MEASUREMENT OF INFRARED INTENSITIES IN TETRAFLUOROETHYLENE

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Introduction

The infrared spectrum of tetrafluoroethylene gas between 500 and 3200 cm^{-1} has been investigated by Torkington and Thompson[1] firstly and two of the twelve fundamentals have been assigned. Not only the infrared spectrum, but also the Raman spectrum have been studied by Nielsen, Claassen and Smith[2] and all of the fundamental frequencies have been determined, although with some uncertainty for three frequencies obtained from combination bands, and the spectra have been interpreted in detail. However, the infrared intensity has not been previously investigated. The authors have performed the spectral measurement between 750 and 1500 cm^{-1} and obtained the absolute absorption intensities in the 1337, 1186 and 913 cm^{-1} bands by pressurizing tetrafluoroethylene gas at low partial pressures with nitrogen up to the total pressure of a maximum of 24 kg/cm^2, according to the previous method[3].

On the other hand, the mercury photosensitized reaction of tetrafluoroethylene gas has been studied by Atkinson[4], and the thermal reaction by Atkinson and Trenwith[5], Lacher, Tompkin and Park[6], and Duus[7], and the mechanism of decomposition and polymerization has been discussed. The authors have performed the spectral measurement between 750 and 1050 cm^{-1} for the gas reacted photochemically or thermally and observed the enhancement of the bands at 767, 807, 839, 853, 963, 983, 1037 and 1042 cm^{-1} which is attributed to the reaction products.

Experimental

Three samples of tetrafluoroethylene gas were used in this experiment. The photosensitized reaction was conducted by irradiating the gas at a pressure of 55 cm Hg in the presence of mercury vapour or in the absence of it with a 160-watt mercury lamp for 4 hours through a quartz window of the reaction vessel. The thermal reaction

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[1] P. Torkington and H. W. Thompson, *Trans. Farad. Soc.*, 41, 236 (1945)

[2] J. R. Nielsen, H. H. Claassen and D. C. Smith, *J. Chem. Phys.*, 18, 812 (1950)

[3] R. Kiyama, S. Minomura and K. Ozawa, *Proc. Japan Acad.*, 30, 758 (1954); *This Journal*, 24, 56 (1955)

[4] B. Atkinson, *J. Chem. Soc.*, 2684 (1952)

[5] B. Atkinson and A. B. Trenwith, *ibid.*, 2082 (1953)

[6] J. R. Racher, G. W. Tompkin and J. D. Park, *J. Am. Chem. Soc.*, 74, 1693 (1952)

[7] H. G. Duus, *Ind. Eng. Chem.*, 47, 1445 (1955)

was conducted by heating the gas at a pressure of 55 cm Hg at 400°C for 4 hours.

D-42 Hilger infrared spectrometer equipped with NaCl prism and FT-16 Hilger vacuum thermopile, and glass absorption cell with KCl window 25.18 cm long and steel cell 16.96 cm long were used for the spectral measurement. The slit width was 20 (glass cell) or 14 cm^{-1} (steel cell) between 1000 and 1500 cm^{-1} and 10 or 8 cm^{-1} between 750 and 1000 cm^{-1}.

The measurement was performed between 750 and 1500 cm^{-1} for tetrafluoroethylene gas at various pressures from 0.009 to a maximum of 5.53 cm Hg pressurized with nitrogen at the total pressure of 1, 12 or 24 kg/cm^2. The absolute absorption intensity was obtained for the 1337, 1186 and 913 cm^{-1} bands. The low partial pressure below 0.1 cm Hg was determined by the expansion method (46.8-fold). From the spectral measurement for the gas reacted photochemically or thermally a few reaction products were determined and the impurity contained in the tetrafluoroethylene gas discussed.

