149. Perfluoroalkyl Compounds of Nitrogen. Part II.* The Vibrational Assignment of Trifluoronitrosomethane.

By (Mrs.) J. Mason (Miss J. Banus) and J. Dunderdale.

The infrared spectrum of gaseous trifluoronitrosomethane has been examined in the region 3800—420 cm.$^{-1}$. Eight of the observed bands have been assigned to ten of the possible twelve fundamental vibrational modes. The frequency of a further fundamental vibration has been inferred from the evidence of combination bands and overtones. The spectrum gives no information as to the magnitude of the CN torsional frequency.

Improved methods of preparation and physical constants are given for the nitroso-compounds.

The preparation of perfluoronitrosoalkanes by the action of ultraviolet light on gaseous mixtures of the alkyl iodide and nitric oxide at just under atmospheric pressure, in the presence of mercury, was described in Part I * (where a historical account supplementing that given by Barr and Haszeldine [1] can be found). Spectroscopic examination of the products confirmed the suspicion, which was mentioned in the case of trifluoronitrosomethane, that they were still impure after repeated purifications with the methods then available (ampoule-to-ampoule distillation, and low-temperature filtration through a constriction in the case of trifluoronitrosomethane, and distillation with —78° reflux in the case of heptafluoro-1-nitrosopropane), and steps were taken to improve the products for spectroscopy and for determination of better physical constants.

First, the apparatus for irradiation was improved, so that the reaction time was reduced from 2—3 hr. to 15 min. [cf. 3—7 days (Haszeldine [2]), or 20—25 hr. (Barr and Haszeldine [1])], which improved the purity since the nitroso-compounds are unstable to light. It was found, too, that the reaction proceeds as well, if not better, in the absence of mercury. A globule of mercury was added in the earlier experiments to remove iodine, and it also removes dinitrogen tetroxide, the presence of which would reduce the yield of nitroso-compound considerably; however, mercury does this very inefficiently unless the vessel is shaken, in which case the yield is very poor, probably because of photo- or photo-sensitised reaction (the reaction with mercury is very slow in the dark †). But very little dinitrogen tetroxide is formed if the apparatus is leak-tight and if the irradiation time is short, so the mercury served no useful purpose, since the reaction is not reversible.

Next, a simple apparatus (see Fig. 1) was designed for the filtration of trifluoronitrosomethane at liquid-air temperatures, and from this it was possible to isolate a pure sample of the contaminant persisting after distillation. This gas had a molecular weight of 44, and sublimed at about —80°, and in the crystalline state resembled carbon dioxide; but it was insoluble in alkali, and infrared spectroscopy showed it to be nitrous oxide. This could be formed during the preparation of nitric oxide, or by the action of ultraviolet light on nitric oxide or trifluoronitrosomethane. Since nitrous oxide boils at —88·5° (m. p. —90·9°) and is very inert it is not surprising that a complete separation had not been effected.‡

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* Part I, *J.*, 1953, 3755.

† The experiment to which Barr and Haszeldine [1] take exception, in which trifluoronitrosomethane was completely decomposed by being shaken with mercury for 20 hr. (Banus [3]) was performed without exclusion of light. Its relevance is to the preparative method described by Haszeldine,[2] in which the fluoroiodide was shaken with excess of mercury and nitric oxide in a silica vessel with ultraviolet irradiation for 3—7 days, after which it is claimed that there was a 75% " yield " of trifluoronitrosomethane, the conversion of iodide into nitroso-compound being given as 10% (*i.e.*, a 10% yield of trifluoronitrosomethane, 13% of the iodide being consumed and 87% recovered). The static method of preparation is much superior to irradiation with shaking, and the omission of mercury altogether is best of all.

‡ *E.g.*, the spectrum (C.S. no. 82) deposited by Jander and Haszeldine [4] with the Chemical Society shows their specimen to contain the impurities, nitrous oxide and trifluoroiodomethane (the former probably still unsuspected by them, the latter acknowledged later [1]), which delayed our determination of good physical constants and infrared spectra.

[1] Barr and Haszeldine, *J.*, 1955, 1881.

