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INFRARED AND ULTRAVIOLET SPECTRUM OF THE FREE RADICAL FCO

by

Dolphus E. Milligan, Marilyn E. Jacox, Arnold M. Bass,
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* NBS Group, Joint Institute for Laboratory Astrophysics at the University of Colorado.
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Dolphus E. Milligan, Marilyn E. Jacox, Arnold M. Bass[*],
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ABSTRACT

FCO has been obtained in a CO and in an Ar matrix at 14-20°K by

the reaction with CO of F atoms produced upon photolysis of OF_2 or of

$t-N_2F_2$, as well as by the photolysis of F_2CO or of HFCO. The three

vibrational fundamentals of the free radical FCO appear at 1855, 1018,

and 626 cm^{-1}. Experiments employing $^{13}C^{16}O$ and $^{12}C^{18}O$ confirm the

infrared identification of FCO. In ultraviolet absorption studies on

matrix-isolated FCO an extensive series of bands has been observed

between 2200 and 3400 A. The most prominent progression in this system

involves bands spaced at approximately 650 cm^{-1} intervals. It is likely

that this progression is associated with the upper state bending mode

of FCO. F_2CO and $(FCO)_2$ are also produced in the reaction of F atoms

with a CO matrix, and features of their infrared spectra are reported.

A supplementary observation of the ultraviolet absorption spectrum of

gaseous F_2CO shows a band system between 1800 and 2100 A, with spacings

of approximately 1700 cm^{-1}. Presumably this system in contributed by

the n → π* carbonyl transition. The approximate geometric structure

and the nature of the chemical bonds of FCO are discussed, and the

mechanisms of formation of this species and of the other observed

products are considered. An estimate of the thermodynamic properties

of FCO is given.

INTRODUCTION

The formyl radical, HCO, has been produced by Ewing, Thompson, and Pimentel[1] in sufficient concentration for direct study of its vibrational spectrum. Crucial to the success of these experiments was their use of the reactive matrix technique. H atoms produced by the photolysis of HBr or of HI were found to react with the CO matrix, with stabilization of the highly reactive reaction intermediate HCO. Recently, Milligan and Jacox[2] have extended this work and have succeeded in resolving several problems associated with the earlier vibrational assignments for HCO and DCO.

In the course of these and other studies, it has been found that H atoms have considerable mobility in CO and in inert gas matrices at cryogenic temperatures. The observations of Milligan and Jacox[3] on the behavior of the infrared absorptions assigned to NCl and NBr when these species are subjected to prolonged photolysis in a matrix environment suggest that Cl and Br atoms may also be able to undergo at least limited diffusion in solids. Given a suitable source of halogen atoms, it appeared feasible to undertake experiments analogous to those on HCO, designed to produce the various haloformyl radicals in an environment suitable for spectroscopic study.

As the following discussion will show, several photolytic sources of F atoms have been found, and FCO has been isolated in a matrix environment in sufficient concentration to permit assignment of all three of its vibrational fundamentals.

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EXPERIMENTAL DETAILS

Four photolytic sources of F atoms and/or of FCO were used in the production of FCO. $t-N_2F_2$ (Air Products, Inc.) was found to contain a small amount of NF_3, which did not appear to photolyze under the conditions of the present experiments. OF_2 (General Chemical Division, Allied Chemical Corp.) was specified as being 99.2% OF_2, with small amounts of O_2, CO_2, and CF_4 as the principal impurities. F_2CO was prepared by the direct reaction of an $Ar:F_2$ = 10 mixture with gaseous CO. The product was freed of Ar by passage through a trap cooled with liquid nitrogen. HCOF was prepared by the procedure described by Morgan, Staats, and Goldstein[4].

Ar and CO (Matheson Co., Inc., C. P. Grade) were used without further purification, except for passage through a P_2O_5 column to remove traces of water. CO enriched to 56% ^{13}CO, as well as CO enriched to 90% $C^{18}O$, were used in some experiments. Samples were prepared using standard manometric procedures. Typical mole ratios CO:(F atom source) ranged between 100 and 400 for the infrared observations. The ultraviolet experiments employed a mole ratio of 160. Experiments were also conducted on three-component systems, Ar:CO:(F atom source). A typical mole ratio for such a system is 200:2:1. Because of its high reactivity, it was necessary to suspend OF_2 in an Ar matrix to use this material as an F atom source.

The cryostats used in these experiments are similar to that described by Milligan[5]. Samples were condensed on a cesium iodide window for the infrared studies and on a lithium fluoride window for

the ultraviolet observations.

All of the infrared observations were made at 14°K, the triple point of hydrogen. The ultraviolet observations were made at 20°K.

The radiation source for photolysis was a medium-pressure mercury arc. For the infrared experiments, photolysis was by direct irradiation through a potassium bromide or, in most experiments, a sodium chloride window, using a quartz focusing lens. To permit observations at wavelengths as short at 1600 A, lithium fluoride windows and a lithium fluoride lens were used for the ultraviolet experiments.

