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IR MATRIX ISOLATION SPECTRA OF SOME PERFLUORO ORGANIC-FREE RADICALS

PART 1. C_2F_5

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SUMMARY

The pentafluoro ethyl radical has been prepared by the pyrolysis of C_2F_5I in a platinum effusion tube at ≈650°C and isolated in an argon matrix. By elimination of absorption bands attributable to known fluorine compounds and from relative intensity measurements on the remaining bands, twenty frequencies were assigned C_2F_5 in the spectral range 4000-200 cm^{-1}. Fourteen of these frequencies were assigned as fundamentals of C_2F_5, with C_s symmetry, and the remainder to combination or overtone modes of the radical.

INTRODUCTION

The matrix isolation technique in conjunction with a variety of spectroscopic methods is now widely used for studying organic-free radical species [1]. In the majority of past studies free radicals have been generated by photolysis of suitable precursors in situ in the matrix, after, or during its deposition. Alternatively chemical abstraction reactions during the deposition process have been widely used [2]. The generation of radicals in molecular beams by pyrolysis of suitable precursors, with subsequent isolation in matrices, has, by comparison with the above approaches, rarely been used.

Some years ago in this laboratory the pyrolyses of CH_3I, $(CH_3)_2Hg$ [3], CF_3I, and C_2F_4 [4] were used to generate the radicals CH_3, CF_3, and CF_2, respectively, for subsequent trapping in neon matrices. The three IR active frequences of CH_3 were first identified in these studies as a subsequent investigation verified [5]. Despite this success of the pyrolysis approach, few other workers tried the technique. Possibly the rather complex appearance of the resulting spectra, due to the presence of a variety of stable and unstable products formed either in the pyrolysis, or by subsequent reaction in the matrix, detered other workers.

Recently we have had the opportunity to retry the pyrolsis generation of free radicals for IR matrix isolation studies. Perfluoro radicals have been investigated exclusively. In general, these species are considerably more stable than their hydrogenated analogues and this may have contributed in some measure to the success of the present studies. Much cleaner spectra have been obtained than reported in our earlier studies [3,4]. In this paper we present data on the IR spectrum of C_2F_5 formed via the pyrolysis of C_2F_5I.

EXPERIMENTAL

The experimental arrangement used in the present studies was very similar to that reported earlier [3,4], but with some variations which will be outlined. The liquid helium cold finger was replaced with an Air Products CS202 Displex closed cycle refrigerator capable of temperatures at the cold finger of 10-11 K. A platinum pyrolysis tube similar in dimensions to that used previously was inductively heated. The end of the tube closest to the matrix window was not attached to a water-cooled plate as required in the earlier configuration when resistance heating was used, but remained free. To minimize radiation from the pyrolysis tube reaching the matrix window, a water-cooled baffle with suitable skimmer orifice was interposed. Temperatures could be measured with an optical pyrometer. The pyrolysis temperatures were much lower than in the previous study (≃1300°C) [3,4], and in practice, the temperature was fixed by setting the current output of the rf. generator at a given value. It is estimated that pyrolysis temperatures were in the range 600-700°C.

C_2F_5I was stored in a 1-liter flask and its flow into the pyrolysis reactor controlled by a Granville Phillips all stainless steel leak valve. The low pressure side of the variable leak valve was monitored by an MKS Baratron capacitance pressure gauge. The C_2F_5I was leaked into the pyrolysis tube at rates of 8×10^{-7} to 4×10^{-5} moles hr^{-1}. From the geometry of the system, it was estimated that between 1-10% of the effusate reached the cooled window. Argon was used as a matrix gas in all experiments being bled in at $(2\text{-}4.5) \times 10^{-3}$ mole hr^{-1}. Matrices were deposited over periods of time ranging from 2-30 hrs. Spectra were recorded on a Perkin Elmer 621 spectrophotometer. Reported frequencies are believed accurate to ± 1 cm^{-1} in the 2000-200 cm^{-1} region examined.

MATERIALS

Linde Ultra High Purity Grade argon was used for the matrix gas. The following halocarbons--CF_4, C_2F_4, C_2F_6, C_3F_6, n-C_4F_8, and C_2F_5I--were obtained either from Matheson or Peninsular Research Chemicals, Inc. Stated purities ranged from 97 to 99.7%. All these materials were subjected to trap-to-trap distillation at liquid nitrogen temperature prior to use.