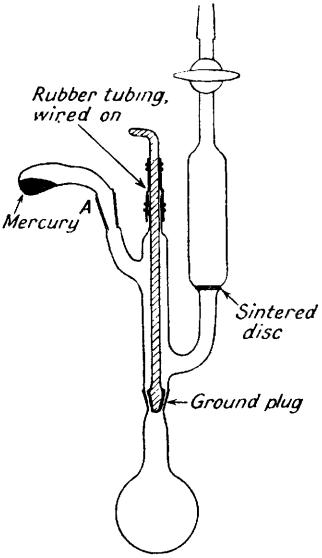
[2] Haszeldine, *J.*, 1953, 2075.

[3] Banus, *J.*, 1953, 3755.

[4] Jander and Haszeldine, *J.*, 1954, 912.

Purification of trifluoronitrosomethane by gas chromatography was therefore chosen. Nitrous oxide, of which the critical diameter, since it is linear, is presumably that of nitrogen (*ca.* 3 Å) would be expected to be sorbed more readily in intercrystalline channels than trifluoronitrosomethane, of which the critical diameter would be nearer 5 Å (cf. 4·94 for CF_3Cl, 4·84 for CHF_3, according to Barrer and Brook [5]). A separation was effected by the use of Doucil, a sodium aluminosilicate gel (J. Crosfield and Sons, Ltd.).

FIG. 1.



For gas chromatographic purposes, Doucil was ground, degassed *in vacuo* at 240° for 24 hr., and used as a sorbent at −80°. The nitrous oxide was adsorbed, probably on internal surfaces, as well as coloured impurities and about 5% of the trifluoronitrosomethane, probably on external surfaces. The trifluoronitrosomethane that passed through was spectroscopically pure, except for a trace of nitrous oxide. The sorbate was released at diminished pressure at room temperature.

Other sorbents may be more selective than Doucil, which has a wider distribution of pore sizes than, in particular, zeolites. However, chabazite, for example, appears to promote an unusual reactivity in the sorbate (*e.g.*, the dehydrohalogenation of chlorodifluoromethane [5]) and trifluoronitrosomethane is in any case a very reactive compound.* A recent report [8] (which appeared after the work described here was done) states that nitric oxide readily disproportionates on chabazite, which adsorbs it strongly, but not on Doucil, which adsorbs it less strongly.

Trifluoronitrosomethane was distilled through an improved low-temperature column, shielded from light and with −80° reflux. Vapour-pressure equations for the purified nitroso-compounds are :

$CF_3{\cdot}NO$: $\log p$ (mm.) $= 7{\cdot}690 - 907{\cdot}2/T$, giving b. p. (extrapolated) −84·5°, L_e 4133 cal., and Trouton coefficient 21·9.

$C_3F_7{\cdot}NO$: $\log p$ (mm.) $= 8{\cdot}077 - 1364{\cdot}2/T$, giving b. p. (extrapolated) −11·5°, L_e 6225 cal., and Trouton coefficient 23·8.

Assignment of the Vibrational Frequencies.—The trifluoronitrosomethane molecule is bent and so belongs to the symmetry point group C_s (cf. methanol [9]). Hence there should be twelve fundamental vibrations, all infrared and Raman active, eight of which will be symmetric with respect to the plane of symmetry (species A') and four antisymmetric (A''). However it is likely that twelve distinct frequencies will not in practice be observed. If the $C{\cdot}N{:}O$ group were linear, the molecule would belong to the point group C_{3v} and would have four singly and four doubly degenerate vibrations; the lowering of symmetry due to the non-linearity of this group will not necessarily cause any considerable splitting of the frequencies corresponding to the modes which would be degenerate in the more symmetrical case. In the present assignment there are two such frequencies which appear not to be split.

Table 1 lists the frequencies observed in the region 3800—420 cm.$^{-1}$ for gaseous

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* Barr and Haszeldine [1] describe as " completely fallacious " the statements by Banus [3] about the decomposition of perfluoronitrosoalkanes at room temperature. We re-affirm the reality of this decomposition : it is rapid in standard apparatus, accelerated by light, much slower in the dark, giving, *inter alia*, nitrous oxide, and the orange compound originally described by Jander and Haszeldine [6] as $(CF_3)(CF_3{\cdot}O)N{:}NO$ (but see Tarte [7]).

