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LASER-INDUCED REACTIONS OF NITROGEN FLUORIDES WITH NITROGEN OXI--ETC(U)  
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TECHNICAL REPORT RR-82-1

LASER-INDUCED REACTIONS OF NITROGEN  
FLUORIDES WITH NITROGEN OXIDES

J. A. Merritt, J. K. McDonald, and V. F. Kalasinsky  
Research Directorate  
US Army Missile Laboratory

JANUARY 1982



**U.S. ARMY MISSILE COMMAND**

*Redstone Arsenal, Alabama 35809*

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| 20. ABSTRACT (Continue on reverse side if necessary and identify by block number)<br>Some laser-induced reactions of tetrafluorohydrazine (N <sub>2</sub> F <sub>4</sub> ), nitrogen tri-<br>fluoride (NF <sub>3</sub> ) with nitric oxide (NO), nitrous oxide (N <sub>2</sub> O), nitrogen dioxide<br>(NO <sub>2</sub> ) or nitrosyl chloride (ClNO) have been studied. Absorption in the<br>nitrogen fluorides of infrared radiation from a CW CO <sub>2</sub> laser initiated a<br>number of reactions. In all cases, the major product was FNO, and when N <sub>2</sub> O<br>or NO <sub>2</sub> were used, FNO <sub>2</sub> was also produced. The quantities of the products<br>depended upon laser power and sample pressures. The laser-induced reactions |                                      |                                                                |

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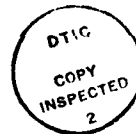
probably proceed through a nonequilibrium thermal process rather than a true multiphoton dissociation, but certain pieces of the data are not totally consistent with this interpretation. A decomposition reaction was induced in CINO through laser absorption by a combination band. Possible mechanisms for the various reactions and the implications of pursuing studies of laser-induced chemical processes are discussed.

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## 1. INTRODUCTION

Discretely tunable infrared lasers have been found to be useful in many areas of research in chemical physics. One particularly important application relates to the possibility of initiating and controlling chemical reactions by exciting specific vibrational modes within the reacting molecules. The infrared output of pulsed or continuous-wave carbon dioxide (CO<sub>2</sub>) lasers can be tuned to match molecular infrared absorption frequencies, and absorption of the laser radiation can promote molecules into reactive, vibrationally excited energy states. The various theoretical aspects and experimental applications of laser-induced chemical processes have been discussed in appropriate reviews.<sup>1-7</sup>

Unimolecular reactions in the gas phase can be induced by infrared laser output, and many studies employing pulsed-laser techniques, where large energy fluences could be achieved, have been reported.<sup>8-11</sup> Considerable effort has been directed toward isotope separation. Selective excitation of isotopically substituted molecules is possible in laser-induced reactions because of the differences in molecular vibrational absorptions which are caused by differences in atomic masses, and some success in isotope separations has been reported for gaseous<sup>12,13</sup> and solid phase<sup>14</sup> reactions. Molecular ionization can be accomplished using laser excitation,<sup>15</sup> and energy deposition and transfer studies have also been reported.<sup>16</sup> In a more synthetic application, considerable work has been concerned with bimolecular and more complicated reactions in the gas phase<sup>17</sup> or involving reactions of or production of solids.<sup>18,19</sup> The interest in these reactions stems primarily from the fact that they are not feasible at ordinary temperatures but proceed rapidly when exposed to infrared laser radiation.

Many of the laser-induced reactions carried out at room temperature follow pathways similar to those observed in ordinary pyrolytic reactions whereas other laser-induced reactions are more difficult to describe mechanistically. Indeed, the mechanisms of laser-induced reactions have been discussed in terms of thermal and multiphoton processes.<sup>1-4,6</sup> In the context applicable to laser-induced chemistry, a multiphoton process refers to one in which there is absorption of enough monochromatic infrared photons in a specific vibrational mode to cause dissociation of a molecule. The resulting, highly energetic species thus produced either rearranges or reacts with another species. However, if the absorption of radiation is not sufficient to induce dissociation or if the relaxation of the vibrational energy is very rapid, an alternative mechanism is possible. The absorbed vibrational energy can be non-radiatively transferred to other rovibrational states and translational modes, and the molecule becomes vibrationally heated. The resulting "hot" molecule can react by thermal mechanisms which are similar to those operative in ordinary, equilibrium pyrolytic reactions. Recent results obtained using supersonic molecular beams and laser excitation indicate that in relatively large molecules, which have many degrees of vibrational freedom, the relaxation of vibrational energy is rapid enough to compete with laser-induced multiphoton dissociation.<sup>6,7,20</sup> This implies that the absorption of monochromatic infrared laser photons can result in a nonequilibrium thermal process or vibrational excitation in a manifold other than simply the one which is resonant with the incident infrared radiation.

Regardless of the exact mechanism involved, a laser-induced reaction can be more specific and more efficient than ordinary pyrolytic reactions. Recent theoretical and experimental work has been aimed at understanding the possible pathways in which laser-induced reactions proceed, and it appears that there can be considerable branching.<sup>21</sup> The effects of experimental parameters, such as pressure, temperature, and laser power, are currently under study, and it appears that relative kinetic barriers and more detailed reaction mechanism can be evaluated.

The vast interest in and applicability of laser-induced chemical process has made it necessary to continue to pursue a number of experiments. The results of these experiments and their implications are reported herein.

## 2. EXPERIMENTAL

Commercially available tetrafluorohydrazine, nitrogen trifluoride (Air Products), nitric oxide (NO), nitrous oxide (N<sub>2</sub>O), nitrogen dioxide (NO<sub>2</sub>), and nitrosyl chloride (ClNO) (Matheson) were employed in the studies. Their infrared spectra<sup>22-28</sup> showed only minor impurities, and the samples were used without further purification. The spectra of these and other compounds (FNO and FNO<sub>2</sub>)<sup>29,30</sup> are summarized in Table I.

The reactions were carried out in stainless steel cells (5 x 10 cm) equipped with O-rings seals for securing windows (5 cm diameter) onto the cells. The infrared laser beam entered through ZnSe windows at either end of the cell (traversing a 10 cm path), and any visible emission was observed through a sapphire window. Evidence of side reactions was observed when KCl and Pyrex windows were used.

Infrared laser excitation in the range of 10.4 or 9.4  $\mu\text{m}$  was provided by a Coherent Radiation Laboratories model 41 continuous-wave CO<sub>2</sub> laser. The exact laser frequencies were verified using an optical engineering CO<sub>2</sub> spectrum analyzer. In single-line operation, output powers between 50 and 150 W could be obtained by varying the CO<sub>2</sub>-N<sub>2</sub>-He gas mixture in the laser. The beam size was measured from burn patterns and was found to be approximately circular with a 4 mm diameter. The ZnSe window on the sample cell was found to transmit only 64% of the incident infrared radiation, so a measure of the laser power available to the samples must be adjusted accordingly.

Infrared spectra were collected on a Digilab FTS-20B interferometer equipped with a KBr/Ge beamsplitter and a triglycine sulfate (TGS) detector. Interferograms were transformed after applying a trapezoidal apodization function with an effective spectral resolution of 1.0  $\text{cm}^{-1}$ .

## 3. RESULTS AND DISCUSSION

### Reaction of NO with NF<sub>3</sub> or N<sub>2</sub>F<sub>4</sub>

Nitric oxide (NO) is a diatomic molecule whose single vibration is centered at 1876  $\text{cm}^{-1}$ . Due to the  $^2\Pi$  ground electronic state, the vibration-rotation spectrum of NO exhibits a Q-branch in addition to the normal P-R structure expected for a diatomic molecule. Since this transition is not resonant with the output of the CO<sub>2</sub> laser, the reaction of NO and a nitrogen fluoride will necessarily be the result of laser excitation of the latter.



In all reactions of NO and NF<sub>3</sub> induced by the P(36) [0001 - 1000] (929.02 cm<sup>-1</sup>) line of the CO<sub>2</sub> laser, the major product was FNO. Prominent features at 1844 and 766 cm<sup>-1</sup> in the spectra of reaction products (Figures 1, 2, and 3) are due to the  $\nu_1$  and  $\nu_3$  fundamentals, respectively, of FNO. Under certain conditions, quantities of N<sub>2</sub>F<sub>4</sub> were also produced.

Figure 1 shows the spectra of the products of laser-induced reactions of equal molar amounts of NO and NF<sub>3</sub> (30 torr each). A small amount of N<sub>2</sub>O is observed at 2224 cm<sup>-1</sup>, and unreacted NO (1876 cm<sup>-1</sup>) and NF<sub>3</sub> (1032 and 905 cm<sup>-1</sup>) are also evident. When 100 W of laser power was used (1 sec), a trace of N<sub>2</sub>F<sub>4</sub> was produced, but considerable N<sub>2</sub>F<sub>4</sub> was produced when the reactants were irradiated for relatively long periods of time (15 sec) with 50 W of power. These two cases are shown in detail in Figure 2 where selected regions of the spectra from Figure 1 are displayed.