RESULTS AND DISCUSSION

The general experimental approach used in the present study was first to obtain matrix spectra of C_2F_5I and its possible stable pyrolysis products (the fluorocarbons listed above); second, to obtain matrix spectra of products from the C_2F_5I pyrolysis; third, to identify known stable and unstable halocarbons (CF_2 and CF_3) in the resulting spectra; and fourth, to make relative intensity measurements on the remaining unknown absorption bands to identify common precursor species.

The pyrolysis of C_2F_5I is expected to result in the scission of the C_2F_5—I bond (C—I bond energy = 220 ±4 kJ mol^{-1}) [6]. In preliminary experiments, various pyrolysis temperatures were tried, from approximately 600°C up to about 750°C. At the lower temperature very little pyrolysis occurred, whereas at the higher temperature, decomposition of the C_2F_5I was extensive, with formation of quite large amounts of CF_3 and CF_2, in addition to other unknown species being recognized easily from the spectra. The pyrolysis temperature used in the final experiments was a compromise between maximizing C_2F_5I decomposition and minimizing CF_3 and CF_2 formation; this temperature, as noted earlier, was in the range 600-750°C, resulting in approximately 20-40% decomposition of the C_2F_5I.

Under the optimum experimental conditions used in most of this study, the pyrolysis of C_2F_5I resulted in matrix spectra, which, from a cursory examination, appeared to consist of only two major components, unreacted C_2F_5I and a second unknown compound. Weak absorption bands attributable to CF_4, CF_3, CF_2, CF_3I, and possibly C_2F_4 were usually identifiable in the spectra, increasing in intensity somewhat at the higher pyrolysis temperatures. No positive identification of absorption bands attributable to C_2F_6, C_3F_6, C_3F_8, or n-C_4F_{10} was ever made in a total of some 25 pyrolysis experiments.

In organic fluorine compounds, carbon-fluorine stretching modes usually occur with strong absorption intensities while the bending modes are typically some one to two orders of magnitude weaker [7]. Because of this, characteristic matrix deposition times of 1-2 hrs sufficed to obtain moderate absorption band intensities for the C–F stretching modes in the 1400-1050 cm^{-1} region, whereas up to 30 hrs deposition time was required to obtain moderate, and in some cases still quite weak intensities, for the lower frequency bending modes.

As noted above, C_2F_5I was a major species present in all the pyrolysis spectra and for this reason several reference spectra of this compound were obtained at low and high intensity for comparison purposes. At moderate and high optical densities, the C_2F_5I spectra contained numerous absorption bands, and the spectra were carefully compared with those in the literature [8]. A total of some 34 overtone and combination bands were identified in the 2000-200 cm^{-1} region which had not previously been reported. They could all be accounted for in terms of the originally assigned fundamental modes [8] of C_2F_5I. These data are not included here since they in no way alter the earlier vibrational assignment for the molecule.

In Figures 1, 2, 3, and 4 the spectra of C_2F_5I pyrolysis products in the region of interest are presented. Spectra were carefully examined at short, medium, and long deposition times with comparable spectra (similar optical density) of C_2F_5I and the other fluorine species noted above. Absorption features attributable to known molecular species were assigned, leaving a total of some 20 absorption bands for which obvious assignment to known species was not possible.

Optical densities for these 20 absorption bands were measured and are shown in Table 1. The omissions in the table are due to the particular absorption feature being too weak or too strong for meaningful measurement. Absorption bands at 703 and 604 cm^{-1} were chosen as reference features and the relative intensities of all the other unknown absorption bands with respect to these two were calculated. The band at 703 cm^{-1} was selected since it was of medium intensity and could potentially provide a good reference, both for the stronger stretching modes in the higher frequency regions and the weaker bending modes at lower frequencies. Unfortunately, this band overlapped the ν_2 frequency of CF_3 at 701 cm^{-1}. The latter is one of the weaker bands of CF_3, but since the amount of CF_3, which was generally small, varied somewhat from experiment to experiment, due to the rather imprecise temperature control, its value as a reference band was in some measure

