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THE PREPARATION AND IDENTIFICATION OF
N-FLUORO-N'-TRIFLUOROMETHYLDIAZINE-N'-OXIDE

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THE PREPARATION AND IDENTIFICATION OF
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ABSTRACT

The compound N-fluoro-N'-trifluoromethyldiazine-N'-oxide (CF_3NONF) has been prepared from the reaction of CF_3I, NO, and N_2F_4 by ultraviolet and thermal activation. Its structure has been shown to be $CF_3-\overset{\overset{O}{\uparrow}}{N}=NF$.


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N-fluoro-N'-trifluoromethyldiazine-N'-oxide (CF_3NONF) was first found as a by-product of reaction (1) when the starting compounds

$$CF_3I + N_2F_4 \longrightarrow CF_3NF_2 + I + NF_2 \qquad\qquad (1)$$
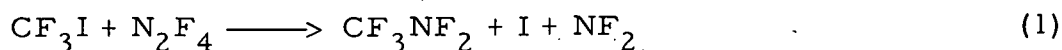
were activated by ultraviolet light ($\geq 2750 \text{Å}$) in Pyrex. The necessary nitric oxide was supplied by reaction (2).

$$N_2F_4 + SiO_2 \longrightarrow 2NO + SiF_4 . \qquad\qquad (2)$$

Thermal activation of CF_3I and N_2F_4 in Pyrex can also be used for the synthesis of CF_3NONF.

The syntheses by uv excitation were carried out in a 4π Pyrex reactor[1] which was thermostated at $26 \pm 5°C$ or $46 \pm 5°C$ by circulating water. A 200-watt low-pressure mercury arc was used as an excitation source. All thermally induced reactions were carried out in Pyrex bombs of ~75 cc capacity. The starting materials were always at a total pressure of less than one atmosphere and present in mole-ratios equivalent to the indicated stoichiometry.

Identification of the reaction products was made by gas chromatography, mass spectrometry and infrared data. Usually the initial separation and purification of the reaction products was made by gas chromatography and the quantity of the purified compounds determined by P-V-T measurements.
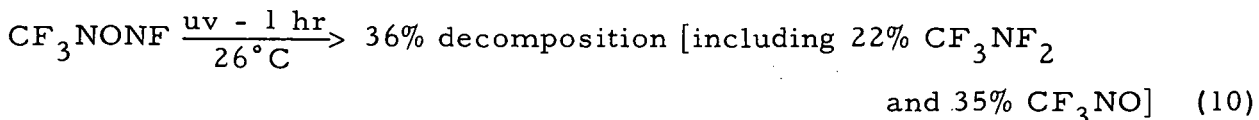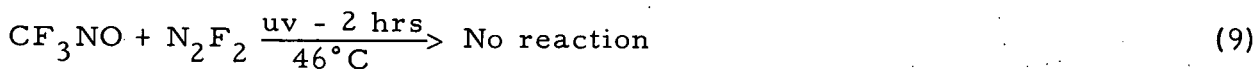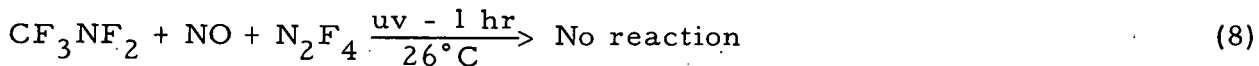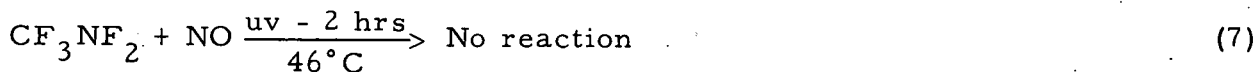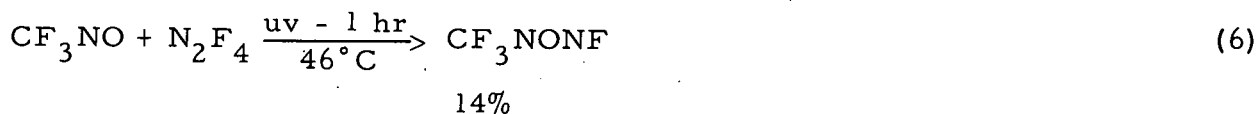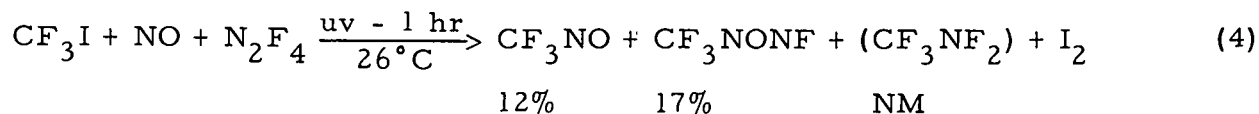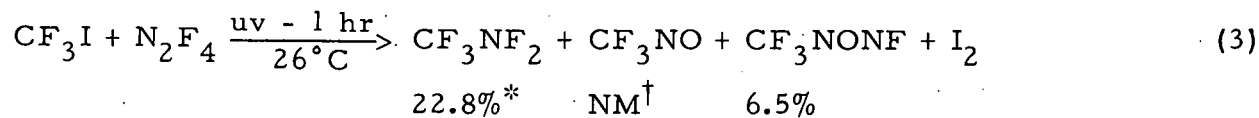
The chromatographic columns often reacted with the by-products. Because of this problem and the difficulty of separating and determining all the products, only compounds in appreciable quantities containing the elements carbon, fluorine, and nitrogen and/or oxygen were quantitatively determined.