The results of studies in which an excess of NO (60 torr NO, 30 torr NF<sub>3</sub>) was used are shown in Figure 3. With a laser power of 100 W, a localized glow was observed as the beam traversed the cell; no such glow was observed when 50 W was used. Unreacted NO and NF<sub>3</sub> were found after both reactions, and it is interesting to note that approximately equal amounts of N<sub>2</sub>F<sub>4</sub> were produced. N<sub>2</sub>O and FNO were produced in both reactions, but more of each product was observed for the higher power reaction. A comparison of relative amounts of FNO in two spectra is often facilitated by viewing the combination band ( $\nu_1 + \nu_2$ ) at 2365 cm<sup>-1</sup> rather than the fundamentals.

With an excess of NF<sub>3</sub> (30 torr NO and 60 torr NF<sub>3</sub>), all the NO was consumed, and large amounts of FNO and N<sub>2</sub>F<sub>4</sub> were produced while very small amounts of N<sub>2</sub>O were observed. These results were the same whether short pulses (~ 1 sec) of 100 W or longer exposure (10-25 sec) of 50 W of laser power were used. The relative amounts of N<sub>2</sub>F<sub>4</sub> were slightly different, however, with more having been produced at the lower power. These reactions make it clear that the laser-induced reactions are much more likely when relatively high pressures of NF<sub>3</sub> are used.

When NO was allowed to react with N<sub>2</sub>F<sub>4</sub>, large amounts of FNO and NF<sub>3</sub> were produced. With 20 torr of each reactant, some unreacted N<sub>2</sub>F<sub>4</sub> was present, but when excess NO was used (40 torr NO and 20 torr N<sub>2</sub>F<sub>4</sub>), the N<sub>2</sub>F<sub>4</sub> was completely consumed, and small amounts of N<sub>2</sub>O were produced along with the FNO and NF<sub>3</sub>.

Mechanistically the reactions of NO with NF<sub>3</sub> or N<sub>2</sub>F<sub>4</sub> should be similar, since the formation of FNO requires the transfer of a fluorine atom. If NF<sub>3</sub> supplies that atom, then a reactive ·NF<sub>2</sub> radical would exist, and this radical is known to be involved in an equilibrium with N<sub>2</sub>F<sub>4</sub>. A set of reactions which can account for the essential features of the observed overall reactions is given on the next page.



The formation of short-lived NF in reaction (3) has not been verified experimentally, but its existence could provide atomic nitrogen as indicated in reaction (4). Varying amounts of  $\text{N}_2\text{O}$  are observed in the infrared spectra, and  $\text{N}_2$  has been identified in a mass spectrometer, so a source of atomic nitrogen must exist if these are produced according to reactions (5) and (6).

Naturally it would require considerable amounts of laser energy to initiate reaction (1), and the necessary duration of the initiating laser pulse indicates that the reaction depends upon thermal excitation. It seems, too, that the distribution of final products depends upon the thermodynamics of the various reactions and the relative concentrations of reacting species.

With the exception of reaction (1), the same series of steps can be applied to the reaction of NO and  $\text{N}_2\text{F}_4$ . Clearly a significant difference would be that laser excitation of the  $\text{N}_2\text{F}_4$  would force the equilibrium in reaction (2) in the reverse direction and supply a reactant for reaction (3).

#### Reaction of ClNO with $\text{NF}_3$ or $\text{N}_2\text{F}_4$ and Unimolecular Reaction of ClNO

The nitrogen fluorides are known to be especially good fluorinating agents in laser-induced reactions, and since FNO was found to be produced in the reactions involving NO, the reactions of ClNO were investigated.

Equimolar mixtures of ClNO and  $\text{NF}_3$  (25 torr each) were subjected to laser irradiation. When a given mixture was irradiated with successively increasing laser powers at  $929.02 \text{ cm}^{-1}$ , P(36) [0001 - 1000] the evolution of reaction products could be followed. For example, in Figure 4 the results of irradiations of 70W, 100W, and 150W are shown. After irradiation with 70W, the presence of NO was observed, but there appeared to be no change in the  $\text{NF}_3$  concentration (Figure 4B). A mixture of ClNO ( $1800 \text{ cm}^{-1}$ ) and FNO ( $1844, 766 \text{ cm}^{-1}$ ) was observed after irradiation with 100W (Figure 4C), and the ClNO was totally consumed after 150W was used (Figure 4D). The amount of  $\text{N}_2\text{O}$  also increased as the production of FNO proceeded, and some  $\text{N}_2\text{F}_4$  was also ultimately produced.

By comparison, when a similar equimolar mixture was irradiated with 100W the results were similar to the final results of the experiments described immediately above, and this can be verified by Figure 5A. With an excess of ClNO (50 torr ClNO, 25 torr  $\text{NF}_3$ ), FNO,  $\text{N}_2\text{O}$ , NO and a small amount of  $\text{N}_2\text{F}_4$  were produced (Figure 5B) by the P(36) [0001 - 1000] laser line (120 W).

Similar results were also observed when the laser line at  $1031.48\text{ cm}^{-1}$ , P(36) [00<sup>0</sup>1 - 02<sup>0</sup>0], was used. This line is resonant with a different vibration ( $\nu_1$ ) of  $\text{NF}_3$ , but the same reaction took place.

In a similar manner,  $\text{N}_2\text{F}_4$  also reacts with  $\text{ClNO}$ . When 25 torr of each were mixed and irradiated with 120W of P(36) [00<sup>0</sup>1 - 02<sup>0</sup>0],  $\text{FNO}$ ,  $\text{NF}_3$  and  $\text{N}_2\text{O}$  were produced. While the stoichiometry is slightly different, the reaction seems to proceed in the same way as that involving  $\text{NF}_3$ .

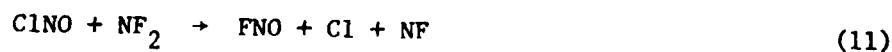
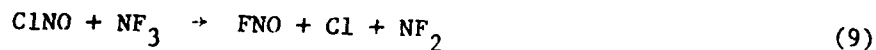
The reaction of  $\text{ClNO}$  and  $\text{NF}_3$  at low levels of laser irradiation raised an interesting question. From Figure 4A it would appear that, with 70W,  $\text{NO}$  is formed,  $\text{ClNO}$  is depleted, and the amount of  $\text{NF}_3$  remains constant, and the explanation of this behavior can be either that  $\text{NF}_3$  sensitizes the decomposition of  $\text{ClNO}$  at low power or that  $\text{ClNO}$  undergoes a unimolecular decomposition. The latter possibility was tested by irradiating 50 torr of  $\text{ClNO}$  with 125W of power at  $929.02\text{ cm}^{-1}$  and at  $1031.48\text{ cm}^{-1}$ . The formation of  $\text{NO}$  was observed after irradiation at  $929.02\text{ cm}^{-1}$  (Figure 6) but not after irradiation at  $1031.48\text{ cm}^{-1}$ .

As indicated in Table I,  $\text{ClNO}$  has fundamental vibrations at 1800, 332, and  $605\text{ cm}^{-1}$ , and none of these are resonant with the laser output described above. However, the  $\nu_2 + \nu_3$  combination band<sup>29</sup> is at  $926\text{ cm}^{-1}$ , and the laser-induced reaction apparently proceeds due to absorption of this band. This certainly explains why no reaction is induced by irradiation at  $1031.48\text{ cm}^{-1}$ . Furthermore, this appears to be the first unimolecular reaction which proceeds through excitation of a combination band.

The unimolecular decomposition of  $\text{ClNO}$  appears to be a thermally induced reaction as evidenced by the relatively long irradiation times which were necessary. The reaction is probably not truly unimolecular, since collisions probably contribute to the reaction. The individual steps are probably those given below.



The reaction of  $\text{ClNO}$  and  $\text{NF}_3$  can be visualized in either of two ways. First of all, it is known that  $\text{NF}_3$  reacts with  $\text{NO}$ , and it is possible that this reaction (Reactions (1) - (6)) follows the decomposition of  $\text{ClNO}$ . Alternatively, there can be a direct reaction between  $\text{ClNO}$  and  $\text{NF}_3$  as a result of laser excitation of  $\text{NF}_3$ . This latter possibility can proceed as follows:





Molecular chlorine has not been identified, but there was no evidence for other chlorine-containing compounds. Additionally, when the product was left unattended at ambient temperatures, the FNO was converted back to ClNO.

