Infrared Emission from the $CF_3 + NO_2$ Reaction

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The reaction of the CF_3 radical with NO_2 has been investigated by using time-resolved FTIR emission spectroscopy. Strong infrared emission has been attributed to products, CF_2O and FNO, excited in the ν_2 and ν_1 modes, respectively. The direct one-step production pathway 1a is suggested as a major reaction channel: $CF_3 + NO_2 \rightarrow CF_2O + FNO$, $\Delta H°_{298} = -267$ kJ mol^{-1} (1a); $\rightarrow CF_2O + F + NO$, $\Delta H°_{298} = -31$ kJ mol^{-1} (1b). The rate constant for reaction 1 was measured to be $(2.4 \pm 0.5) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}. The F atom formation pathway 1b is the minor channel: the relative branching ratio of reactions 1a and 1b was estimated as 1 : 0.015. The formation of the FON isomer formed via a five-center intermediate is discussed as a possible carrier of an unidentified emission band near 1880 cm^{-1}. The $CF_3O + NO$ reaction was investigated by the same technique. Lower emission intensities from the same reaction products were observed, with proportionally less vibrational excitation in the CF_2O product.

Introduction

The role of the CF_3 radical in stratospheric chemistry has been the subject of much research, both experimental[1] and theoretical.[2] The species is also of importance in the field of plasma chemistry, particularly in etching processes, in which free radical reactions are initiated by the dissociation of halocarbon precursor molecules, and in the pyrolysis of fluorocarbon polymer materials exposed to high temperature.[3] Absolute rate coefficients and reaction mechanisms for these elementary halocarbon radical reactions are therefore required in the modeling of these environments.

Kinetic and molecular dynamic information has been reported for the elementary reactions between CF_3 and the atomic species, O,[4] N,[4] H,[5] F,[6] and I,[7] and a variety of molecules, such as O_2,[1,8] NO,[9] NO_2,[10−15] and the self-recombination reaction of the CF_3 radical has also been investigated.[16] In particular, the mechanisms and kinetics of the reactions of NO, NO_2, O_3, and HO_2 with either the CF_3 radical or the related CF_3O and CF_3O_2 species have been emphasized by several authors because of their possible roles in the chemistry of the stratosphere.[13,17−24] Interest has been focused on the various $CF_3/CF_3O + NO_x$ reactions, since these can reduce NO_x in the stratosphere, but substantial uncertainties remain in the nitration mechanisms. For example, although the CF_2O molecule has been identified as a major end product of the reaction between CF_3 and NO_2, estimates of the quantum yield of CF_2O have been conflicting, as the contribution of the addition reaction to form CF_3NO_2 (or CF_3ONO) is uncertain (see refs 14, 15, and 25). Furthermore, the role of the CF_3O radical in the $CF_3 + NO_2$ reaction is not clear.

There have been several studies on the $CF_3 + NO_2$ reaction. Using a very-low-pressure-photolysis (VLPP) molecular beam sampling apparatus combined with mass spectroscopy, Rossi et al. observed the production of CF_2O from infrared multiple photon dissociation (IRMPD) of CF_3I in the presence of NO_2.[10] The rate coefficient of the $CF_3 + NO_2$ reaction was found to be $(2.7 \pm 0.5) \times 10^{-12}$ cm^{3}molecule^{-1} s^{-1} at 298 K, and the following reaction mechanism was suggested:

$$CF_3 + NO_2 \rightarrow CF_3O + NO \quad (1c)$$

$$CF_3O \rightarrow CF_2O + F \quad (2)$$

$$F + CF_3I \rightarrow CF_3 + FI \quad (3)$$

In a later series of experiments, Sugawara et al. applied time-resolved diode laser spectroscopy to follow directly the decay of the CF_3 radicals in the $CF_3 + NO_2$ reaction.[11] The rate coefficient obtained, $(2.5 \pm 0.3) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 300 K, was, however, a factor of 10 greater than that measured by Rossi et al. One possible explanation advanced for the discrepancy between the two measurements involved the known tendency of NO_2 to dissolve in Teflon and thus to affect the concentration assumed in the VLPP technique.[10] If such an explanation were correct, it would suggest that the rate coefficient measured by Sugawara et al. is the more reliable. Furthermore, Sugawara et al. observed absorption lines for transitions of the ν_1 band of nitrosyl fluoride, FNO, at very early reaction times (∼15 μs), an observation which prompted the authors to propose mechanism 1a involving a four-centered transition state:

$$CF_3 + NO_2 \rightarrow CF_2O + FNO \quad (1a)$$

A further investigation of the $CF_3 + NO_2$ reaction was performed by Francisco and Li, using IRMPD of CF_3I in the presence of NO_2.[12] Strong but spectrally unresolved IR emission was observed and assigned to CF_2O, and the rate constant for the reaction was taken to be that for the rising portion of this emission, yielding a value identical to that of Sugawara et.al.[11] Francisco and Li suggested that the major products of the $CF_3 + NO_2$ reaction were $CF_2O^{\ddagger}$ and vibrationally cold FNO, despite FTIR analysis showing no evidence of FNO as an end product.[12]

The final products of the $CF_3 + NO_2$ reaction have been investigated in a flow tube reactor coupled to a chemical ionization mass spectrometric (CIMS) detector by Bevilacqua et al.[13] The various products observed were CF_2O (major product), FNO, and CF_3NO_2 or CF_3ONO. CF_3O was confirmed by monitoring a decline of the peak by reaction with isobutane. Three competing reaction channels were suggested:

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$$CF_3 + NO_2 \rightarrow CF_2O + FNO \quad (1a)$$

$$\rightarrow CF_3O + NO \quad (1c)$$

$$\rightarrow CF_3ONO \quad (1d)$$

Pathway 1a was found to be the major channel. The overall rate coefficient for reaction 1 was found to be $k_1 = (1.0 \pm 0.7) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}. O'Sullivan et al. also reported that reaction of CF_3 radicals with NO_2 resulted in the formation of CF_2O (~75% yield) and CF_3NO_2 (or CF_3ONO) (~25%), and no other C-containing compounds were detected in the IR spectra.[14] Furthermore, O'Sullivan et al. inferred the possibility that CF_2O and FNO could also be dissociative products of CF_3-ONO. Very recently, the title reaction was studied at 296 ± 2 K using IR fluorescence and UV absorption spectroscopy and a branching ratio of (reaction 1a):(reaction 1c) was estimated to be (70 ± 12)%:(30 ± 12)%.[15] In contrast, other mass spectroscopic analyses showed that the quantum yield of CF_2O as a final product of the $CF_3 + NO_2$ reaction is unity.[25]