Tables 1 and 2 list the uv and thermally activated reactions explored during the synthesis of CF_3NONF. Synthesis conditions are indicated with each reaction plus yield data based on the available (CF_3-). Synthesis of CF_3NONF can be accomplished by either uv excitation or thermal activation of CF_3I plus N_2F_4 in a Pyrex reaction vessel (reactions 3 and 11 in Tables 1 and 2). The addition of NO to the starting materials $(CF_3I$ plus $N_2F_4)$ enhances the CF_3NONF yield (reaction 4 and 12). If NO is not added as a starting material CF_3NONF cannot be synthesized until the NO is produced by reaction (2).

The CF_3NONF yield of the thermally activated reaction is considerably greater than that of the uv activated reaction. This is due at least in part to the difference in the stability of CF_3NONF with respect to uv excitation and to heat. When the CF_3NONF is very pure, there is no decomposition in Pyrex at 120°C in 24 hours (reaction 16), but the uv irradiation of the compound results in a 36% decomposition in one hour (reaction 10).

From the synthesis of CF_3NONF the only other compounds of interest were CF_3NF_2 and CF_3NO. N,N-difluorotrifluoromethylamine (CF_3NF_2) was present regardless of whether the synthesis was carried out by uv excitation or thermal activation. However, CF_3NO was only present when the synthesis was carried out by uv excitation. The thermally induced reaction of CF_3I and NO does not yield CF_3NO (reaction 14).

When CF_3NF_2 plus NO are subjected to the same conditions used for the synthesis of CF_3NONF no reaction occurs (see reactions 7 and 15). It is

Table 1 — Reactions Activated by Ultraviolet Excitation ($\geq 2750\text{Å}$).

$$CF_3I + N_2F_4 \xrightarrow[26°C]{uv - 1 \text{ hr}} CF_3NF_2 + CF_3NO + CF_3NONF + I_2 \qquad (3)$$
$$22.8\%^* \qquad NM^\dagger \qquad 6.5\%$$

$$CF_3I + NO + N_2F_4 \xrightarrow[26°C]{uv - 1 \text{ hr}} CF_3NO + CF_3NONF + (CF_3NF_2) + I_2 \qquad (4)$$
$$12\% \qquad 17\% \qquad NM$$

$$CF_3I + NO \xrightarrow[26°C]{uv - 1 \text{ hr}} CF_3NO + I_2 \qquad (5)$$
$$29\%$$

$$CF_3NO + N_2F_4 \xrightarrow[46°C]{uv - 1 \text{ hr}} CF_3NONF \qquad (6)$$
$$14\%$$

$$CF_3NF_2 + NO \xrightarrow[46°C]{uv - 2 \text{ hrs}} \text{No reaction} \qquad (7)$$

$$CF_3NF_2 + NO + N_2F_4 \xrightarrow[26°C]{uv - 1 \text{ hr}} \text{No reaction} \qquad (8)$$

$$CF_3NO + N_2F_2 \xrightarrow[46°C]{uv - 2 \text{ hrs}} \text{No reaction} \qquad (9)$$

$$CF_3NONF \xrightarrow[26°C]{uv - 1 \text{ hr}} 36\% \text{ decomposition [including } 22\% \text{ } CF_3NF_2$$
$$\text{and } 35\% \text{ } CF_3NO] \qquad (10)$$

* Yield values as based on the available CF_3 groups.

