Laser Emission and Energy Partitioning in the Reaction of Oxygen Atoms with 3,3,3-Trifluoromethylacetylene

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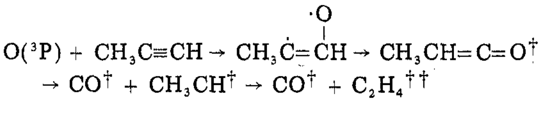
The vibrational energy distributions of HF and CO formed in the $O(^3P) + CF_3C_2H$ reaction have been measured by means of HF laser emission and CO laser resonance absorption methods. CO was found to be vibrationally excited to $v = 3$ with a Boltzmann vibrational temperature of 2200 K. The observed CO distribution is consistent with those predicted by different statistical models, indicating the presence of a long-lived reaction intermediate ($CF_3CH{=}CO$). The observed HF distribution ($N_1/N_0 = 0.38 \pm 0.06$), however, was found to be twice as much as that predicted by these models, presumably due to the presence of other more exothermic secondary reactions, such as CF_3CH + O and NO_2, the photochemical source of the O atom.

Introduction

The results of eariler studies[1,2] show that the vibrationally excited CO formed in the $O(^3P) + CH_3C\equiv CH$ reaction can be quantitatively accounted for by the following mechanism:[1-4]



$$O(^3P) + CH_3C{\equiv}CH \rightarrow CH_3\overset{\cdot O}{\dot{C}}{=}\dot{C}H \rightarrow CH_3CH{=}C{=}O^\dagger \rightarrow CO^\dagger + CH_3CH^\dagger \rightarrow CO^\dagger + C_2H_4^{\dagger\dagger}$$

Since the isomerization reaction, $CH_3CH \rightarrow C_2H_4$, takes place after the complete separation of the CO and CH_3CH, the energy released (~68 kcal/mol)[1] by the isomerization is not available to the CO. The good agreement between the observed and the statistically predicted vibrational population distribution for the CO formed indicated that a long-lived intermediate ($CH_3CH{=}C{=}O$) was involved, and that the reaction energy was completely randomized among all degrees of freedom of the dissociating complex. The study[1] showed conclusively that CH_3CH, and not C_2H_4, was formed initially in the reaction.

In this work we investigated the analogous reaction of fluorine-substituted methylacetylene, CF_3C_2H, with $O(^3P)$. It is well known that excited fluorohydrocarbons may eliminate HF, so besides the possibility of CO formation as in the methylacetylene reaction, there may be a second channel, that of HF formation, available to the O + CF_3C_2H reaction. Indeed, it was found that both vibrationally excited CO and HF were produced. These results are reported in this paper.

Experimental Section

Descriptions of the UV flash laser apparatus[5] and the CO laser probing[6] system have been published. Briefly, the UV apparatus consisted of a 1.4 m long, 1.2 cm (i.d.) Pyrex laser tube fitted with a BaF_2 Brewster window and connected to a greaseless, all glass vacuum line. The Pyrex tube was positioned in an optical cavity formed by two 2.5 cm diameter, 3 m radius gold-coated mirrors, one of which was used internally. The gap between the Brewster window and the external mirror was continually flushed with dry N_2 to avoid atmospheric water absorption of emitted radiation.

A 3.0 cm (i.d.) × 80 cm quartz flash tube, coaxially sealed to the laser tube, and using 20 Torr of 1% Xe/Ar as the light source, provided the flash output for the photolysis. The 1.6-kJ energy for the flash was produced by a Universal Voltronics Model BAC-16-30 18-kV dc power supply and stored in a 14-μF capacitor. An EG & G TM-11 30-kV pulse generator was used to trigger the spark gap. The flash output had a rise time of 5 μs and a half-width of 7 μs.

HF laser emissions coupled out of the Brewster window were analyzed by a half-meter Minuteman Model 305M13 monochromator fitted with a kinematically mounted grating (150 lines/mm, blazed at 6 μm), and were observed with a liquid N_2 cooled Ge:Au detector in conjunction with a Tektronix 7633 storage oscilloscope.