Infrared spectra were recorded on a double-beam, prism-grating spectrometer (Beckman IR-9). Under the conditions of a typical experiment, the resolution and frequency accuracy are both approximately 1 cm^{-1} in the spectral range of interest for the present observations $(400-2000 \text{ cm}^{-1})$.

The ultraviolet absorption spectrum was recorded with an evacuable scanning Ebert-Fastie monochromator[6]. This instrument has a plane grating ruled with 1200 grooves per mm. With the slit widths used (100 microns), the spectral resolution was about 1 A. The detector was an end-on photomultiplier tube (EMI No. 6255B) with a sodium salicylate coating. The background continuum was provided by a hydrogen discharge lamp with a "Suprasil" window, so that the wavelength region 1600-4000 A could readily be scanned.

OBSERVATIONS

The behavior of the infrared absorption spectrum of a typical

CO:t-N_2F_2 sample as a function of the duration of photolysis is given in Table I. The spectra recorded in another typical experiment are reproduced in Figure 1. Except for one weak absorption, it has been possible to assign all of the features appearing in these spectra. Not recorded in Table I, but present in Fig. 1, are features at 895 and 1027 cm^{-1}, contributed by NF_3 impurity in the t-N_2F_2 and unchanged upon photolysis. In addition, the 660 cm^{-1} CO_2 peak has been omitted, as have been its isotopically substituted counterparts in the later discussion. It was difficult to remove traces of CO_2 and of O_2 from the CO sample. This small O_2 impurity accounts for the growth in the CO_2 absorption during photolysis. Supplementary experiments on the system CO_2:t-N_2F_2 show no evidence for the appearance of products of a photolytically-induced reaction. The broad, weak feature appearing in Fig. 1 near 1980 cm^{-1} is a t-N_2F_2 combination band. The possibility that any of the observed features are contributed by HCOF has been excluded by direct observation of the infrared spectrum of this substance in a CO matrix. Relatively small matrix shifts have been observed for F_2CO suspended in CO, compared with the gas phase spectrum of F_2CO reported by Nielsen, Burke, Woltz, and Jones[7]. It is of some interest to note that the Fermi resonance between ν_2 and $2\nu_1$ of this species, indicated in the gas phase spectrum by a shoulder at 1907 cm^{-1} on the broad, very intense 1942 cm^{-1} band, is clearly resolved in the spectrum of F_2CO isolated in a CO matrix; absorptions of nearly equal intensity appear at 1913 and 1941 cm^{-1}. Corresponding to the medium intensity gas phase absorptions of F_2CO at 584 and at 626 cm^{-1}, a relatively thick film of

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F_2CO suspended in CO is found to have absorptions of approximately equal intensity at 585 and at 619.5 cm^{-1}. Both of these absorptions are too weak to appear in the experiment described by Table I. Tullock[8] has observed the most intense absorptions of gaseous oxalyl fluoride, $(FCO)_2$, at approximately 1110, 1263, 1862, and 1876 cm^{-1}. The intense product absorptions appearing near these frequencies have been assigned to this species. The absorptions assigned to $(FCO)_2$ near 1100 and 1270 cm^{-1} are doubled. Saksena et al.[9] have postulated the occurrence of cis-trans isomerism in $(ClCO)_2$ to explain certain features of the infrared and ultraviolet spectrum of this species. The occurrence of cis and trans isomers would explain the doubling of the antisymmetric C—F stretching mode of $(FCO)_2$. A multiple site effect in the matrix also may play an important role in the appearance of this doubling. As will later be shown, the behavior of the less intense absorption at 676 cm^{-1} in the 56% ^{13}CO matrix experiments is appropriate to a species containing two carbon atoms, suggesting that it, too, should be assigned to $(FCO)_2$.

The absorptions assigned to FCO in Table I all diminish in intensity and ultimately disappear when the sample is warmed to a temperature at which diffusion can occur in the matrix, whereas the absorptions assigned to $(FCO)_2$ and to F_2CO change relatively little. The F_2CO absorption at 1941 cm^{-1} diminishes markedly in intensity during the warmup operation, while the absorption at 1913 cm^{-1} grows. Presumably this anomaly occurs as a result of changes in vibration frequencies of the F_2CO molecule on going from an isolated to an associated state.