Table 1

INTENSITY MEASUREMENTS (ABSORBANCE UNITS) OF POSSIBLE C_2F_6 ABSORPTION BANDS

	Band	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R	S	T
Expt.	Frequency (cm^{-1})	1410	1398	1273	1227	1193	1184	1117	1040	1012	956	898	820	703	694	604	514	419	366	227	211
1a		-	-	0.218	0.182	-	0.290	0.153	-	-	-	-	-	0.0185	-	-	-	-	-	-	-
1b		-	-	0.714	0.588	-	0.871	0.416	-	-	-	-	-	0.0783	-	0.0249	-	-	-	-	-
1c		-	-	-	-	-	-	-	-	-	-	-	-	0.392	-	0.124	-	-	-	-	-
2a		-	-	0.460	0.415	-	0.562	0.283	-	-	-	-	-	0.0480	-	-	-	-	-	-	-
2b		-	-	-	-	-	-	-	-	-	-	-	-	0.295	-	0.106	-	-	-	-	-
3		-	-	0.385	0.354	-	0.476	0.221	-	-	-	-	-	0.0411	-	0.0140	-	-	-	-	-
4a		-	-	0.225	0.240	-	0.287	0.146	-	-	-	-	-	0.0191	-	-	-	-	-	-	-
4b		-	-	0.433	0.410	-	0.577	0.262	-	-	-	-	-	0.0484	-	0.0143	-	-	-	-	-
5		-	-	0.162	0.097	-	0.207	0.107	-	-	-	-	-	0.0150	-	weak	-	-	-	-	-
6		-	-	-	-	0.031	-	-	0.020	-	weak	-	-	0.208	-	0.063	0.047	0.011	-	0.035	0.039
7		-	0.056	-	-	0.017	-	-	0.014	-	weak	-	-	0.151	-	0.047	0.033	-	-	0.021	0.025
8		0.015	0.129	-	-	0.030	-	-	0.019	-	0.008	-	-	0.201	-	0.061	0.042	0.008	-	0.033	0.040
9a		0.059	0.256	-	-	0.046	-	-	0.039	*	0.020	*	*	0.395	0.006	0.139	0.086	0.019	0.008	0.089	0.082
9b		0.052	0.253	-	-	0.046	-	-	0.047	*	0.036	*	*	0.568	0.010	0.197	0.141	0.027	0.011	0.141	0.132
10a		0.024	0.227	-	-	0.020	-	-	0.019	*	0.021	*	*	0.287	weak	0.098	0.063	0.011	weak	0.054	0.066
10b		0.054	0.357	-	-	0.047	-	-	0.044	*	0.051	*	*	0.572	0.010	0.195	0.142	0.024	0.010	0.139	0.144
10c		0.076	0.485	-	-	0.049	-	-	0.072	*	0.077	*	*	0.931	0.009	0.308	0.233	0.053	0.015	0.247	0.225

*Too badly overlapped with C_2F_5I band to make intensity measurement.