Result and Consideration

The spectra between 1100 and 1500 cm^{-1} for samples No. 1 (real line) and No. 2 (dotted line) of tetrafluoroethylene at five partial pressures pressurized with nitrogen at the total pressure of 1 kg/cm^2 are shown in Fig. 1. The 1186 cm^{-1} band with three sub-maxima (1181, 1186 and 1195 cm^{-1}) and the 1337 cm^{-1} band with a pair of maxima (1332 and 1342 cm^{-1}) have been interpreted as B_{3u} and B_{2u} fundamentals by Torkington

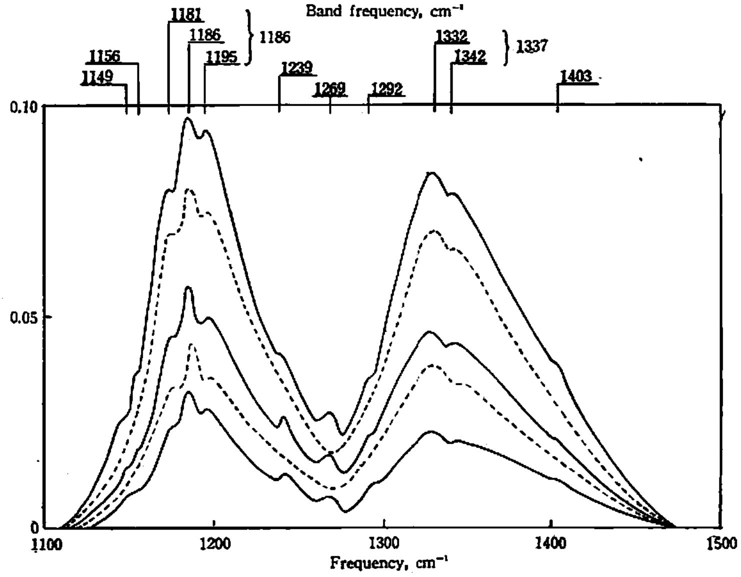

Fig. 1 The spectra between 1100 and 1500 cm^{-1} of tetrafluoroethylene gas pressurized with nitrogen at the total pressure of 1 km/cm^2

	sample No.	partial pressures of C_2F_4
real line	1	0.39, 0.19 and 0.09 mm Hg
dotted line	2	0.33 and 0.16 mm Hg

et al. and Nielsen *et al.* As the description of the band contour *A* and *B* types in Badger-Zumwalt's terminology[8] are given for both bands respectively from the separation of the maxima of the rotational branches. The very weak bands at 1149, 1156, 1239, 1269, 1292 and 1403 cm^{-1} are shown for sample No. 1, but not shown for sample No. 2. These band frequencies coincide with the spectrum of octafluorocyclobutane investigated by Claassen[9].

The apparent absorption in the 1186 and 1337 cm^{-1} bands non-pressurized or pressurized with nitrogen at 1 and 12 kg/cm^2 is plotted against the equivalent path length of tetrafluoroethylene in Fig. 2. The difference between in the intensities in samples No. 1 and No. 2 is not found. The enhancement of the apparent absorption which is interpreted as the broadening of the rotational structure is caused by pressurizing with nitrogen, but the difference between the effects at 1 and 12 kg/cm^2 is hardly observed. The comparison between the intensities non-pressured and pressurized estimated as the limiting slope at zero of the equivalent path length is made for both bands in the Table. The absolute absorption intensities are shown by the values in the condition pressurized.

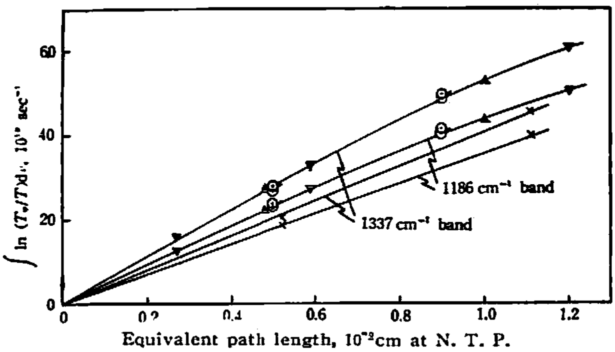

Fig. 2 Intensities in the 1186 and 1337 cm^{-1} bands

×	non-pressurized	sample No. 2	*glass cell*
▽	pressurized at 1 kg/cm^2	sample No. 1	
△	pressurized at 1 kg/cm^2	sample No. 2	
⊙	pressurized at 1 kg/cm^2	sample No. 2	*steel cell*
⊙	pressurized at 12 kg/cm^2	sample No. 2	

Table Intensities of 1186 and 1337 cm^{-1} bands
(in sec^{-1} cm^{-1} at N. T. P.)

