776. *Perfluoroalkyl Compounds of Nitrogen. Part IV.*† *Electronic Absorption Spectra of Perfluoro-nitroso- and -nitro-alkanes, and Related Molecules.*

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The electronic absorption spectra of perfluoronitrosoalkanes are presented, and compared with those of other *C*-nitroso- and of typical *O*-nitroso- and *N*-nitroso-compounds, for the gas phase and for solution, and also with the electronic spectra of perfluoronitroalkanes.

The energy and intensity of the longest-wavelength bands in the spectra of $\mathrm{Y{-}\ddot{N}{=}O}$ molecules suggest that they are due to n_N–π^* transitions, and this is supported by the solvent effects. The consequences of the transition in the CF_3·NO molecule are discussed.

The visible band in the CF_3·NO spectrum shows complex, though relatively diffuse, vibrational structure, which is insensitive to temperature. Some of the regularities can be identified with vibrational modes, in particular the N=O stretching mode, which is strongly excited in the n_N–π^* absorption of almost all $\mathrm{Y{-}\ddot{N}{=}O}$ molecules. The ultraviolet band near 2700 Å for the perfluoronitrosoalkanes, 2800 Å for the nitro-compounds, is due to an n_O–π^* transition. At the minimum between this and the strong π–π^* absorption at shorter wavelengths there is weak vibrational structure in the perfluoronitrosoalkane spectra.

Perfluoronitrosoalkanes decompose by an excited-molecule mechanism when they absorb visible light, and by bond rupture when they absorb ultraviolet light.

The electronic spectra of trifluoronitrosomethane and perfluoronitrosopropane [1] have been measured, for the gases and their solutions, with a Cary recording spectrophotometer. The blue colour is due to weak absorption in the red, of *f*-value (oscillator strength) 0·0002, and there is no absorption between this band and a weaker one (*f*-value 0·00005) at 3200—2400 Å, beyond which the absorption rises steeply. The visible bands are drawn in Fig. 1, and extinction coefficients for the gases are given in Table 1.

Table 1.

		$\lambda_{max.}$			$\lambda_{min.}$	
	$\varepsilon_{max.}$	(Å)	(cm.$^{-1}$)	$\varepsilon_{min.}$	(Å)	(cm.$^{-1}$)
CF_3·NO	23·8	6925	(14,440)	17·3	6870	(14,560)
	21·3	6730	(14,860)			
	1·8	2695	(37,100)	0·8	2400	(41,670)
C_3F_7·NO	22·7	6840	(14,620)	—	—	—
	20·2	7075	(14,130)			
	2·1	2715	(36,830)	1·0	2410	(41,490)
CF_3·NO_2	11·2	2775	(36,030)	2·0	2395	(41,750)
C_3F_7·NO_2	41·6	2795	(35,770)	5·0	2367	(42,240)

The visible band in the spectrum of gaseous trifluoronitrosomethane shows considerable vibrational structure, and small inflections can be seen at and beyond the ultraviolet minimum; but for the larger molecule the vibrational bands are very poorly resolved.

Solvent Effects.—The effect of solvents on the visible band of trifluoronitrosomethane was examined for diagnostic purposes. Fig. 1 shows, as well as the spectrum of the gas, the visible absorption of solutions of the substance in *cyclo*hexane, chloroform, and water. The spectra of its solutions in 2N-hydrochloric acid and 100% sulphuric acid were similar to that of the aqueous solution.

The spectrum of *cyclo*hexane solutions was like that of the gas, though considerably less sharp, and the band had moved very slightly towards longer wavelengths. With