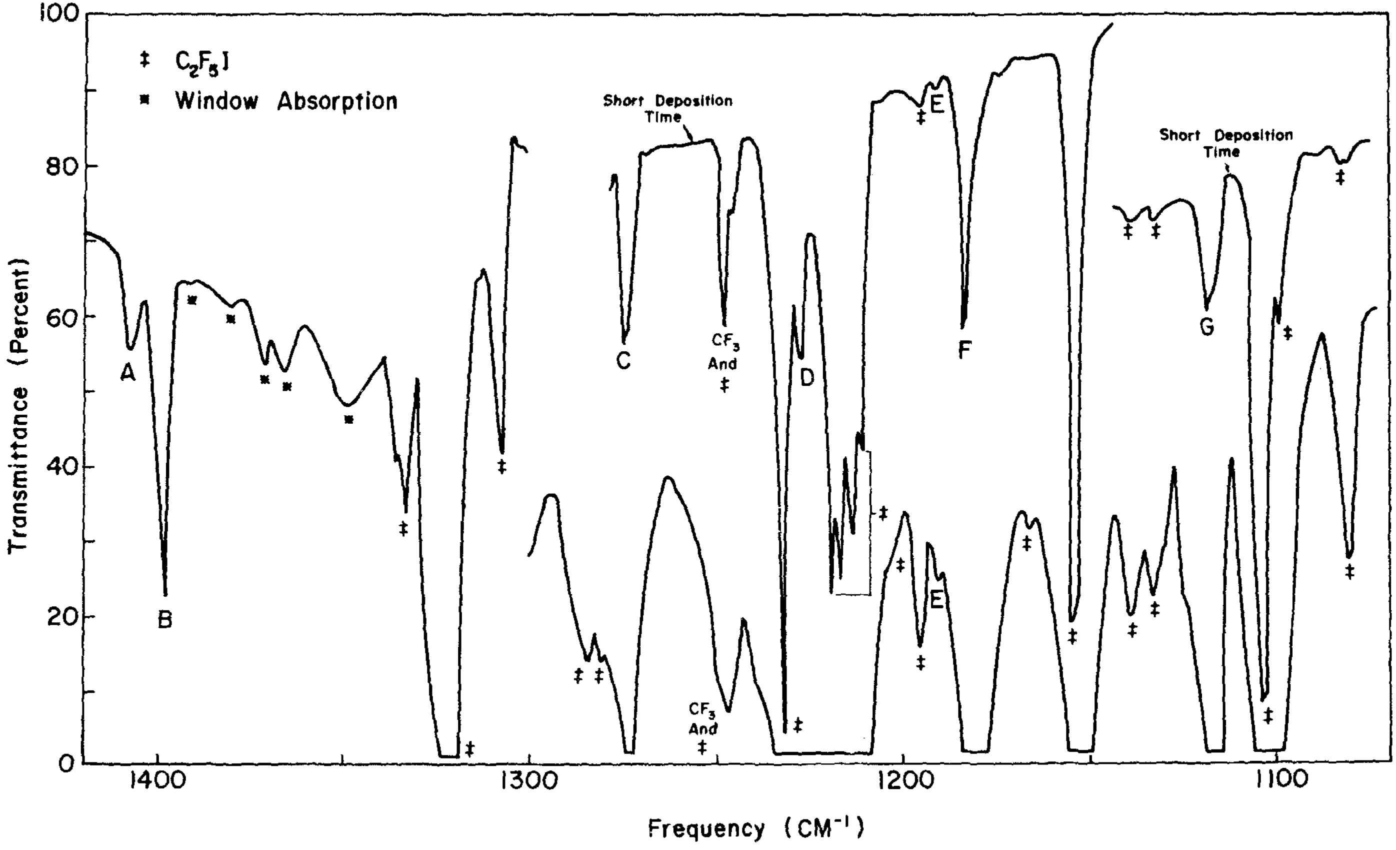

Fig. 1 MATRIX ISOLATION SPECTRUM OF PYROLYSIS PRODUCTS OF C_2F_5I (20hr. Deposition)