Table II gives the time dependence of the optical density of

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t-N_2F_2 and of the two more intense absorption pairs assigned to $F^{12}CO$ and $F^{13}CO$ for a thin film of CO ($56\% ^{13}CO$):t-N_2F_2 = 125. Because a small sample was used in this experiment, the FCO absorption near 626 cm^{-1} and the (FCO)$_2$ and F_2CO absorptions were not sufficiently intense for inclusion in this table. Figure 2 shows the resulting absorption pattern after photolysis of a thicker deposit of CO ($56\% ^{13}CO$):t-N_2F_2. Table II and Figure 2 demonstrate that the 1018 (995) and 1855 (1814) cm^{-1} absorptions are contributed by a species containing one carbon atom, and Table II shows that this species is itself subject to photolytic and/or chemical processes which prevent an indefinite buildup in its concentration. When this sample was subjected to prolonged photolysis, beyond the period reported in the table, the peaks assigned to (FCO)$_2$ and to F_2CO continued to grow in intensity. In Fig. 2, the intensity pattern of the 620-626 cm^{-1} pair is also appropriate to a species containing one carbon atom, except that the 620 cm^{-1} peak is slightly more intense than that at 626 cm^{-1}. However, appreciable F_2CO was produced in this experiment, and $F_2{}^{12}C^{16}O$ has a medium-intensity peak at 620 cm^{-1} in a CO matrix. An experiment on Ar:CO ($56\% ^{13}CO$):t-N_2F_2 = 100:2:1 in which very little FCO or (FCO)$_2$ was produced but a high yield of F_2CO was obtained showed that the ^{13}C splitting of this 620 cm^{-1} peak is less than 2 or 3 cm^{-1}. Thus, the slightly greater intensity of the 620 cm^{-1} peak in Fig. 2 may well be due to contributions by $F_2{}^{12}CO$ and $F_2{}^{13}CO$.

Table III summarizes the features which have been observed in studies of the photolysis of t-N_2F_2 in ordinary CO and in CO enriched to 56% $^{13}C^{16}O$ or to 90% $^{12}C^{18}O$. The sample of $^{12}C^{18}O$ was too small to permit observation

of weaker features, such as the absorption anticipated for $F^{12}C^{18}O$ in

the 610-620 cm^{-1} region. A detailed assignment of the features appearing

in the isotopically substituted systems is not attempted in Table III,

except for the designation of the frequencies appearing for $F_2^{13}CO$ in

the Ar:CO (56% ^{13}CO):t-N_2F_2 experiment mentioned above.

Although most of the experiments here reported have used the photo-

lysis of t-N_2F_2 as the source of F atoms, the features tentatively as-

signed to FCO also appear when a CO:F_2CO mixture is subjected to pro-

longed photolysis, and features assigned both to HCO and, tentatively,

to FCO appear when a CO:HCOF mixture is photolyzed. The latter system

has the advantage of minimizing the production of species containing two

F atoms. In fact, only the features due to HCO and those tentatively

assigned to FCO are observed in this system.

As in the CO matrix experiments, all of the spectroscopically

observable products in three-component systems, with an Ar matrix, appear

to involve F and CO. The absorptions are somewhat broader, and bands

assigned to (FCO)$_2$ appear weakly, if at all. This behavior is to be

anticipated at the concentrations of CO (near 1%) employed in the three-

component experiments. The features attributed to FCO have also been

observed following the photolysis of Ar:CO:OF$_2$ mixtures. In an Ar matrix,

several of the features appearing after photolysis, including the 1913-

1941 cm^{-1} Fermi resonance pair of F_2CO, are doubled.

Prior to photolysis, the CO:t-N_2F_2 samples used for the ultraviolet

studies displayed a strong, continuous absorption at wavelengths shorter

than 2400 A, and absorbed weakly toward longer wavelengths. There was

no indication of any discrete structure in the absorption over the range 1700-3600 A. After a ten-minute photolysis period, a series of bands could be observed in the region 2200-3400 A. Continued photolysis produced a growth in the intensity of these bands, but after about two hours of photolysis their intensity had virtually "levelled off", the strongest bands having somewhat less than 20% absorption. This behavior parallels that of the infrared absorptions tentatively assigned to FCO;the concentrations of $(FCO)_2$ and of F_2CO have been found to increase steadily upon prolonged photolysis.

The 2200-3400 A system consists of a series of fairly regularly spaced bands showing slowly varying intensity. The bands are fairly broad, with half-intensity widths in the range 250-400 cm^{-1}. As is usual for matrix observations, no indication of any structure could be observed in any of the bands, but the shape of a number of the bands was somewhat asymmetric, with a tapering off toward shorter wavelengths. The wavelengths of the maxima of the observed bands are listed in Table IV. The principal progression appears to have a spacing of approximately 650 cm^{-1}. In addition, most of the more intense peaks are accompanied by a secondary peak about 240 cm^{-1} to the short wavelength side of the main peak. These secondary peaks may persist in gas phase studies and may play an important role in their analysis. On the other hand,/shifts matrix of the order of 200-300 cm^{-1} are common in ultraviolet observations, and it is also conceivable that this secondary sequence is related to the occurrence of multiple sites.

Supplementary ultraviolet observations were made on HFCO and on

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F_2CO in the gas phase and in a CO matrix. The HFCO spectrum, which has been studied in the gas phase by Giddings and Innes[10], shows a very complex system of absorptions between 1850 and 2600 A. There is no similarity between the HFCO spectrum and the newly observed system. The gas phase (15 cm. path length, 4 mm. partial pressure F_2CO in CO) ultraviolet spectrum of F_2CO, previously unreported, exhibits a group of five bands, shaded to longer wavelengths, between 1800 and 2100 A. The observed F_2CO bands are listed in Table V. Because of a lack of good wavelength standards in this experiment, the wavelength accuracy in Table V is approximately $\pm$ 5 A, although the relative positions are probably correct to within 1 A. In a CO matrix, the absorptions of HFCO and F_2CO showed no discrete band structure, but exhibited continuous absorption at wavelengths shorter than 2300 A.

