The Review of Physical Chemistry of Japan Vol. 26 No. 1 (1956)

INDUCED INFRARED ABSORPTION IN GASEOUS ACETYLENE AT PRESSURE, II

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Introduction

In the infrared spectra for gases at pressure the induced absorption corresponding to the fundamental vibrational transition, which is forbidden by the infrared selection rules, are exhibited and a characteristic enhancement of the absorptions of pure gases is caused by the addition of foreign gases.[1-5] Such changes in the spectra are attributed to the dipole moments induced by intermolecular interaction. The author has observed such induced absorption of the totally symmetric fundamental ν_2 at 1974 cm^{-1} for acetylene at gaseous pressures up to 24 kg/cm^2 in the previous investigation[6] and the integrated absorption coefficient per unit Amagat density of acetylene has been found to increase linearly with increasing density. The author has investigated the pressure effect of foreign gases (oxygen and hydrogen) up to 20 kg/cm^2 on the infrared absorption of the fundamental ν_4 at 1627.5 cm^{-1} of ammonia and the integrated absorption coefficient has been found to increase with increasing density of the foreign gases.[7]

In the present investigation the induced ν_2-band at 1974 cm^{-1} of acetylene has been observed for the pure gas at pressures up to 14.3 kg/cm^2 and for the mixtures with foreign gases (nitrogen, argon and hydrogen) at pressures up to 100 kg/cm^2 at room and elevated temperatures. The effect of density and temperature on the integrated absorption coefficient and the distribution of intensity for the induced ν_2-band have been discussed.

Experimentals

Lithium fluoride crystal, 1.1 cm in thickness and 2.4 cm in diameter, was used as an optical window of the absorption cell tube for high pressure gases.[6] The free area for admitting the trasmission of light was 1.8 cm in diameter and the path length was 16.6 cm. The window was designed by Bridgman's unsupported area

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principle,[8] the polished surfaces of the window and its supporting plug for sealing pressure being cemented. It was used for gases at pressures up to 100 kg/cm^2 and the pressure applied on the supporting area was over 200 kg/cm^2, although the apparent elastic limit of lithium fluoride crystal cited in the literature[9] was 83 kg/cm^2. Throughout the present investigation only a small crack was produced in the supporting area, but no visible change in the free area, and the light transmission of the window was reproduced for measuring high pressure gases. The temperature was raised by an electric heater coiled on the cell tube.

The infrared spectrometer used was a D.42 Hilger instrument equipped with a NaCl prism and FT-16 Hilger vacuum thermopile. The source was a 30 watt Hilger Nernst lamp stabilized with an electric voltage regulator. The slit width was 50 cm^{-1}.

Gaseous acetylene from calcium carbide and water was refined by passing at the normal pressure through a dry mixture of $FeCl_3$, $HgCl_2$, copper acetate and acid clay and through 30∼40% aqueous solution of sodium hydroxide. The gas was found with aqueous solution of bromine to be in the purity of 99.6%, and by the spectral measurement in the frequency range of the induced ν_2-band of acetylene to show the 1812 and 2176 cm^{-1} bands contributed to the impurities. But the two bands disappeared by being preserved in compressed state with the dry refining mixture and sodium hydroxide for 48 hours and the optical pure acetylene can be prepared. Compressed nitrogen, argon and hydrogen from commercial bombs were used as the foreign gases. The Amagat densities of the gases under the experimental conditions for pressure × volume = 1 at 1 atm and 0°C were calculated from the pressure-volume-temperature data available in the literature[10]. It was assumed for the gaseous mixtures that the density of each gas could be calculated from its partial pressure.

Readings of the absorption, $\log_{10}(T_r/T)$, were taken at an interval of 0.02μ over the wavelength range 4 to 6μ. In this expression T_r and T are the intensities of light transmitted through hydrogen at 1 kg/cm^2 in the reference cell and gases under the various experimental conditions in the absorbing cell respectively and corrected for stray light and change of room temperature. The absorption for gaseous mixture was determined by subtracting the absorption of the foreign gas at its partial pressure.