The rate coefficients and products of the reaction of the related CF_3O radical with NO and NO_2 have been reported.[13,17-24] The CF_3O radical is an important haloalkoxy radical formed during the tropospheric oxidation of CFC substitutes which contain a CF_3 group. The reaction products and rate coefficients are

$$CF_3O + NO \rightarrow CF_2O + FNO \qquad k_4 = (5.2 \pm 2.7) \times 10^{-11}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1} \quad (4)$$

$$CF_3O + NO_2 \rightarrow CF_3ONO_2 \qquad k_5 = (5.1 \pm 0.6) \times 10^{-12}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1} \quad (5a)$$

$$\rightarrow CF_2O + FNO_2 \quad (5b)$$

The rate coefficient of reaction 4 is taken from a recent study investigated by a pulsed radiolysis UV absorption technique at 254 and 276 nm by Sehested et al.[18] Studies of reaction (4) have been used to show that CF_2O is the only C-atom-containing product.[19] However, the FNO product was not detected, possibly as a result of its efficient destruction by collision with the walls of the reactor: the failure to detect FNO may not be used as evidence to exclude its production in the CF_3O + NO reaction. For reaction 5, the rate coefficient is taken from recent studies by photolysis/FTIR absorption methods[19] and laser photolysis/LIF.[20] Chen et al. used photolysis of CF_3NO to prepare CF_3O_2 and subsequently CF_3O in 700 Torr of air at 297 ± 2 K and found that the formation of CF_3ONO_2 is the dominant channel ($k_{(5a)}/[k_{(5a)} + k_{(5b)}] > 90\%$).[21]

Notwithstanding the improved accuracy in recent measurements of the rate coefficient for the $CF_3 + NO_2$ reaction, the mechanism of the reaction, the branching ratio of the product channels, and the role of the CF_3O radical in the mechanism, remain unclear. In this study, IR emission assigned to the CF_2O, FNO, and HF (with H_2 added) products of the $CF_3 + NO_2$ reaction was observed and interpreted to show that the emitting products are formed via the mechanism:

$$CF_3 + NO_2 \rightarrow CF_2O + FNO \qquad \Delta H^\circ_{298} = -267\ \text{kJ mol}^{-1} \quad (1a)$$

$$\rightarrow CF_2O + F + NO \qquad \Delta H^\circ_{298} = -31\ \text{kJ mol}^{-1} \quad (1b)$$

$$F + H_2 \rightarrow HF(v) + H \qquad \Delta H^\circ_{298} = -135\ \text{kJ mol}^{-1} \quad (6)$$

The discussion in this report is concerned with the determination of the products of the $CF_3 + NO_2$ reaction, the measurement of the rate coefficient, the establishment of the reaction mechanism, and the measurement of the relative branching ratio for reactions 1a and 1b. The related reaction of CF_3O + NO was also investigated to compare two different reaction channels which yield the same products. The comparison of the two reactions $CF_3 + NO_2$ and CF_3O + NO support the conclusion that both CF_2O and FNO from the $CF_3 + NO_2$ reaction are vibrationally excited.

Experimental Section

The time-resolved FTIR emission technique and the experimental procedures have been described previously in detail.[26] A brief summary is presented here. The CF_3 radical was produced from IRMPD of either CF_3I or CF_3Br using radiation at 1074.6 cm^{-1} from a pulsed CO_2 laser (the 9R(14) line). At low CO_2 laser fluence, the majority of CF_3I (or CF_3Br) precursor molecules are dissociated in an IRMPD scheme:

$$CF_3I + nh\nu \rightarrow CF_3 + I \quad (7a)$$

The fluence is insufficient to promote the less favorable dissociation (7b):

$$CF_3I + nh\nu \rightarrow F + \text{products} \quad (7b)$$

At high fluence, F atoms are formed by process 7b, and thus in order to avoid the side reactions caused by F atoms, all time-resolved FTIR emission spectra for the $CF_3 + NO_2$ reaction were carefully taken at low fluence (0.5−3.0 J cm^{-2}). IR emission was passed through a modified Michelson interferometer operating in stop-scan mode, and recorded either with a HgCdTe detector (detection range 1100−2400 cm^{-1}, with an optical filter used to block scattered CO_2 laser radiation below 1100 cm^{-1}) or with an InSb detector (detection range 1850−4500 cm^{-1}, with a filter combination). Time-resolved signals were captured with a custom built transient recorder (1 μs time resolution). In some cases, narrow band IR filters were used to isolate emission from the products of interest. The gases used in this study were CF_3I, Fluorochem, >99%; CF_3Br, Fluorochem, >99%; H_2, BOC, 99.7%; Ar, BOC, 99.998%; NO_2, BOC. All thermodynamic data in this study are taken from the literature.[27]

Results

1. Time-Resolved FTIR Emission Studies of the $CF_3 + NO_2$ Reaction. IR emission was observed over the range 1100−4500 cm^{-1} when CF_3I was irradiated in the presence of NO_2. Figure 1 shows a survey of the infrared emission spectrum obtained over this range summed between 0−300 μs after the dissociating laser pulse and taken with both the HgCdTe and InSb detectors. In the range covered by the HgCdTe detector, 1100−2400 cm^{-1}, we identify five emission bands marked as a−f on the upper panel of Figure 1, namely at 1184, 1250, 1625, 1844, 1880, and 1950 cm^{-1}. We first deal with feature a at 1184 cm^{-1}, which is assigned to the precursor molecule $CF_3I^\ddagger$ (ν_4) excited by IR multiple-photon excitation (IRMPE),[28,29] as these emission bands were also detected at early times (<30 μs) without NO_2 present. Feature b also appeared in the absence of NO_2 and is again in the position expected for emission from CF_3I ($\nu_2 + \nu_5$), but with NO_2 present it persisted for longer time periods than before. Emission near 1625 cm^{-1}, feature c, was attributed to the asymmetric stretch of NO_2, which appears to be excited through an energy transfer process.[30] Strong emission in the features d, e, and f are in the regions expected for FNO at 1844 cm^{-1},[31-34] FON near 1880 cm^{-1},[32-34] NO at