The CO laser probing system consisted of a 1.7-m liquid nitrogen cooled continuous wave CO laser sealed by two CaF_2 Brewster windows. Mixtures of CO, He, N_2, and a trace amount of NO were continuously pumped through the tube. The laser cavity was formed by a 240 lines/mm grating blazed at 3.75 μm and a 3-m radius output coupling dielectric-coated germanium mirror (3% transmission between 4.7 and 6.0 μm). The mirror was mounted on a Lansing piezoelectric transducer that stabilized the laser to line center. The output from the mirror passed through the reaction tube, a focusing lens, and an IR filter before being observed by a Ge:Au detector in conjunction with a Tektronix 555 oscilliscope equipped with a Polaroid C-12 camera.

All gases used in this work were obtained from the Matheson Gas Products, except the CF_3C_2H, which was obtained from PCR Inc. Condensable chemicals were subjected to trap-to-trap distillation using appropriate slush baths. Noncondensables were used without further purification. The $O(^3P)$ atoms were produced by the photodissociation of NO_2 in Pyrex ($\lambda \geq 300$ nm).

Results

I. *HF Laser Emission.* HF laser emission was observed when mixtures of CF_3C_2H, NO_2, and Ar or SF_6 were flash photolyzed in the laser cavity. NO_2 was found to be necessary for laser action. The NO_2 dependence, inert gas effect, and total pressure dependence were studied. These results are presented as follows.

1. *NO_2 Dependence.* The total HF laser emission intensity was studied as a function of the NO_2:CF_3C_2H ratio. Mixtures of 1 Torr of CF_3C_2H and varying amounts of NO_2 and Ar to make a total pressure of 60 Torr were flashed

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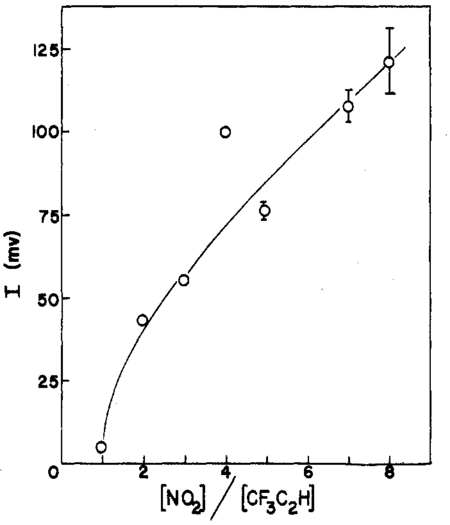


Figure 1. HF laser intensity as a function of $[NO_2]/[CF_3C_2H]$ ratio. CF_3C_2H (1 Torr) was added to varying amounts of NO_2 and Ar to make a total pressure of 60 Torr, flashed with 1.6-kJ energy.

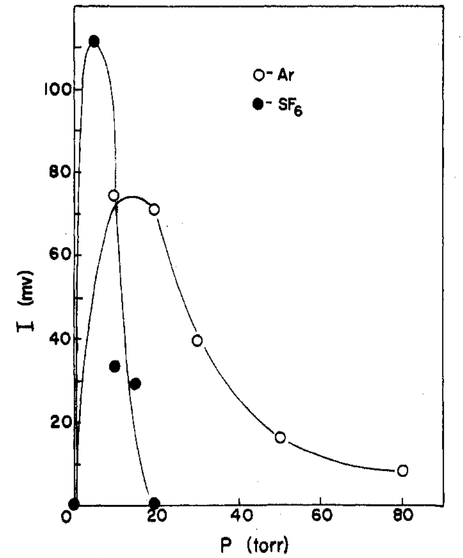


Figure 2. The effects of Ar and SF_6 on HF laser intensity. Mixtures (3 Torr) of 1:2 $CF_3C_2H:NO_2$ and 5 Torr mixtures of 1:4 $CF_3C_2H:NO_2$ were diluted with Ar and SF_6, respectively. Flash energy was maintained constant at 1.6 kJ.