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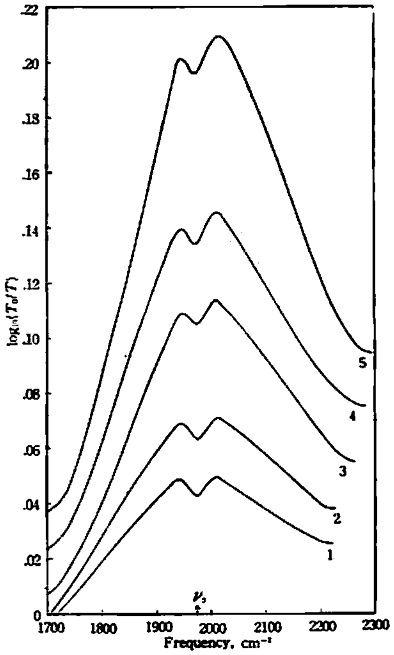

Fig. 1 The induced ν_2-band of gaseous acetylene at various pressures at 17°C

curve	
1	4.9 kg/cm²
2	6.6 "
3	9.3 "
4	11.2 "
5	14.3 "

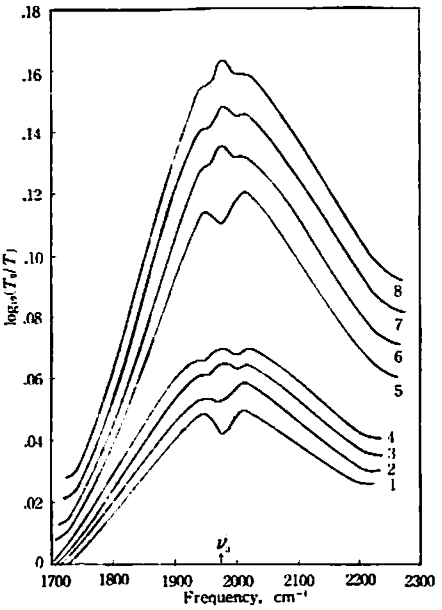

Fig. 2 The enhancement of the induced ν_2-band of acetylene by nitrogen at 17°C

	curve	
acetylene	1	4.6 kg/cm²
acetylene + nitrogen	2	50 "
	3	75 "
	4	100 "
acetylene	5	9.4 kg/cm²
acetylene + nitrogen	6	50 "
	7	75 "
	8	100 "

Experimental Results

For acetylene at pressures up to 14.3 kg/cm² the induced ν_2-band is shown in Fig. 1. In the figure the position of the band origin ν_0 (1974 cm^{-1}) is marked on the frequency axis. The band consists of two branches which indicate the maximum absorptions at 1944 and 2009 cm^{-1} respectively and overlaps in the bands tails with the 1328 cm^{-1} band ($\nu_4+\nu_5$) and the 2701.5 cm^{-1} band ($\nu_2+\nu_5$). At the partial pressures of 4.6 to 10.2 kg/cm² for mixtures of acetylene with foreign gases (nitrogen, argon and hydrogen) which were added up to the total pressures of 50, 75 and 100 kg/cm² the induced ν_2-band was observed. The absorption increases in all cases by the addition of the foreign gases. The enhancement is highest for nitrogen and lowest for hydrogen. The band for high pressure mixtures consists of three branches because of the remarkable enhancement of the absorption at the band origin. The spectra are shown only for an acetylene-nitrogen mixture in Fig. 2. The enhancement of the induced ν_2-band by increasing temperature was observed for acetylene and its mixtures with foreign gases at a certain density. For acetylene the complement between the two branches was caused by the enhancement of the absorption at the band origin, as shown in Fig. 3. For acetylene-foreign gas mixtures the enhancement of the absorption by increasing temperature is highest for nitrogen and lowest for hydrogen. The splitting of the three branches is more remarkable by the enhancement of absorption at the band origin in all cases. The spectra are shown only for an acetylene-nitrogen mixture in Fig. 4.