The reaction which proceeds with irradiation by laser powers of 100W or more probably follows these steps. Irradiation at  $929.02 \text{ cm}^{-1}$  can initiate both the decomposition of ClNO and the fluorination of ClNO, but irradiation at  $1031.48 \text{ cm}^{-1}$  can only induce the latter reaction. Since both laser lines give the same sets of products it is likely that in both cases reactions (9) - (15) are operative.

At low laser power at  $929.02 \text{ cm}^{-1}$ , the competition between various pathways becomes evident (Figure 4). Low levels of power are apparently insufficient (at the pressures used) to induce a reaction involving the  $\text{NF}_3$  presumably because of the stability of  $\text{NF}_3$ . On the other hand, sufficient energy is available to induce a cleavage of the Cl-N bond. The reactions of  $\text{NF}_3$  are known to be extremely rapid and exothermic, and these will dominate the reaction system at higher power levels.

#### Reaction of $\text{N}_2\text{O}$ and $\text{NF}_3$ or $\text{N}_2\text{F}$

The infrared spectra of  $\text{N}_2\text{O}$  and a mixture of  $\text{NO}_2$ - $\text{N}_2\text{O}_4$  are shown in Figure 7. None of the fundamental vibrations for  $\text{N}_2\text{O}$  are resonant with the output of the  $\text{CO}_2$  laser, so the reactions described herein are the result of the absorption of infrared radiation by the appropriate nitrogen fluoride.

The laser power required for a reaction was quite high relative to the other reaction systems described. For example, Figure 8A shows the spectrum of a mixture of 55 torr  $\text{N}_2\text{O}$  and 30 torr  $\text{NF}_3$ . Extended irradiation (10-20 sec) by 100W of power at  $929.02 \text{ cm}^{-1}$ , did not induce a reaction. The effects of 140W of power on a mixture of 60 torr  $\text{N}_2\text{O}$  and 40 torr  $\text{NF}_3$  are indicated in Figure 8B and 8C. Although unreacted  $\text{N}_2\text{O}$  and  $\text{NF}_3$  were present in relatively large amounts, significant amounts of FNO were produced, and the presence of  $\text{FNO}_2$  was confirmed by the weak Q-branches at  $1793$  and  $822 \text{ cm}^{-1}$ . The spectrum in Figure 8B was recorded after five three-second irradiations of the initial mixture, and five additional three-second exposures were carried out before the spectrum in Figure 8C was recorded. The additional irradiation caused increases in the concentrations of FNO and  $\text{FNO}_2$ .

When different relative amounts of reactants were used, different results were observed. In particular, with a mixture of 40 torr  $\text{N}_2\text{O}$  and 50 torr  $\text{NF}_3$ , four three-second exposures of 140W of P(36)  $[00^01 - 10^00]$  radiation produced FNO and  $\text{FNO}_2$  (Figure 9A), but additional exposures caused an increase in the amount of FNO and a decrease in the amount of  $\text{FNO}_2$ . As larger and larger relative amounts of  $\text{NF}_3$  were used, the same effect was observed at even lower

laser powers. With a mixture of 30 torr  $N_2O$  and 60 torr  $NF_3$ , extended irradiation (20-30 sec) with 110W of P(36) laser power was sufficient to completely deplete the  $FNO_2$ . Similar results were also observed for the reaction of  $N_2O$  with  $N_2F_4$ . In these reactions,  $NF_3$  was also observed in the mixture of reaction products.

The reactions of  $N_2O$  with the two nitrogen fluorides cannot be accounted for in as straightforward a manner as other reaction systems. An important question relates to whether the  $N_2O$  molecules undergo N-N or N-O bond cleavage, and it may be that both processes are possible. If binary collisions only are considered, the reactions can be described reasonably well by the following steps:



For N-N bond cleavage, reactions (16)-(18) indicate a mechanism which can result in the large quantities of FNO observed in the spectra. The only reasonable binary reaction which can result in the formation of  $FNO_2$  is shown in reaction (19). It has been observed that the production of  $FNO_2$  is more favorable when larger relative amounts of  $N_2O$  are present. The depletion of  $FNO_2$  is shown in a stoichiometric fashion in reaction (23), but it is conceivable that other nitrogen fluoride species contribute to the process.

Any more detailed description of the mechanism would require extensive further experimentation including temporal studies and the use of isotopically labelled ( $^{15}N$ ) reactants.

#### Reaction of $NO_2$ with $NF_3$ or $N_2F_4$

The reaction of  $NO_2$  and  $N_2F_4$  is known to be spontaneous and probably proceeds because of the existence of small quantities of  $NF_2$  which are in equilibrium with the  $N_2F_4$ . Reportedly, the only product of the reaction is

FNO, <sup>31</sup> but our data show that FNO<sub>2</sub> and NF<sub>3</sub> are also produced. The similarities between the reactivities of N<sub>2</sub>F<sub>4</sub> and NF<sub>3</sub> in laser-induced reactions is well known, so a study of the reaction of NF<sub>3</sub> with NO<sub>2</sub> was undertaken.

No spontaneous reaction between NO<sub>2</sub> and NF<sub>3</sub> was observed, and the laser-induced reactions required at least 50W of power at 929.02 cm<sup>-1</sup>. This laser power was used on an equimolar mixture (45 torr each) of NO<sub>2</sub> and NF<sub>3</sub>, and the results are shown in Figure 10A. FNO and FNO<sub>2</sub> are the main products, and the unreacted NO<sub>2</sub> and N<sub>2</sub>O<sub>4</sub> can be identified by comparison with their spectra in Figure 7 and their frequencies in Table I. Similar results were obtained with different total pressures and different laser powers. When an excess of NO<sub>2</sub> (60 torr NO<sub>2</sub>, 30 torr NF<sub>3</sub>) was used, 50W of laser power induced only a slight reaction, but with 130W (Figure 10B), FNO and small amounts of FNO<sub>2</sub> were produced.

Mixtures of 30 torr NO<sub>2</sub> and 60 torr NF<sub>3</sub> provided rather interesting results. When the mixture was irradiated with 140W at 929.02 cm<sup>-1</sup>, FNO and FNO<sub>2</sub> were produced (Figure 11B). When this latter mixture was further irradiated with 140W of power, additional FNO was produced and the FNO<sub>2</sub> was completely depleted. Two important points can be made on the basis of these results. First of all, for a given set of concentrations of reactants, the amount of FNO<sub>2</sub> depends upon the laser power, and secondly, the FNO<sub>2</sub> can be converted into FNO if suitable quantities of NF<sub>3</sub> are available.

This latter observation deserved further investigation, and the NO<sub>2</sub> - N<sub>2</sub>F<sub>4</sub> reaction system was used to accomplish this task. With a large excess of N<sub>2</sub>F<sub>4</sub> (approximately 10 torr NO<sub>2</sub>, 40 torr N<sub>2</sub>F<sub>4</sub>), all of the NO<sub>2</sub> was consumed in the spontaneous production of FNO and FNO<sub>2</sub> (Figure 12A). When this mixture was subjected to irradiation by 140W of power, the FNO<sub>2</sub> and N<sub>2</sub>F<sub>4</sub> were completely consumed, and FNO and NF<sub>3</sub> were produced.

Since the possibility existed that atomic oxygen could be involved in the conversion of FNO<sub>2</sub> to FNO the laser-induced reaction of O<sub>2</sub> and NF<sub>3</sub> was studied. Laser powers of 140W were necessary for a reaction, and with 10 torr O<sub>2</sub> and 60 torr NF<sub>3</sub> the only product was FNO<sub>2</sub> in trace amounts. When 30 torr O<sub>2</sub> and 60 torr NF<sub>3</sub> were used, trace amounts of FNO and FNO<sub>2</sub> were produced. When this mixture was exposed to further irradiation, the FNO<sub>2</sub> was depleted and more FNO was produced.

The reactions involving NO<sub>2</sub> can be described by the following scheme:





As noted, reaction (26) is spontaneous at room temperature, and the formation of FNO by this route is very favorable. Also reaction (27) is probably the source of FNO<sub>2</sub> in the spontaneous reaction. Reactions (24) and (25) propose the production of products from NF<sub>3</sub> in the laser-induced initiation step. The cleavage of an N-F bond and the production of atomic fluorine seems like an unlikely step but no other mechanism would be plausible for this reaction system. Indeed, perhaps such a step is operative in all the reactions of nitrogen fluorides with nitrogen oxides. Also important in the formation of this conclusion is the apparent production of atomic fluorine in reaction (28), but this reaction (or a more complicated one) must be operative in the laser-induced decomposition of FNO<sub>2</sub> by N<sub>2</sub>F<sub>4</sub> (Figure 12).