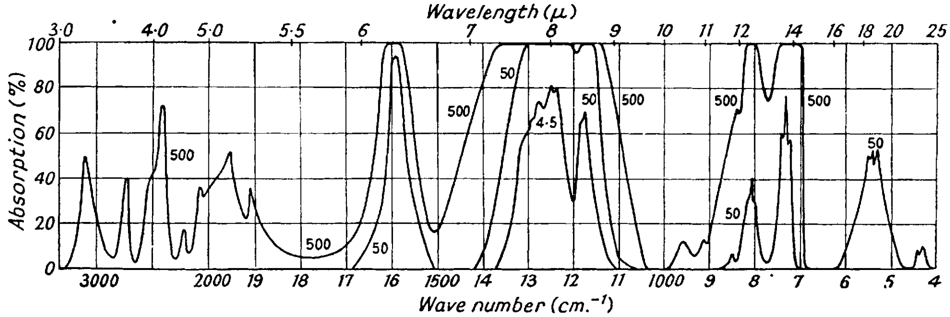
The difficulties of working with perfluoronitrosoalkanes, namely, low yields and impure products, have now largely been overcome.

[5] Barrer and Brook, *Trans. Faraday Soc.*, 1953, **49**, 940.
[6] Jander and Haszeldine, *J.*, 1954, 696.
[7] Tarte, *J. Chem. Phys.*, 1955, **23**, 979.
[8] Addison and Barrer, *J.*, 1955, 757.
[9] Herzberg, " Infrared and Raman Spectra," Van Nostrand, New York, 1945, p. 334.

trifluoronitrosomethane (Fig. 2). A spectrum of this compound was published [4] after these results were obtained. There is general agreement between this spectrum, which covered only the sodium chloride region, and ours, except that weak bands observed at *ca.* 2210, 1835, 1460, 1115, 1028, and 976 cm.$^{-1}$ were not found by us in pure samples, though we did observe bands at 1835, 1028, and 976 cm.$^{-1}$ in impure samples; the band at 2210 cm.$^{-1}$ in Jander and Haszeldine's spectrum appears to form a doublet with the band at 2227 cm.$^{-1}$, and is probably due to the presence of nitrous oxide.[10] This spectrum does not show bands observed by us at 903, 1237, and 1310 cm.$^{-1}$.

Four sets of values for the moments of inertia of trifluoronitrosomethane were calculated, from assumed molecular dimensions, and the symmetry factors ρ and S, described by Badger and Zumwalt [11] were then evaluated. From these the separation of the P and the R branch were calculated for each of the band types A, B, and C, which correspond to electric moments or changes of moment parallel to the A, B, and C axes (of least, intermediate, and greatest moment of inertia), respectively. The usefulness of this method was, however, limited, as the values of the P–R separation are rather similar for the different band types. Further, the A' vibrations will produce components of electric moment parallel to both the I_x and I_z axes (respectively parallel and perpendicular to the NO bond, in the CNO plane), so that such bands will be hybrids of types A and B.

FIG. 2. *Infrared spectrum of trifluoronitrosomethane.*



Numerals are gas pressures (mm.). There is a slight shoulder on the low-frequency side of the band centred at 438 cm.$^{-1}$, which the diagram does not show.

Inspection of the spectrum suggests that the bands at 1590, 1181, 811, 731, 542, and 438 cm.$^{-1}$ are fundamental frequencies, and that at least one and probably two others are in the region of strong absorption between 1300 and 1230 cm.$^{-1}$.

The assignment is based largely on considerations of the probable regions of absorption appropriate to the different modes of vibration, and the work of Edgell and May [12] and of Plyler and Acquista [13] on trifluoromethyl compounds has been very helpful in the assignment of the CF vibrations. Edgell and May suggest that the " natural " frequencies of the CF_3 group, if there is not much interaction with other modes, should lie near 700 and 1100 cm.$^{-1}$ for the symmetrical deformation and the symmetrical stretching mode, respectively, and near 520 and 1180 cm.$^{-1}$ for the corresponding degenerate vibrations. The bands in the trifluoronitrosomethane spectrum at 731 and 1181 cm.$^{-1}$ are therefore assigned to the A' deformation and stretching mode, respectively, and the band at 542 cm.$^{-1}$ to the antisymmetric A'' deformation vibration. The contours of these bands are similar to those of corresponding bands in trifluoronitromethane,[14] bromotrifluoromethane, and trifluoroiodomethane.[12, 13] The degree of splitting of each degenerate vibration of the CF_3 group in trifluoronitrosomethane, to give one A' and one A'' vibration, depends on the interaction between the two halves of the molecule. This interaction seems to be small