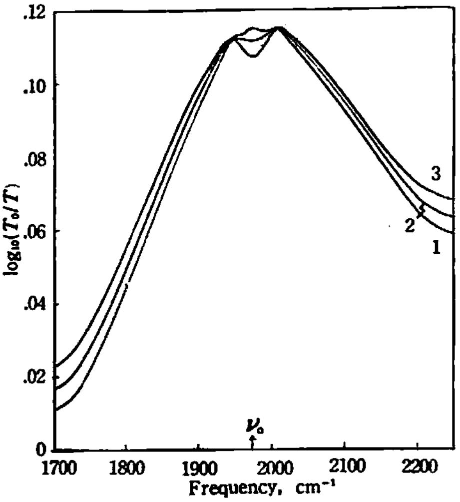

Fig. 3 The effect of temperature on the induced ν_2-band for acetylene

9.16 Amagat acetylene at 17°C
curve 1 at 17°C
2 at 36°C
3 at 62°C

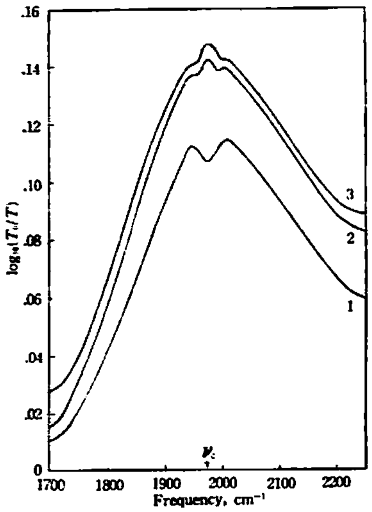

Fig. 4 The effect of temperature on the induced ν_2-band for acetylene-nitrogen mixture

curve 1 9.16 Amagat acetylene at 17°C
2 9.16 Amagat acetylene + 59.7 Amagat nitrogen at 17°C
3 9.16 Amagat acetylene + 59.7 Amagat nitrogen at 62°C

Discussion

The effect of density and temperature on the integrated absorption coefficient

Fig. 5 shows that the maximum absorption of the induced ν_2-band for acetylene, which is given by the absorption at 2009 cm^{-1} in Fig. 1, increases as the square of the density. Fig. 6 shows that the integrated absorption coefficient per unit Amagat density of acetylene $\int a d\nu$ (sec^{-1}/cm/Amagat C_2H_2), which is given by the area under the curve in Fig. 1, increases linearly to the density, ρ_a. The slope a_1 of the straight line in the diagram can be expressed by the following relation,

$$\int a d\nu = a_1(\rho_a - 2.43) + 1.5, \qquad (1)$$

where the constant 1.5 is the ordinate at a density of 2.43. The value of a_1 (sec^{-1}/cm/(Amagat $C_2H_2)^2$) is given in Table 1. Such a proportional relation between the integrated absorption coefficient and density coincides with the observations[2-3] for the induced fundamental absorption in homonuclear diatomic molecules. But at high

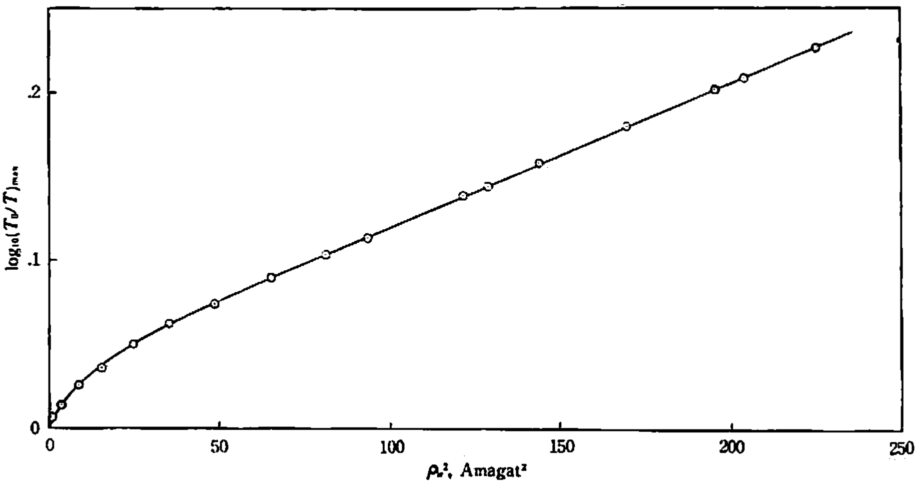

Fig. 5 The diagram of the maximum absorption of the induced ν_2-band for acetylene against the square of the density, ρ_a

density a plot of $\int a d\nu$ against the density has been found by Welsh *et al.*1) to show a curve indicating that the integrated absorption coefficient increases more rapidly than increasing density.