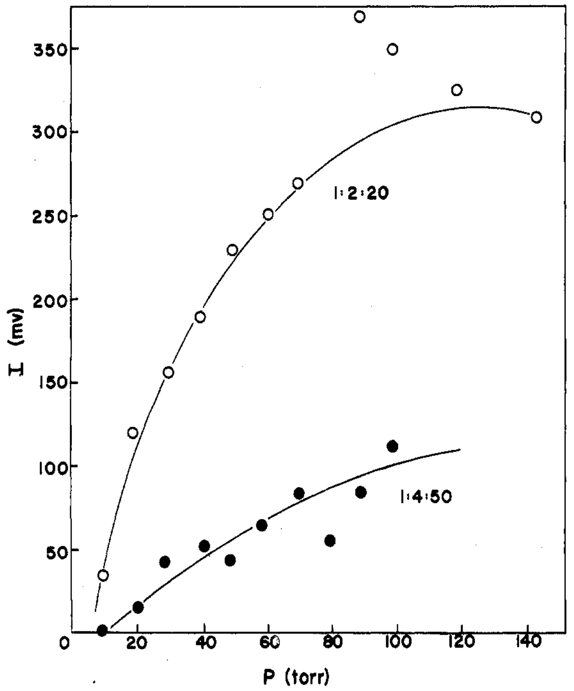


Figure 3. Total pressure dependence of HF laser emission for 1:2:20 and 1:4:50 $CF_3C_2H:NO_2:Ar$ mixtures. Flash energy 1.6 kJ.

TABLE I: HF Vibrational Population Measurements from Various Mixtures (Flashed at 1.6 kJ)

Mixture ($CF_3C_2H:NO_2:Ar$)	Total pressure, Torr	Lines obsd	Appearance time, μs
1:2:20	50	$P_{1\to 0}$ (6)	7.2
		(7)	7.6
		(8)	10.0
1:4:50	50	$P_{1\to 0}$ (6)	9.8
		(7)	10.6
1:4:70	50	$P_{1\to 0}$ (6)	12.6
1:4:70	100	$P_{1\to 0}$ (6)	9.2

and the total laser intensity measured. As shown in Figure 1, laser intensity rises rapidly as the ratio of $NO_2:CF_3C_2H$ increases. No laser emission was observed in the absence of NO_2, indicating that HF is produced from the reaction of O with CF_3C_2H, and not from the direct dissociation of CF_3C_2H. There was no sign of decreasing laser intensity up to ratios of 8:1 $NO_2:CF_3C_2H$, indicating that any relaxation of HF by NO_2 is more than compensated for by the enhanced rate of HF production at higher $NO_2:CF_3C_2H$ ratios.

2. *Inert Gas Effect.* Figure 2 shows the effect of the dilution of $CF_3C_2H:NO_2$ mixtures with Ar or SF_6. Mixtures (3 Torr) of 1:2 $CF_3C_2H:NO_2$ were diluted with various pressures of Ar, and 5 Torr mixtures of 1:4 $CF_3C_2H:NO_2$ were diluted with SF_6, and HF laser intensity was measured. Addition of low pressures of Ar and SF_6 resulted in an increase in laser power due to lowering of the rotational-translational temperature of the system. At higher inert gas pressures, this relaxation diminished rather drastically the already weak HF emission. It is known that neither Ar nor SF_6 effectively relaxes vibrationally hot HF, so the quenching effect shown in Figure 2 must be due to the relaxation of the reaction intermediate, CF_3CHCO.

3. *Total Pressure Dependence.* In Figure 3, the total HF laser intensity is plotted as a function of the total pressure for 1:2:20 and 1:4:50 $CF_3C_2H:NO_2:Ar$ mixtures. The intensity increases with pressure in a similar manner for both mixtures, but the total intensity is about twice as large for the 1:2:20 mixture as it is for the 1:4:50 mixture.

4. *Identification of Transitions.* The individual HF vibrational-rotational transitions that appeared when various $CF_3C_2H:NO_2:Ar$ mixtures were photolyzed are summarized in Table I. An attempt was made to use a grating (~90% efficiency between 2.7 and 3.2 μm) to achieve a single-line oscillation, but the gain of the system was too low to have oscillation.

Only $v = 1 \to v = 0$ transitions were found in all of the mixtures investigated. As very few lines were observed, it was a straightforward procedure to determine the relative population ratio with a plot of relative gain vs. population ratio based on the gain (or absorption) equation given later. In all mixtures, P_{10} (6) appeared first, so N_1/N_0 is estimated to be 0.38 ± 0.06.

In a separate experiment, D_2 was added to the reaction mixture, but no DF emission was observed. From this result it is concluded that F atoms are not produced to any significant extent.

Possible mechanisms for the production of the vibrationally excited HF are discussed in the next section.