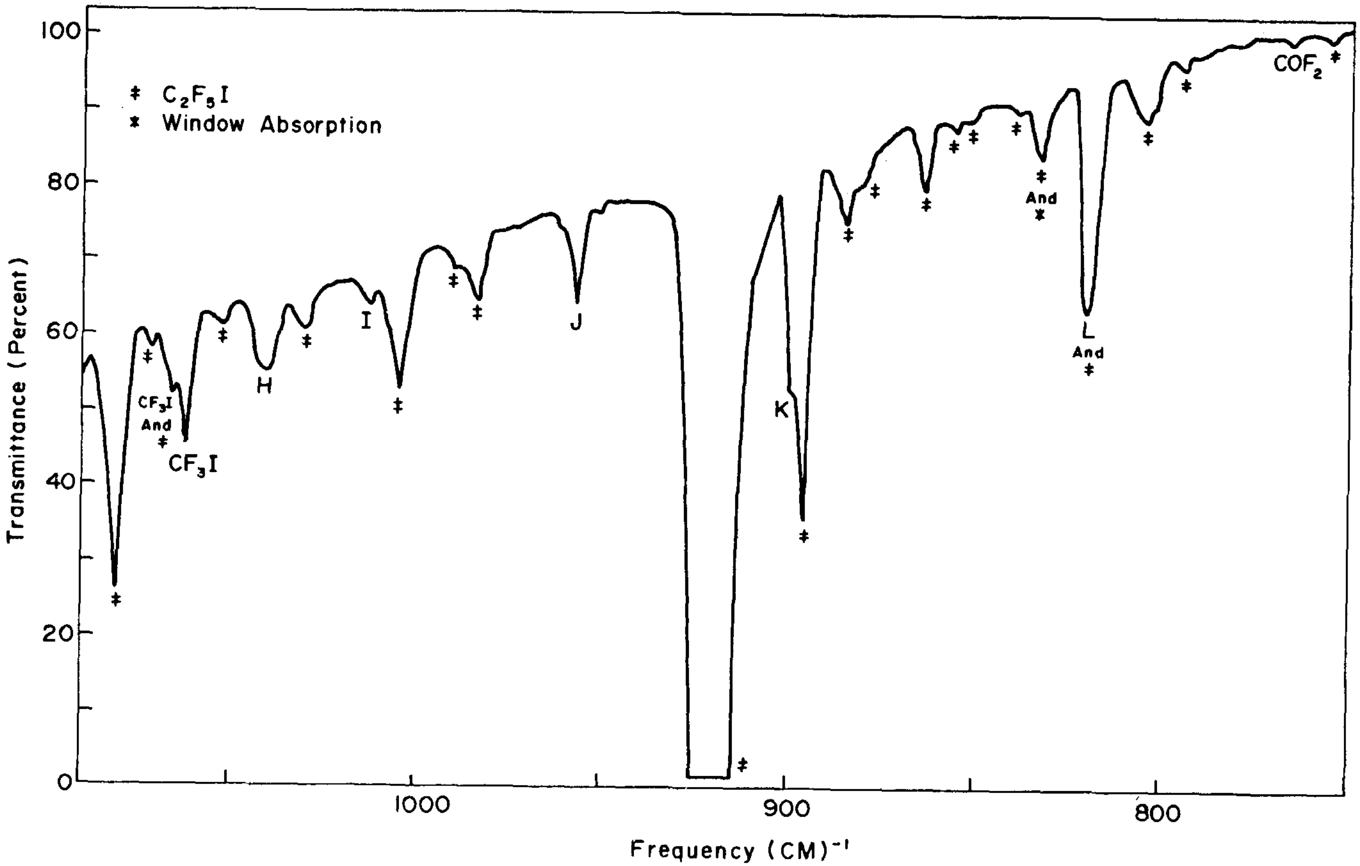

Fig. 2 MATRIX ISOLATION SPECTRUM OF PYROLYSIS PRODUCTS OF C_2F_5I (20hr. Deposition)

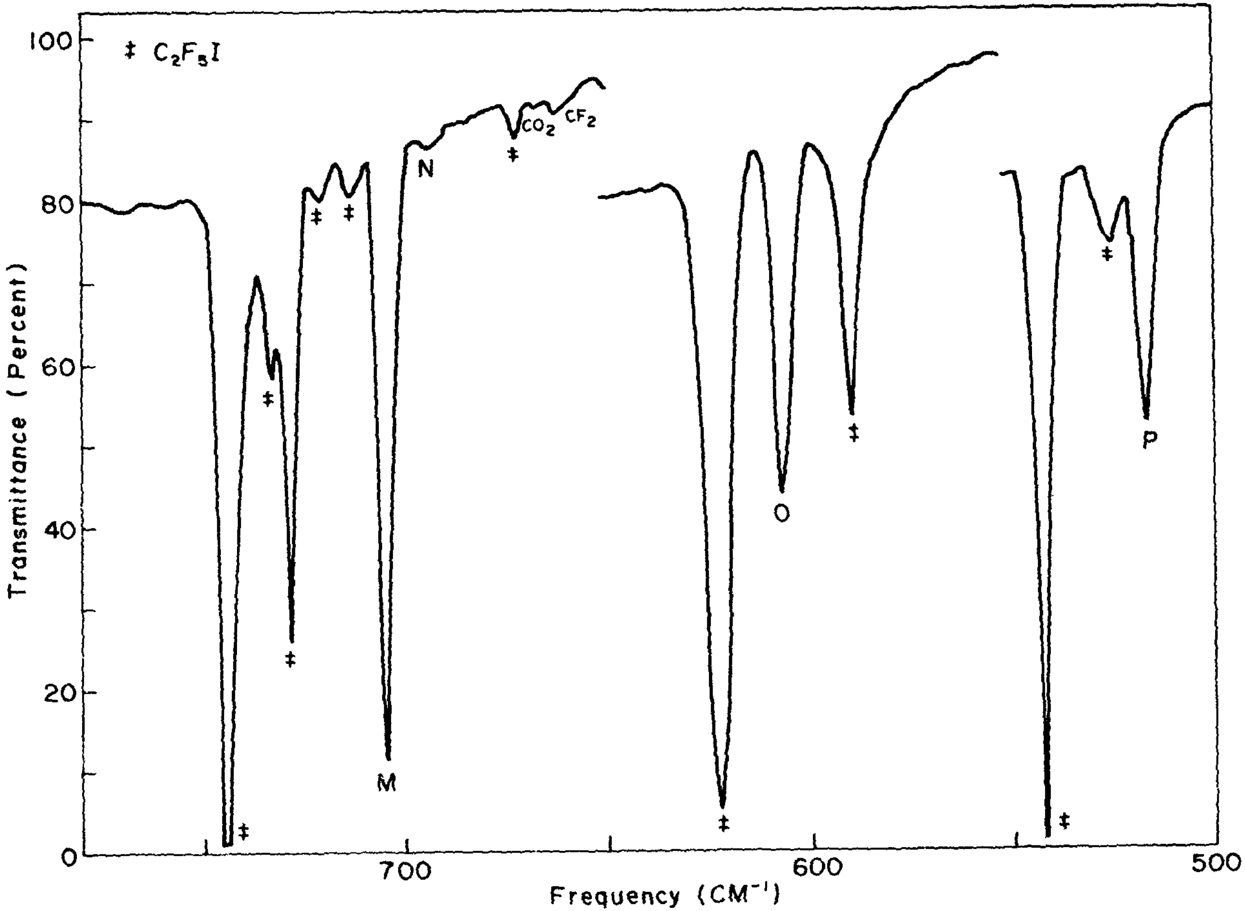

Fig. 3 MATRIX ISOLATION SPECTRUM OF PYROLYSIS PRODUCTS OF C_2F_5I (20hr. Deposition)