The increment of the integrated absorption coefficient per unit Amagat density of acetylene $\int (a_f - a_0) d\nu$ by the addition of foreign gases is not proportional to the densities of the foreign gases, ρ_f and the departure from linearity is significant in all cases. In this expression a_0 and a_f are the absorption coefficients for acetylene and acetylene-foreign gas mixtures respectively. As shown in Fig. 7, the quantity $1/\rho_f(a_f - a_0) d\nu$ (sec⁻¹/cm/Amagat C_2H_2/Amagat foreign gas) plotted against ρ_f is found to show a straight line in all cases. Therefore the increment of the integrated

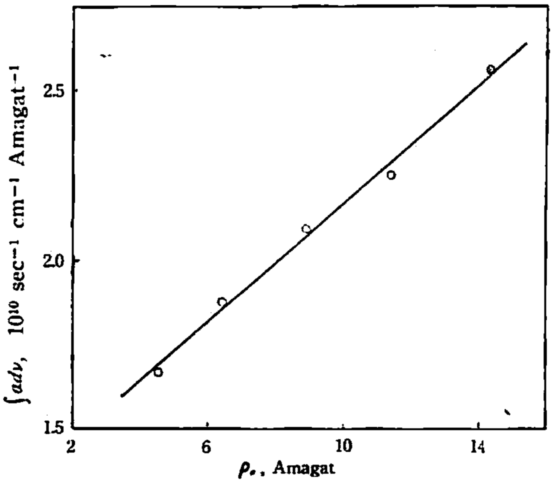

Fig. 6 The relation between the integrated absorption coefficient and the density of acetylene, ρ_a

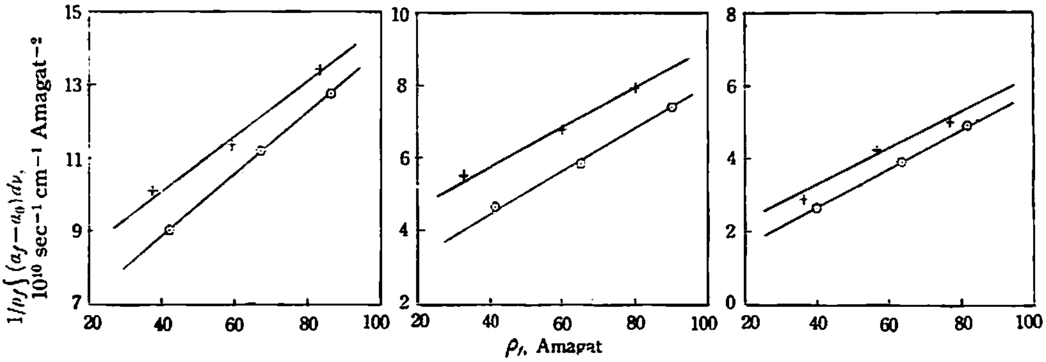

Fig. 7 The relation between the integrated absorption coefficient and the density of foreign gas, ρ_f

+9.38 Amagat acetylene +9.42 Amagat acetylene +8.68 Amagat acetylene
⊙4.60 Amagat acetylene ⊙4.43 Amagat acetylene ⊙4.21 Amagat acetylene

absorption coefficient per unit Amagat density of acetylene by the addition of the foreign gases is of the form

$$\int(a_f-a_0)d\nu=a_1\rho_f+a_2\rho_f^2, \tag{2}$$

wher a_1 and a_2 are the constants. a_1(sec^{-1}/cm/Amagat C_2H_2/Amagat foreign gas) is given by the ordinate which is extrapolated to the straight line in Fig. 7 to zero density of foreign gas and it is comparable with a_1 in Eq. (1). a_2(sec^{-1}/cm/Amagat C_2H_2/(Amagat foreign gas)^2) is given by the slope of the straight line in Fig. 7. The values of a_1 and a_2 determined for acetylene-foreign gas mixtures are summerized in Table I.