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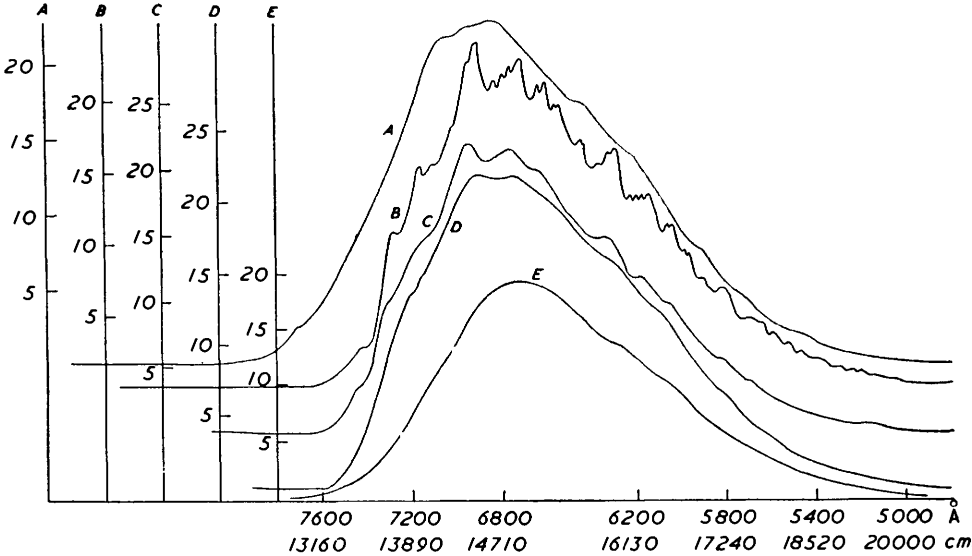
† Part III, *J.*, 1956, 759.

[1] Banus, *Nature*, 1953, **171**, 173; *J.*, 1953, 3755; Mason (Banus) and Dunderdale, *J.*, 1956, 754.

chloroform or ethyl ether as solvent the spectrum was less sharp again and the band had now moved very slightly, if at all, to wavelengths shorter relatively to the spectrum of the gas. However, the spectrum of the aqueous solution was very greatly smoothed out, so that almost no vibrational structure was discernible, and the band had moved about 300 cm.$^{-1}$ to wavelengths shorter relatively to the spectrum of the gas, and about 350 cm.$^{-1}$ relatively to the spectrum of the hydrocarbon solution. This blue shift is equivalent to an increase of about 1 kcal./mole in the energy of the transition, 37 kcal. at 13,000 cm.$^{-1}$.

FIG. 1. *Absorption spectra of gaseous perfluoronitrosopropane (A), and of trifluoronitrosomethane in the gaseous state (B) and in solution in (C)* cyclo*hexane, (D) chloroform, and (E) water.*



The blurring or obliteration of the vibrational structure and the blue shift, as one passes from non-polar to aqueous solutions,[2-7] indicate that electrostatic interaction with a polar solvent stabilises the ground state of the molecule, relative to the excited state at the instant of formation, so that more energy is required for the transition. This is a consequence of the Franck–Condon principle when there is a change in size or of charge distribution of the molecule on excitation, since the excited solute molecule has to be formed inside a grouping of solvent molecules that is appropriate to the ground state.

We should expect trifluoronitrosomethane to form hydrogen bonds in hydroxylic solvents, and to participate in weaker non-specific interactions in polar non-hydroxylic solvents. The change in dimensions of the molecule on excitation must be small, from the shape and small extent of the spectrum and its insensitivity to temperature (see below). However there should be some change in charge distribution in the transition; the low oscillator strength suggests, in the present case, that the overlap between the ground-state and the excited-state orbitals is small.

The stabilisation of the electronic ground state of trifluoronitrosomethane in aqueous solution (about 1 kcal./mole) is less than the usual energy of hydrogen bonds from water to nitrogen, but the presence of fluorine and oxygen considerably reduces the basicity of the nitrogen atom; that it is not protonated in 100% sulphuric acid is shown by the

[2] Kasha, *Discuss. Faraday Soc.*, 1950, **9**, 14.
[3] Brealey and Kasha, *J. Amer. Chem. Soc.*, 1955, **77**, 4462.
[4] McConnell, *J. Chem. Phys.*, 1952, **20**, 700.
[5] Platt, *J. Opt. Soc. Amer.*, 1953, **43**, 252.
[6] Bayliss and McRae, *J. Phys. Chem.*, 1954, **58**, 1002, 1006.
[7] Halverson and Hirt, *J. Chem. Phys.*, 1949, **17**, 1165; 1951, **19**, 711.

persistence of the nitroso-absorption. Thus the hydrogen bond will be relatively weak, and the association constant of the hydrogen bonding[3] low.

It has been suggested[6] that the blurring of the vibrational structure of n–π^* bands for molecules in polar solutions is a consequence of the uncertainty principle, as the relaxation of the solvent cage interferes with the quantisation of the vibrations of the excited solute molecule. However, such a dynamic picture contravenes the Franck–Condon principle for an absorbing molecule. It is the variation of the polar environment that causes the spread in the sizes of the vibrational quanta absorbed at the same time as the electronic (0,0) quantum.