† NM — not measured quantitatively.

Table 2 — Reactions Activated by Heating in Pyrex at 120°C for 1 hour.

$$CF_3I + N_2F_4 \longrightarrow CF_3NONF + CF_3NF_2 + I_2 \qquad (11)$$
$$35\% \qquad\qquad 11\%$$

$$CF_3I + NO + N_2F_4 \longrightarrow CF_3NONF + CF_3NF_2 + I_2 \qquad (12)$$
$$45\%^* \qquad\qquad NM^\dagger$$

$$CF_3NO + N_2F_4 \longrightarrow CF_3NONF + CF_3NF_2 \qquad (13)$$
$$45\% \qquad\qquad 20\%$$

$$CF_3I + NO \longrightarrow No\ reaction \qquad (14)$$

$$CF_3NF_2 + NO \longrightarrow No\ reaction \qquad (15)$$

$$CF_3NONF \longrightarrow No\ decomposition\ in\ 24\ hours \qquad (16)$$
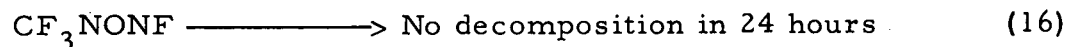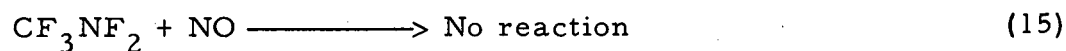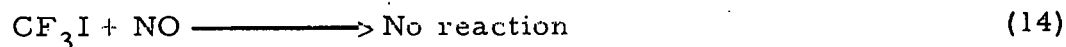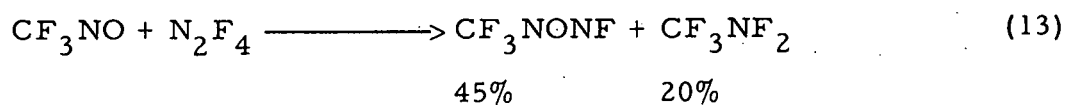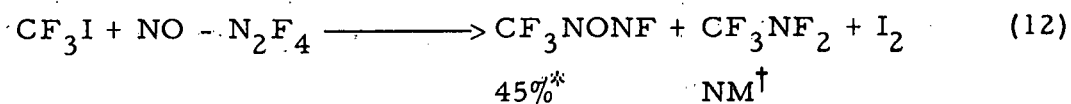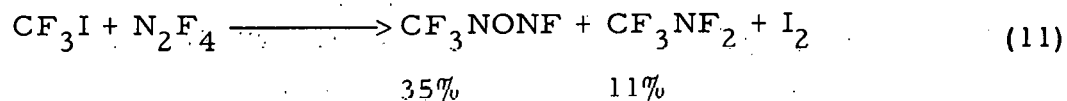
* Yield values as based on the available CF_3-groups.

† NM — not measured quantitatively.

therefore concluded that CF_3NF_2 is an end-product in the synthesis of CF_3NONF. This suggests that the groups in CF_3NONF are not arranged in the order of (CF_3)-(NF)-(NO).

When CF_3NO plus N_2F_4 are uv or thermally activated (reactions 6 and 13) CF_3NONF is synthesized. This suggests that the groups in CF_3NONF are arranged in the order (CF_3)-(NO)-(NF).

Since CF_3NO can only be an intermediate compound, in the uv activated reactions there must be at least two different mechanisms by which CF_3NONF can be synthesized. Two such possible mechanisms are suggested below:

$$CF_3I \xrightarrow{uv} CF_3 + I \qquad (17)$$

$$CF_3 + NO \xrightarrow{uv} CF_3NO \qquad (18)$$

$$N_2F_4 \rightleftharpoons 2NF_2 \qquad (19)$$

$$CF_3NO + NF_2 \xrightarrow{uv \ or \ \Delta} CF_3NONF + F \qquad (20)$$

and

$$NO + NF_2 \xrightarrow{uv \ or \ \Delta} NONF_2 \qquad (21)$$

$$CF_3I + NONF_2 \xrightarrow{uv \ or \ \Delta} CF_3NONF + F + I. \qquad (22)$$

JOHNSON and COBURN[2] have reported the thermal free-radical decomposition of N_2F_4 at ambient temperature, making these overall mechanisms attractive.