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[10] *Op. cit.*, p. 277.
[11] Badger and Zumwalt, *J. Chem. Phys.*, 1938, **6**, 711.
[12] Edgell and May, *ibid.*, 1954, **22**, 1808.
[13] Plyler and Acquista, *J. Res. Nat. Bur. Stand.*, 1952, **48**, 92.
[14] Part III, following paper.

for the A'' deformation, whose frequency is close to that of the same degenerate mode in trifluoro-nitro-, -bromo-, and -iodo-methane, so this frequency, 542 cm.$^{-1}$, has also been assigned to the A' deformation vibration.

Although Herzberg[9] considers that the internal modes of the CX_3 group are less likely to be split than those of the $CX_3{\cdot}YZ$ chain, in the present case the interaction seems to be large, for there is a considerable shift of the antisymmetrical CF stretching frequency from the " natural " frequency of 1180 cm.$^{-1}$ to the 1300—1230 cm.$^{-1}$ region. It is therefore proposed that both A' and A'' frequencies, derived from the E stretching of CF_3, lie within this range. If we choose the band centred at 1250 cm.$^{-1}$, with the shoulder at 1237 cm.$^{-1}$ as its P branch, for one of these vibrations, the other could be the band centred at 1298 cm.$^{-1}$, since this band does not appear to be a combination or overtone frequency. Of the two, the band at 1298 cm.$^{-1}$ has been chosen, rather arbitrarily, as the A'' mode, since the least symmetrical stretching vibration in CF_3 compounds usually has the higher frequency.

The only other CF frequencies to be assigned are those of the A' and A'' rocking modes. The band at 438 cm.$^{-1}$ has been chosen for both of these, in view of its similarity, in position and contour, to the band assigned to the CF_3 rocking vibration in other CF_3 compounds, especially trifluoroiodomethane.[12, 13]

Of the other fundamentals, the intense absorption centred at 1595 cm.$^{-1}$ can be immediately assigned, on grounds of frequency and intensity, to the NO stretching vibration, and similarly the band centred at 811 cm.$^{-1}$ to the CN stretching vibration (cf. 800—920 cm.$^{-1}$ for the lower nitroalkanes[15] and 944 cm.$^{-1}$ suggested for trichloronitrosomethane[16]). The contours of the bands at 811 and 1181 cm.$^{-1}$ are very similar, so that the former must also arise from an A' mode. Evidence from overtones and combination bands points to the existence of a band at about 405 cm.$^{-1}$, which has been assigned to the C·NO deformation mode. The CN torsional vibration will have a fundamental frequency of about 200 cm.$^{-1}$, but no indication of the magnitude can be found in the infrared spectrum.

The remaining frequencies have been assigned as binary or ternary (below and above 1930 cm.$^{-1}$ respectively) combination bands of the 11 fundamentals. The band at 1277 cm.$^{-1}$ is stronger than one would expect; this may be due to Fermi resonance between the overtone at 1273 cm.$^{-1}$ and the fundamental at 1298 cm.$^{-1}$. The intensity of the combination band at 1273 cm.$^{-1}$ may also be enhanced by the overlapping of the P and the R branch of the bands centred at 1298 and 1250 cm.$^{-1}$ respectively.

The fundamentals are listed in Table 2, with an approximate description of the motion involved, and a complete interpretation of the spectrum is given in Table 1. No complete assignment of the heptafluoro-1-nitrosopropane spectrum has been attempted, but the following fundamental frequencies can be picked out: NO antisymmetrical stretching and symmetric stretching at 1603 and 1310 cm.$^{-1}$, CN stretching at 855 cm.$^{-1}$, and CF bending at 746 cm.$^{-1}$.