The small red shift in the spectrum of the hydrocarbon solution compared with the vapour spectrum corresponds with Bayliss's polarisation red-shift.[6]

Solvent Effects on the Long-wavelength Electronic Spectra of Other $\mathrm{Y{-}\dot{N}{=}O}$ *Molecules.*—The only other molecules of this type for which solution spectra of the low-energy bands have been determined are alkyl nitrites, nitrous acid, nitrite ion, and dialkyl nitrosamines. Specimen solvent shifts are given in Table 2. For nitrous acid and alkyl nitrites the vibrational structure is only slightly diminished in solution in non-polar or in polar solvents, and the solvent shifts refer to the presumed origin, or if a range is given the first figure refers to the presumed origin, and the second to the band as a whole. However, for trifluoronitrosomethane, nitrite ion, and alkylnitrosamines, where the vibrational structure is considerably reduced for solutions in non-polar solvents, and almost obliterated when the compound is in aqueous solution, so that the origin is no longer discernible, the shifts are those of the band maximum, or of the band as a whole. The experimental error may be about 100 cm.$^{-1}$.

TABLE 2. *Solvent shifts* (*cm.*$^{-1}$) *in the low-energy bands of* $\mathrm{Y{-}\dot{N}{=}O}$ *molecules.*

	Red shifts		Blue shifts	
$CF_3{\cdot}NO$ ……	Gas—HC *	70	HC—$CHCl_3$	100
			HC—ether	100
			HC—water	350
HO·NO ……	Gas[a,b]—ether[e]	400—600	Ether—water[a,e]	300—200
			Water—N-$HClO_4$[c,d]	100—400
			N-$HClO_4$—(N-$HClO_4$ + 6N-$NaClO_4$[c])	100
MeO·NO ……	Gas—HC	150	HC—MeOH	0—100
	HC—DMF †	50—100		
$O{\cdot}NO^-$	—		Crystal[f]—EtOH	350
(as $NaNO_2$)			EtOH—water	150
$Me_2N{\cdot}NO$[g,h]	—		Gas—HC	150
			HC—ether	150
			HC—$CHCl_3$	700
			HC—EtOH	1200
			HC—water	2450 (7 kcal./mole)

* HC = hydrocarbon. † DMF = dimethylformamide.[g]

[a] Tarte, *Bull. Soc. chim. belges*, 1950, **59**, 365. [b] Porter, *J. Chem. Phys.*, 1951, **19**, 1278. [c] Bunton and Stedman, unpublished results. [d] Singer and Vamplew, *J.*, 1956, 3972; Longstaff and Singer, *J.*, 1954, 2604. [e] Kortum, *Z. phys. Chem.*, 1939, **43**, *B*, 418. [f] Sidman, *J. Amer. Chem. Soc.*, 1956, **78**, 2911. [g] Haszeldine and Mattinson, *J.*, 1955, 4172. [h] Thompson and Purkis, *Trans. Faraday Soc.*, 1936, **32**, 674, 1466.

Table 2 shows, in general, that with increase in the polar character of the solution (*e.g.*, the dielectric constant of the organic solvent, or the ionic strength of the aqueous solution) the absorption band shifts to the blue as the vibrational structure disappears. These solvent effects are very striking in the case of dialkylnitrosamines, and evident for nitrous acid and trifluoronitrosomethane, but small for alkyl nitrites (for which, however, no aqueous-solution spectrum has been recorded).

The Nature of the Transition.—All the evidence points to an n_N–π^* transition[2,5,8] as the result of the absorption of red light by trifluoronitrosomethane; one of the (nearly) non-bonding electrons of the nitrogen is excited to an anti-bonding π (*i.e.*, π^*)-orbital.

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[8] (*a*) Orgel, *J.*, 1953, 1276; Nakamoto and Suzuki, *J. Chem. Phys.*, 1952, **20**, 1971; (*b*) Nakamoto and Rundle, *J. Amer. Chem. Soc.*, 1956, **78**, 1116.

This will be the transition requiring the least energy, since the n_N electrons are the most loosely held, and the lowest unoccupied orbital is π^*. More energy will be required for the π–π^* transitions, and also for the n–π^* transitions from oxygen [9] (since this is more electronegative than nitrogen) and these give rise to ultraviolet absorption.

The distinction can also be made on grounds of intensity. Since such an n–π^* transition is allowed by symmetry, the low oscillator strength (though much higher than singlet–triplet f-values for atoms of this weight [5, 10]) shows that the transition is almost "overlap forbidden." Intensities of the symmetry-allowed π–π^* bands are much higher (f-values 0·1—1·0) owing to the much better overlap between the ground-state and the excited-state wave-functions.