Band / Condition	1186 cm^{-1}	1337 cm^{-1}
Non-pressurized	3611×10^{10}	4103×10^{10}
Pressurized at 1 or 12 kg/cm^2	4909×10^{10}	6010×10^{10}

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[8] R. M. Badger and L. R. Zumwalt, *J. Chem. Phys.*, 6, 711 (1938)
[9] H. H. Claassen, *ibid.*, 18, 543 (1950)

The spectra between 750 and 1000 cm^{-1} for samples No. 2 (real line) and No. 3 (dotted line) at five partial pressures are shown in Fig. 3. The 913 cm^{-1} band with

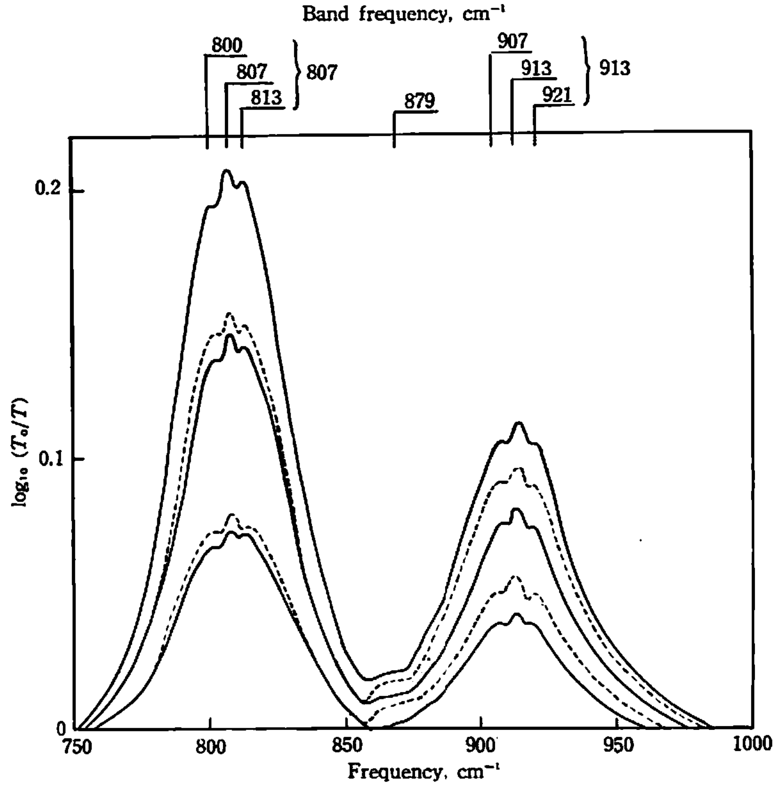

Fig. 3 The spectra between 750 and 1000cm^{-1} of tetrafluoroethylene gas

	sample No.	pressures of C_2F_4
real line	2	4.20, 2.82 and 1.38 cm Hg
dotted line	3	3.91 and 1.97 cm Hg

three sub-maxima (907, 913 and 921 cm^{-1}) has been interpreted as 407 cm^{-1} (B_{1u} fundamental) + 510 cm^{-1} (B_{2g} fundamental) = 917 cm^{-1} (B_{3u}) which has A type of contour by Nielsen *et al.* The very weak band at ~879 cm^{-1} is assigned as 510 cm^{-1} + 778 cm^{-1} (A_g fundamental) − 407 cm^{-1} = 881 cm^{-1} (B_{3u}) which has A type of contour, or 407 cm^{-1} + 2 × 245 cm^{-1} (B_{2u} fundamental) = 897 cm^{-1} (B_{1u}) which has C type of contour. The band with three sub-maxima is shown at 807 cm^{-1}, but the band for sample No. 3 is weaker than that for sample No. 2. The 807 cm^{-1} band is also shown in the spectrum observed by Torkington *et al.* and given A type as the description of the band contour, but it is several-fold weaker than the band observed by the authors. The band is not shown in the spectrum observed by Nielsen *et al.* For this reason, it is concluded that the 807 cm^{-1} band is due to an impurity contained in tetrafluoroethylene.

