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MEASUREMENT OF INFRARED ABSORPTION INTENSITY FOR STRETCHING VIBRATION OF CARBON DISULFIDE MOLECULE*

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Introduction

The authors have previously reported, as for acetylene¹⁾ and ammonia²⁾, the influences of pressure on the infrared absorption in pure gases and gases mixed with infrared inactive gases. In this paper the absolute absorption intensity of the infrared active stretching fundamental vibration, ν_3-band (1523 cm^{-1}) of gaseous carbon disulfide molecule is reported.

According to Willson and Wells' extrapolation method³⁾, D. Z. Robinson⁴⁾ has already obtained the absolute absorption intensity of the ν_3-band of carbon disulfide gas by using an atmospheric air as broadening gas. Its value was 7560×10^{10} cm^{-1}sec^{-1} at N. T. P.. On the other hand, S. S. Penner and D. Weber⁵⁾ have mentioned that in the measurement of infrared intensity for pressurized carbon monoxide gas, the adsorption of the gas on the walls of stainless steel cell occurred, and so it was necessary to coat the absorption cell for some gas such as carbon monoxide.

In the present investigation, by using the steel cell uncoated or coated with trifluorochloroethylene resin film and the glass cell, the adsorption phenomena were compared with each other, and then the pressure effect for the apparent absorption intensity of the ν_3-band of carbon disulfide gas pressurized with nitrogen as broadening gas up to 1 kg/cm^2 and 24 kg/cm^2 was studied

Experimentals

The sample of carbon disulfide gas was obtained by the distillation from the com-

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* *This investigation has been done by K. Ozawa, being in the postgraduate course, under the direction of Prof. R. Kiyama.*

1) R. Kiyama, S. Minomura and K. Ozawa, *Proc. Japan Acad.*, **30**, 758 (1954)
   S. Minomura, *This Journal*, **24**, 49 (1955)
2) R. Kiyama, S. Minomura and K. Ozawa, *ibid.*, **24**, 56 (1955)
3) E. B. Willson and A. J. Wells, *J. Chem. Phys.*, **14**, 578 (1946)
4) David Z. Robinson, *ibid.*, **19**, 881 (1951)
5) S. S. Penner and D. Weber, *ibid.*, **19**, 807 (1951)

mercial reagent. The nitrogen as broadening gas was added from a commercial bomb.

The absorption cells used in this work were the glass cell 25.04 cm in path length which could be used for the gases at total pressure below 1 kg/cm² and the steel cell, described in the previous papers[1], 17.31 cm in path length, which was used for the high pressure gases in uncoating or coating with trifluorochloroethylene resin film.

The equivalent path length, *Le* (cm at N. T. P.), of carbon disulfide gas is varied from zero to 0.0164 cm at N. T. P.. (The partial pressures of carbon disulfide gas were in the range of 0 ~ 0.719 mmHg at 0°C for 17.31 cm path length.) The filling at low pressure of the carbon disulfide gas was performed by the dilute-mixing of the gas of several mmHg with nitrogen gas at the ratio of about 1 to 10 or 1 to 30 and the pressurizing of the gaseous mixture of several mmHg with nitrogen gas at total pressure of 1 kg/cm² or 24 kg/cm². The measurements were carried out within 10 minutes after the end of filling, over the frequency range of 1350 ~ 1700 cm^{-1} at room temperature of 20 ~ 22°C.

In order to ascertain the adsorption phenomena, the variations in the apparent absorption intensity with the lapse of time were measured by using uncoated steel cell at $Le = 0.0144$ cm at N.T.P. of carbon disulfide gas (the partial pressure of gas = 0.634 mmHg at 0°C).

Results and Considerations

The apparent absorption intensity, $\mathcal{B} = \int \ln(T_0/T)d\nu\,(\sec^{-1})$ of the ν_3-band as a function of the equivalent path length, *Le* (cm at N.T.P.), of carbon disulfide gas is shown in Fig. 1. Here T_0/T is a reciprocal of apparent fraction of light transmmited by the gas and ν is the frequency. In the figure, curve I is the data in the case of a glass cell and curve II is that of a steel cell. The values at total pressures of 1 kg/cm² and 24 kg/cm² in uncoated cell are marked with ⊙ and ● respectively, and the results obtained at cor-