As is evident from the spectrum, the change in molecular dimensions on excitation is small; this is a feature of n–π^* transitions, since bonding electrons are not involved. Finally, the solvent effects are appropriate to the excitation of an n-electron, for which their diagnostic use has been recommended.[2–7] Similar solvent effects may be observed in π–π^* transitions for heteronuclear systems such as N=O, or in symmetry-forbidden π–π^* transitions,[4] but in the present case the distinction is clear on grounds of intensity, energy, and the symmetry of the molecule, and is supported by the solvent effects.

The visible and near ultraviolet (*i.e.*, low-energy) and low-intensity absorption of alkyl nitrites, nitrite ion, dialkylnitrosamines, nitrosyl halides, azo-, azoxy-, and diazo-compounds, azides, (aromatic) oximes, and azines [7, 11] are due to similar n–π^* transitions from nitrogen.

The Band Origin.—An attempt was made to find the band origin in the visible spectrum of trifluoronitrosomethane, from the effect of changes of temperature on the long-wavelength bands. The gas was examined at +100°, −80° (carbon dioxide–ether), and −111·6° (melting carbon disulphide); at −183° a solution in mixed hydrocarbons was used since trifluoronitrosomethane is not volatile enough for a vapour spectrum to be measurable at this temperature with reasonable path-lengths.

Slight inflections at 13,200 cm.$^{-1}$ and possibly at 12,900 cm.$^{-1}$ are visible in spectra taken at 760 mm. and room temperature in a 10 cm. cell. These inflections are slightly enhanced at +100°, but persist at −80° and at −112°. They could not be discerned in the spectra taken at −183° of hydrocarbon glassy solutions, but then much of the vibrational detail was missing here, just as in the hydrocarbon solutions at room temperature; there was no sharpening of the bands at low temperatures.

The effective origin must then be taken to be at 13,200, possibly at 12,900 cm.$^{-1}$, or less probably at longer wavelengths.

Since one would expect the band origin to be near the band maximum if the change of molecular dimensions in the transition is very small (although it may not, in this case, be *very* small), the possibility was considered that these long-wavelength bands may belong to another band system, as has been suggested for the α-chloronitroso-compounds.[12] Elkins and Kuhn [13] considered that the 3200—4000 Å spectrum of alkyl nitrites arises from two different electronic transitions, for they found the circular dichroism and anisotropic factor of optically active nitrites to vary across the spectrum. According to Tarte such a hypothesis would also explain anomalies of the vibrational structure in spectra of alkyl nitrites [14] and nitrous acid.[15]

However, all such molecules can exist as rotational isomers, and hydrogen bonding in the *cis*-form would further alter the electronic distribution. No such possibility exists for trifluoronitrosomethane, and the only other transition that could give rise to absorption

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[9] McMurry, *J. Chem. Phys.*, 1941, **9**, 231, 241.

[10] McClure, *ibid.*, 1949, **17**, 905.

[11] Rush and Sponer, *ibid.*, 1952, **20**, 1847; Orgel, *J.*, 1955, 121; Mason, *J.*, 1955, 2336.

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

[13] Elkins and Kuhn, *J. Amer. Chem. Soc.*, 1935, **57**, 296.

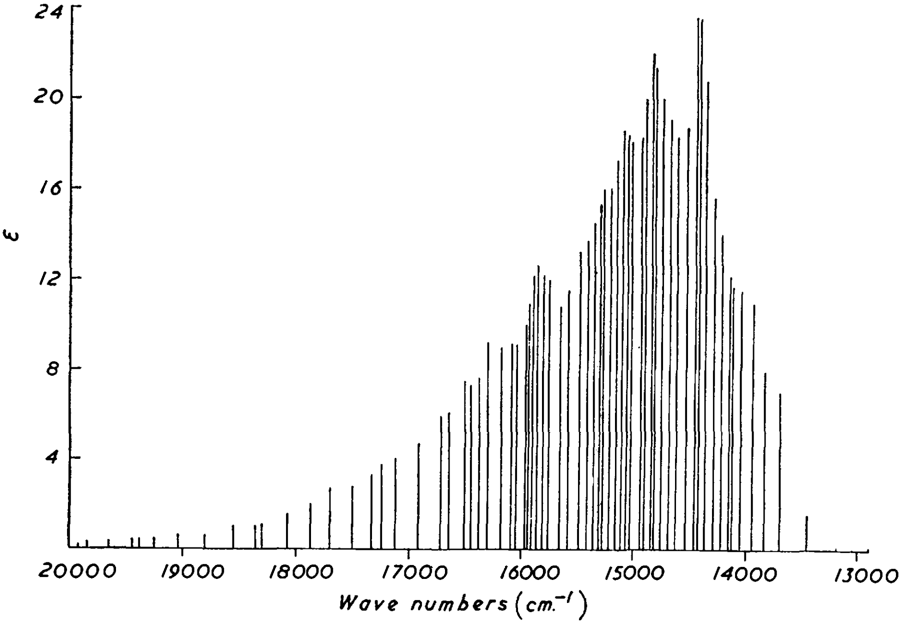
[14] Tarte, *J. Chem. Phys.*, 1952, **20**, 1570.