The spectra between 750 and 1050 cm^{-1} for sample No. 3 of tetrafluoroethylene and for the gas irradiated with a mercury lamp in the presence of mercury vapour or in the absence of it at a pressure of 3.91 cm Hg are shown in Fig. 4. The enhancement

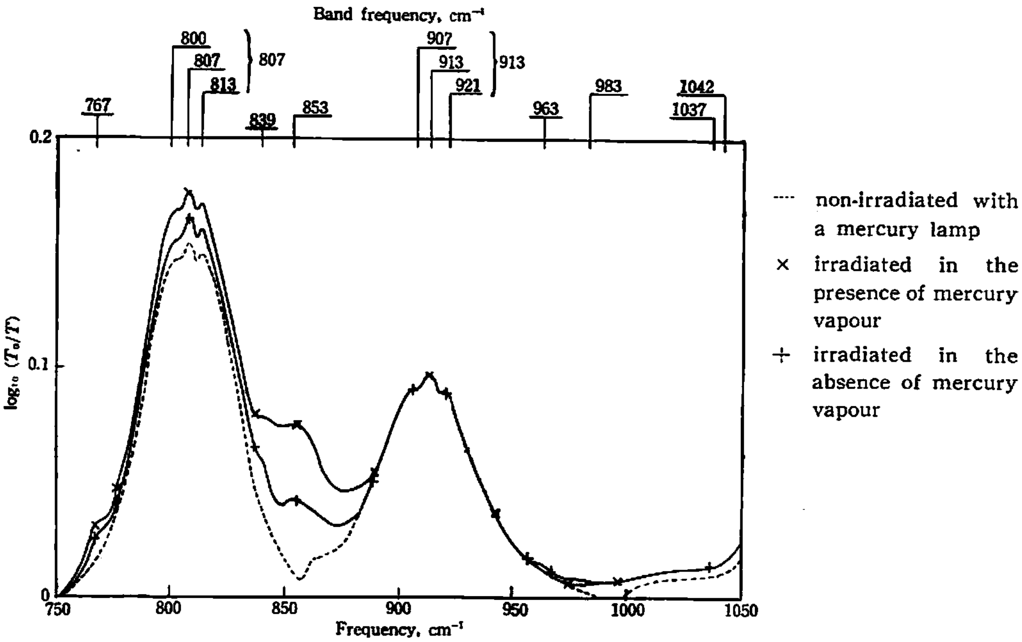

Fig. 4 The change of the spectrum between 750 and 1050 cm^{-1} of tetrafluoroethylene gas (sample No. 3) at the pressure of 3.91 cm Hg by the photosensitized reaction

of the bands which is attributed to the products of the photosensitized reaction is observed at 767, 807, 839, 853, 963, 983, 1037 and 1042 cm^{-1}, although the diminution of the 913 cm^{-1} band is scarcely found. The enhancement is more remarkable and the quantity of white powder formed on the wall of the reaction vessel increases in the presence of mercury vapour. The spectra between 750 and 1050 cm^{-1} for tetrafluoroethylene and for the gas heated at 400°C are shown in Fig. 5. The disappearance of the 913 cm^{-1} band and the enhancement of the 767, 807, 963, 983, 1037 and 1042 cm^{-1} bands are brought about by the thermal reaction. The band frequencies of 963, 983, 1037 and 1042 cm^{-1} coincide with the spectrum octafluorocyclobutane investigated by Claassen, and those of 767 and 1037 cm^{-1} coincide with the spectrum of hexafluoropropene investigated by Young and Murray$^{10)}$, and Nielsen and Claassen$^{11)}$. As the band frequencies of 839 and 853 cm^{-1} do not coincide with the spectra of two compounds above described and of octafluorobutene-1, -2, or isomer investigated by Brice *et al.*$^{12)}$, the bands will be ascribed to the reaction products of carbon number above 4.