From the mass spectrum data (Table 3) CF_3NONF was shown to contain (CF_3), (NO), and (NF) groups. The infrared spectrum (Fig. 1) showed absorption bands in the regions where these groups are normally active. A determination of the molecular weight by the method of limiting densities yielded a value of 132.1 versus 132.0 calculated for a compound CF_4N_2O (CF_3NONF). This agrees with the molecular weight (132) obtained by mass spectrum data. The compound is therefore limited to just one of each of the groups (CF_3), (NO), and (NF).

This compound is a gas at room temperature and a clear liquid in the condensed phase. The vapor pressure can be expressed by $\log_{10} P_{cm}$ $= 5.0989 - \dfrac{415.09}{T} - \dfrac{116667}{T^2}$ over the range 238° to 267° Kelvin. The boiling point is $-7.5 \pm 0.2°C$.

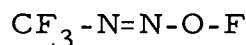The possible structures of CF_3NONF are

$$\overset{O}{\underset{\uparrow}{CF_3-N=NF}} \qquad CF_3-O-N=N-F \qquad CF_3-N=N-O-F \qquad \overset{F}{\underset{|}{CF_3-N-N=O}}$$
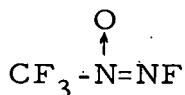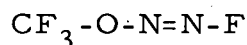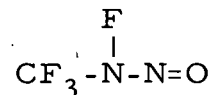
$$\quad I \qquad\qquad\qquad II \qquad\qquad\qquad III \qquad\qquad\qquad IV$$

Table 3 — Mass Spectrum Data for CF_3NONF

m/e	Ion assignment	Pattern (%)	
		$I_m = 247MA$	$I_m = 426MA$
12	C^+	2.89	
14	N^+	4.20	
16	O^+	4.56	
19	F^+	1.75	
28	N_2^+	7.28	
30	NO^+	36.87	
31	CF^+	10.13	
33	NF^+	3.89	
44	N_2O^+	10.92	8.60
45	CFN^+	1.04	1.39
47	N_2F^+	16.35	16.88
50	CF_2^+	9.74	12.10
63	$NONF^+$		0.12
64	CF_2N^+		0.82
66	CF_2O^+		0.59
69	CF_3^+	100.0	100.0*
99	CF_3NO^+		0.94
132	CF_3NONF^+		1.83

*CF_3^+ sensitivity = 73.9 div/μ.

shown by I through IV. From the synthesis data structure I was preferred; this assignment was confirmed by NMR and ultraviolet absorption spectra data.

The F^{19} spectrum of the two fluorine resonance peaks was observed at 40.0 Mc (Fig. 2). The chemical shift of the two peaks relative to the CF_3 in trifluoroacetic acid is given in parts per million. The peak at -118.7 ppm is broad and shows no structure, while the signal at -7.0 ppm shows six peaks and appears to be 3 sets of doublets. Double irradiation at a nitrogen frequency of 3,072,050 ± 25 cycles changed the -7.0 peak to a doublet. From this behavior it is evident that the -7.0 ppm peak is coupled to a nitrogen and also to another nucleus of spin 1/2. The only nuclear species present of spin 1/2 is fluorine, and it therefore must be a single fluorine at -118.7 ppm coupled to the fluorines at -7.0 ppm. It is concluded that the peak at -7.0 ppm arises from a $-CF_3$ group and from measurements on the original and de-coupled spectra the spin coupling constants are:

$$J_{CF_3 - F_{-118.7}} = 7.1 \pm 0.5 \text{ cps}$$

$$J_{CF_3 - N} = 11.9 \pm 0.5 \text{ cps} .$$

The broadness of the single fluorine at -118.7 is reasonable if it is split into a quartet by the $-CF_3$ group and then further coupled to a nitrogen giving a broad unresolvable set of lines.

Additional double irradiation experiments were performed to show that the -118.7 ppm peak is indeed coupled to a nitrogen and, furthermore, this is a different nitrogen than the one coupled to the $-CF_3$ group. One irradiation was already mentioned previously as detecting a $N--CF_3$ coupling which could be removed by saturating a particular nitrogen at 3,072,050 ± 25 cycles. For the purposes of identification this nitrogen has been labeled $N(CF_3)$.