[15] D'Or and Tarte, *Bull. Soc. roy. Sci. Liège*, 1951, **12**, 685.

at these long wavelengths is the singlet–triplet n–π^*, which may well absorb in the neighbourhood of the singlet–singlet banb.[10, 16] However, the intensity of the band due to this multiplicity-forbidden transition should be too small to be observed with the apparatus available. Spectra of trifluoronitrosomethane in solution in di-iodomethane were examined in case the atomic-number effect [17] might enhance the intercombination sufficiently to make it visible, but no change in the spectrum could be seen. In fact, the vibrational structure was much more blurred than for chloroform solutions, so that very small changes could not have been discerned.

The Vibrational Structure.—The CNO chain in trifluoronitrosomethane is bent in the electronic ground state, so that it belongs to the symmetry group C_s, possessing only a plane of symmetry. The n–π^* transition moment is perpendicular to the CNO plane, *i.e.*, $^1A' \longrightarrow {}^1A''$, where species A′ is symmetric and species A″ antisymmetric to the plane.

FIG. 2. *Spacings of the vibrational bands of trifluoronitrosomethane.*



The transition is thus allowed by symmetry, and we might expect any of the normal vibrations to be excited, the A′ ones more strongly. However, since the ground state is vibrationless, as shown by the insensitivity of the spectrum to changes of temperature, A″ vibrations would not be expected in the excited state.

The anti-bonding contribution in the excited state, when the π^*-orbital becomes half-filled, will increase the N=O bond length and decrease the N=O stretching frequency, as compared with the ground state; the effect on the deformation frequency will be of the second order.

The contraction of the n_N-orbital in the transition will allow the CNO angle to open slightly; the electronegativity of the nitrogen will increase and the s-character of the nitrogen σ-bonds diminish. (The n_N-electrons, which would be wholly s in character in CF_3·NO bent at 90°, still have more than their share of the s-character in the normal ground state, which is approximately trigonally hybridised. In addition, the bonding orbitals in tervalent-nitrogen compounds usually sacrifice s-character, and σ-bond strength, to economise the rather large energy of promotion of an s-electron to a half-filled p-orbital.)

[16] Goodman and Shull, *J. Chem. Phys.*, 1954, **22**, 1138; Reid, *ibid.*, 1953, **21**, 1906.

[17] Kasha, *ibid.*, 1952, **20**, 71.

As the C–N and N=O bonds become more directional, their stretching and deformation frequencies should increase slightly, although for the N=O stretching frequency such an increase would be more than offset by the weakening effect of the anti-bonding electron.

The effect of the transition on the C–N torsion frequency is difficult to predict, as the consequences of the N=O bond lengthening and the opening of the CNO angle will be opposed. Vibrations of the CF_3 group may well be excited.[18]

Fig. 2 shows the spacings of the vibrational bands, with some omission of detail, for clarity. Regularities at intervals of 1300—1400, 700—800, 450—500, and *ca.* 240 cm.$^{-1}$ can be seen, and may be the upper-state values of the following ground state frequencies (cm.$^{-1}$; Mason and Dunderdale $^{1)}$): N=O stretching 1595, C–N stretching 811, N=O deformation 405, and C–N torsion about 200 (conjectural); although the last is an A″ vibration. A regularity with a spacing of 60—80 is particularly prominent. Such a frequency is rather high for a rotation, and too low for a vibration. It may perhaps be a highest common factor † (or small multiple of this) of two excited-state frequencies. Since none of these bands is eliminated at low temperatures, they must be considered as belonging to progressions rather than to sequences.