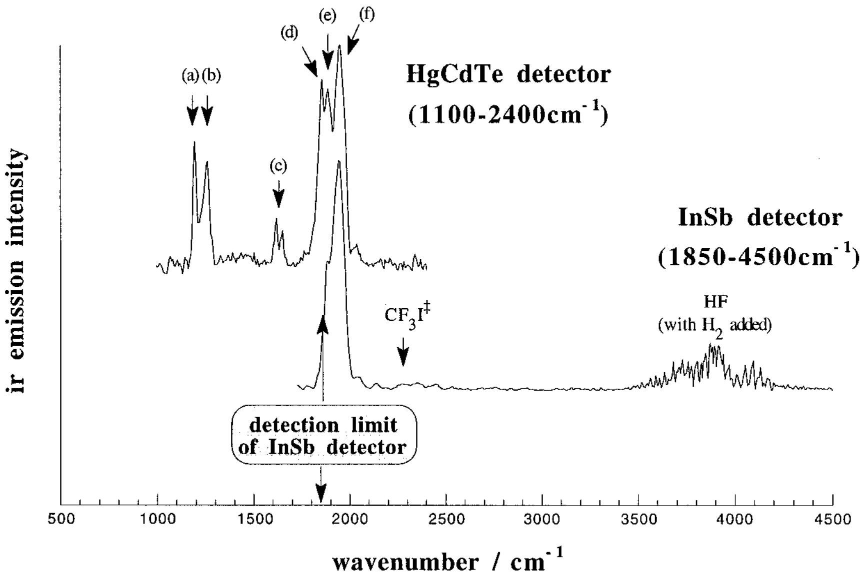


Figure 1. The infrared emission spectrum obtained following the $CF_3 + NO_2$ reaction over the detection range of 1100−4500 cm^{-1}, summed between 0−300 μs. Instrumental resolution is 6 cm^{-1}. Conditions were 50 mTorr CF_3I, 100 mTorr NO_2, and 5 Torr Ar. Bands a−f shown in the figure are identifed in the text.

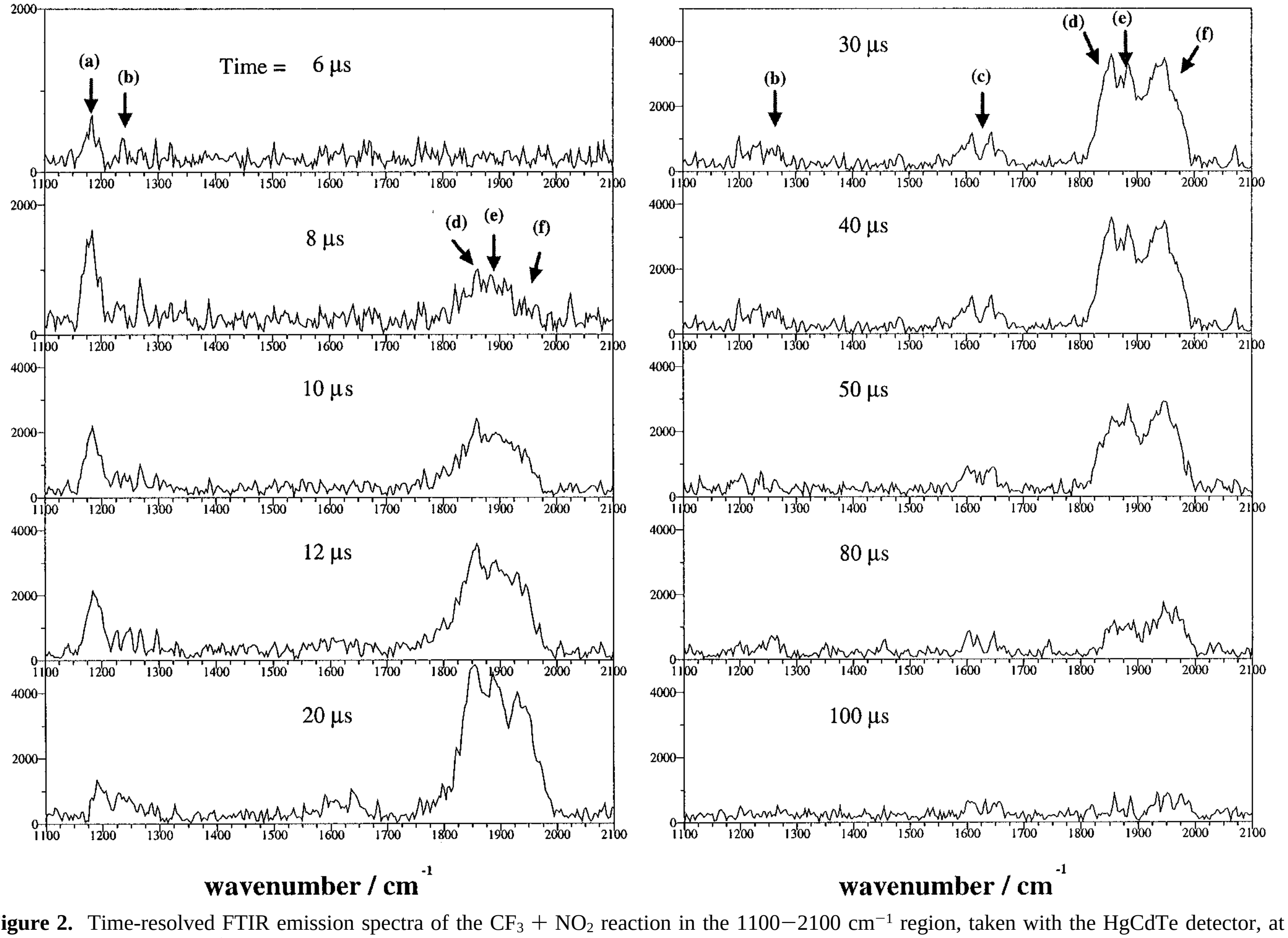


Figure 2. Time-resolved FTIR emission spectra of the $CF_3 + NO_2$ reaction in the 1100−2100 cm^{-1} region, taken with the HgCdTe detector, at low fluence with a 6 cm^{-1} resolution: 50 mTorr CF_3I, 100 mTorr NO_2, and 5 Torr Ar. Emission intensity is in arbitrary units. Each spectrum in the result of averaging over a 2 μs window at the times shown following the CO_2 laser pulse. Features a−f are as in Figure 1.

1876 cm^{-1}, and CF_2O at 1944 cm^{-1} (ν_2),[17,35] all potential products of reaction 1. The major additional feature seen in the InSb spectrum (Figure 1) is emission at 4000 cm^{-1} from vibrationally excited HF formed when H_2 was added to the reaction mixture and indicating the presence of F atoms which react in process 6.