Table I Absorption coefficient of the induced ν_2-band for acetylene and the mixtures with foreign gases at room temperature 17 to 26°C

Perturbing gas	Density of acetylene Amagat	Absorption coefficient	
		a_1 10^{10} sec^{-1} cm^{-1} Amagat^{-2}	a_2 10^{10} sec^{-1} cm^{-1} Amagat^{-3}
Acetylene	4.72~14.30	87×10^{-3}	—
Nitrogen	9.38	7.0×10^{-3}	7.6×10^{-5}
	4.60	5.4×10^{-3}	8.5×10^{-5}
Argon	9.42	3.5×10^{-3}	5.5×10^{-5}
	4.43	2.0×10^{-3}	6.0×10^{-5}
Hydrogen	8.68	1.2×10^{-3}	5.1×10^{-5}
	4.21	0.5×10^{-3}	5.4×10^{-5}

The values of a_1 obtained above for nitrogen, argon and hydrogen are of the same order, but the values of a_2 are of the order of 10 times as much as those of the constants determined by Welsh *et al.*[1] for hydrogen and the mixtures with foreign gases. It is ascribed to the fact that the enhancement of the induced ν_2-band of acetylene by the addition of foreign gases is much higher than that of the induced fundamental absorption in hydrogen. The order of the magnitude of a_1 and a_2, $N_2>A>H_2$, coincides with that of the polarizability of molecules.

The absorption coefficient a_1 of the induced fundamental absorption for hydrogen has been found by Welsh *et al.* to decrease linearly with decreasing temperature. On the assumption of such proportional relation the increment of a_1 of the induced ν_2-band per Kelvin degree is determined for acetylene and the mixtures with foreign gases. Table II gives the increment of a_1 in Eq. (1) for acetylene and those of a_1 in Eq. (2) at a certain density of acetylene for the mixtures per Kelvin degree.

Table II Temperature coefficient of the absorption coefficient a_1 of the induced ν_2-band for acetylene and the mixtures with foreign gases

Perturbing gas	$\Delta a_1/\Delta T$ 10^{-10} sec^{-1} cm^{-1} Amagat^{-2} degree^{-1}
Acetylene	50×10^{-5} (290−309°K) 49×10^{-5} (290−335°K)
Acetylene + nitrogen	6.5×10^{-5} ″
Acetylene + argon	5.7×10^{-5} ″
Acetylene + hydrogen	4.2×10^{-5} ″

The value for acetylene obtained above is of the order of 130 times as much as that for hydrogen[1].

The distribution of intensity Since acetylene is a molecule of the same point group $D_{\infty h}$ to hydrogen, the rotational transitions of three branches of the induced ν_2-band for acetylene-foreign gas mixtures would coincide respectively with those of three components Q_P, Q_Q and Q_R of Q branch of the induced fundamental absorption for hydrogen-foreign gas mixtures obtained by Welsh *et al.* It has been assumed for the splitting of the Q branch that the relative kinetic energy of the absorbing molecule and its neighbours is altered by the absorption of the light quantum. The ν_2-band of acetylene corresponding to the totally symmetric ($\parallel$) vibrational transition of $D_{\infty h}$ molecules such as $\sum_g^+ \leftarrow \sum_g^+$, is Raman active and it consists of O, Q, and S branches corresponding to the rotational transitions $\Delta J=-2$, 0, and 2, respectively. Assuming that the induced absorption is caused by the distortion of the electronic charge distribution of the molecules during close two-body collisions,[1] acetylene molecules behave as rigid rotator with dipole moment perpendicular to the axis of rotation. Therefore, the branches obeying the infrared selection rules in addition to the Raman would be observed for the induced ν_2-band of acetylene. Since the infrared absorption band corresponding to the antisymmetric ($\perp$) vibrational transition of $D_{\infty h}$ molecules, such as $\sum_u^+ \leftarrow \sum_g^+$, consists of P and R branches without Q branch, the two branches at lower and higher frequency sides than the band origin ν_0 would correspond to the rotational transition $\Delta J=-1$ and 1, respectively. The enhancement of the absorption at the band origin by the addition of foreign gases and by increasing temperature would correspond to $\Delta J=0$. It is supported by the fact that the enhancement of the absorption corresponding to the rotational transition $\Delta J=0$ is caused by applying static electric field, which produces the same effect to the polarizability of molecules, on hydrogen at pressure[11)].