DISCUSSION

It has been noted that the intensities of the absorptions appearing at 1855, 1018, and 626 cm^{-1} increase somewhat more slowly than do the intensities of the other product absorptions when a typical sample is subjected to prolonged photolysis. Thus, it is suggested that these features may be contributed by a single species. The assignment of the 626 cm^{-1} feature to F_2CO, which has a gas phase absorption at this frequency, has been precluded by the observation of the corresponding F_2CO absorption at 619.5 cm^{-1} in a CO matrix. The disappearance of the three absorptions during the warmup operation confirms their assignment to a single species and indicates that this species is highly reactive. Since these features appear in several systems (e.g., $CO:F_2CO$, $CO:HFCO$,

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and Ar:CO:OF$_2$) in which no nitrogen is present, the species which contributes them cannot contain nitrogen. Their appearance upon photolysis of HFCO is especially suggestive that they result from a species containing only one F atom. Their appearance when F$_2$CO is photolyzed also suggests that only one F atom is involved; it would be anticipated that a C-F bond would undergo photolytic rupture more readily than the C=O bond, and HCO is known to be produced in the photolysis of H$_2$CO. Because each of these features appears in the 56% ^{13}CO matrix experiments, paired with a set of features of approximately equal intensity at somewhat lower frequencies, the species must contain one and only one carbon atom. The presence of oxygen is demonstrated by the observation of a frequency shift for the two higher frequency features in the 90% C^{18}O experiment. In summary, all of the experimental evidence is consistent with the assignment of the 1855, 1018, and 626 cm^{-1} features to the C=O stretching mode, the C-F stretching mode, and the bending mode, respectively, of the free radical FCO.

Structure, Force Constants, and Thermodynamic Properties of FCO

Since no structural data have previously been obtained for FCO, it is necessary to assume suitable geometric parameters in order to estimate force constants for this species. The infrared spectrum attributed to FCO has several points of close similarity to that of the more familiar species HFCO. Thus, it seems reasonable to assume that the two bond lengths are the same as those determined for HFCO (i.e., r_{CF} = 1.34 A, r_{CO} = 1.18 A)[11]. The semiquantitative arguments of Walsh[12] suggest that the valence angles of FCO, HCO, and NO$_2$ should be

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comparable. Ritchie, Walsh, and Warsop[13] have found a valence angle
of 134° for NO_2, while Johns, Priddle, and Ramsay[14] have found HCO
to have a ground state valence angle of 119.5°. This latter value was
derived assuming a C-H bond distance of 1.08 A. However, there is
reason to believe that the C-H bond in HCO is atypical[2]. In view of
the similarity between the infrared spectrum of FCO and that of HFCO,
it may also be significant to note that the FCO angle in HFCO has been
found by Miller and Curl[11] to be 122.8°. Although there is considerable
uncertainty in the estimate of the FCO valence angle, an estimate of the
force constants of FCO appears to be feasible, since force constants
and infrared absorption frequencies are not highly sensitive to geometric
parameters.

Table VI summarizes the valence force constants calculated for FCO
using the bond distances found for HFCO and a valence angle of 135°.
Because it has been found that the approximate separation of the 1855 cm^{-1}
frequency is not too satisfactory, it has been necessary to solve the
unfactored secular determinant for the three force constants. The form
of the secular equation used for these calculations is that derived by
Ruth and Philippe[15], in which all but one of the force constants is
eliminated, resulting in a polynomial with terms up to the sixth power
in this force constant. The C=O stretching force constant was chosen
for this expression, and roots of the equation lying between 12.0 and
15.0 mdyn/A, the range in which this force constant is expected to
occur, were sought using a successive approximation procedure. Only
one value, 12.82 mdyn/A, was found to satisfy the equation within this

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range. Given this value, the other two force constants of Table VI were obtained using the expressions for these summarized by Ruth and Philippe. When a valence angle of 120° was chosen and the procedure repeated, a value for the C=O stretching force constant of 13.28 mdyn/A was obtained, but the C-F stretching force constant was exceptionally large. However, this inconsistency need not exclude the possibility that the valence angle of FCO is near 120°, since the actual bond distances of FCO may differ somewhat from those assumed or, an even more likely possibility, the assumed valence force potential may be inadequate.

The stretching force constants for FCO given in Table VI compare quite closely with those obtained for F_2CO by Overend and Scherer[16]. However, the values given for this latter molecule were based on a Urey-Bradley force field. Because of the relatively great interaction of the nonbonded F atoms, the FCO bending constant for F_2CO is not entirely comparable to that obtained from a simple valence force field. Thus, it is not feasible to compare the bending force constants. Agreement between the force constants calculated for FCO and those obtained by Morgan, Staats, and Goldstein[4] for HFCO is also reasonably good. However, comparison of the C=O stretching force constants of HCO and of FCO suggests that the partial triple bond character of the carbonyl bond of HCO does not have its analog in FCO. Similarly, although the C-H stretching force constant of HCO has been found[2] to be unusually small, the C-F stretching force constant of FCO is quite comparable to that in other molecules.