II. *CO Production.* Mixtures of CF_3C_2H, NO_2, and SF_6 were flash photolyzed at 1-kJ energy in the CO laser

TABLE II: CO Vibrational Population Distribution Measured by the CO Laser Probing Method

Reaction mixture (CF_3C_2H:NO_2:SF_6)	N_0	N_1	N_2	N_3
2:4:34.0[a]	1.00	0.247 ± 0.046	0.0744 ± 0.0168	0.0194 ± 0.0045
2:4.4:33.6[a]	1.00	0.225 ± 0.027	0.0710 ± 0.0048	0.0123 ± 0.0022
Av	1.00	0.236 ± 0.035	0.0727 ± 0.0109	0.0158 ± 0.0043

[a] Average of three sets of data taken at 300 K with 1.0-kJ flash energy.

probing system. The results obtained from two different reaction mixtures are summarized in Table II. CO was found to be produced and vibrationally excited to $v = 3$. Time-resolved CO absorption curves were obtained for the vibrational levels populated by the reaction. The CO vibrational population was determined by analyzing the early portion of the absorption curves with a computer using the gain equation:[6]

$$\alpha_v(J) = (8\pi^3/3kT)(Mc^2/2\pi kT)^{1/2} \times |R_v|^2 J F_{vr} \{N_{v+1}B_{v+1}\exp[-B_{v+1}J(J-1)hc/kT] - N_v B_v \exp[-B_v J(J+1)hc/kT]\}$$

where v and J are the vibrational and rotational quantum numbers of the lower level, $|R_v|^2$ is the rotationless matrix element for the $v \rightarrow v + 1$ transition, F_{vr} is the Herman–Wallis factor, and B_v is the rotational constant for the vth vibrational level. The sources of these molecular constants can be found in ref 6. The initial population distribution was evaluated by extrapolating the N_v/N_0 ratios evaluated from the above equation to the appearance time of absorption, in order to eliminate any effects of vibrational relaxation of CO and possible secondary reactions that might generate CO. The results obtained from the average of six sets of experiments are shown in Figure 4. The excited CO was found to have an average of 2.0 ± 0.2 kcal/mol of vibrational energy ($\langle E_v \rangle = \sum N_v E_v / \sum N_v$) with a Boltzmann vibrational temperature of 2200 K.

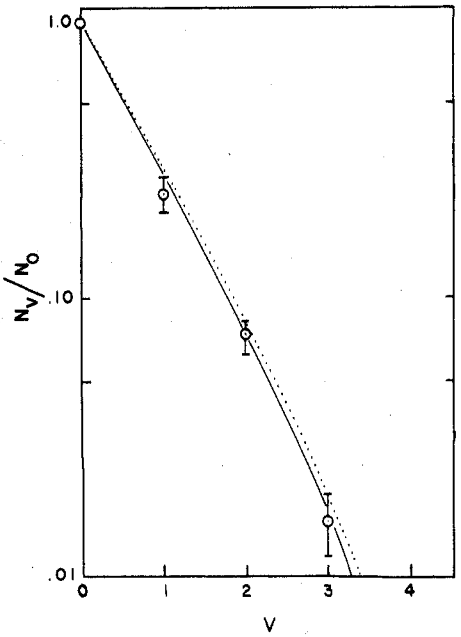
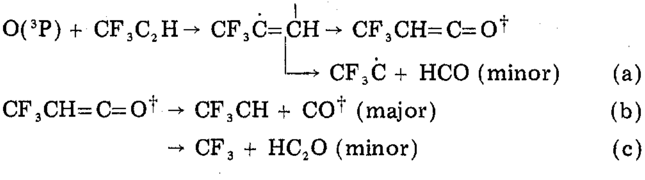


Figure 4. Initial CO vibrational energy distribution observed in the O + CF_3C_2H reaction. Experimental conditions are shown in Table II: (solid curve) statistical distribution evaluated from eq I, as described in ref 1; (dotted curve) prior statistical distribution evaluated according to the method described in ref 10.