Another frequency was found in the nitrogen region which would sharpen the F^{19} peak at -118.7 ppm. The nitrogen irradiation frequency was 3,071,930 ± 25 cycles. Since it was necessary to reduce the dc magnetic field 111.7 ppm (118.7 - 7.0 ppm) to go from the CF_3 peak to the single fluorine, the precession frequency of the $N(-CF_3)$ would have also been reduced by $(111.7 \times 10^{-6}) \times (3.072 \times 10^6) = 342$ cycles, and its precession frequency during the time we were observing the single fluorine decoupling was then 3,072,050-342 cycles = 3,071,708 cycles. This precession frequency is 222 cycles different from the 3.071930 Mc frequency which did have a decoupling influence on the -118.7 peak. Therefore, the two types of fluorines are coupled to two different nitrogens. The magnitude of the coupling of the F(-118.7 ppm) to its nitrogen, N(F), is not known accurately but is estimated to be of the order of 50 cycles from the fact that the F(-118.7 ppm) peak begins to show structure if the sample is examined at room temperature. Most of the initial measurements were made near zero degrees.

Double irradiation of the nitrogens while holding the field constant were carried out to confirm the above conclusions. In this case the dc magnetic field was held constant while using just enough sweep field to span the peak under observation. The fluorine resonances were stimulated with a variable but stable 40-Mc oscillator and the output of the probe observed through the NMR receiver. With the field fixed, the 40.0-Mc oscillator frequency was adjusted to bring one of the fluorine resonances on to the oscilloscope. The nitrogen frequency was searched until a decoupling of the fluorine was observed. With the field still unchanged and the nitrogen saturating oscillator fixed at its decoupling value, the 40.0-Mc oscillator was changed to bring the other fluorine signal on to the oscilloscope to see if there was any decoupling of the second fluorine. The observed results are given in Table 4.

Table 4 – Values of the Double Irradiation Experiments.

Nitrogen frequency	Effect on CF$_3$ peak, F^{19} at 40.000100 Mc	Effect on single F^{19}, F^{19} at 40.004571 Mc
3.072025 Mc ± 25 cycles	Decoupled to a doublet	No effect
3.072225 Mc ± 25 cycles	No effect	Peak sharpened

The two approaches for measuring the chemical shift of the nitrogens relative to each other gave 222 (frequency constant) and 200 (field constant) cycles respectively. Because the strength of the saturating rf must be high in order to achieve the decoupling, the frequency position of maximum decoupling effect is sufficiently uncertain to make this deviation reasonable.

The observed spectra and decouplings are most consistent with structure I. Structure II is unlikely because it is felt that a N--CF$_3$ spin coupling of the observed magnitude would not be carried through a F-C-O-N bond system. The apparently large N--F coupling (about 50 cycles) is much larger than would be expected through a -N-O-F bond arrangement as in structure III. On the other hand the -118.7 chemical shift is in the region commonly measured for fluorines bonded to nitrogen. Structure IV would indicate that both types of fluorine should be spin coupled to the same nitrogen. The double irradiation experiments proved that the two types of fluorines were actually coupled to different nitrogens thus ruling out structure IV.

The absorption spectrum of CF$_3$NONF consists of a weak absorption band with a maximum at 2770Å (ϵ_{max} = 7.3) and a shallow minimum at 2670Å (ϵ_{min} = 6.9) followed by a strong ultraviolet absorption with a maximum at 2125Å (ϵ_{max} ~ 4500). The compound exhibits no absorption bands with ϵ > 0.05 between 3500Å and 12,000Å.

The ultraviolet spectrum of CF_3NONF yields strong evidence for the identification of the compound with structure I.

Structure IV contains the group $X - N = O$ where X has a nonbonded pair of electrons. Compounds containing this group have absorptions with considerable band structure in the 3000 to 4000Å region,[3] see Fig. 3 (b,c). Structure II is electronically similar to IV and to methyl nitrite and would be expected to have a similar absorption spectrum. Since the spectrum of CF_3NONF does not have an absorption with band structure in this region of the spectrum, structures II and IV seem unlikely.

The ($N \overset{O}{\underset{O}{\diagup\kern-0.6em\diagdown}} NF$) group of structure I is electronically similar to the nitro group ($N \overset{O}{\underset{O}{\diagdown\kern-0.6em\diagup}}$). Compounds containing the nitro group have a weak continuous absorption with a maximum at roughly 2750Å followed by a strong continuum. This is the type of absorption exhibited by CF_4N_2O. The similarity in position and strength of the ultraviolet absorptions of CF_3NONF and those of the nitro compounds [see (Fig. 3 (d, e, f) and Table 5)] is strong evidence in favor of structure I as the structure of the compound CF_3NONF described.