Utilizing the force constants of Table VI, the frequencies summarized in Table VII have been calculated for $F^{13}C^{16}O$ and for $F^{12}C^{18}O$. Considering that all of the geometric parameters for FCO were assumed and that the $O \cdots F$ interaction was neglected, the agreement appears to be reasonably good.

Despite the uncertainty remaining in the geometric parameters of FCO, an estimate of the thermodynamic properties of this species appears to be feasible, since these properties are not highly sensitive to molecular dimensions. For example, if the FCO valence angle is as low as $120°$, the values of $-(F° - H_0°)/T$ and of $S°$ given in Table VIII would each be increased by 0.31 cal/mole-°K, compared to the values tabulated for $135°$. The values of $C_p°$ and of $(H° - H_0°)/T$ would not be changed.

Electronic Transitions of FCO

The most prominent sequence of the observed ultraviolet band system, attributed to FCO, contains some eighteen bands with a fairly regular spacing of approximately 650 cm^{-1}. (Note the bands marked with an asterisk in Table IV.) This progression conceivably could be attributed either to the upper state C-F stretching mode or to the upper state bending mode. However, analogy with the behavior of related molecules, including HCO and CF_2, and consideration of the molecular orbitals most likely to be concerned in the transition both suggest that most probably a long progression in the upper state bending mode should occur.

Johns, Priddle, and Ramsay[14] have found that the absorption system of HCO between 7500 and 4500 A should be assigned to a $^2A''II - ^2A'$
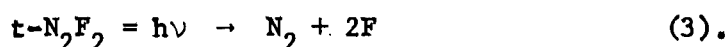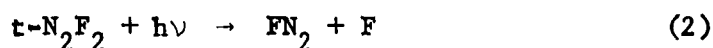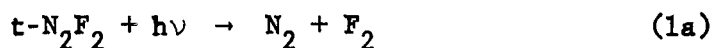
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transition involving the promotion of the unpaired electron, largely localized on the C atom in the ground state, to a higher orbital. In this transition the HCO valence angle goes from approximately 120° to 180° in the upper state. The C=O and C-H bond lengths appear to change relatively little in this transition; most of the bands can be assigned to a progression in the upper state bending frequency. Because predissociation can occur for this species, alternate transitions (to $v_2' = 2n$, n an integer) are diffuse. Splittings due to the Renner effect are also found to play an important role in the analysis of the progression in v_2'.

Walsh[12] has predicted that the haloformyl radicals, XCO, should behave quite similarly to HCO. The ground state of each of these species is predicted to have the unpaired electron largely localized on the C atom. In each case one of the lowest allowed electronic transitions should involve promotion of the unpaired electron to a higher orbital of a" symmetry, which correlates with the same π state for the linear molecule as does the ground state orbital of this electron. For HCO this transition causes the molecule to become linear. However, Walsh predicts that for XCO this higher orbital may still favor a bent molecule, although the valence angle should be considerably larger than in the ground state. Thus, a long progression in the upper state bending frequency is predicted, although the complications of predissociation and of the Renner effect may or may not be present in the upper state of XCO.

Because of the added molecular orbitals when an F atom is substituted for an H atom, still other low-lying electronic transitions

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Mechanism of the Reactions Occurring in the Matrix

Little is known regarding the detailed mechanism of the photo-chemical decomposition of the F atom precursors used for the present experiments. Reactions (1) to (3) represent the possible modes by which F atoms may be produced on photolysis of $t-N_2F_2$:

$$t-N_2F_2 + h\nu \rightarrow N_2 + F_2 \qquad (1a)$$

$$F_2 + h\nu \rightarrow 2F \qquad (1b)$$

$$t-N_2F_2 + h\nu \rightarrow FN_2 + F \qquad (2)$$

$$t-N_2F_2 = h\nu \rightarrow N_2 + 2F \qquad (3).$$

If the primary photolytic process is that of Reaction (1a), it is necessary that Reaction (1b) occur very readily in the matrix environment, since Tables I and II give no hint of an induction period for the formation of FCO in the system $CO:t-N_2F_2$. The trans configuration of the F atoms also somewhat disfavors the occurrence of Reaction (1a). The production of alkyl radicals when the azoalkanes are photolyzed also suggests that Reaction (2) or (3) is more likely. It is, however, more difficult to distinguish between these two possibilities. Apparently, insufficient FN_2 is stabilized in the matrix to permit observation of its infrared spectrum. However, this species may undergo unimolecular decomposition or may photolyze very readily. If it is present, one might expect that recombination of the molecular fragments within the "cage" might lead to the appearance during the course of photolysis of some $c-N_2F_2$. Supplementary observations indicate that this species photolyzes in an Ar matrix at a rate comparable to that observed for $t-N_2F_2$. However, there is no spectroscopic evidence for the production of a significant concentration of $c-N_2F_2$. Although these

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observations may be interpreted as favoring Reaction (3), they do not exclude the possibility that the primary photolytic process is that of Reaction (2).