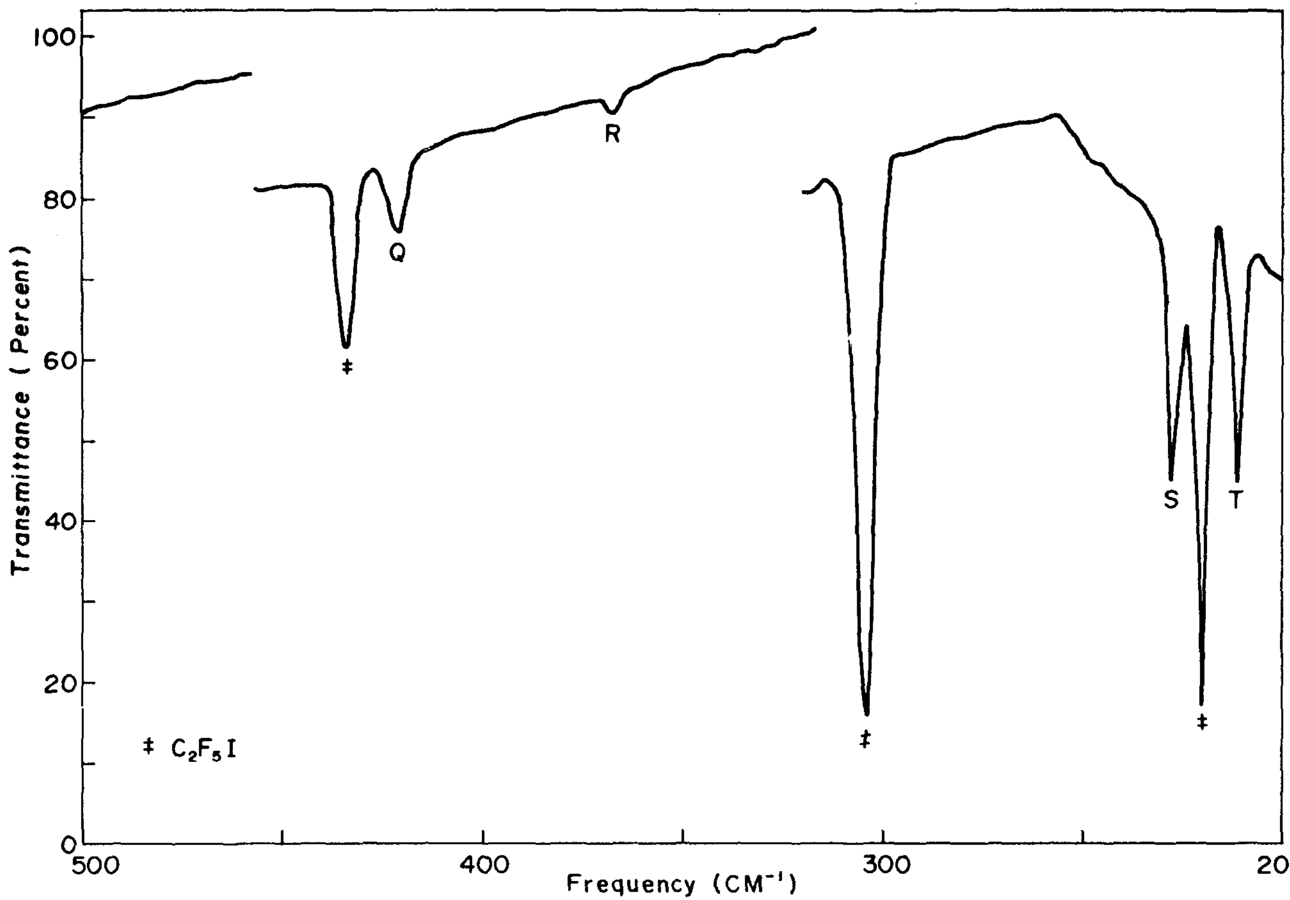

Fig. 4 MATRIX ISOLATION SPECTRUM OF PYROLYSIS PRODUCTS OF C_2F_5I (20hr. Deposition)

compromised. Because of this difficulty, the weaker 604 cm^{-1} absorption band was also used as a reference since it did not suffer interference from any known species.