Table 5 — Absorption Characteristics of CF_3NONF, CF_3NO_2, and CH_3NO_2.

Compound	Weak continuum					Strong continuum	
	λ_{max}	ϵ_{max}	λ_{min}	ϵ_{min}	$f \times 10^4$	λ_{max}	ϵ_{max}
CF_4N_2O (I)	2770	7.3	2670	6.9	2	2125	>3000
CF_3NO_2 [4]	2775	11.2	2370	2.0	-	-	>3000
CH_3NO_2 [5,6]	2750	8.1	2450	3.9	2.5	1975	>3000

We conclude that structure I is the structure of the compound CF_3NONF since it is the only structure of those considered which is consistent with all

the data. It is thought the reactions described are quite general and will result in a series of new compounds containing the group -NONF.

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(1) Available from Hanovia Chemical and Mfg. Co., Newark, New Jersey.

(2) F. A. JOHNSON and C. B. COLBURN, "The tetrafluorohydrazine-difluoro-amino radical equilibrium." Presented at the American Chemical Society Meeting, St. Louis, Missouri, March 21-30, 1961.

(3) C. H. PURKIS and H. W. THOMPSON, Trans. Faraday Soc. 32 674, 1466 (1936).

(4) J. MASON, J. Chem. Soc., 1957 3904.

(5) N. S. BAYLISS and E. G. MCRAE, J. Phys. Chem. 58 1006 (1954).

(6) S. NAGAKURA, Molecular Physics 3 152 (1960).

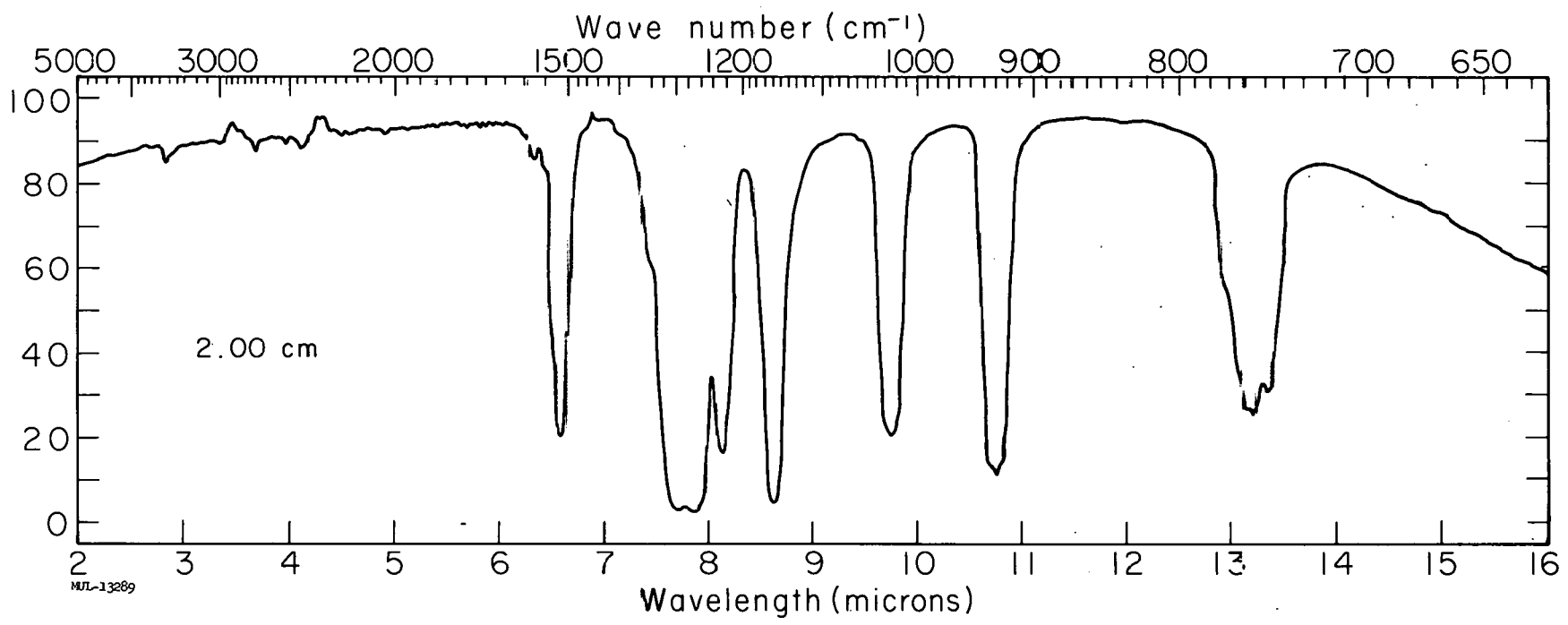(7) R. N. HASELDINE and B. J. H. MATTINSON, J. Chem. Soc. 1955, 4172.