The apparent absorption in the 913 and 807 cm^{-1} bands non-pressurized or pressurized

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10) E. G. Young and W. S. Murray, *J. Am. Chem. Soc.*, **70**, 2814 (1948)

11) J. R. Nielsen and H. H. Claassen, *J. Chem. Phys.*, **22**, 1916 (1952)

12) J. J. Brice, J. D. Lazerte, L. J. Halsand and W. H. Pearlson, *J. Am. Chem. Soc.*, **75**, 2698 (1953)

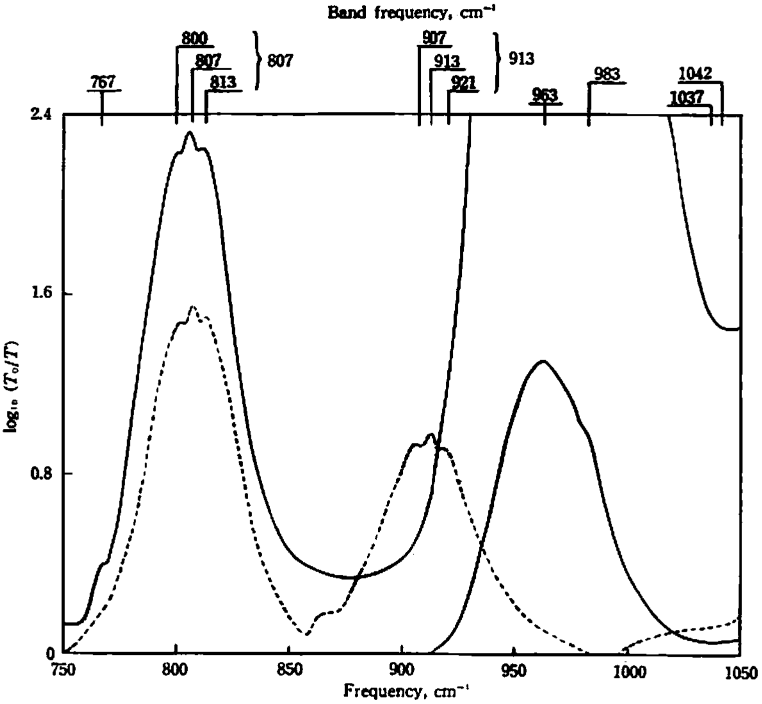

Fig. 5 The change of the spectrum between 750 and 1050 cm^{-1} of tetrafluoroethylene gas (sample No. 3) by the thermal reaction at 400°C

		pressures of C_2F_4
dotted line	non-heated	3.91 cm Hg
real line	heated	3.92 and 0.38 cm Hg

with nitrogen at 1 and 24 kg/cm^2 is plotted against the equivalent path length of tetrafluoroethylene in Fig. 6. Sample No. 2 has the same intensity for the 913 cm^{-1}

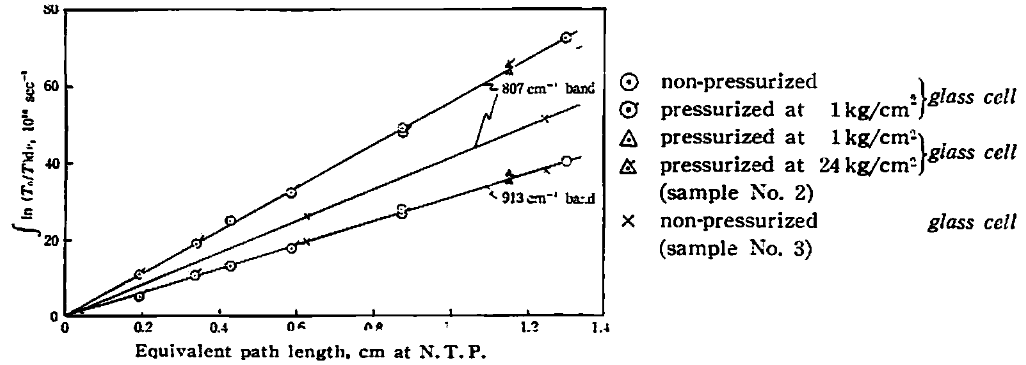

Fig. 6 Intensities in the 807 and 913 cm^{-1} bands

band, but is 1.5-fold stronger for the 807 cm^{-1} band in comparison with sample No. 3. The pressurizing effect with nitrogen is hardly found for both bands. The absolute absorption intensity in the 913 cm^{-1} band is $31 \times 10^{10} sec^{-1} cm^{-1}$ at N. T. P.

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