Figure 2 shows time-resolved FTIR spectra in the range 1100−2100 cm^{-1} following the reaction of $CF_3 + NO_2$ taken at 2 μs time intervals and at a resolution of 6 cm^{-1}. The spectra clearly show that the emission near 1200 cm^{-1}, band a, from excited $CF_3I^{\ddagger}$ peaks at very early time and disappears quickly, while the emission bands d−f attributed to reaction products

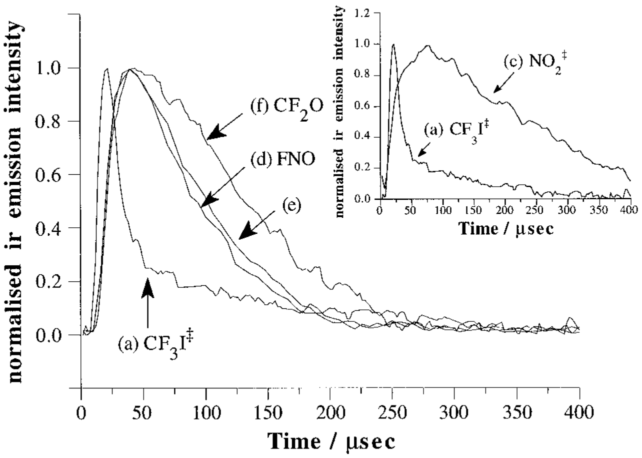


Figure 3. The intensity versus time traces of each emission extracted from Figure 2. Emission from excited precursor (emission a) appears earlier than that assigned to FNO (emission d) and CF_2O (emission f), and both CF_2O and FNO are formed with the same production rate. The evolution rate of NO_2 emission (emission c) is compared with the relaxation rate of the $CF_3I^{\ddagger}$ emission on the top right-hand side.

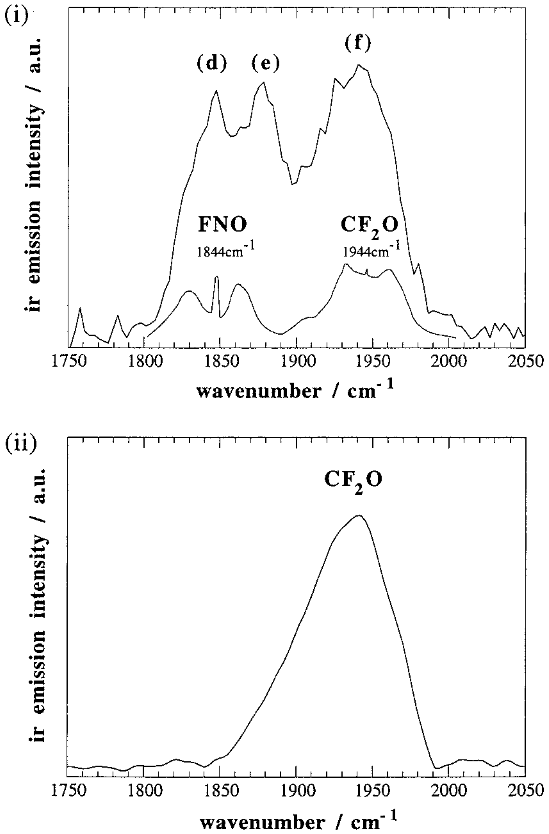


Figure 4. Comparison of the emission bands near 1800−2000 cm^{-1} following the $CF_3 + NO_2$ reaction (i) and with the emission band of CF_2O itself (ii). CF_2O in Figure 4ii was generated from the oxidation reaction of the CF_3 radical with O_3 in the absence of NO/NO_2. Band d is identified as FNO, band e discussed in the text, and band f identified as CF_2O are marked in the Figure 4i. Also shown in Figure 4i are the absorption bands of FNO and CF_2O taken from ref 17.

appear later and last longer. The $CF_3I^{\ddagger}$ band near 1250 cm^{-1} is overlapped by potential emission from CF_2O (ν_4). After the excited precursor emission near 1184 cm^{-1} has disappeared (for example, at 80 μs), the emission at 1250 cm^{-1} remains and then decays with the same kinetics as for band f near 1944 cm^{-1}.

Figure 3 shows the intensity versus time traces of the peaks of each emission feature extracted from Figure 2. What is clear from these traces is that the rise times for features (a) and (c) are markedly different from those of the major emissions d, e, and f. For feature a, attributed to vibrationally excited precursor, rapid formation during the CO_2 laser pulse is followed by rapid quenching, as has been observed in many previous studies of IRMPE.[29] Bands d and f are seen to rise with the same rate, but decay somewhat differently. Band e shows the same kinetic behavior as band d. The emission from NO_2 at 1625 cm^{-1}, band c, appeared to be excited by slower energy transfer from excited products of the reaction of $CF_3 + NO_2$ or excited precursor molecules. Figure 3 also compares the evolution rate of NO_2 emission with the relaxation rate of the $CF_3I^{\ddagger}$ emission.

Infrared emission between 1850−4500 cm^{-1} was investigated using the InSb detector. Compared to the HgCdTe detector, the InSb detector had a higher detection sensitivity in this region, and thus spectra near 1944 cm^{-1} were obtained with a better signal to noise ratio, as can be seen in Figure 1, but, owing to the InSb detector cutoff (~1850 cm^{-1}), only emission band f and a part of band e were observed. Two other weak emissions were seen, one assigned to excited precursor $CF_3I^{\ddagger}$ near 2100−2400 cm^{-1} ($2\nu_1$ at 2146 cm^{-1}, $\nu_4 + \nu_1$ at 2258 cm^{-1}, and $2\nu_4$ at 2370 cm^{-1}) and one near 3851 cm^{-1}, in the position expected for the overtone transition $2\nu_2$ of CF_2O. The different time evolutions of the bands near 2100−2400 and 3851 cm^{-1} were consistent with them being from excited precursor and from the same source as feature f, respectively.

When CF_3Br was used as a source for the CF_3 radical, the same infrared emissions in the 1800−2000 cm^{-1} region, bands d, e, and f were detected. The similarity of the spectra with those generated in the experiments which used CF_3I as the precursor for the CF_3 radical show that other photolytic products from the precursor, for example, I or Br, do not interfere significantly with the $CF_3 + NO_2$ reaction.

2. Emission Bands near 1800−2000 cm^{-1}. The main problem of this study is to identify the emission bands from reaction products near 1800−2000 cm^{-1}. Figure 4i shows the observed emission bands, d, e, and f, detected from the $CF_3 + NO_2$ reaction, together with the infrared absorption spectra of FNO (ν_1 band origin at 1844 cm^{-1})[31−34] and CF_2O (ν_2 band origin at 1944 cm^{-1}).[17,35] The resolution of the present observations (6 cm^{-1}) is such that positive identification through rotational structure of an emission band is not possible, and thus the assignments of the bands in this region necessarily remain tentative. Bands d and f are in the positions expected for the strong $\Delta\nu_1$ and $\Delta\nu_2 = -1$ transitions in FNO and CF_2O, respectively, and are identified as such. The source for band e is not immediately obvious. It could be argued that band e could come from highly vibrationally excited CF_2O emitting in a red-shifted region. In order to test this, the emission from CF_2O only was generated from the reaction of the CF_3 radical with O_3 reaction 8 in the absence of NO/NO_2:

$$CF_3 + O_3 \rightarrow CF_2O^{\ddagger} + FO_2 \qquad \Delta H^\circ_{298} = -284 \text{ kJ mol}^{-1} \tag{8a}$$

$$\rightarrow CF_2O^{\ddagger} + F + O_2 \qquad \Delta H^\circ_{298} = -231 \text{ kJ mol}^{-1} \tag{8b}$$