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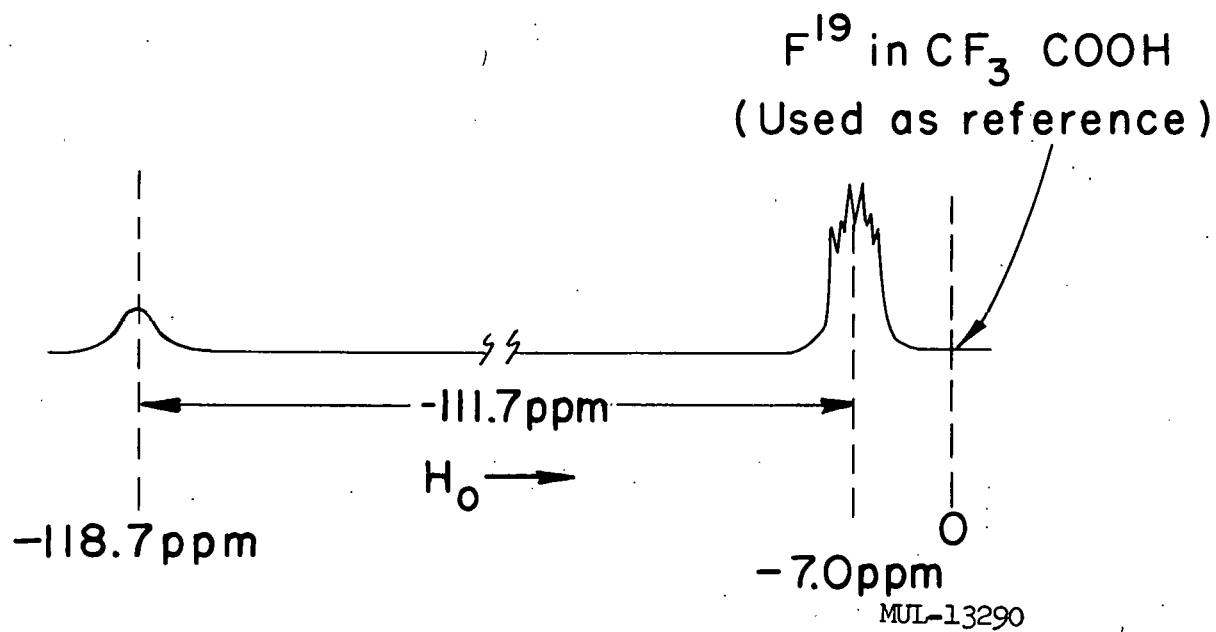Fig. 1. The infrared spectrum of CF$_3$NONF.
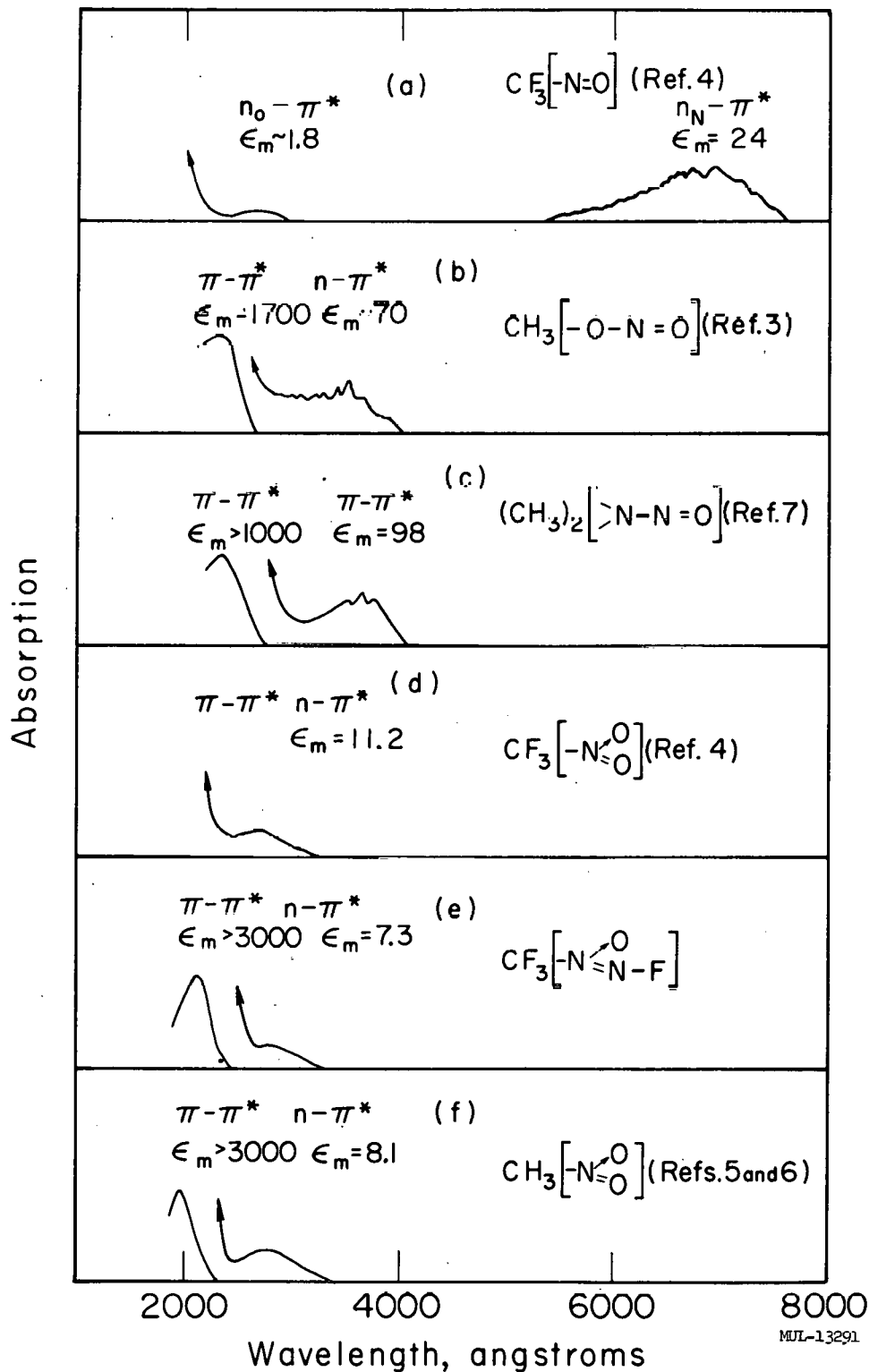
Fig. 2.   The NMR spectrum of CF_3NONF at 40.0 Mc.