Once produced, F atoms apparently can undergo limited diffusion in the matrix. These atoms may react with CO (Reaction (4)) even when CO is present

$$F + CO \rightarrow FCO \qquad (4)$$

in relatively small concentration in an Ar matrix. Thus, although a significant activation energy is required for the reaction of H atoms with CO, there does not appear to be an appreciable activation energy required for Reaction (4). Especially in the CO matrix, it is likely that this reaction occurs in sites near those in which the F atoms are produced. Since the usual F atom precursors for these experiments possess two F atoms, Reactions (5) and (6) also occur quite readily even in the early stages of photolysis.

$$FCO + FCO \rightarrow (FCO)_2 \qquad (5)$$

$$FCO + F \rightarrow F_2CO \qquad (6)$$

Because FCO would diffuse only with difficulty in an Ar or a CO matrix at 14°K, and because the diffusion of CO is also inhibited in Ar matrices at 14°K, it is likely that Reaction (5) occurs primarily by the combination of FCO radicals initially formed on adjacent sites. The failure to observe the production of appreciable $(FCO)_2$ in the Ar matrix experiments is in accord with this hypothesis. On the other hand, Reaction (6) is not inhibited in the Ar matrix, since it would require only the diffusion of F atoms.

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The observation of Reaction (7), the reverse of Reaction (6), is of

$$F_2CO + h\nu \rightarrow FCO + F \qquad (7)$$

some further interest. This photolytic reaction occurs relatively slowly, excluding the possibility that FCO is produced by the reaction of F_2, produced by Reaction (1), with CO (Reaction (8)), followed by the

$$F_2 + CO \rightarrow F_2CO \qquad (8)$$

photolysis of F_2CO. Therefore, F atoms must play a major role in the initial formation of FCO when OF_2 or $t-N_2F_2$ is used as the F atom precursor.

In summary, although the details of the photolytic decomposition of F atom precursors such as $t-N_2F_2$ have not yet been completely clarified, consideration of the likely reactions of F atoms and of FCO radicals in the present experiments can account for all of the observed products.

CONCLUSIONS

The vibrational fundamentals of $F^{12}C^{16}O$ have been observed in a matrix environment at 626, 1018, and 1855 cm^{-1}. Observations involving ^{13}C and ^{18}O substitution confirm these results. The products of more extensive reaction, F_2CO and $(FCO)_2$, have also been observed, although the production of the latter is inhibited when an Ar matrix is employed. The C-F and C=O stretching force constants derived from the infrared data for FCO are comparable to those reported for more stable molecules. An ultraviolet absorption system extending between 2200 and 3400 A can be assigned to FCO. The principal progression, with spacings of approximately 650 cm^{-1}, appears to be associated with the upper state bending mode of this species. However, a definite assignment of this

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transition must await gas phase studies. The 1800-2100 A band system, with spacings of approximately 1700 cm^{-1}, which has been observed in supplementary studies on gaseous F_2CO appears to be associated with the $n \rightarrow \pi^*$ transition of the carbonyl group of F_2CO. A consideration of the possible reactions of F atoms, CO, and FCO can account for all of the products observed in the present experiments.

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Table I

TIME DEPENDENCE OF OPTICAL DENSITIES

$CO:t-N_2F_2 = 250$;   12.8 μmole $t-N_2F_2$

Frequency (cm^{-1})	Duration of Photolysis				Assignment
	0 min.	10 min.	20 min.	40 min.	
626	.....	0.024	0.042	0.058	FCO
676	.....	0.021	0.037	0.071	$(FCO)_2$
764	.....	0.016	0.018	0.048	F_2CO
804	.....	.....	0.009	0.022	?
966	0.007	0.016	0.033	0.062	F_2CO
980		100% absorbing			$t-N_2F_2$
1018	.....	0.274	0.400	0.526	FCO
1082	.....	0.015	0.034	0.060	$(FCO)_2$
1101	.....	0.039	0.082	0.186	$(FCO)_2$
1239	.....	0.051	0.108	0.222	F_2CO
1268	.....	0.048	0.083	0.158	$(FCO)_2$
1275	.....	0.014	0.043	0.069	$(FCO)_2$
1855	.....	0.442	0.594	0.735	FCO
1863	.....	0.067	0.149	0.310	$(FCO)_2$
1888	.....	0.052	0.096	0.192	$(FCO)_2$
1913	.....	0.046	0.082	0.183	F_2CO
1941	.....	0.046	0.086	0.187	F_2CO

Table II

TIME DEPENDENCE OF OPTICAL DENSITIES

CO (56% ^{13}CO):t-N_2F_2 = 125; 6.0 μmole t-N_2F_2

Frequency	Duration of Photolysis				Assignment
(cm^{-1})	0 min.	10 min.	40 min.	80 min.	
980	0.502	0.455	0.339	0.249	t-N_2F_2
995	.....	0.019	0.033	0.033	$F^{13}CO$
1018	.....	0.019	0.034	0.034	$F^{12}CO$
1814	.....	0.042	0.086	0.088	$F^{13}CO$
1855	.....	0.040	0.081	0.088	$F^{12}CO$