The integrated absorption coefficient per unit Amagat density of acetylene can be expressed by the following relation, assuming the induced dipol moment μ as the linear function of the normal coordinates, Q_i,[12)]

$$\int_i a d\nu \equiv A_i = \frac{N\pi}{3C}\left(\frac{\partial\mu}{\partial Q_i}\right)^2, \tag{3}$$

where N is the number of molecules per cm^3, and C the velocity of light. Q_i is linearly related to the internal coordinates, R_k, by the normalized transformation coefficient, $(L^{-1})_{ik}$,

$$Q_i = \sum_k (L^{-1})_{ik} R_k. \tag{4}$$

$(L^{-1})_{ik}$ is calculated by the kinetic energy matrix (**G**) and the potential energy matrix (**F**) for acetylene.

Using Eq. (4), the following relation is obtained,

$$\frac{\partial\mu}{\partial R_k} = \sum_i \left(\frac{\partial\mu}{\partial Q_i}\right)(L^{-1})_{ik}. \tag{5}$$

The rate of change of the induced dipole moment with C≡C bond length, R_2, is of the form from Eq. (5),

$$\frac{\partial\mu}{\partial R_2} = \left(\frac{\partial\mu}{\partial Q_1}\right)(L^{-1})_{12} + \left(\frac{\partial\mu}{\partial Q_2}\right)(L^{-1})_{22}. \tag{6}$$

$\partial\mu/\partial Q_2 = \pm 4.7$ (c. g. s. units) is obtained by substituting $A_2 = 2.1\times 14^{10}$ sec^{-1}/cm/Amagat C_2H_2 for 10 Amagat of acetylene and other physical constants in Eq. (1). A_1 is unknown, but assuming $A_1 = A_2$, $\partial\mu/\partial Q_1 = \partial\mu/\partial Q_2$ is obtained. Substituting $(L^{-1})_{12} = 1.2\times 10^{-12}$ and $(L^{-1})_{22} = 3.1\times 10^{-12}$ (c.g.s. units) in Eq. (6), $\partial\mu/\partial R_2 = \pm 0.2\times 10^{10}$ (c.g.s. units) is found. On the other hand, $\partial\mu/\partial R_1 = \pm 0.5 \sim 0.6\times 10^{10}$ (c. g. s. units), where R_1 is C—H bond length, is found for the ν_3-band (3287 cm^{-1}) of the antisymmetric CH (‖) vibration[13)] and for the ν_5-band (729 cm^{-1}) of the antisymmetric CH (⊥) vibration[14)]. The rate of change of the induced dipole moments with C≡C bond at 10 Amagat of acetylene is of the order comparable with that of dipole moments with C—H bond.

Welsh *et al.*[1)] have assumed with respect to the induced absorption in homonuclear diatomic molecules and the mixtures with foreign gases that dipole moments are caused by distortion of the electronic charge distribution of molecules during close

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two-body collisions. The number of collisions per unit volume and per unit time derived from the kinetic theory of gas is proportional to the square of density. It coincides with the fact that the integrated absorption coefficient per unit Amagat density of acetylene for the induced ν_2-band increases linearly with the density. The increment of the absorption coefficient by increasing temperature depends on the increment not only of the number of collisions, which is proportional to the square root of temperature, but also of the factor due to the relative kinetic energy of the colliding pair. The form of the dependence between the absorption coefficient and temperature by collisions is not decided. Vodar *et al.*[15] have assumed, with respect to the induced absorption in heteronuclear diatomic molecules by foreign gases, that dipole moments obeying the rotational selection rules $\Delta J=0,\pm2$, are caused by the reaction field of the polarizable foreign gas molecules in its neighbourhood. It supports that the enhancement of the absorption at the band origin of the induced ν_2-band of acetylene by the addition of foreign gases corresponds to the rotational transitions $\Delta J=0$. Kranendonk and Bird[16] have assumed two terms due to overlap and quadrapole forces in the calculation of the intensity of the induced absorption in hydrogen. Since quadrapole rotation-vibration spectrum of hydrogen consists of Q and S branches according to Herzberg,[17] the existence of quadrapole interaction is supposed from the enhancement of the absorption at the band origin (Q branch) of the induced ν_2-band of acetylene, which is molecule of the same point group $D_{\infty h}$ to hydrogen, by the addition of foreign gases.

The author has great pleasure in expressing his sincere thanks to Prof. Ryo Kiyama for his advice and encouragement throughout the course of this investigation. He is also indebted partly to the Department of Education for the Grant in Aid for Fundamental Scientific Individual Research (The Physico-Chemical Researches on Acetylene) shared out to Prof. Ryo Kiyama.

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