The standard deviation of the derived relative intensity ratios is presented in Table 2 together with some comments as to experimental difficulties associated with the individual measurements. Not mentioned in this connection are the difficulties associated with spectrometer response. In experiments with heavy matrix deposits, matrix transparency was markedly reduced in the higher (>1,000 cm^{-1}) frequency region. For the weaker bands in this range, optical density measurements are likely to have considerable error. In the low frequency range below 250 cm^{-1}, although matrix transparency was never really bad, the intrinsic spectrometric performance was not very good, due to a combination of low energy and background water vapor absorption.

Because of the above difficulties related to the optical density measurements, it was considered unrealistic to select a single criterion for all the absorption features (i.e., some arbitrary upper limit to the precision of the relative intensity measurements) for determining which absorption bands could have common precursors. Rather, each intensity correlation measurement and its associated standard deviation was considered to see if it fell within a range commensurate with the measurement problems, if indeed the two bands did have a common source. Assuming good instrument response and no problem with defining the correct base line, individual relative intensity measurements can be expected to be accurate to within about 2-12% in the 5-95% transmission range. For bands designated as vvw (Table 2) or those for which peak definition is complicated by partial overlap with other species, making correct base line definition uncertain, the higher limit to the expected accuracy is probably about 45%.

With the above considerations, the intensity correlation data shown in Table 2 may reasonably be taken to indicate that all absorption bands listed could have a common precursor. Assuming the correctness of the conclusion, a better correlation obtains for the data based on the 604 cm^{-1} band (average standard deviation $\bar{\sigma} = \pm 15.7\%$) than that obtained from the 703 cm^{-1} band ($\bar{\sigma} = \pm 19.1\%$). This is consistent with expectations mentioned earlier due to partial overlap of the 703 cm^{-1} band.

At this point, it will be assumed that the most likely candidate responsible for the absorption bands listed in Table 2 is the radical C_2F_5 and an attempt will be made to assign the observed frequencies on this basis.

Table 2

Relative Intensity Ratios For The 24 'Unknown' Absorption Bands In The Spectrum of The Pyrolysis Products Of C_2F_5I

Band	Frequency (cm^{-1})	Intensity Correlation With Band at 703 cm^{-1}	Intensity Correlation With Band at 604 cm^{-1}	Remarks
A	1410 (vw)	± 21.2%	± 24.6%	partially overlapped with band at 1398 cm^{-1}
B	1398 (w)	± 27.1%	± 18.4%	some interference from window absorption
C	1273 (vs)	± 11.7%	± 4.8%	
D	1227 (s)	± 20.0%	± 10.0%	partially overlapped with a C_2F_5I band
E	1193 (vvw)	± 38.2%	± 40.6%	some overlap with a strong C_2F_5I band
F	1184 (vs)	± 13.2%	± 9.4%	
G	1117 (s)	± 17.9%	± 7.6%	
H	1040 (vw)	± 14.6%	± 17.2%	
I	1012 (vvw)	?	?	partially overlapped with a C_2F_5I band
J	956 (vw)	± 32.6%	± 27.5%	
K	898 (vw?)	?	?	overlapped with a C_2F_5I band
L	820 (vw?)	?	?	overlapped with a C_2F_5I band
M	703 (m)	reference	± 6.4%	reference band for intensity correlations
N	694 (vvw)	± 31.2%	± 23.9%	
O	604 (w)	± 6.4%	reference	reference band for intensity correlations
P	514 (w)	± 7.0%	± 6.9%	
Q	419 (vw)	± 14.6%	± 16.9%	
R	366 (vvw)	± 10.4%	± 7.9%	some interference from a C_2F_5I band
S	227 (vw)	± 23.9%	± 18.9%	partially overlapped with a C_2F_5I band
T	211 (vw)	± 14.9%	± 10.7%	

Very little is known of the structure of C_2F_5. An EPR experiment covering a broad temperature range led to the conclusion that the radical site was pyramidal [14], as in trifluormethyl, and that there was a barrier to rotation about the C—C bond of 11.9 kJ mol^{-1}. Such a structure implies the radical belongs to the C_s point group in which all 15 fundamental frequencies are IR active.