Table III

FREQUENCIES (cm^{-1}) OF FEATURES APPEARING AFTER PHOTOLYSIS OF $t-N_2F_2$ IN ISOTOPICALLY SUBSTITUTED CO MATRICES

$^{12}C^{16}O$	$^{13}C^{16}O$ (56%)	$^{12}C^{18}O$ (90%)	Assignment (for $^{12}C^{16}O$)
	620		
626	626		FCO
	670 sh		
	673		
676	676		$(FCO)_2$
	731		
	740 *		
764	763		F_2CO
	942 w		
	962		
966	965	950	F_2CO
	995		
1018	1018	1016	FCO
	1055		
	1068		
	1074		
1082	1084	1080 w	$(FCO)_2$
1090 w	1089		
1101	1101	1098	$(FCO)_2$

Table III—Continued

$^{12}C^{16}O$	$^{13}C^{16}O$ (56%)	$^{12}C^{18}O$ (90%)	Assignment (for $^{12}C^{16}O$)
	1204 *		
	1208 sh		
	1216 w		
	1235		
1239	1240	1240	F_2CO
	1253		
1268	1268	1268	$(FCO)_2$
1276	1276 w		$(FCO)_2$
	1814	1813	
	1819	1822	
	1823	1828	
	1841	1849	
1855	1855	1854 w	FCO
1863	1862		$(FCO)_2$
	1866	1868 w	
	1875 *	1876	
		1878	
1888	1887		$(FCO)_2$
		1907	
1913	1912		F_2CO
1941	1940		F_2CO

* Independently determined to be contributed by $F_2^{13}C^{16}O$.

Table IV

WAVELENGTHS OF MAXIMA OF THE ULTRAVIOLET BANDS OF FCO

Relative Intensity	λ_{air} (Å)	ν_{vac} (cm^{-1})	$\Delta\nu^{(a)}$ (cm^{-1})
5	2214.4	45144.8	
15	2227.5	44879.4	
10	2243.6	44557.4	
25	2256.7	44298.7 *	
20 sh[b]	2276.4	43915.4	625.0
30	2289.0	43673.7 *	
15 sh	2309.6	43284.2	631.7
40	2322.6	43042.0 *	
20 sh	2334.8	42817.1	604.8
60	2355.7	42437.2 *	
20 sh	2378.6	42028.7	643.9
50	2392.0	41793.3 *	
15 sh	2414.6	41402.1	640.0
65	2429.2	41153.3 *	
30 sh	2452.4	40764.0	650.2
70	2468.2	40503.1 *	
30 sh	2495.9	40053.6	644.3
90	2508.1	39858.8 *	642.6
90	2549.2	39216.2 *	656.4
100	2592.6	38559.8 *	
	2619.4	38165.3	

Table IV—Continued

Relative Intensity	λ_{air} (Å)	ν_{vac} (cm^{-1})	$\Delta\nu^{(a)}$ (cm^{-1})
50 sh	2628.1	38039.0	657.8
100	2637.6	37902.0 *	
25 sh	2668.0	37470.1	656.6
90	2684.1	37245.4 *	
25 sh	2718.5	36774.1	667.7
90	2733.1	36577.7 *	
70	2782.8	35924.4 *	653.3
65	2837.7	35229.5 *	694.9
70	2891.4	34575.2 *	654.3
45	2928.9	34132.6	661.5
60	2947.8	33913.7 *	
75	2990.8	33426.1	
70	3013.3	33176.6	
75	3053.2	32743.0	
40	3081.6	32441.3	
60	3119.5	32047.2	
35	3163.7	31599.4	
55	3187.0	31368.4	
55	3231.2	30939.4	
25	3269.9	30573.2	
35	3305.8	30241.2	
30	3348.0	29860.0	

(a) Difference between adjacent starred frequencies.
(b) sh designates a weaker band that appears as a shoulder or satellite toward the short wavelength of a major peak.

Table V

ABSORPTION SPECTRUM OF GASEOUS F_2CO

Relative Intensity	λ_{air} (Å)	ν_{vac} (cm^{-1})	$\Delta\nu$ (cm^{-1})
100	2062	48495	
			1705
75	1992	50200	
			1695
60	1927	51895	
			1665
50	1867	53560	
			1630
20	1812	55190	

Table VI

FORCE CONSTANTS (mdyn/A) FOR FCO AND RELATED SPECIES

	HCO	HFCO	F_2CO	FCO[*]
k_{CO}	14.07	11.34	12.85	12.82
k_{CF}	.....	4.76	4.53	4.55
k_{FCO}	.....	1.43	.....	0.94

[*] Assuming r_{CO} = 1.18 A, r_{CF} = 1.34 A, and $\angle FCO = 135°$.

