

Absorption Spectra Observed during the Flash Photolysis of Mixtures of Carbonyl Sulphide and Nitrogen Trifluoride

THE isothermal flash photolysis of mixtures of nitrogen trifluoride and carbonyl sulphide, and nitrogen trifluoride and carbon disulphide, has been investigated, as part of a study of the reactions of atomic sulphur with a series of volatile inorganic fluorides. The ground state (3P) sulphur atom, obtained on photolysing carbon disulphide with light of wavelength $< 2200 \text{ \AA}$, was found to be unreactive towards nitrogen trifluoride, while the excited (1D) atom, obtained on photolysing carbonyl sulphide, was found to react slowly.

Nitrogen trifluoride prepared by the electrolysis of molten ammonium hydrogen fluoride, carbonyl sulphide obtained from the reaction of concentrated sulphuric acid with a cold concentrated solution of potassium thiocyanate and carbon disulphide were purified by distillation *in vacuo* until their high pressure infra-red spectra showed the absence of impurities. The flash photolysis apparatus used was identical to that described elsewhere¹ and spectra were recorded on Ilford Q and Ilford 'Solochrome' plates using a Littrow type spectrograph (Hilger E.742).

Absorption spectra obtained at short delay times after a mixture of carbonyl sulphide, nitrogen trifluoride and argon (in the ratio 1 : 2 : 20) had been flash photolysed—using 5 mm mercury partial pressure of carbonyl sulphide—showed strong S_2 absorption which was observed to reach its maximum intensity at the shortest delay time used, that is, 15 μsec . In addition, a new complex series of weak bands was obtained in the region 3300–4200 \AA . As a result of the weak nature of these bands, it was difficult to obtain accurate measurements of the wavelengths. Attempts to improve the intensity of the system by varying the ratio of the mixture were unsuccessful. Table 1 lists the band head wavelengths and intensities (scale of ten)—all bands were degraded to the red.

It was not possible to fit all the bands into one vibrational scheme; however, they could be arranged in two systems, that is, 3286.5–3655.7 \AA and 3703.1–4189.4 \AA . The mean differences in the 3286.5 \AA system are 440 cm^{-1} and 644 cm^{-1} , while those of the 3703.1 \AA system are 412 cm^{-1} and 634 cm^{-1} . Photometric measurements on the strongest bands of the 3703.1 \AA system showed that it reached its maximum intensity at about 60–70 μsec delay, while the 3286.5 \AA system seemed to reach its maximum intensity at about 50–60 μsec . It was not possible, however, to carry out accurate photometry on the latter system because of its weak nature. Both systems decayed to zero intensity after 500 μsec .

Investigation of the spectral region 2200–2800 \AA when a mixture of carbonyl sulphide, nitrogen trifluoride and argon (in the ratio 1 : 2 : 25) was flash photolysed—using 2 mm mercury partial pressure of carbonyl sulphide—showed in addition to S_2 the presence of an appreciable concentration of NS in the reaction mixture even at 15 μsec delay. The NS reached maximum intensity at about 50 μsec and had disappeared by 250 μsec .

A range of mixtures each containing 5 mm mercury partial pressure of carbonyl sulphide but varying amounts

of nitrogen trifluoride (between 0 and 15 mm mercury) were flash photolysed isothermally, and spectra recorded at 80 μsec delay. Although the complex system of bands in the region 3300–4200 \AA were too weak for accurate photometry to be carried out, a visual examination of the strongest bands at 3979.5 \AA and 4008.0 \AA showed that their intensity at 80 μsec was increased by increasing the partial pressure of nitrogen trifluoride. The intensity of S_2 , however, was only decreased very slightly by increasing the partial pressure of nitrogen trifluoride.

All spectra obtained during the experiments were closely examined for the presence of NF_2 absorption² at 2600 \AA , but no banded absorption other than S_2 was observed in this region at any delay time.

An increase in the partial pressure of nitrogen trifluoride only resulted in slight suppression of the S_2 intensity, and because of this the reaction of S (1D) with nitrogen trifluoride must be slow compared with the reaction of S (1D) with carbonyl sulphide. The initial reaction of S (1D) with nitrogen trifluoride could result either in abstraction to give SF and NF_2 radicals or addition to give a "hot" SNF_3^* molecule which could then lose energy by decomposition to species such as SNF_2 and SNF. The absence of NF_2 absorption must result either from the slow nature of the abstraction reaction or from some fast reaction of NF_2 with carbonyl sulphide, S_2 or S (1D).

The new transient 3300–4200 \AA system could therefore either arise from unstable fluorides of nitrogen and sulphur (for example, NF_2 , NF, SF, SF_2 , SF_3) or from species such as SNF_3 , SNF_2 and SNF. The species SNF_3 and SNF have been reported to be relatively stable molecules although their ultra-violet spectra have not been reported in the literature. The ultra-violet spectrum of the NF_2 radical has been reported². From the nature of the 3300–4200 \AA bands it would seem likely that they belong either to two different transitions of a diatomic radical, or to a triatomic radical. They might therefore arise from one of the species SF, SF_2 or NF.

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¹ McGrath, W. D., and Morrow, T., *Trans. Farad. Soc.* (in the press).

² Johnson, F. A., and Colburn, C. B., *J. Amer. Chem. Soc.*, **83**, 3043 (1961).

Vibrational Spectrum of Liquid Crystalline Methyl Stearate

METHYL STEARATE, $\text{CH}_3(\text{CH}_2)_{16}\text{COOCH}_3$, occurs in the form of liquid crystals between 22° and 38° C (ref. 1). Optical examination of the textures exhibited by the mesophase indicated that the structure is smectic. The infra-red absorption spectra of this compound were reported by Jones *et al.*^{2,3} for thin films and also in carbon disulphide solution. We have investigated the spectrum of methyl stearate in the liquid crystalline state to ascertain the distinctive characteristics of the spectrum of this phase.

Fig. 1 shows the infra-red spectra of the liquid (a), liquid crystalline (b) and crystalline (c) phases recorded with a 'Zeiss UR-10' spectrophotometer. The important features of the spectrum of the liquid crystalline phase are summarized here. It was found that these features become increasingly pronounced the lower the temperature of the liquid crystal.

(1) Sharp peaks appear at 764, 785 and 813 cm^{-1} in the spectrum of the liquid crystal. These peaks are absent from the spectrum of the liquid, but present in that of the solid with greater intensity and sharpness.

(2) The peak at about 888 cm^{-1} is broad in the liquid, but becomes progressively sharper on passing from the liquid through the liquid crystalline to the solid phase.

Table 1. WAVELENGTHS OF BAND HEADS OBSERVED DURING THE FLASH PHOTOLYSIS OF MIXTURES OF CARBONYL SULPHIDE AND NITROGEN TRIFLUORIDE

Wavelength (in air) $\pm 0.2 \text{ \AA}$	Relative intensity (visual estimate)	Wavelength (in air) $\pm 0.2 \text{ \AA}$	Relative intensity (visual estimate)
3286.5	8	3703.1	7
3335.7	8	3761.6	7
3358.6	5	3818.5	3
3384.8	8	3854.7	7
3410.0	5	3878.4	5
3432.7	8	3916.5	10
3460.6	8	3942.8	5
3485.7	8	3950.2	3
3515.6	7	3979.5	10
3540.4	8	4008.0	10
3570.3	6	4042.0	3
3596.4	8	4083.0	5
3655.7	8	4145.3	3
		4189.4	4