The NO stretching frequency, 1595 cm.$^{-1}$ for trifluoronitrosomethane and 1603 for heptafluoro-1-nitrosopropane is of interest, since few values were available for *C*-nitroso-compounds before Tarte's work;[16] Bellamy[17] favoured the 1420—1310 cm.$^{-1}$ region for this vibration. Tarte lists the NO stretching frequencies for gaseous compounds, and these accord better with our findings; $CCl_3{\cdot}NO$ 1621; $R_2C(NO)Cl$ 1580—1600 (R = alkyl); $Me_3C{\cdot}NO$ 1574; PhNO *ca.* 1523 cm.$^{-1}$.

The NO stretching frequencies of nitrosoalkanes lie close to the corresponding values for the lower nitroalkanes, *i.e.*, 1590—1570 cm.$^{-1}$ (Smith *et al.*[15]), slightly below the value for trifluoronitromethane.[14] However, these are all well below the NO stretching frequencies for NOX compounds: NOBr 1801 (Burns *et al.*[18]); NOCl 1800 (Pulford *et al.*[19]); NOF 1844 (Woltz *et al.*[20]); NO 1876 cm.$^{-1}$ (Herzberg[21]). In the nitrosyl halides

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[15] Smith, Pan, and Nielsen, *J. Chem. Phys.*, 1950, **18**, 706.

[16] Tarte, *Bull. Soc. chim. belges*, 1954, **63**, 525.

[17] Bellamy, " The Infrared Spectra of Complex Molecules," Methuen, London, 1954, p. 254.

[18] Burns and Bernstein, *J. Chem. Phys.*, 1950, **18**, 1669.

[19] Pulford and Walsh, *Trans. Faraday Soc.*, 1951, **47**, 347; cf. ref. 18 and other workers.

[20] Woltz, Jones, and Nielsen, *J. Chem. Phys.*, 1952, **20**, 378.

[21] Herzberg, " The Spectra of Diatomic Molecules," Van Nostrand, New York, 1950, p. 62.

a shorter and stronger NO bond (as compared with the usual NO double bond) is correlated by Ketelaar and Palmer[22] with increased ionic character in the molecule, *i.e.*, a contribution from $X^-(N\vdots O)^+$. According to this interpretation the degree of ionic character falls in the series NOF > NOCl > NOBr > CF_3·NO, as one would expect.

TABLE 1. *Description and assignment of* CF_3·NO *spectrum.*

Band (cm.$^{-1}$) *			Assignment	
405 †		A'	NO deformation	
432	m	A' and A''	CF_3 rocking	
438				
444·5				
532	s	A' and A''	CF deformation	
542				
550				
725·8	s	A'	CF deformation	
731·2				
740·8				
803	s	A'	$2 \times 405 = 810$ CN stretching	A'
810·7				
816				
846·8	s		$405 + 438 = 843$	$A' + A''$
903	vw		?	
957	vw		$405 + 542 = 947$	$A' + A''$
1177	s	A'	CF stretching	
1181				
1187				
1237	s	A'	$438 + 811 = 1249$ CF stretching	$A' + A''$
1250				
—				
1277	s		$731 + 542 = 1273$	$A' + A''$
—	sh	A''	CF stretching	
1298				
1310				
1588	vs		$405 + 1181 = 1586$	A'
1595		A'	NO stretching	
1911	vw		$731 + 1181 = 1912$	A'
1955	vw		$405 + 731 + 811 = 1947$	A'
2080	vw		$542 + 731 + 811 = 2084$	$A' + A''$
2227	vw		N_2O trace	
2405	w		$811 + 1591 = 2402$	A'
2514	vw		$2 \times 1250 = 2500$; $542 + 731 + 1250 = 2523$	A' $A' + A''$
2741	vw		$405 + 731 + 1591 = 2727$	$A' + A''$
3104	vw		$731 + 2 \times 1181 = 3093$	A'

* w = weak; m = medium; s = strong; sh = shoulder; v = very.
† From combination bands.

TABLE 2. *Fundamental frequencies.* CF_3·NO, C_s.