Initially it was thought that N-O bond cleavage in NO<sub>2</sub> and production of atomic oxygen might accompany the formation of FNO, but this does not seem to be very likely based on all the available data. The reaction of O<sub>2</sub> with NF<sub>3</sub> is also somewhat puzzling. This reaction seems to indicate the FNO<sub>2</sub> is formed preferentially but ultimately depleted as in reactions (28) and (29). Therefore, an insertion reaction (FNO<sub>2</sub> formation) appears to be preferred to a replacement reaction (formation of FNO and O).

The formation of FNO from NO<sub>2</sub> and N<sub>2</sub>F<sub>4</sub> in the spontaneous reaction has been described as proceeding through a complex of the form F<sub>2</sub>N-O-NO followed by a rearrangement.<sup>31</sup> There is no direct evidence to contradict this conclusion, but the formation of significant amounts of FNO<sub>2</sub> cannot be explained by this relatively simple mechanism. Also it is clear that FNO<sub>2</sub> and large quantities of nitrogen fluorides react under laser excitation to produce FNO. The overall mechanism may involve simply a step in which NO<sub>2</sub> is fluorinated, and a step in which the resulting FNO<sub>2</sub> decomposes to FNO. A clear resolution of these possibilities require extensive further experimentation.

#### 4. CONCLUSIONS AND RECOMMENDATIONS

The reactions of NF<sub>3</sub> and N<sub>2</sub>F<sub>4</sub> with the nitrogen-oxygen compounds discussed above form an extremely interesting group of reactions. Thus far the reaction mechanisms are not clearly understood, but certain features have been gleaned from the studies reported herein. The laser-induced reactions seem to be the

result of nonequilibrium thermal excitation of the absorbing molecules (either  $\text{NF}_3$  or  $\text{N}_2\text{F}_4$ ). The decomposition of  $\text{N}_2\text{F}_4$  into  $\text{NF}_2$  radicals by pumping the N-F stretches with an infrared laser has been demonstrated,<sup>32</sup> and presumably this mechanism is operative in the reactions described in the previous section.

The laser-induced reactions of  $\text{NF}_3$  and the nitrogen oxides appear to follow the same pathways as those for the  $\text{N}_2\text{F}_4$ -nitrogen oxide systems. An explanation for that observation is that  $\text{NF}_3$  gives rise to  $\text{NF}_2$  radicals. The basic question, however, is whether the  $\text{NF}_2$  radicals form as a result of laser-induced decomposition of  $\text{NF}_3$  or laser-induced reactions of  $\text{NF}_3$  with other molecules which abstract a fluorine atom. Given the stability of  $\text{NF}_3$  and the reaction conditions, the latter possibility seems more likely, but the reactions involving  $\text{NO}_2$  seem to indicate the presence (even if for only a short time) of fluorine atoms.

For reactions which occur very rapidly, a detailed mechanism can only be determined by appropriate temporal studies in which the dominant intermediate species can be identified. Unlike other laser induced reactions,<sup>33</sup> the ones described in the previous section are relatively slow and require extended laser irradiations. Therefore, these reactions may serve as a unique model system for the study of the mechanism of laser-induced reactions of  $\text{NF}_3$  and  $\text{N}_2\text{F}_4$ . Time-resolved studies of infrared and ultraviolet or visible absorptions would be extremely useful, and similar time-resolved studies of the infrared emission spectra of these reaction systems could provide the insight necessary for unraveling the mechanistic questions. The temporal studies may be possible by using conventional techniques, but more detailed information can be obtained by using additional lasers, and appropriate detectors, to probe the reaction volume within the cells as the reactions proceed.

Research in the area of laser-induced chemistry is still in its infancy. The basic theoretical models and explanations have been developed for unimolecular reactions, but very little effort has been placed on more complicated and more realistic chemical systems. Thermal and multiphoton mechanisms for laser-induced chemistry have been discussed, and a thorough understanding of laser-induced chemistry will require a knowledge of the relative importance of these two processes. For large molecules, both processes are probably operative and it will be necessary to undertake additional experiments to determine which process predominates for a given molecular system under specific experimental conditions. The exact course of a laser-induced chemical reaction will generally depend on the predominant mechanism as well as on the relative thermodynamic stabilities of reactants and products.

Research programs in laser-induced chemistry deserve continued attention and support. Many fundamental experiments have yet to be carried out, even though the applicability of laser-induced reactions touches all areas of chemistry. And while the distinction between multiphoton and thermal processes is fundamentally important to both the theorist and the experimentalist, the fact remains that regardless of the exact mechanism which initiates a reaction, laser-induced reactions are more efficient and far more selective than ordinary pyrolytic reactions. Laser-induced reactions generally proceed to completion and they can be controlled, to a certain extent, by adjusting reaction conditions at ambient temperatures.



TABLE I. FUNDAMENTAL VIBRATIONS (cm<sup>-1</sup>) OF SOME  
NITROGEN-CONTAINING COMPOUNDS

|                                            |                           |                         |                       |
|--------------------------------------------|---------------------------|-------------------------|-----------------------|
| NO                                         | $\nu_1 = 1876^*$          |                         |                       |
| N <sub>2</sub> O                           | $\nu_1 = 1286^*$          | $\nu_2 = 589$           | $\nu_3 = 2224^*$      |
| NO <sub>2</sub>                            | $\nu_1 = 1318$            | $\nu_2 = 750^*$         | $\nu_3 = 1618^*$      |
| N <sub>2</sub> O <sub>4</sub>              | $\nu_1 = 1380$            | $\nu_2 = 808$           | $\nu_3 = 226$         |
|                                            | $\nu_4 =$                 | $\nu_5 = 1712$          | $\nu_6 = 482$         |
|                                            | $\nu_7 = 429$             | $\nu_8 = 672$           | $\nu_9 = 1748^*$      |
|                                            | $\nu_{10} = 381$          | $\nu_{11} = 1262^*$     | $\nu_{12} = 750^*$    |
| CINO                                       | $\nu_1 = 1800^*$          | $\nu_2 = 332$           | $\nu_3 = 605$         |
| FNO                                        | $\nu_1 = 1844^*$          | $\nu_2 = 521$           | $\nu_3 = 766^*$       |
| FNO <sub>2</sub>                           | $\nu_1 = 1312^*$          | $\nu_2 = 822^*$         | $\nu_3 = 460$         |
|                                            | $\nu_4 = 1793^*$          | $\nu_5 = 570$           | $\nu_6 = 742$         |
| NF <sub>3</sub>                            | $\nu_1 = 1032^*$          | $\nu_2 = 647$           | $\nu_3 = 905$         |
|                                            | $\nu_4 = 493$             |                         |                       |
| N <sub>2</sub> F <sub>4</sub> <sup>+</sup> | $\nu_1 = 1039, 1023^*$    | $\nu_2 = 719, 737$      | $\nu_3 = 601, 590$    |
|                                            | $\nu_4 = 354, 300$        | $\nu_5 = 964^*, 1010^*$ | $\nu_6 = 252, 423$    |
|                                            | $\nu_7 = 131, 116$        | $\nu_8 = 873, 934^*$    | $\nu_9 = 494, 284$    |
|                                            | $\nu_{10} = 999^*, 946^*$ | $\nu_{11} = 542, 518$   | $\nu_{12} = 467, 242$ |

\*Bands observed in the infrared spectra under the experimental conditions described herein.

+Vibrations are numbered according to the C<sub>2h</sub> symmetry of the trans conformation and the frequencies for the corresponding motions for the gauche conformation are also given.