Discussion

The kinetics and mechanism of the $O(^3P)$ + CF_3C_2H reaction are not well known. Recently, Blumenberg et al.[7] investigated this reaction using a low pressure, crossed free jet reactor and a mass spectrometer for analysis of the products. They were able to detect the reaction intermediate, CF_3CHCO, and determined that the major reaction channel is the one that produces CO + CF_3CH. The assignment of m/e 82 to CF_3CH was based on the fact that the observed cracking pattern was different from that of trifluoroethylene. A minor route observed corresponded to the formation of CF_3 + HC_2O. CF_3C and HCO were also detected, but may be decomposition products of the addition intermediate. These results could be accounted for by the following reaction scheme:



$$O(^3P) + CF_3C_2H \rightarrow CF_3\dot{C}{=}\overset{\cdot O}{\overset{|}{C}}H \rightarrow CF_3CH{=}C{=}O^{\dagger}$$
$$\hookrightarrow CF_3\dot{C} + HCO \text{ (minor)} \quad \text{(a)}$$
$$CF_3CH{=}C{=}O^{\dagger} \rightarrow CF_3CH + CO^{\dagger} \text{ (major)} \quad \text{(b)}$$
$$\rightarrow CF_3 + HC_2O \text{ (minor)} \quad \text{(c)}$$

The fact that CO is a product of the major reaction channel is consistent with the results of our laser absorption measurement. However, HF was not observed in their study, although stimulated emission was detected in our experiments at very early stages of reaction. The mechanism of HF production will be discussed later.

The CO formed in the present reaction carried an average vibrational energy of 2.0 kcal/mol, compared with a value of 2.3 kcal/mol for the O + CH_3C_2H reaction. If the effects of fluorine substitution on the heats of formation of CF_3C_2H and CF_3CH are approximately the same, then the energy released in the CO production channel (b) should be about 53 kcal/mol,[1] based on that of the methylacetylene reaction. We have used this value to compute the theoretical CO vibrational energy distribution according to the statistical model employed previously to account for the CO vibrational energy distribution observed in the O + CH_3C_2H reaction. The model assumes that the total available reaction energy (E_{tot}) is completely randomized among all vibrational modes of the dissociating complex. The total angular momentum constraint that may affect the partitioning reaction energy between the separating fragments is ignored.

On the basis of this assumption, we have arrived at the following expression for the relative vibrational energy distribution:[1]

$$N_v/N_0 = \Sigma P(E_{tot} - E_v)/\Sigma P(E_{tot}) \qquad \text{(I)}$$

where N_v is the population and E_v is the vibrational energy of CO at the vth level, and $\sum P(E)$, the total energy level sum of the dissociating complex at energy E, which was evaluated by means of the Whitten and Rabinovitch approximation.[8] As shown in Figure 4, the CO distribution predicted by eq I (the solid curve) agrees quantitatively with the observed values. A similar calculation based on the method of Levine and Bernstein[9] as extended by Bogan and Setser[10] (the dotted curve) also agrees reasonably with the experimental result. This latter statistical model treats the (relative) translational and all vibrational and rotational degrees of freedom of both products (CO and CF_3CH) as active. This model, which also ignores the angular momentum effect, is equivalent to the loose model previously employed.[1] The fact that the experimental and predicted CO distributions agree closely indicates that in the present reaction CF_3CH rather than CF_2CHF is initially produced, analogous to the production of CH_3CH observed in the O + CH_3C_2H reaction. The formation of CF_3CH is considered to be more likely in the CF_3C_2H reaction because the C–F bond is considerably stronger than the C–H bond.

The fate of the CF_3CH radical in the present system (containing O, NO_2, and NO) is not clear. The long lifetime of the CF_3CH radical may be intimately related to the observation of HF laser emissions in the present system.

The vibrationally excited HF may be produced from the following three possibilities.

(1) The direct elimination from vibrationally excited $CF_3CH{=}C{=}O$:

$$CF_3CH{=}C{=}O^\dagger \rightarrow HF^\dagger + CF_2{=}C{=}C{=}O \qquad \text{(d)}$$

This is a very likely process although it may not be the only possibility. The vibrationally excited $CF_3CH{=}C{=}O$, according to the thermochemistry of the O + $CH_3C_2H \rightarrow CH_3CH{=}C{=}O$ reaction, may possess as much as 123 kcal/mol of internal energy. On the basis of the RRK theory of unimolecular reaction, the relative rate of HF and CO production can be approximately given by

$$\frac{R_{HF}}{R_{CO}} \approx \frac{A_{HF}}{A_{CO}}\left(\frac{E_{int} - E_{HF}}{E_{int} - E_{CO}}\right)^{s-1}$$

Taking the following reasonable values: $A_{HF} \approx 10^{13}$–10^{14} and $A_{CO} \approx 10^{14}$–10^{15} s^{-1}, $E_{HF} \approx 65$, $E_{CO} \approx 75$ kcal/mol, and $s = 18$, we obtained $R_{HF}/R_{CO} \approx 0.3$–$30$. This indicates that the production of HF from CF_3CHCO may be as important as CO. This is indirectly supported by the fact that CO absorption signals are considerably weaker in the present system than in the O + CH_3C_2H reaction.