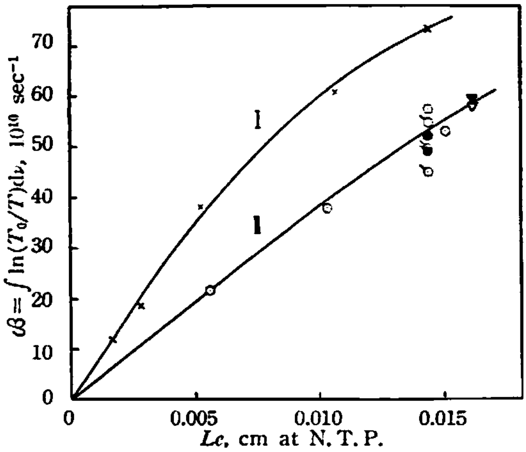

Fig. 1 The values of $\mathcal{B}$ against *Lc* of CS_2

Curve I: in the glass cell
× ; at total pressure of 1 kg/cm²

Curve II: in the steel cell
⊙ ; at total pressure of 1 kg/cm² } using uncoated cell
⊙ ; in the lapse of time at total pressure of 1 kg/cm² } using uncoated cell
● ; at total pressure of 24 kg/cm² } using uncoated cell
● ; in the lapse of time at total pressure of 24 kg/cm² } using uncoated cell

▽ ; at total pressure of 1 kg/cm² } using coated cell
▼ ; at total pressure of 24 kg/cm² } using coated cell

responding pressures in coated cell are shown with ▽ and ▼ respectively. At $Le=0.0144$ cm at N. T. P., the plots of $\mathcal{B}$ which bear the marks of ○ and ● are the values measured with the lapse of time after the end of filling at total pressurs of 1 kg/cm^2 and 24 kg/cm^2 respectively.

The values of $\mathcal{B}$ as a function of the time at total pressures of 1 kg/cm^2 and 24 kg/cm^2 are shown in Fig. 2. On the behavior of $\mathcal{B}$ with the lapse of time in the cases of the coated steel cell and the glass cell, in the coated cell the decrease of comparable order which was observed for the uncoated steel cell could be detected, while in the glass cell the change scarcely be observed. The above mentioned discrepancy of $\mathcal{B}$ between the glass cell and the steel cell and the decrease of $\mathcal{B}$ with the time suggest that carbon disulfide gas is adsorbed on the steel walls of cell. This adsorption was still observed in the same degree as in the case of the coated cell by trifluorochloroethylene resin film. The adsorption rate on the walls of steel cell, by reference to Fig. 2, was smaller at the pressurized state with nitrogen up to 24 kg/cm^2 than 1 kg/cm^2. In view of the fact that the values of $\mathcal{B}$ at total pressure of 24 kg/cm^2 is on the curve of 1 kg/cm^2, the broadening effect was sufficient below a total pressure of 1 kg/cm^2 for the equivalent path length range of carbon disulfide in this study.

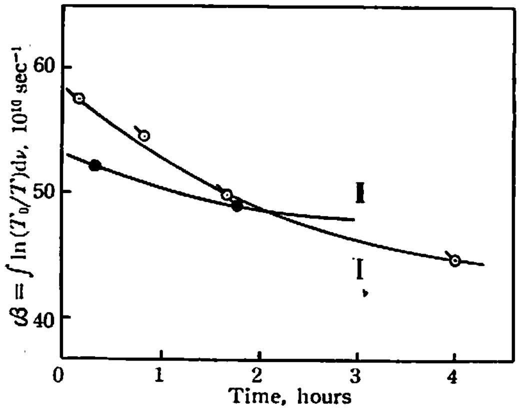

Fig. 2 The values of $\mathcal{B}$ against the time after the end of filling at total pressures of 1 kg/cm^2 (curve I) and 24 kg/cm^2 (curve II) for Le of CS_2 $=0.0144$ cm at N. T. P.

On the other hand, the absolute absorption intensity of band A can be esimated as the slope of the curve at $Le=0$ from the relation $A=\lim_{Le\to 0}\frac{\mathcal{B}}{Le}$. The absolute absorption intensities obtained in this study are listed in Table, making a comparison with the value of D. Z. Robinson.

Table Absolute absorption intensities of stretching vibration, ν_3 of CS_2 molecule (in cm^{-1} sec^{-1} at N. T. P.)

	Present study		Robinson
	using glass cell	using steel cell	
A	7450×10^{10}	4160×10^{10}	7560×10^{10}

The result on the glass cell is in good agreement with the value reported by D. Z. Robinson.

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