If one takes the longest-wavelength band to be at 13,200 (or 12,900) cm.$^{-1}$, the separation from the strongest band is 1200 (or 1500) cm.$^{-1}$. This frequency might perhaps be identified with the N=O stretching vibration, but it represents an amount of energy that would certainly not be available at −112°. The same is true of the smaller separations between the weak long-wavelength bands. Thus, although at first sight the strongest band seems a more likely origin of progressions, such an origin must be at the electronic origin at longer wavelengths, since the transition is allowed; there can be no question of a vibrational quantum as prerequisite.

The observed vibrational structure has been described as insensitive to temperature since the variation with change of temperature (—110° to +100° for gaseous trifluoronitrosomethane) of the intensity distribution within the band is much smaller than would be required by Boltzmann factors for molecules vibrationally excited in the ground state. There is some effect of temperature, however: at low temperatures, compared with room temperature, the intensities are reduced by 10—20% on the long-wavelength side, increased by a similar amount near the two maxima, and increased by a smaller amount on the long-wavelength side.

Excited-state Frequencies in Other $Y-\ddot{N}=O$ *Molecules.*—The N=O stretching vibration is strongly excited in the $n_N-\pi^*$ absorption of almost all such molecules. A possible exception[19] is dinitrogen trioxide (although this has not been examined in the vapour phase), but in this the Y–N bond is very weak indeed. The vibrational structure of the $n_N-\pi^*$ bands of other $Y-\ddot{N}=O$ compounds is much simpler than in the case of trifluoronitrosomethane, and this is not always correlated with a greater complexity of the group Y; the only upper-state interval in the spectra of methyl nitrite and dimethylnitrosamine is that of the N=O stretching vibration, and the spectra of their higher homologues are not noticeably more diffuse. In contrast, there is a striking loss of vibrational structure in the nitroso-compound spectra as the perfluoroalkyl groups become more complex.

The greater diffuseness of the spectra of methyl nitrite and dimethylnitrosamine may be a result of the extra modes of internal rotation in these molecules, as compared with trifluoronitrosomethane. Predissociation may be suggested as an alternative (or as an additional) explanation, and to account for the lack of resolution in the spectrum of trifluoronitrosomethane as well, but if this were present the blurring should increase across the bands to shorter wavelengths, which is not observed. For trifluoronitrosomethane there may be the

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† Sponer and Teller [18] describe a similar regularity in the electronic spectrum of methylamine. They refer to it as the "smallest common denominator" of two larger frequencies, but it is clear that the "largest common factor" was intended.

[18] Sponer and Teller, *Rev. Mod. Phys.*, 1941, **13**, 75.

[19] Mason (Banus), unpublished work.

further argument against predissociation, that the energy available may be insufficient (see below).

It is more likely that the lack of resolution in the trifluoronitrosomethane band is due to the " solvent " or " loose-bolt " effect of the alkyl group, this effect increasing sharply up the homologous series because of the relative rigidity of the smallest member, trifluoronitrosomethane, compared with methyl nitrite and dimethylnitrosamine where the damping effect is already evident, because of the extra internal degrees of freedom.

The n–π^* band of the orange compound formed by trifluoronitrosomethane on irradiation has $\varepsilon_{\text{max.}}$ 20 at 3720 Å, and no vibrational structure. The inflections reported [20] are due to nitrogen dioxide, which is a photodecomposition product and can be removed by shaking with mercury.

Table 3 shows values of excited-state and ground-state frequencies of the N=O stretching vibration, and of other modes in the very few cases where they have been observed in the excited state.

TABLE 3. N=O *stretching frequencies* (*cm.*$^{-1}$) *in the ground and the excited states* (*values in parentheses refer to other modes*).

Compound *	Excited state	Ground state	Refs.
CF_3·NO	1300—1400	3595	*a*
C_3F_7·NO	,,	1603	*a*
CCl_3·NO	1350—1450	1621	12
Me_2CCl·NO, etc.	,,	1580—1600	
Pr^i_2CBr·NO	*ca.* 1400	—	*b*
Ph·NO	(*ca.* 500	NO def. 810—50)	*b*, 8*b*
	—	1500	*c*
NOCl	1580	1799	*d*
	(380	NCl str. 592)	
HO·NO †	970—1160	1640, 1696	15, *e*, *f*, *g*
	(255—270	?NO torsion, 637, 543)	*f*, *g*.
DO·NO †	1040—1180	1610, 1690	as for HO·NO
	(160—220	?NO torsion, 508, 416)	
HO·NO acid soln.	similarly	—	*h*
MeO·NO †	900—1100	1625, 1681	14, *i*
Me_2N·NO	850—950	1490	12, *i*
ON·O$^-$ (cryst.)	1018	NO sym. str. 1337	*j*
	(632	NO def. 829)	

* Gaseous, unless otherwise stated. † Of the two values for the ground state the first refers to the *cis*- and the second to the *trans*-form.