Time-resolved FTIR emission spectra of reaction 8 showed that the emission from high vibrational levels of CF_2O predominated, with a cascade to lower levels shifting the spectrum to higher wavenumbers as time progressed, eventually leading to emission from the ground vibrational state of CF_2O near 1944 cm^{-1}. Figure 4 illustrates a comparison of the emission bands near 1800−2000 cm^{-1} following the $CF_3 + NO_2$ reaction: Figure 4i, with the emission band of CF_2O itself formed from the $CF_3 + O_3$ reaction, Figure 4ii, summed over the same time interval and under similar precursor pressures. The time evolution of these two spectra shows that band e behaves very differently from the low-wavenumber emission from vibrationally excited CF_2O shown in Figure 4ii, the former retaining its separation from the main CF_2O peak at 1944 cm^{-1} over all times later than ~20 μs from reaction initiation. Considering that the available energy in the vibrationally excited CF_2O in the two reactions 1 and 8, are similar, 267 and 231 kJ mol^{-1},[27] respectively, it appears that band e in Figure 1 cannot be from highly vibrationally excited CF_2O.

NO has an emission band near 1874 cm^{-1}, exactly in the position observed for band e. To test this, a cold gas filter experiment was performed to quantify the amount of NO ($v = 1 \rightarrow 0$) emission. When a low pressure of NO (2 Torr) was present in the cold gas filter cell, the intensity of the emission between 1840−1920 cm^{-1} isolated by a filter and reaching the detector was not significantly decreased, a result which implied that the only a small portion of the emission was from NO (v=1) (if the emission is entirely from the excited NO, ~75% of the emission would be resonantly absorbed in a 10 cm cell under these conditions). The result of cold gas filter experiments gave an estimate of the fraction of NO ($v=1 \rightarrow 0$) in the emission observed over 10−100 μs near 1840−1920 cm^{-1} as 1.65%.

Comparison of the spectra in Figure 4 and the result of NO cold gas filter experiment indicate that the emission band e is from neither CF_2O nor NO. A possible candidate for band e is FON; this will be discussed later in detail.

3. CO_2 Laser Fluence Dependence of the Emitting Species. In the low CO_2 laser fluence region (<3 J cm^{-2}), the intensities of the emissions identified as from CF_2O, FNO, and $CF_3I^‡$ were monitored as a function of laser fluence. The CF_2O and FNO emissions showed the same fluence dependencies with a threshold for the formation of the CF_3 radical near 0.6 J cm^{-2}. Excited precursor emissions, at 1184 and near 2250 cm^{-1}, show in contrast a much lower fluence threshold, well below that for the production of the CF_3 radical. Thus, it was confirmed that the emissions from CF_2O and FNO originated in the CF_3 radical pathway 1a, and not from the reaction of $CF_3I^‡ + NO_2$.

4. Kinetics of the Product Emission. The time dependencies of the emission features were investigated at various NO_2 concentrations. These experiments were performed at low fluence in order to avoid any side reactions involving F atoms formed from the precursor.[29] A narrow band-pass optical filter (1840−1920 cm^{-1}) was placed in front of the HgCdTe detector to measure the emission from bands d, e, and f: this wavenumber range was chosen to encompass emission from the most highly vibrationally excited CF_2O formed to avoid the cascade of vibrational population from higher levels. It should be emphasized, however, that the peaks of these emission bands showed very similar rising rates, as shown in Figure 3. The time dependence of the emission showed a characteristic double-exponential rising and falling behavior (one for reaction and one for relaxation), the rates of which both increased with increasing NO_2 pressures. A plot of the rising rates versus NO_2 pressure was linear, as shown in Figure 5, with a slope of $(2.4 \pm 0.5) \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1}, which was consistent with two previous measurements of the rate coefficient of the $CF_3 + NO_2$ reaction within error range.[11,12] The falling rates were also increased with a slope of $(6.4 \pm 0.4) \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} as a function of the NO_2 pressure. From such behavior, however, it is not possible unequivocally to identify the rising rate with process 1 (as was done in the IR emission study of Francisco and Li[12]), as fast relaxation and slow reaction would produce the same double-exponential kinetics. To separate these rate processes, a comparison of the quenching effect of the emission by N_2 and O_2 was investigated. N_2 or O_2 (0−2.5 Torr) were added in turn to a gas sample consisting of 20 mTorr CF_3I, 100 mTorr NO_2, and 5.8 Torr Ar. When N_2 was added to the gas sample, the rising rates were unchanged but the falling rates were increased with N_2 pressure with a slope of 1.24×10^{-13} cm^3 $molecule^{-1}$ s^{-1}, which is identified with the quenching rate of the vibrationally excited products by N_2. However, when O_2 was added to the gas sample, both rising and falling rates were increased, with slopes of 1.08×10^{-12} and 2.14×10^{-13} cm^3 $molecule^{-1}$ s^{-1}, respectively: the slope for the falling rates corresponds to quenching of the emission by O_2 and the observation of increased rising rates at higher O_2 pressure was consistent with the loss rate of the CF_3 radical by reaction with O_2 under the present experimental conditions.[1,8] The precursor pressure dependence of the emission was also investigated. The rising rates were again found to be independent of CF_3I pressure, and the amplitude of the emission increased linearly with CF_3I pressure. It seems that the production of CF_2O is not affected by any subsequent reactions with other products from the $CF_3 + NO_2$ reaction. The time dependence of the emission on the pressure of added H_2 was also investigated. The emission showed a simple quenching response with increased H_2; rising rates were found to be independent of H_2 pressure and falling rates were increased at higher H_2 pressures. This result implies that the production mechanism for CF_2O is independent of H_2 and that the subsequent $H_2 + CF_2O$ reaction 9 is not significant on the timescale of the current experiments:

$$H_2 + CF_2O \rightarrow \text{products} \tag{9}$$

The above results confirm that the rising rates are consistent with the loss of the CF_3 radical, i.e., the CF_2O production by reaction 1, and falling rates are the relaxation of vibrationally excited products. Therefore, the observed slope of the rising rates as a function of NO_2 pressure, $(2.4 \pm 0.5) \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1}, represents the rate constant for the $CF_3 + NO_2$ reaction.