Table VII

CALCULATED[*] AND OBSERVED FREQUENCIES FOR ISOTOPICALLY SUBSTITUTED FCO

Species	ν_{obs} (cm^{-1})	ν_{calc} (cm^{-1})
$F^{12}C^{16}O$	1855	....
	1018	....
	626	....
$F^{13}C^{16}O$	1814	1810
	995	991
	620	622
$F^{12}C^{18}O$	1813	1818
	1016	1013
	....	612

[*] Assuming r_{CO} = 1.18 A, r_{CF} = 1.34 A, and $\sphericalangle FCO$ = 135°.

Table VIII

THERMODYNAMIC PROPERTIES OF FCO (cal/mole-°K)
assuming $r_{CO} = 1.18$ Å, $r_{CF} = 1.34$ Å, and $\angle FCO = 135°$

T (°K)	C_p^o	$\dfrac{H^o - H_o^o}{T}$	$\dfrac{-(F^o - H_o^o)}{T}$	S^o
273.16	9.10	8.26	50.29	58.54
298.16	9.32	8.34	51.01	59.35
300	9.33	8.34	51.06	59.40
400	10.12	8.69	53.51	62.20
500	10.78	9.04	55.49	64.53
600	11.32	9.38	57.17	66.55
700	11.76	9.69	58.63	68.32
800	12.11	9.97	59.95	69.92
900	12.39	10.22	61.13	71.36
1000	12.62	10.45	62.22	72.68
1100	12.80	10.66	63.23	73.89
1200	12.95	10.84	64.16	75.01
1300	13.07	11.01	65.04	76.05
1400	13.17	11.16	65.86	77.02
1500	13.26	11.30	66.64	77.93
2000	13.52	11.82	69.96	81.78
3000	13.73	12.43	74.88	87.31

Figure 1

CO:t-N_2F_2 = 140

———— 9.2 μmole t-N_2F_2; before photolysis

— — — 19.1 μmole t-N_2F_2; 15 min. photolysis

- - - - 28.3 μmole t-N_2F_2; 20 min. additional photolysis
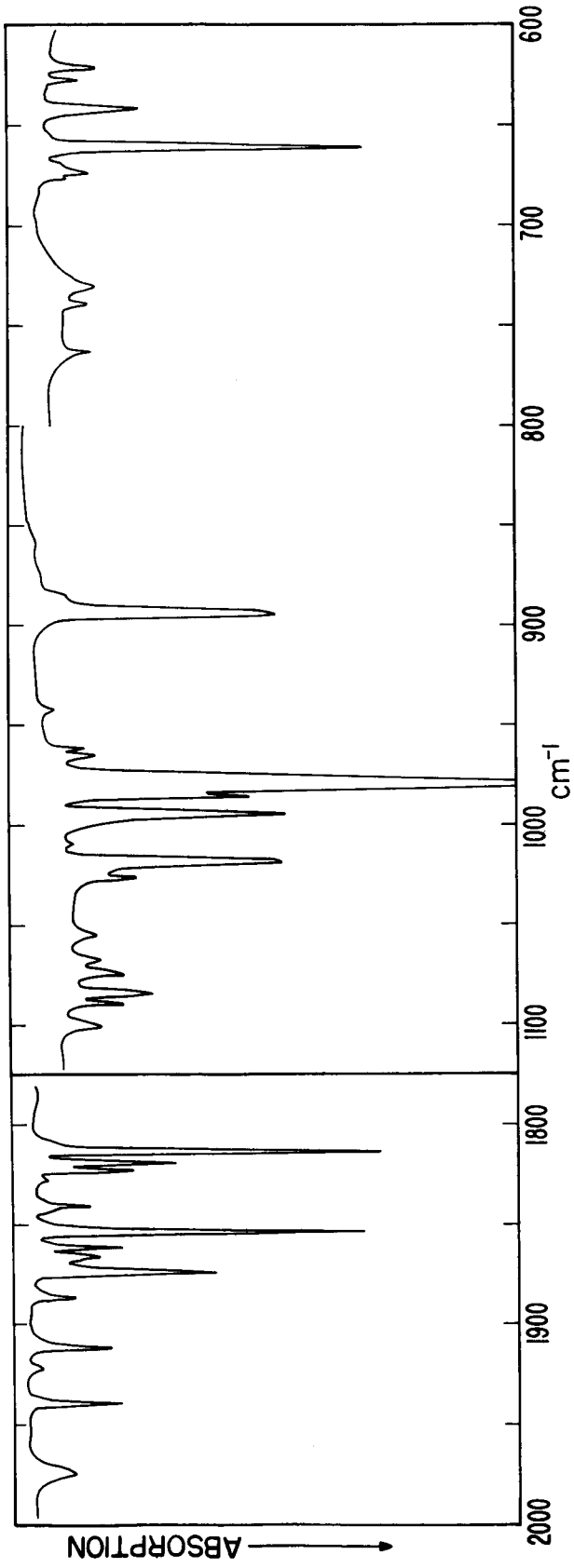
Figure 2

CO (56% ^{13}CO):$t-N_2F_2$ = 200

23.1 μmole $t-N_2F_2$

simultaneous deposition and photolysis, over course of 100 min.