[a] Mason and Dunderdale.[1] [b] Lewis and Kasha, *J. Amer. Chem. Soc.*, 1945, **67**, 994. [c] Glusker and Thompson, *Spectrochim. Acta*, 1954, **6**, 434; Lüttke, *J. Phys. Radium*, 1954, **15**, 633. [d] Goodeve and Katz, *Proc. Roy. Soc.*, 1939, *A*, **172**, 432; Woltz, Jones, and Nielsen, *J. Chem. Phys.*, 1952, **20**, 378. [e] Tarte, *Bull. Soc. chim. belges*, 1950, **59**, 365; D'Or and Tarte, *Bull. Soc. roy. Sci. Liège*, 1951, 16, 478, 685. [f] Jones, Badger, and Moore, *J. Chem. Phys.*, 1951, **19**, 1599. [g] Porter, *J. Chem. Phys.*, 1951, **19**, 1278. [h] Bunton and Stedman, unpublished work; Singer and Vamplew, *J.*, 1956, 3972; Longstaff and Singer, *J.*, 1954, 2604. [i] Thompson and Purkis, *Trans. Faraday Soc.*, 1936, **32**, 674, 1466. [j] Sidman, *J. Amer. Chem. Soc.*, 1956, **78**, 2911.

The nitroso-compounds HNO and DNO have been found to absorb near 7500 Å, in the flash-photolysis [21] of *e.g.*, nitroethane, but no vibrational structure has been published as yet. Walsh [22] considers that the long-wavelength transition in HNO will open the angle. Sidman [23] records that the bond angle in the nitrite ion in sodium nitrite crystal increases slightly in the excited state, in the 3000—3700 Å absorption.

The Photodecomposition of Trifluoronitrosomethane. The bond dissociation energy for CH_3–NO_2 is estimated [24] as 57 or [25] as 52—57 kcal./mole, and that for CF_3–NO_2 will be similar or slightly less, since the perfluorination of methyl groups is usually found not

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[20] Jander and Haszeldine, *J.*, 1954, 696.
[21] Dalby, *Nature*, 1956, **178**, 969.
[22] Walsh, *Ann. Rev. Phys. Chem.*, 1954, **5**, 169.
[23] Sidman, *J. Amer. Chem. Soc.*, 1956, **78**, 2911.
[24] Gray, *Trans. Faraday Soc.*, 1955, **51**, 1367.
[25] Cottrell, " The Strengths of Chemical Bonds," Butterworths, London, 1954, p. 207.

to alter bond-dissociation energies significantly, or else to lower them slightly, in the molecules that have been studied, *e.g.*, CF_3–H,[26] CF_3–Hal.[27] The C–N bond in trifluoronitrosomethane will be a little weaker than in trifluoronitromethane, because of the non-bonding electrons in the former. The relative values of the C–N stretching frequencies bear out these assumptions: CH_3·NO_2 [28] 918, CF_3·NO_2 [29] 863, CF_3·NO [30] 811 (cm.$^{-1}$). We can therefore estimate that the bond-dissociation energy for CF_3–NO is *ca.* 50 kcal./mole, or somewhat less (cf. the value [31] 46 kcal./mole for CH_3–N:N·CH_3).

Thus the energy absorbed by trifluoronitrosomethane in the visible region, 41 kcal./mole at the maximum (6930 Å), and at the most 55 kcal./mole at the short-wavelength limit (about 5000 Å), is insufficient to break the C–N bond, unless other bonds are formed at the same time. The energy required to break a bond photochemically [32] is usually about half as much again as the bond-dissociation energy. Jander and Haszeldine state [20] that, on exposure to light, photolysis occurs to form a CF_3 radical and NO, which then add to a second molecule (perhaps involving a third) in one way [20] or another [33] to form an orange dimer, formulated as an *N*-nitroso- [20] or as an *O*-nitrito-compound.[33] In such a primary step there would be a very small gain of energy from the formation of the NO molecule from the NO radical, but there would not be enough to support the mechanism advocated. It is more likely from the energetics of the process that photoreaction by an excited-molecule mechanism, rather than photolysis involving a free CF_3 radical, occurs when trifluoronitrosomethane absorbs visible light.

