binary colliding pair at a short distance of molecules A and B is given by:

$$\mu = \mu_A + \mu_B = \alpha_A F_B + \alpha_B F_A \cdot \cdot \cdot \cdot \cdot \cdot \cdot (5)$$

in which μ_A is the moment induced in A by B , α_A is the polarizability tensor of A , and F_B is the electric field acting on A due to the induced charges in B . The Eq. (5) may be developed in a Taylor series for deviations ξ_A and ξ_B , varying periodically with the frequencies ν_A and ν_B respectively from equilibrium positions:

32) M. Mizushima, *Phys. Rev.*, **76**, 1268 (1949); **77**, 149, 150 (1950)

33) J. van Kranendonk, *Physica*, **23**, 825 (1957); **24**, 347 (1958)

$$\mu = \left(\alpha_A^0 + \frac{\partial \alpha_A}{\partial \xi_A} \xi_A + \dots \right) \left(F_B^0 + \frac{\partial F_B}{\partial \xi_B} \xi_B + \dots \right) + \dots$$

$$\dots + \left(\alpha_B^0 + \frac{\partial \alpha_B}{\partial \xi_B} \xi_B + \dots \right) \left(F_A^0 + \frac{\partial F_A}{\partial \xi_A} \xi_A + \dots \right) \dots \quad (6)$$

If the sum of all first order terms with ξ_A is not zero:

$$\alpha_B^0 \frac{\partial F_A}{\partial \xi_A} \xi_A + F_B^0 \frac{\partial \alpha_A}{\partial \xi_A} \xi_A \neq 0 \dots \quad (7)$$

then the induced infrared absorption occurs at the frequency ν_A .

In Eq. (7) the first term represents the perturbation-induced effect which is zero in first approximation, because the electric field due to the dipole contribution from A molecule does not change with a change of ξ_A accompanying the vibration ν_A . However the first one is not zero if considering the field due to the change in the quadrupole moment of A molecule. On the other hand the second term, as the ν_A is the Raman active vibration ($\frac{\partial \alpha_A}{\partial \xi_A} \neq 0$), should not be zero in the case of the presence of molecule B in surroundings.

Thus the resulting induction of dipole moments caused by the reaction field of the polarizable perturbing molecules in its neighbourhood should give rise to a break-down of the selection rules and the enhancement of the forbidden transitions in the infrared spectrum.

V Acknowledgements

The research described in this thesis was supervised by the late Professor R. Kiyama and by Professors W. Jono and R. Goto, to whom the author is greatly indebted for their many suggestions and helpful criticisms during the course of the work and the preparation of this paper. The research was carried out in the Laboratory of the Infrared Spectroscopy, Institute for Chemical Research, Kyoto University, with the approval of Professor R. Goto. The help given by and many discussions with Dr. J. Osugi have been of great benefit. The author wishes also to express his thanks to Dr. S. Minomura for his discussions and valuable assistance in the earlier phases of the experimental work.

This research was partially financed by the Grant in Aid for Fundamental Scientific Individual Research of the Ministry of Education.

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