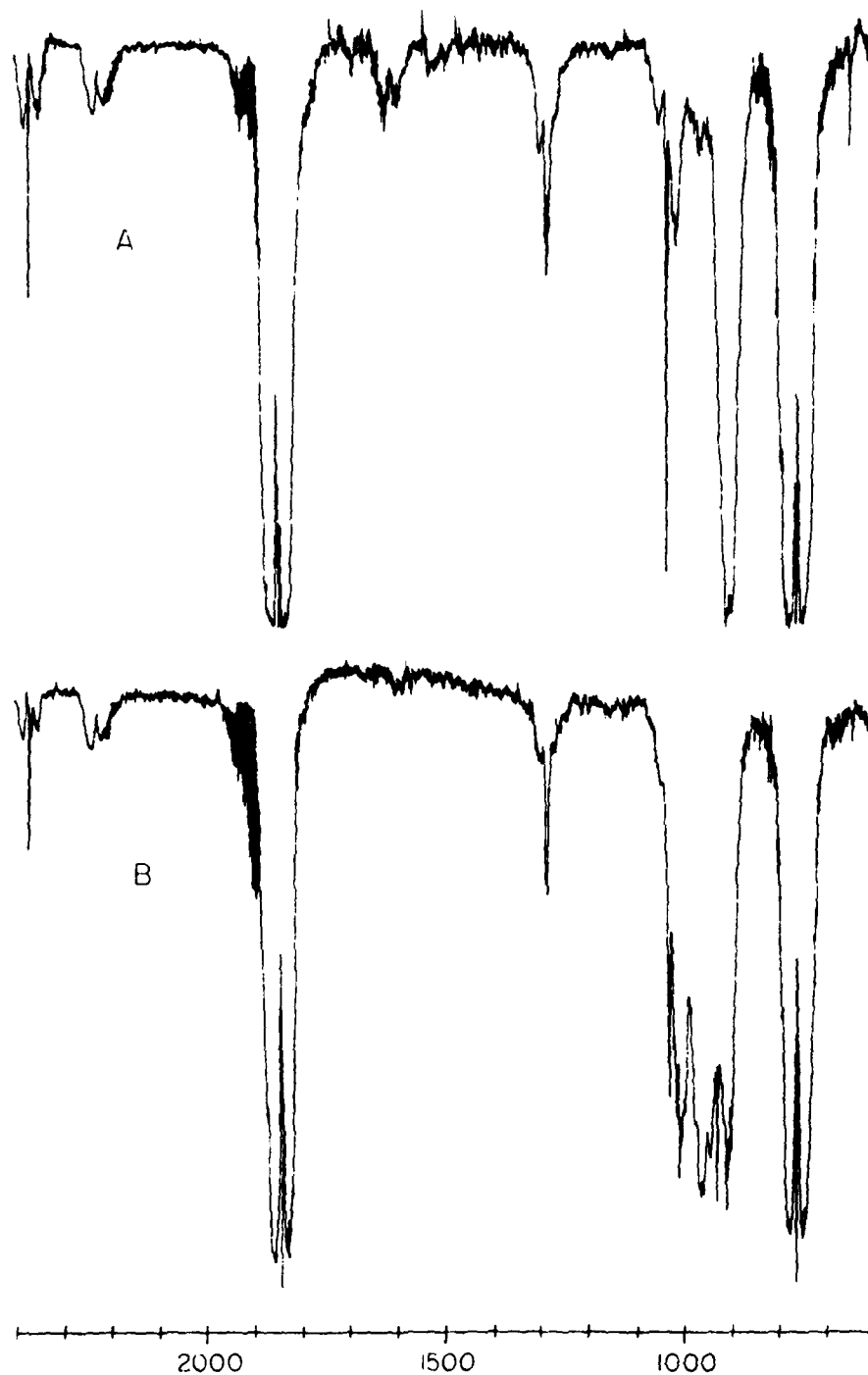


Figure 1. Spectra of the products of the laser-induced reaction of NO and NF<sub>3</sub> (30 torr each) using P(36) [0001 - 1000] at 929.02 cm<sup>-1</sup>; (A) 100W, 1 sec; (B) 50W, three 5-sec exposures.

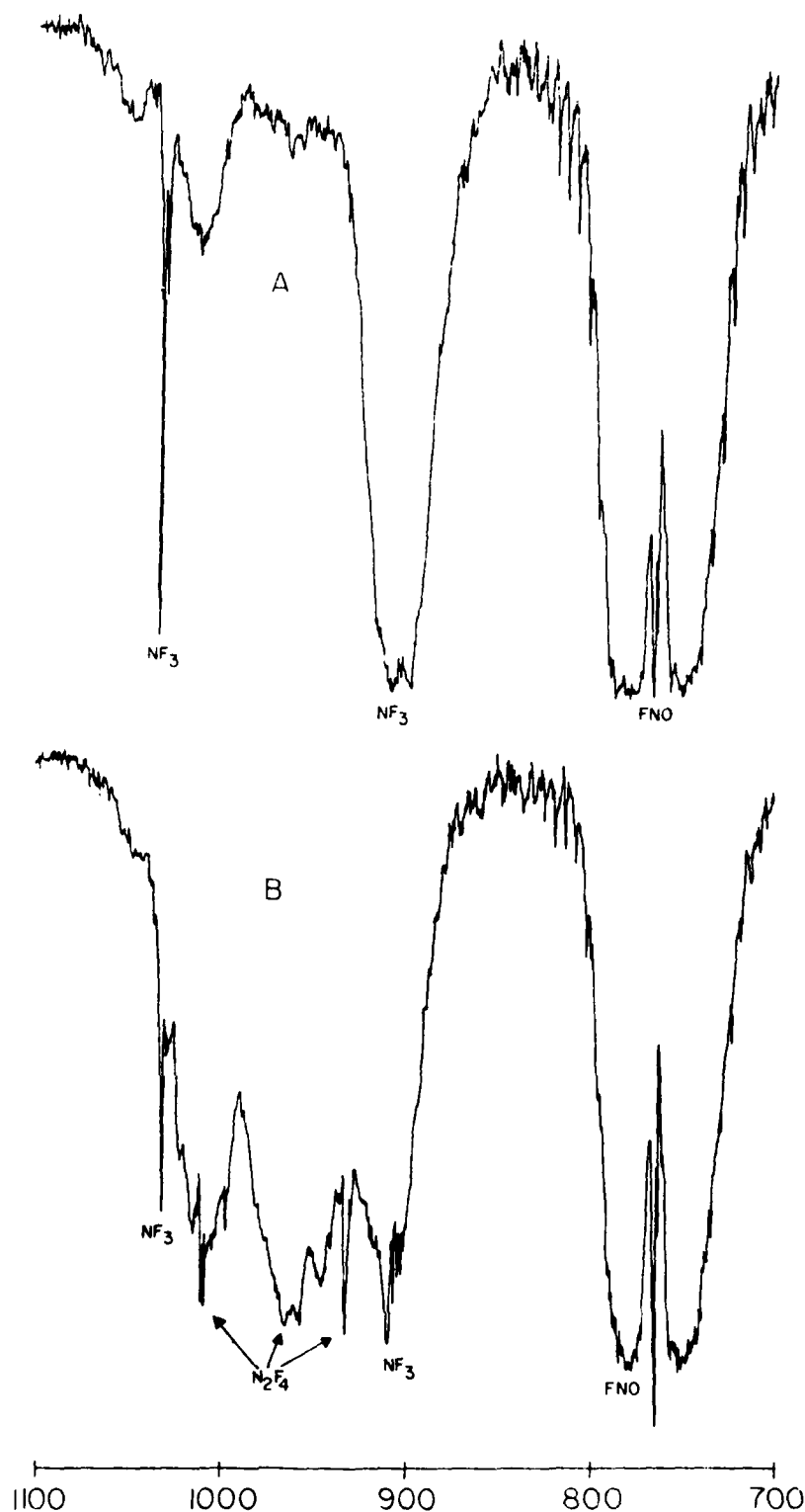


Figure 2. Expanded spectra of the products of the laser-induced reaction of NO and NF<sub>3</sub> (30 torr each) using P(36) [00<sup>0</sup>1 - 10<sup>0</sup>0] at 929.02 cm<sup>-1</sup> (A) 100W, 1 sec; (B) 50W, three 5-sec exposures.