		(cm.$^{-1}$)			(cm.$^{-1}$)
A'	NO stretching	1595 *	A''	CF stretching	1298
Infrared and Raman	CF stretching	1250 *	Infrared and Raman	CF deformation	542
active	CF stretching	1181	active	CF_3 rocking	438
In plane	CN stretching	810·7 *	Out of plane	CN torsion	*ca.* 200
	CF deformation	731·2 *			(conjectural)
	CF deformation	542			
	CF_3 rocking	438			
	NO deformation	405 †			

* Cf. Jander and Haszeldine.[4]

† From combination bands.

EXPERIMENTAL

*Trifluoronitrosomethane and Heptafluoro-*1-*nitrosopropane.*—Trifluoroiodomethane (or heptafluoro-1-iodopropane) and nitric oxide in 1 : 1 gas mixtures at just below atmospheric pressure were irradiated for 15 min. in a Vycor tube of 53 mm. outer diameter and 30 cm. length, enclosed in a spiral mercury lamp. The lamp consisted of 24 turns of 12 mm. silica tubing, the helix being 30 cm. long and 4 cm. in outer diameter, and gave almost pure 2537 Å radiation of high intensity (see Part I). The iodine deposits (large crystals) were not removed when the reaction vessel was emptied and refilled (from a vacuum-system) for another irradiation. With such a short reaction time, the process could readily be made continuous.

The crude product was bubbled through dilute alkali to remove oxides of nitrogen, carbon dioxide, and iodine, then distilled many times through a trap cooled in melting *iso*pentane (−160°). It was further purified at −196°, where it is still liquid, though viscous, and the contaminants are solid. The gas mixture was taken from the vacuum-system into the apparatus shown in the Figure through the joint at the top, and condensed at the liquid-nitrogen level above the sintered disc. Trifluoronitrosomethane runs down through the disc into the bulb at the bottom (the ground plug being raised out of its seating), and the residual perfluoronitrosomethane above the disc is pushed through with dry gaseous nitrogen. The ground plug is then wedged tight, the bath lowered until the liquid-nitrogen surface is below the plug, and mercury quickly dropped in (by rotation of the inner joint at *A* through 180°) to seal the plug. After this the white solid material above the plug can be distilled back into the vacuum-system. This

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[22] Ketelaar and Palmer, *J. Amer. Chem. Soc.*, 1937, **59**, 2629.

material is not completely separated from the deep blue trifluoronitrosomethane, which can be seen to wet it, but a completely colourless sample of the contaminants was obtained by exploiting the observation that this material sublimes at low temperatures without melting. The mixture was condensed into a small cold-finger, which was then warmed with the hand whereupon the liquid trifluoronitrosomethane, which wets the glass, evaporated, leaving some white solid for which the thermal contact with the glass was less good, identified as nitrous oxide (see p. 754). This sample was contaminated with trifluoro-nitro- and -iodo-methane, since in selecting the " purest " fractions of trifluoronitrosomethane the desired molecular weight of 99 had been used as criterion, and the impurities of higher molecular weight had balanced the nitrous oxide. A pure sample of nitrous oxide was isolated by distillation, and its identity confirmed tensimetrically (*M*, 44).

Gas-chromatographic Purification.—" Doucil " was ground and packed in a tube of 8 mm. outer diameter and 120 cm. length, bent 3 times so that it could be slid into a tubular furnace, and from there into a tubular container for solid carbon dioxide, which was crushed and moistened with ether. The sorbent was degassed *in vacuo* at 240° for 24 hr. and then held at $-80°$ while the slightly impure trifluoronitrosomethane was passed through at about 40 mm. pressure at a rate of about 500 c.c. (S.T.P.) per hr., shielded from light. The emerging gas was analytically pure, and was used for the spectroscopic studies. A small amount of material, which was not examined, was desorbed only at higher temperatures.

Infrared Spectra.—Infrared spectra were measured at various gas pressures in a 10 cm. cell with a Hilger D 209 spectrometer (single beam), with fluorite, rock salt, and potassium bromide prisms. It is estimated that the accuracy of measurement of sharp bands is 1 cm.$^{-1}$ at low frequencies and 5 cm.$^{-1}$ at high frequencies. Additional spectra were taken by courtesy of Prof. A. Albert of the Australian National University with a 12C single-beam Perkin-Elmer recording spectrophotometer.

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WILLIAM RAMSAY AND RALPH FORSTER LABORATORIES,
UNIVERSITY COLLEGE, LONDON, W.C.1.

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