Further investigation of the emission was carried out with a filter in the range 1915−1980 cm^{-1}, i.e., covering all of band f. Again double-exponential rising and falling rates were seen,

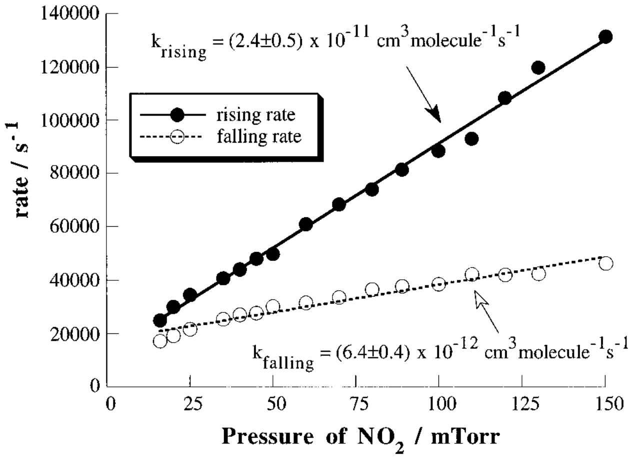


Figure 5. Plots of the rising (●) and falling (○) rates of the CF_2O emission against NO_2 pressure. Conditions were 7 mTorr CF_3I, 5 Torr Ar, and 16, 20, 25, 35, 40, 45, 50, 60, 70, 80, 89, 100, 110, 120, 130, and 150 mTorr NO_2; the emissions were observed through an interference filter FWHM 50 cm^{-1} centered at 1880 cm^{-1}. The straight-line-least-squares-fits to the data give rising and falling rate constants of $(2.4 \pm 0.5) \times 10^{-11}$ and $(6.4 \pm 0.4) \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1}, respectively.

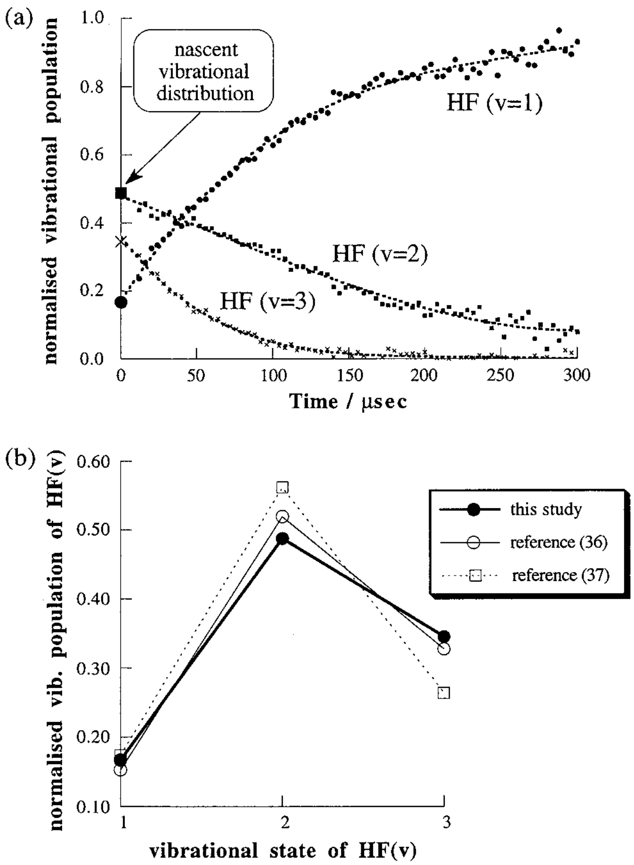


Figure 6. (a) Time evolution of normalized vibrational populations of HF(v) formed in the $CF_3 + NO_2$ reaction in the presence of H_2. Conditions were 7 mTorr CF_3I, 75 mTorr NO_2, 50 mTorr H_2, and 5.2 Torr Ar with a 10 cm^{-1} resolution. Extrapolated values to zero time represent the nascent vibrational distribution of the HF(v) and are plotted in (b). The nascent distribution of HF(v) is compared with the literature values for the $F + H_2$ reaction.

but with a rising rate constant a factor of 2 smaller than that shown in Figure 3. We interpret this lower rate constant as demonstrating the effects of vibrational cascade from higher levels of CF_2O slowing down the production process. Figure 2 shows that as time progresses the peak of feature f is not developed until some 20 μs after reaction initiation, in contrast with the earlier appearance of the resolved peak of feature d. Vibrational cascade will thus affect any kinetic observations which include the high-wavenumber part of peak f and will lead to an underestimation of the true rate constant.

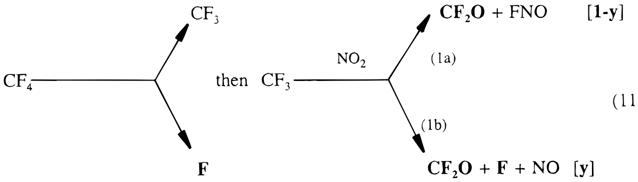
5. F-Atom Formation in the $CF_3 + NO_2$ Reaction. *5.a. Source of Emission from Vibrationally Excited HF.* Further results were obtained when H_2 was added to the reaction system. No HF emission was seen in the absence of NO_2, but when NO_2 was added, HF emission appeared. The fluence dependence of this emission was found to be similar to that from CF_2O and FNO, a result which implied that the source of HF was from reaction of the CF_3 radical.

Figure 6a shows the normalized vibrational populations of HF as a function of delay time after the CO_2 laser pulse. The nascent HF(v) distribution was obtained from an extrapolation of the data shown in Figure 6a to a delay of zero. The HF(v) distribution so obtained compared well with literature values[36,37] for the $F + H_2$ reaction as shown in Figure 6b, a result which implies strongly the reaction as the source of the majority of HF in the present system. The kinetics of formation of HF were found to be consistent with its formation from the reaction sequence 1b and 6. The reaction must, however, be dominated by pathway 1a because, despite the fact that the emission coefficients of HF(v) are known to be larger than those for CF_2O,[38] the intensity of HF(v) emission observed was much smaller than that of CF_2O.