The Ultraviolet Absorption.—It is probable that the largely structureless low-intensity band in the ultraviolet spectrum of trifluoronitrosomethane and perfluoronitrosopropane is due to an n–π^* transition of one of the non-bonding electrons on oxygen. There is a corresponding transition in the corresponding nitro-compounds, and Table 1 gives extinctions and wavelengths for these four gases. Although the oscillator strength is low (the *f*-value for trifluoronitrosomethane is 0·000052), it is still too high for a singlet–triplet n–π^* and too low for a symmetry-allowed π–π^* transition. n_O–π^* bands of similar intensity and energy are shown, for example, by nitromethane [34] ($\varepsilon_{max.}$ 17 at 2780 Å), by acetone [9] ($\varepsilon_{max.}$ 11 at 2760 Å), and by nitrite and nitrate ions [35] ($\varepsilon_{max.}$ respectively 9 at 2900 Å and 7 at 3025 Å, in aqueous solution).

The intense π–π^* absorption begins at *ca.* 2200 and 2300 Å respectively for the perfluoro-nitroso- and -nitro-alkanes.

Since nearly 120 kcal./mole are available at 2400 Å, the ultraviolet absorption will be followed by dissociation, *e.g.*, $CF_3\cdot NO \longrightarrow \cdot CF_3 + NO$, or, less probably, $CF_3\cdot NO \longrightarrow \cdot CF_2\cdot + NOF$. There is considerable fragmentation, and little of the orange compound (which is itself photosensitive) that is formed when trifluoronitrosomethane absorbs visible light, can be recovered.

There are weak vibrational bands in the spectrum of trifluoronitrosomethane at and beyond the minimum on the short-wavelength side of the n_O–π^* band, at 2292, 2303, 2314, 2325, 2337, 2348, 2361, 2373, 2385, 2398, 2410, and possibly at 2438 Å, with separations of about 200—250 cm.$^{-1}$. This interval was observed in the visible spectrum as well, and may be an upper state value of the C–N torsional vibration, with the reservation previously mentioned, that an A″ vibration is unexpected, since these are allowed as sequences only, and the ground state appears to be vibrationless.

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[33] Haszeldine and Mattinson, *J.*, 1955, 4172.

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There is similar structure, though fainter, and perhaps with a larger interval (350—400 cm.$^{-1}$), in the spectrum of perfluoronitrosomethane round the minimum at 2410 Å. There may also be some inflections between 3140 and 3300 Å on the long-wavelength side of the trifluoronitrosomethane n_0–π^* band, but these are very weak.

There are a few ill-defined humps in the n_0–π^* bands for nitro-compounds, but these are even fainter for the perfluoronitroalkanes than for nitromethane.

EXPERIMENTAL

The nitroso-compounds were prepared as in Part II.[30] Other compounds were prepared or obtained and purified by standard methods (Weissberger and Proskauer, Seidell).

The ultraviolet and visible spectra were measured with a Cary recording spectrophotometer. The gases and their solutions were contained in a 2 or 10 cm. silica cell, with a vacuum-tap and joint attached. The gas was let in from a vacuum-system, usually to a pressure of *ca.* 50 mm. If a solvent was required, it was then let in to atmospheric pressure, or to a total of 40 lb. pressure (applied from a nitrogen cylinder) if the solvent was one in which the solute was not very soluble (*e.g.*, trifluoronitrosomethane in water), and the tap was secured with a rubber band. Concentrations are not very accurately known; the absolute values of ε for the solution spectra shown in Fig. 1 may be in error by 5—10%.

For low temperatures the metal cell described by Passerini and Ross[36] was used, with minor modifications to ensure vacuum-tightness of the cells and jacket. Since it was difficult to maintain a vacuum in the jacket at very low temperatures, it was, where possible, filled with dry nitrogen, and hot air was blown on to the outer windows.

For the spectra at −183°, the gases were dissolved in 6 : 1 *iso*pentane–methyl*cyclo*hexane,[37] purified by repeated shaking with concentrated sulphuric acid, treatment with potassium hydroxide pellets, and passage through activated silica. With these precautions the spectra could also be observed in the ultraviolet region.

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