(a) $n_o - \pi^*$ $\epsilon_m \sim 1.8$ $CF_3\left[-N=O\right]$ (Ref. 4) $n_N - \pi^*$ $\epsilon_m = 24$

(b) $\pi - \pi^*$ $\epsilon_m = 1700$ $n - \pi^*$ $\epsilon_m \sim 70$ $CH_3\left[-O-N=O\right]$ (Ref. 3)

(c) $\pi - \pi^*$ $\epsilon_m > 1000$ $\pi - \pi^*$ $\epsilon_m = 98$ $(CH_3)_2\left[>N-N=O\right]$ (Ref. 7)

(d) $\pi - \pi^*$ $n - \pi^*$ $\epsilon_m = 11.2$ $CF_3\left[-N\substack{O \\ \lessgtr O}\right]$ (Ref. 4)

(e) $\pi - \pi^*$ $n - \pi^*$ $\epsilon_m > 3000$ $\epsilon_m = 7.3$ $CF_3\left[-N\substack{O \\ \lessgtr N-F}\right]$

(f) $\pi - \pi^*$ $n - \pi^*$ $\epsilon_m > 3000$ $\epsilon_m = 8.1$ $CH_3\left[-N\substack{O \\ \lessgtr O}\right]$ (Refs. 5 and 6)

Absorption

2000   4000   6000   8000

Wavelength, angstroms

MUL-13291

Fig. 3.   The absorption spectrum of CF_4N_2O and the absorptions of compounds containing various nitrogen-oxygen groups.   The type of transition and absorption coefficient at maximum (ϵ_m) is given above each absorption band.