5.b. Measurement of the CF_2O:F Ratio. A series of experiments based on the IRMPD of CF_4 were carried out to quantify the relative amounts of F and CF_2O produced from the $CF_3 + NO_2$ reaction. CF_4 was chosen as the "reference precursor" because the IRMPD of CF_4 produces CF_3 and F in a 1:1 yield:

$$CF_4 + nh\nu \rightarrow CF_3 + F \qquad \Delta H°_{298} = 545 \text{ kJ mol}^{-1} \quad (10)$$

In the present system both NO_2 and H_2 are present. The CF_3 radicals produced by the IRMPD of CF_4 react with NO_2 via one of two reaction channels (the numbers in square brackets are the branching ratios for the two channels):



(11)

Since the CF_2O species is produced in the reaction of $CF_3 + NO_2$, its emission may be used as a measure of the CF_3 concentration. The emission from HF excited by the $F + H_2$ reaction is related to the F atom concentration: note, however, that F atoms are produced by both the IRMPD of CF_4 and by one branch of the $CF_3 + NO_2$ reaction. Therefore, the ratio of the emission intensities from CF_2O and HF in the presence of NO_2 and H_2 following the IRMPD of CF_4 corresponds to a ratio of $CF_2O : F = 1:(1 + y)$. The concentration ratio of CF_2O:HF from the $CF_3 + NO_2$ reaction is 1:y, when CF_3 is produced from the IRMPD of the CF_3I precursor. The intensity ratio of the CF_2O and HF emissions produced from the CF_3I precursor was measured at low fluence (to avoid IRMPD directly forming F atoms), then compared with that from CF_4 precursor under the same experimental conditions except at high fluence (conditions required for the IRMPD of the precursor). The comparison yielded a value of $y = 0.015 \pm 0.002$, which means that the relative branching ratio of two reaction pathways (reaction 1a):(reaction 1b) is 1:0.015, and is a result which is in good agreement with the estimation of a small amount of NO ($v = 1 \rightarrow 0$) made from the NO cold gas filter experiment. Error limits are estimated from uncertainties in the response of the IR detector over the dynamic range studied. In conclusion, our results are consistent with the products of the $CF_3 + NO_2$ reaction being predominantly CF_2O + FNO with a far smaller quantity of CF_2O + NO + F.

Discussion

1. Band e. We conclude from the evidence presented above that CF_2O and FNO are both formed as major products of the $CF_3 + NO_2$ reaction. However, there is still an unresolved problem in identifying of band e, which emits near 1880 cm^{-1}. The production and relaxation rates of band e were very similar to those of FNO, band d, in Figure 3. A possibility of the formation of the isomer FON via a five-center intermediate was considered. Smardzewski and Fox in 1974 reported the three fundamentals of FON from Ar- and N_2- matrix isolation experiments: 1886.6 (ν_1), 735.1 (ν_2), and 492.2 (ν_3) cm^{-1} in an Ar-matrix; 1904.1 (ν_1), 724.6 (ν_2), and 485.4 (ν_3) cm^{-1} in a N_2-matrix.[32] In each matrix, the peak assigned to FON was blue shifted with respect to that from FNO by ~34 cm^{-1}, identical to that observed between bands d and e in the present

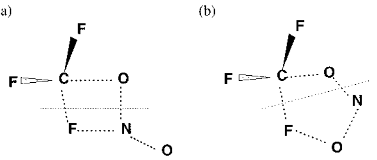


Figure 7. Two possible reaction intermediates in the CF_3+NO_2 reaction leading to CF_2O and F(ON) products.

experiments. No observation of the gas phase absorption spectrum of FON has been reported, but a similar isomeric shift would be expected. It should however be noted that Smardzewski and Fox's results have been questioned : the lack of observation of a peak near 1887 cm^{-1} in a later Ar matrix experiment[33] (in which the isomeric FON was believed to be present) and ab initio studies of the predicted isomeric and isotopic shifts[34] have raised the possibility that the two bands observed in the 1850−1887 cm^{-1} range[32] might be from FNO present in different matrix sites. A simple idea of two possible intermediates (namely, four-center and five-center) of the $CF_3 + NO_2$ reaction is illustrated in Figure 7. If reaction proceeds via a five-center intermediate, then FON can be formed, reaction 1e.

$$CF_3 + NO_2 \rightarrow CF_2O + FNO \qquad \Delta H^\circ_{298} = -267\ \mathrm{kJ\ mol^{-1}} \quad (1a)$$

$$\rightarrow CF_2O + FON \qquad \Delta H^\circ_{298} = -112\ \mathrm{kJ\ mol^{-1}} \quad (1e)$$

The FON isomer is calculated to be the less stable by some 155 kJ mol^{-1}, but has a barrier to isomerisation of some 35 kJ mol^{-1}.[34,39] Even if this interpretation is correct, the data are not of sufficient quality to enable any quantitative conclusions to be drawn concerning the relative quantum yields of channels 1a and 1e, owing to the overlap of the spectral features d, e, and f and their unknown vibrational distributions and emission coefficients. Ab initio calculations of transition state structures similar to those illustrated in Figure 7 would help in deciding the feasibility of forming the (less strained) five-membered ring system leading to FON formation. However, at present such formation must be regarded as speculative.

2. Mechanism for Formation of CF_2O and FNO. Rossi et al. suggested that the production of CF_2O in the $CF_3 + NO_2$ reaction occurs via a two step reaction mechanism via reactions 1c and 2 involving the sequence $CF_3 \rightarrow CF_3O \rightarrow CF_2O$.[10] Under our conditions, process 2 can only take place for CF_3O species having considerable vibrational energy, and from the kinetic evidence presented above, it would seem that process 1c is rate limiting. This two-step scheme, however, suggests the formation of equal quantities of F and CF_2O products, with no FNO produced. Evidence for the F/CF_2O ratio being far smaller (0.015) is not consistent with this scheme. Furthermore, features assigned to vibrationally excited CF_2O and FNO appear with the same production rate, as can be seen in Figure 3, and is further good evidence to support the direct formation of both products such as process 1a. We can discount the possibility of formation of CF_3O by reaction 1c followed by production of vibrationally excited CF_2O by process 5b, its reaction with NO_2. Under our conditions, reaction 5b would be rate determining ($k_5 \cong 0.2k_4$) and would thus result in slower formation rates than those experimentally observed. No emission could be detected in the $CF_3 + NO_2$ system from possible products of the $CF_3O + NO_2$ reaction.[19,21] In a separate experiment, weak infrared emission near 1750 cm^{-1}, which could be from CF_3ONO_2, or more likely FNO_2, was detected when CF_3O was formed in excess NO_2. The CF_3O radical was produced by the following mechanisms when O_2 and NO were added to the system:

$$CF_3 + O_2 + M \rightarrow CF_3OO + M \quad (12)$$

$$CF_3OO + NO \rightarrow CF_3O + NO_2 \quad (13)$$

$$CF_3O + NO \rightarrow CF_2O + F(NO) \quad (4)$$

$$CF_3O + NO_2 \rightarrow CF_3ONO_2 \quad (5a)$$

$$CF_3O + NO_2 \rightarrow CF_2O + FNO_2 \quad (5b)$$

Although the rate coefficient for reaction of CF_3O with NO (4) is ~10 times faster than that with NO_2 (reaction 5), under conditions of excess NO_2 (and O_2), reaction 5 necessarily dominates reaction 4. Our conclusions from these studies are that the mechanism including the CF_3O radical is unlikely.