In making the tentative assignment shown in Table 3, earlier frequency assignments made for C_2F_5X (X = H [9], F [8], Cl [8], Br [8], and I [8]), CF_3COX (X = F [10], Cl [11], and OH [12]), and CF_3NF_2 [13] have been used for comparison. Five C—F fundamental stretching modes are expected in the 1400-1100 cm^{-1} region with good intensity. There are five obvious candidates at 1398, 1273, 1184, and 1117 cm^{-1}. The three higher and the two lower sets of frequencies are assigned to CF_3 and CF_2 stretching modes, respectively [8]. The distribution of the frequencies to the specific vibrational modes of the CF_3 group are somewhat questionable. There are some indications that the symmetric CF_3 stretching mode lies at higher frequency than the unsymmetrical mode in many compounds [10,11,12,13] and on this basis the frequency at 1398 cm^{-1} was so assigned. In C_2F_5X (X = Cl, Br, and H), the highest frequency has been assigned to an a'' rather than an a' mode as in the present case.

The two lowest frequencies in Table 3--at 211 and 227 cm^{-1}--are assigned to the ν_9 (a') and ν_{14} (a'') CF_3 rocking modes. By analogy with other molecules, this assignment seems fairly certain. The value of the torsional mode at 67 cm^{-1} was calculated based on the barrier height to internal rotation obtained in the EPR study [14].

The assignment for the specific CF_3 and CF_2 deformation modes is at best somewhat arbitrary. The unsymmetrical modes appear in the 770-540 cm^{-1} region, while the symmetrical modes lie at somewhat lower average frequencies of 660-310 cm^{-1}. There are obviously several frequencies in Table 2 which could be assigned to the CF_3 and CF_2 deformation modes. A total of seven lie in the expected range for these modes of 770-310 cm^{-1}. Because of this situation, the best that can be said of the assignment in Table 3 for the lower bending frequency modes is that qualitatively they are reasonable, but that several other permutations of the frequencies would be just as acceptable.

A similar situation exists for the assignment of the ν_4, C—C stretching frequency. In other carbon-fluorine compounds, the frequency appears to fall within the range 940-750 cm^{-1}. In Table 2, there are three frequencies at 820, 898, and 956 cm^{-1} which could be considered. In addition, there are two bands at 1012 and 1040 cm^{-1} which, although at somewhat higher frequencies

Table 3

TENTATIVE FUNDAMENTAL FREQUENCY ASSIGNMENT FOR C_2F_5

Vibrational Mode	Frequency cm^{-1}	Approximate Mode Description
Species a'		
ν_1	1398	Sym CF_3 stretch
ν_2	1273	Unsym CF_3 stretch
ν_3	1117	Sym CF_2 stretch
ν_4	820 - 1040?	C–C stretch
ν_5	703	Unsym CF_3 deformation
ν_6	604	Syn CF_3 deformation
ν_7	514	CF_2 deformation
ν_8	419	Sym FCC angle bend
ν_9	227	CF_3 rock
Species a''		
ν_{10}	1227	Unsym CF_3 stretch
ν_{11}	1182	Unsym CF_2 stretch
ν_{12}	694	Unsym CF_3 deformation
ν_{13}	366	Unsym FCC angle bend
ν_{14}	211	CF_3 rock
ν_{15}	67	Torsion

than noted above, might also be candidates. Although by no means compelling evidence in its favor, it is interesting to note that of the above five frequencies, only that at 1040 cm^{-1} cannot be accounted for in terms of sum or difference frequencies of the other assigned fundamentals. Because of these uncertainties, the assigned C–C stretching mode in Table 3 is simply denoted as the extreme limits covered by the five possible observed frequencies.

There are only two other frequencies in Table 2, at 1410 and 1193 cm^{-1}; which have not been discussed. The former can be interpreted in terms of combination modes of the assigned fundamental, but not the latter. Since this feature is extremely weak and in close proximity to the very strong 1182 cm^{-1} band, it is possible that it may represent some matrix effect on this frequency.

The above may only be regarded as a tentative vibrational assignment for C_2F_5. However, the magnitudes of the frequencies are in a range which would be expected of the radical, assuming that the approximate tetrahedral structure at the radical center is retained. Indeed, the frequencies assigned in this investigation to the C_2F_5 radical are almost identical with those estimated by approximating procedures using C_2F_5H as a model compound and eliminating the three carbon-hydrogen vibration frequencies [14,15]. This finding is reassuring since the latter approximating procedures for carbon-fluorine radicals has only been tested to date on CF_3, for which it also works well, and gives added confidence to this method for estimating frequencies that are required in the computation of thermochemical quantities $C_p°$ and $S°$. In the near future, we will present a normal coordinate analysis for the C_2F_5 radical based on these results.

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