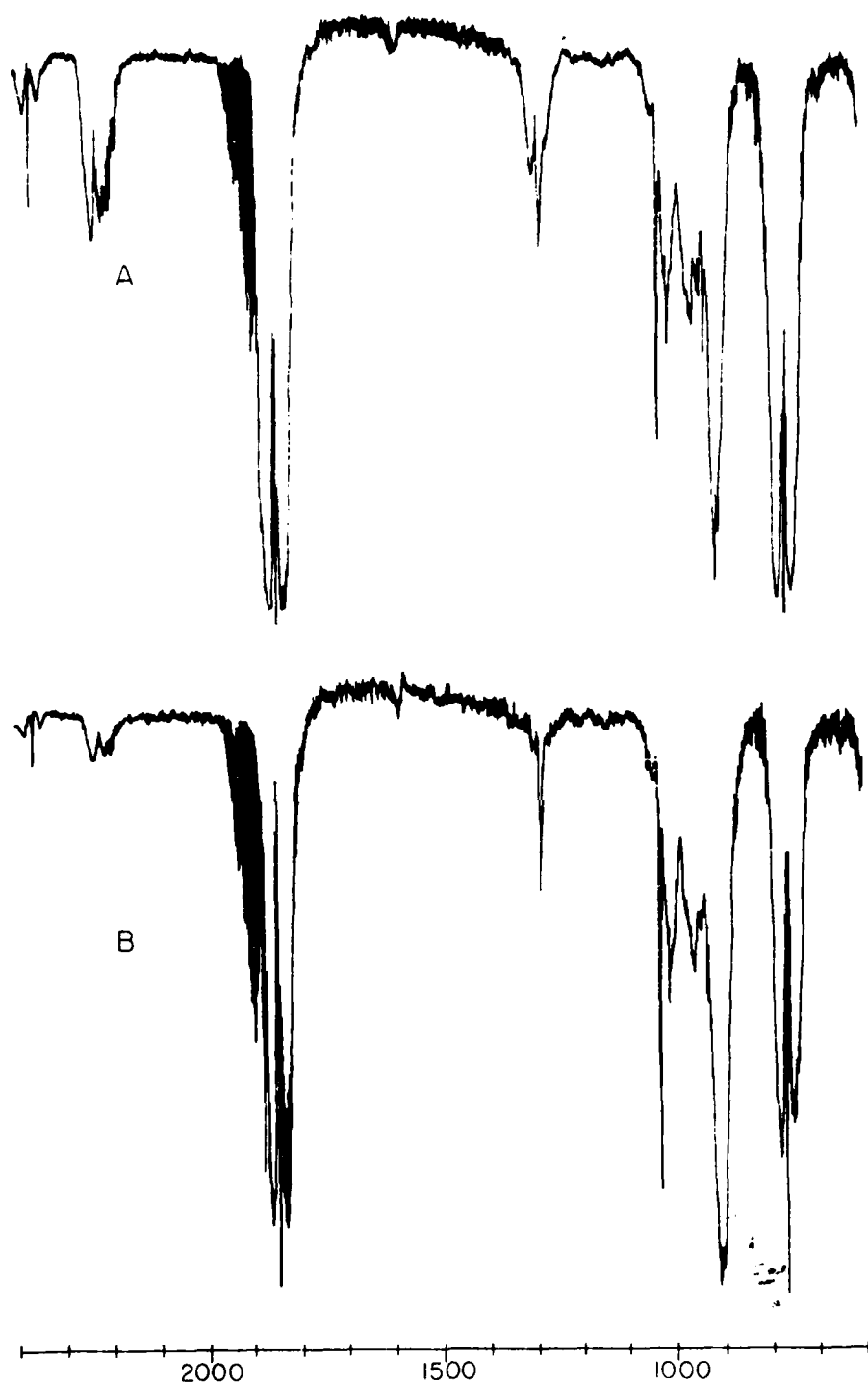


Figure 3. Spectra of the products of the laser-induced reaction of NO (60 torr) and NF<sub>3</sub> (30 torr) using P(36) [00°1 - 100°0] at 929.02 cm<sup>-1</sup>; (A) 100W, 1 sec; (B) 50W, three 8-sec exposures.

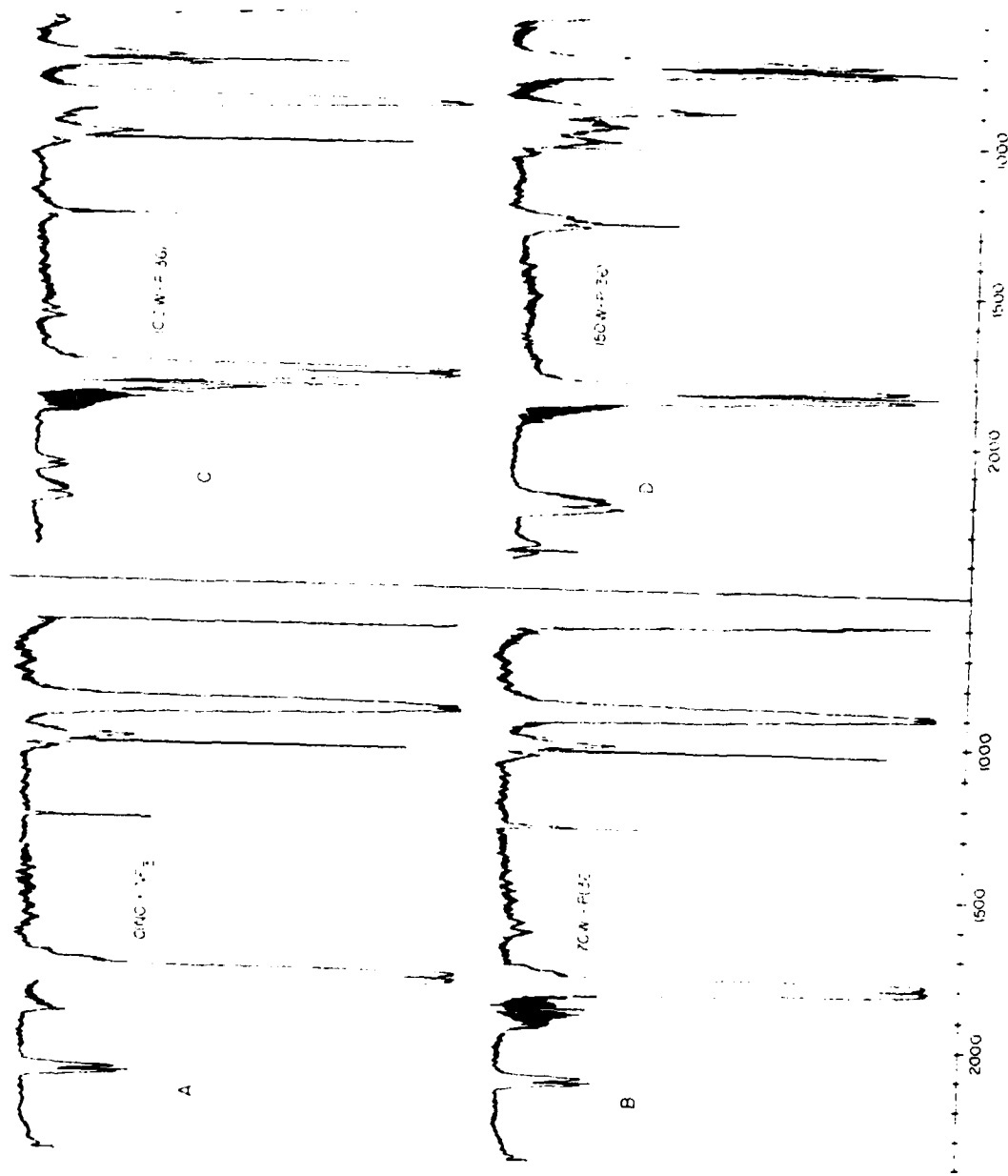


Figure 4. Laser-induced reaction of ClNO and NF<sub>3</sub> (25 torr each): (A) reactant mixture before laser irradiation; (B) 70W, P(36) [0001 - 1000], 1 sec; (C) 100W, P(36), additional 2 sec; (D) 150W, P(36), additional 8 sec.