If HF is directly generated from channel d, the energy released from the overall reaction:

$$O(^3P) + CF_3C_2H \rightarrow HF + CF_2{=}C{=}C{=}O \qquad \text{(e)}$$

was estimated to be ~94 kcal/mol asuming $\Delta H_f°(CF_3C_2H) \approx \Delta H_f°(CH_3C_2H) + \Delta H_f°(CF_3CH_3) - \Delta H_f°(CH_3CH_3) = -114$ and $\Delta H_f°(CF_2C_2O) \approx \Delta H_f°(C_3O_2) + \Delta H_f°(F_2CO) - \Delta H_f°(CO_2) = -82$ kcal/mol. On the basis of the approximate value of 94 kcal/mol, both statistical models described above predict $N_1/N_0 = 0.19$, which is a factor of 2 lower than the experimentally determined value. This crude but reliable estimate seems to suggest strongly the importance of the following alternatives that involve the CF_3CH radial.

(2) Decomposition of vibrationally excited CF_2CHF. The freshly formed CF_3CH radical may carry as much as 40 kcal/mol of internal energy from reaction b, probably sufficient for overcoming the barrier of the isomerization:

$$CF_3\ddot{C}H \rightarrow CF_2{=}CHF \qquad \text{(f)}$$

The above energy aided by the freshly released heat of isomerization (~68 kcal/mol based on $CH_3CH \rightarrow C_2H_4$ mentioned eariler) should provide CF_2CHF with sufficient energy (~108 kcal/mol) to generate highly excited HF. The rate of reaction f may be considerably slower than the rate of nonfluorinated reaction because of the stronger C–F bonds, as mentioned before.

(3) Decomposition of vibrationally excited CF_3CHO. The CF_3CH radical formed by the decomposition of CF_3CHCO may also undergo several secondary bimolecular reactions with oxidants such as O and NO_2 to generate highly excited products, particularly CF_3CHO. For example

$$CF_3CH + O \rightarrow CF_3CHO + {\sim}180\ \text{kcal/mol} \qquad \text{(g)}$$

$$CF_3CH + NO_2 \rightarrow CF_3CHO + NO + {\sim}107\ \text{kcal/mol} \qquad \text{(h)}$$

The exothermicities given above were estimated by assuming $D(CF_3CH{=}O) \approx D(CH_2{=}O) = 180$ kcal/mol. The excited fluorinated acetaldehyde is also expected to produce vibrationally excited HF. Laser emission was actually detected in the reactions of O atoms with partially fluorinated ethylenes, which are believed to occur via vibrationally excited acetaldehyde. For example[11]

$$O + CHF{=}CH_2 \rightarrow CH_2FCHO^\dagger \rightarrow HF^\dagger + CH_2CO + 105\ \text{kcal/mol}$$

The production of more highly excited HF from the above reactions may account for the observed higher N_1/N_0 inversion ratio. Unfortunately, the complexity and uncertainties in both the kinetics and thermochemistry of these side reactions make any attempts to quantitatively interpret the observed inversion ratio ($N_1/N_0 = 0.38$) prohibitively difficult.

Conclusion

The results of the present and other studies indicate that the major primary products of the $O(^3P) + CF_3C_2H$ reaction are CF_3CH and CO. The CO formed in the reaction was found to be vibrationally excited to $v = 3$ with a Boltzmann vibrational temperature of 2200 K. The observed CO vibrational energy distribution agrees closely with those predicted by different statistical models, indicating the presence of a long-lived reaction intermediate which is most likely $CF_3CH{=}C{=}O$. HF laser emission was detected when mixtures of NO_2 and CF_3C_2H were flash photolyzed above 300 nm in a laser cavity in the presence of appropriate amounts of diluents such as SF_6 and Ar. Comparison of the results of a statistical model calculation with the observed HF vibrational energy distribution led us to conclude that the vibrationally excited HF was produced not only from the direct elimination of $CF_3CH{=}CO$, but also from other possible secondary reactions, such as CF_3CH + O and NO_2. The relative abundance CO and HF cannot be determined in this work.

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