A brief investigation was made of the $F + NO_2$ reaction as a possible source of the FNO species as a small fraction of F atoms are produced from the $CF_3 + NO_2$ reaction. F atoms were produced by IRMPD of SF_6 with the 10P(20) line of the CO_2 laser. When 50 mTorr of NO_2 was added to the sample of 30 mTorr SF_6 and 5 Torr Ar, a weak emission near 1800−1900 cm^{-1} was detected, the source of which could have been FNO. However, the intensity of the emission was very small when compared to the FNO emission from the $CF_3 + NO_2$ reaction, even at high SF_6 pressures. Therefore, it seems that the reaction of F atoms with NO_2 is almost certainly not the source of the FNO emission observed near 1800−1900 cm^{-1} in the $CF_3 + NO_2$ reaction.

3. Comparison with the CF_3O + NO Reaction. The CF_3O + NO and $CF_3 + NO_2$ reactions can yield the same products, CF_2O + F(NO).[13,17−24] Emissions were observed in the 1850−4500 cm^{-1} region following the IRMPD of CF_3I in the presence of excess NO and O_2. CF_3O is produced via processes 12 and 13, and $C^{\ddagger}{}_3O$ then reacts with NO to give the observed products of reaction 4. Both NO and O_2 were required to produce emission from CF_2O. The rate coefficient for reaction 13 has been reported as $(1.57 \pm 0.31) \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} from observations of the removal rate of the CF_3OO radical,[23,24] and the reaction of CF_3OO + NO is thought to proceed solely by this path.[24] Another possible source for the CF_3O radical is the self-reaction of CF_3OO, but under the present conditions its contribution to CF_2O production is low.

There is a well known but slow reaction between O_2 and NO to give NO_2 or NO_3.[40] Since both O_2 (600 mTorr) and NO (70 mTorr) are present in the reaction system at relatively high pressures, the reaction between these species could be a significant source of extra NO_2 and could thus react with CF_3 as demonstrated in the earlier part of this study. An experiment was performed in order to quantify this. Both O_2 and NO were introduced to the flow cell through the side arms of the flow tube. The reagent O_2 was introduced from a fixed position, and NO injection point was varied, thus changing the contact time between O_2 and NO. There was no difference in intensity of the CF_2O emission when the injection position of NO was changed. Therefore, the O_2 + NO reaction could not be a source of extra NO_2.

The infrared emission from CF_2O formed in the CF_3O + NO reaction was about four times smaller than that from the $CF_3 + NO_2$ reaction at similar reagent concentrations. The slower production rate of CF_2O and the lower exothermicity of the CF_3O + NO reaction account for this. Figure 8 compares the infrared emission spectra recorded following the CF_3O + NO reaction with that recorded following the $CF_3 + NO_2$ reaction.

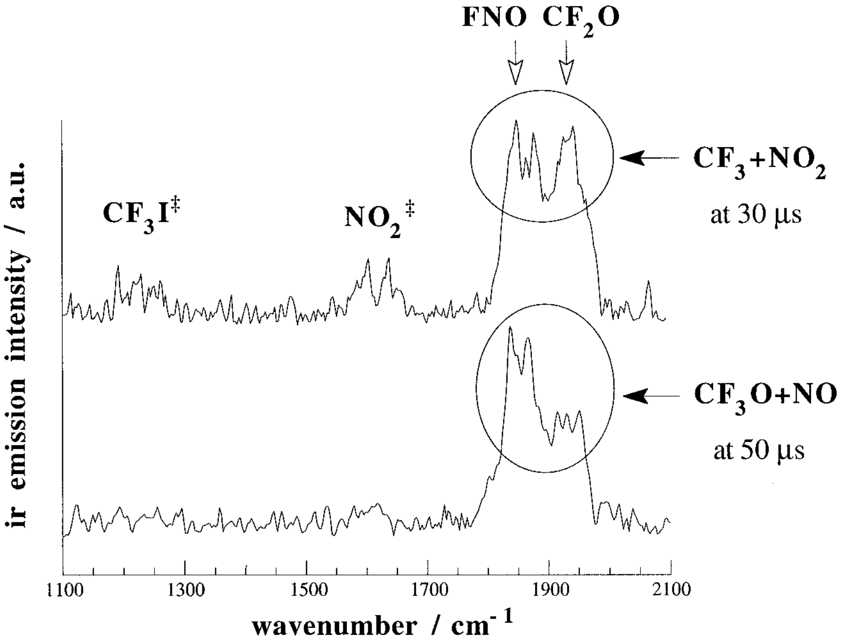


Figure 8. Comparison of the infrared emission spectra recorded following the $CF_3O + NO$ reaction at 50 μs with that recorded following the $CF_3 + NO_2$ reaction at 30 μs. A closer inspection, marked with circle, shows that the ratio of the F(NO) emission intensity to that of the CF_2O emission is greater in the case of the $CF_3O + NO$ reaction.

At first sight, the spectra appear similar, although closer inspection shows that the ratio of the emission intensities of F(NO):CF_2O was greater in the case of the $CF_3O + NO$ reaction. Both reactions are highly exothermic. However, the $CF_3 + NO_2$ reaction involves the formation of two new bonds, the $CF_2{=}O$ and F−(NO) bonds. As a consequence, both products are highly vibrationally excited and produce strong infrared emissions. In contrast, the F-atom transfer pathway in the reaction of CF_3O with NO to give CF_2O and F(NO) involves the formation of only one new bond, the F−(NO) bond, and thus it would be expected that F(NO) is more excited than CF_2O.

Conclusions

The reaction of the CF_3 radical with NO_2 has been investigated by using time-resolved FTIR emission spectroscopy. Emission features near 1850 and 1940 cm^{-1} have been tentatively assigned as originating from the vibrationally excited reaction products FNO and CF_2O respectively, and the possibility of an isomeric FON species emitting at 1880 cm^{-1} is discussed. Two reaction channels 1a and 1b were suggested and the relative branching ratio of reactions 1a and 1b was estimated as 1:0.015.

$$CF_3 + NO_2 \rightarrow CF_2O + FNO \qquad \Delta H^\circ_{298} = -267 \text{ kJ mol}^{-1} \quad (1a)$$

$$\rightarrow CF_2O + F + NO \qquad \Delta H^\circ_{298} = -31 \text{ kJ mol}^{-1} \quad (1b)$$

The rising rate of the product emission was identified with the reaction of CF_3 with NO_2, and the rate constant for reaction 1 was determined to be $(2.4 \pm 0.5) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}. The $CF_3O + NO$ reaction was investigated by the same technique. Emission was again observed from the same products, although the emission from CF_2O relative to that from F(NO) was somewhat smaller than the relative emission intensities from the products of the $CF_3 + NO_2$ reaction. This was explained by the fact that two new bonds are formed in both product species in the $CF_3 + NO_2$ reaction.

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