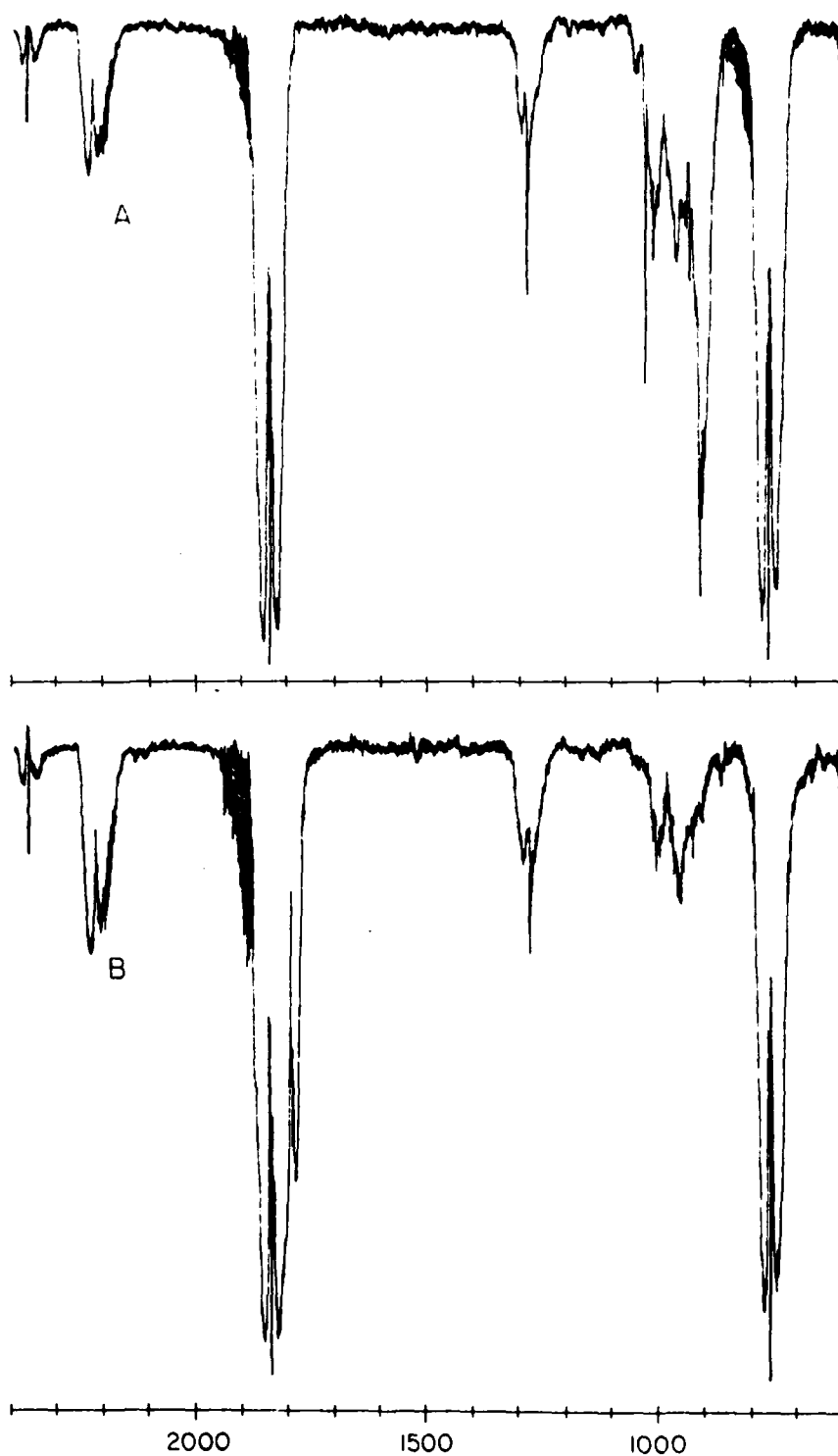


Figure 5. Laser-induced reaction of (A)  $\text{ClNO}$  and  $\text{NF}_3$  (25 torr each); 100W, P(36)  $00^{\circ}1 - 10^{\circ}0$ , five 1-sec exposures; (B)  $\text{ClNO}$  (50 torr) and  $\text{NF}_3$  (25 torr), 125W, P(36)  $[00^{\circ}1 - 10^{\circ}0]$ , five 2-sec exposures.

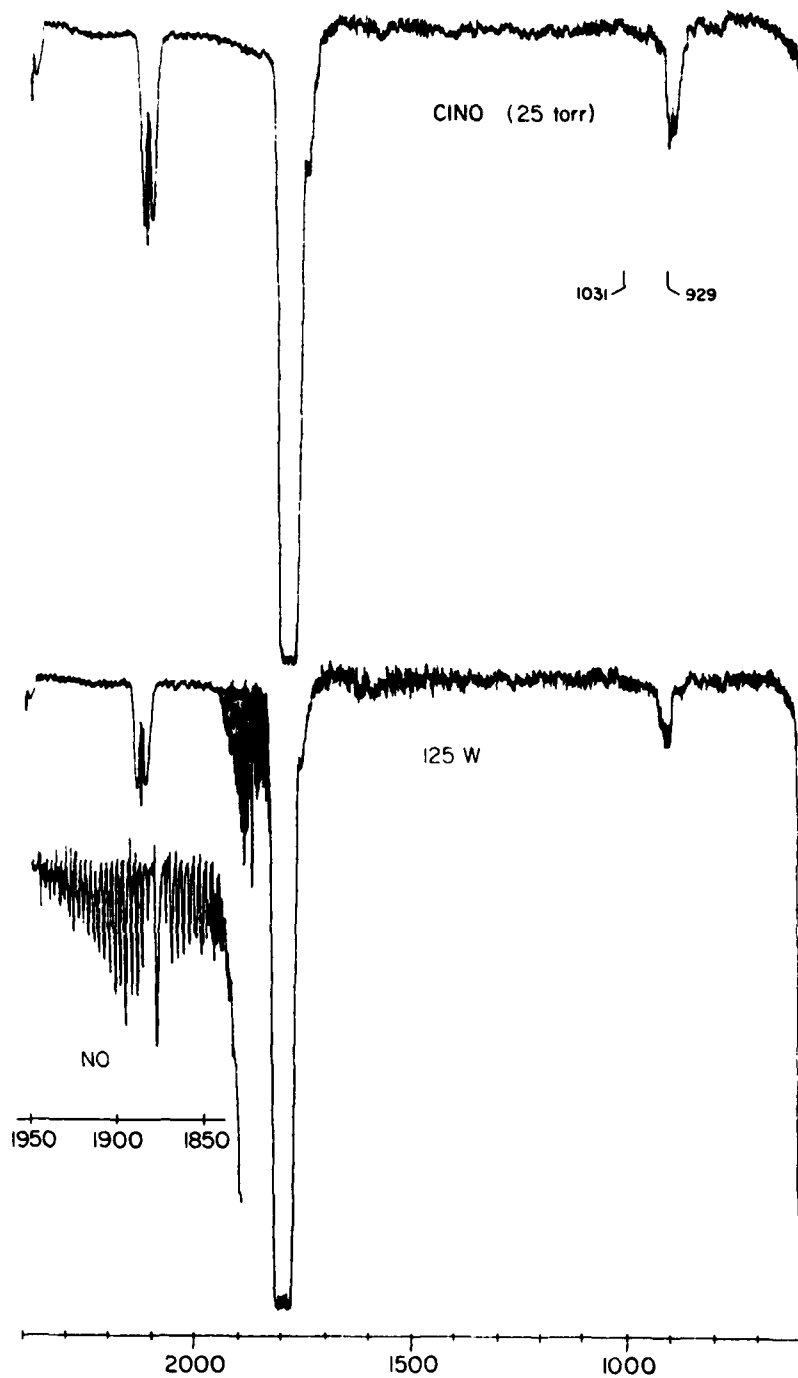


Figure 6. Infrared spectra of (A) 50 torr ClNO, (B) products of laser-induced reaction using P(36) [0001 - 1000] at 929 cm<sup>-1</sup>. Spectrum of NO product is expanded in insert.

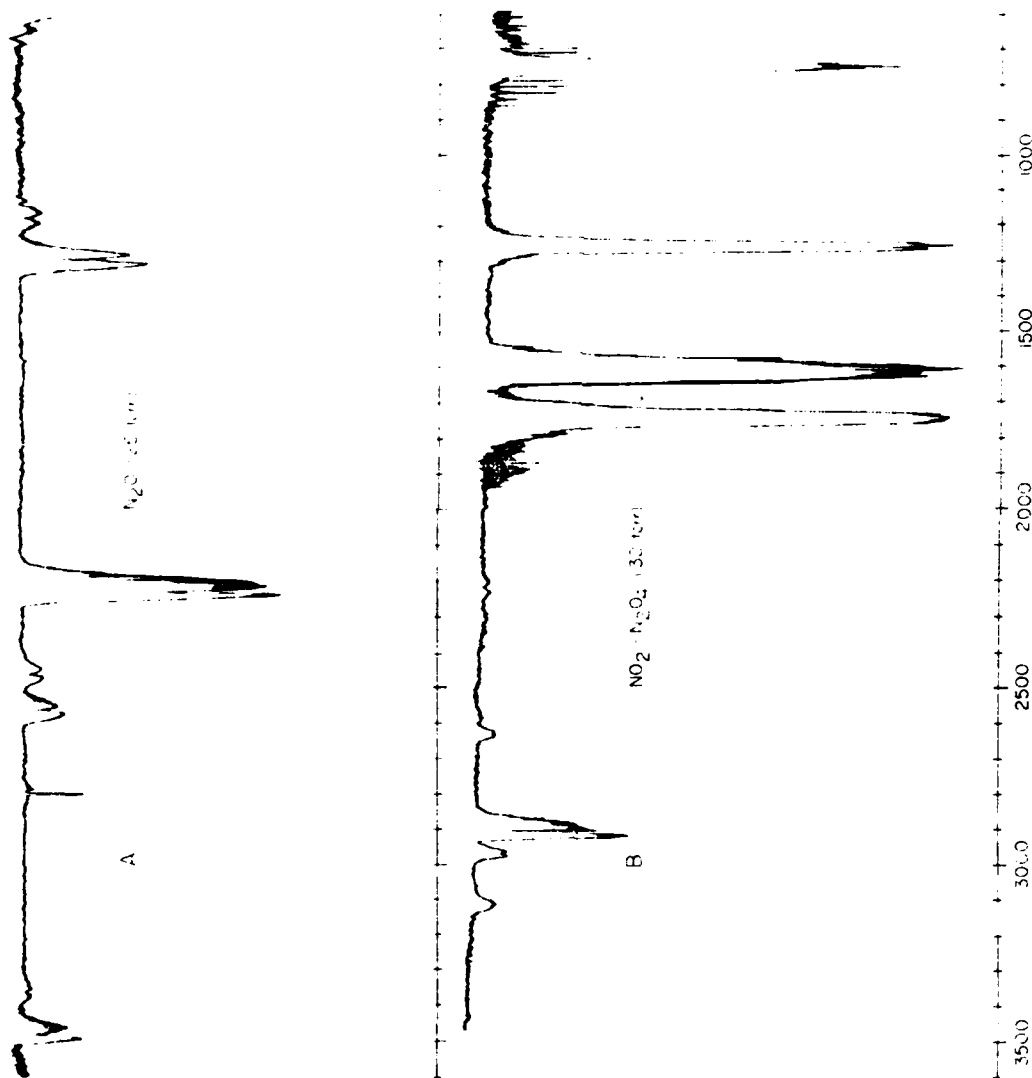


Figure 7. Infrared spectra of (A) 25 torr of  $\text{N}_2\text{O}$ , (B) 30 torr of  $\text{NO}_2 - \text{N}_2\text{O}_4$  mixture.



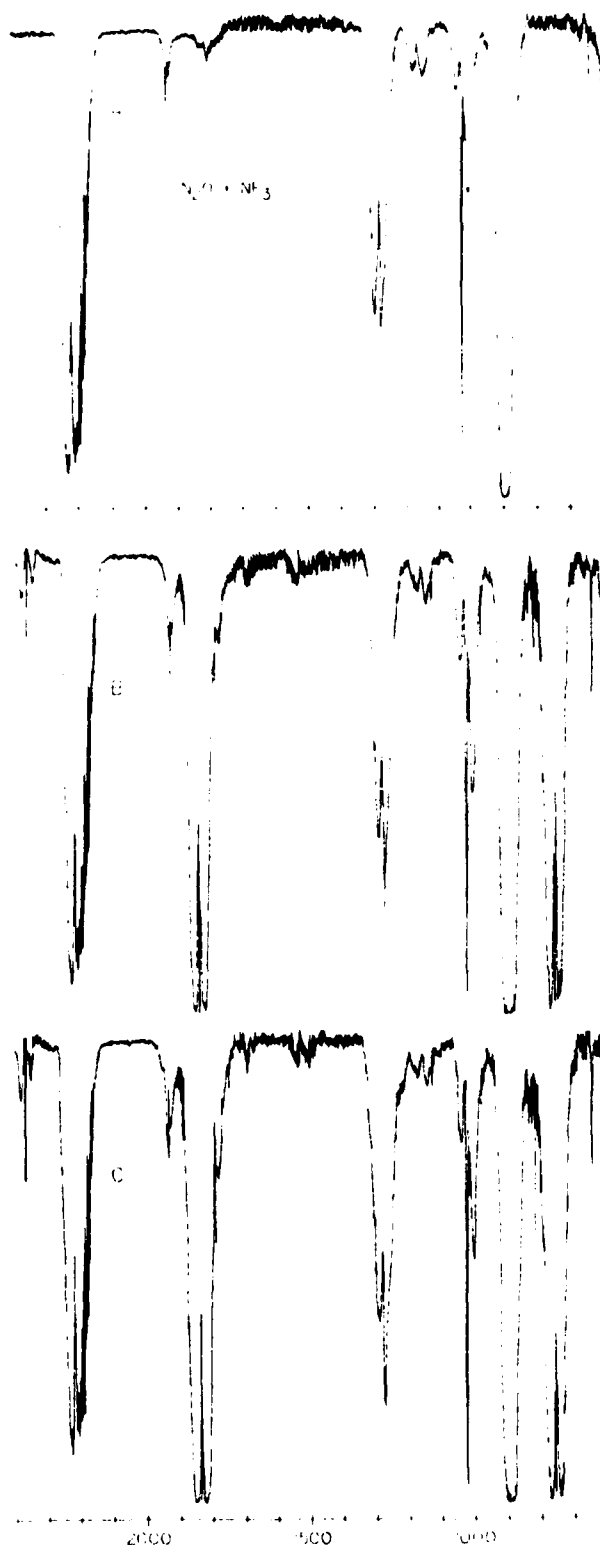


Figure 8. Infrared spectra of (A)  $\text{N}_2\text{O}$  (55 torr) -  $\text{NF}_3$  (30 torr) mixture; (B) products of laser-induced reaction of  $\text{N}_2\text{O}$  (60 torr) and  $\text{NF}_3$  (40 torr) using P(36) [0001 - 1000], 140W, five 3-sec exposures, (C) 140W, P(36), five additional 3-sec exposures. Bands at 1793 and 822  $\text{cm}^{-1}$  arising from  $\text{FNO}_2$  are marked with •).

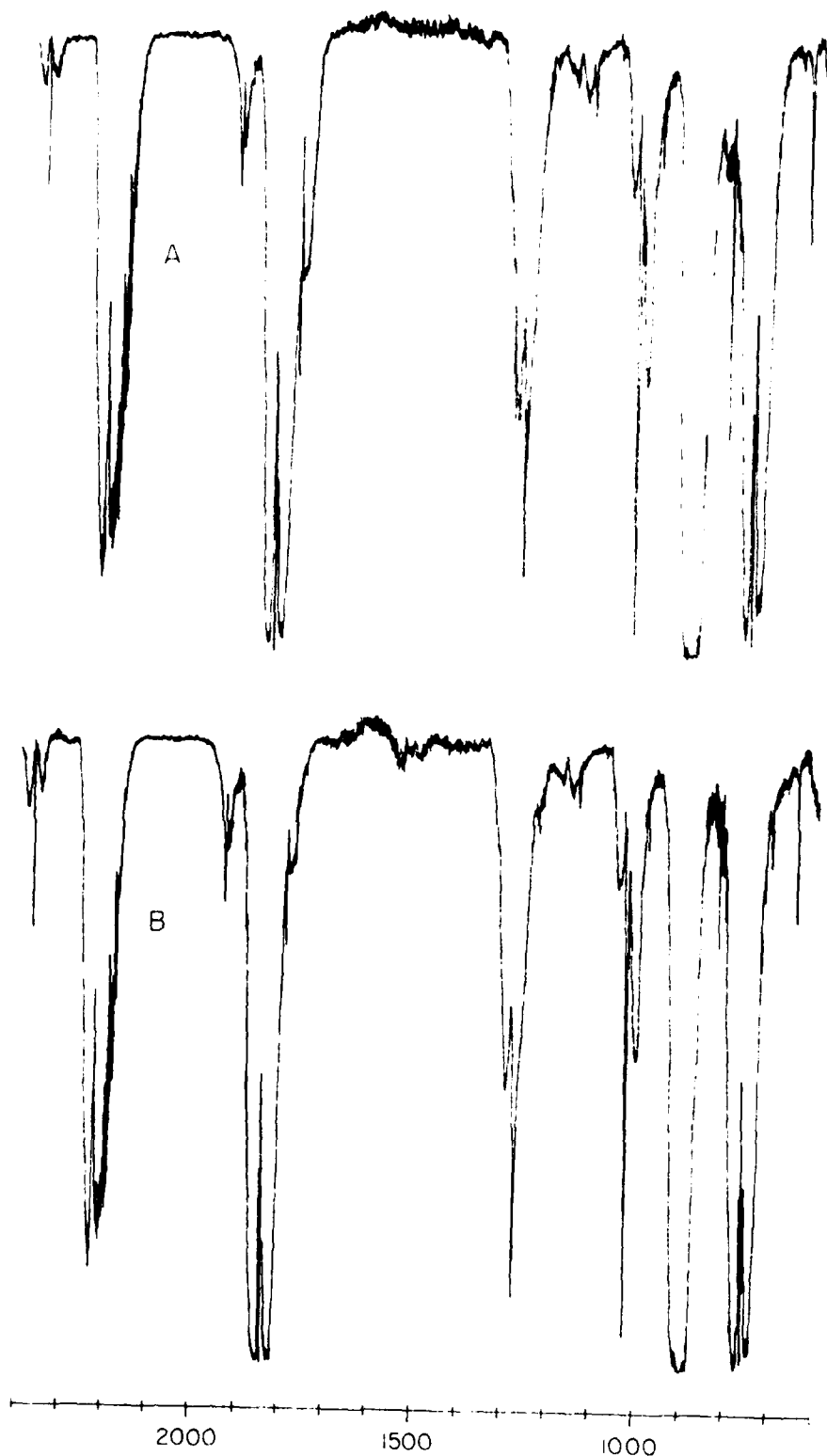


Figure 9. Infrared spectra of the products of the laser-induced reaction of  $\text{N}_2\text{O}$  (40 torr) and  $\text{NF}_3$  (50 torr) using P(36)  $[00^\circ 1 - 10^\circ 0]$ ; (A) 140W four 3-sec exposures (B) 140W, four additional 3-sec exposures.

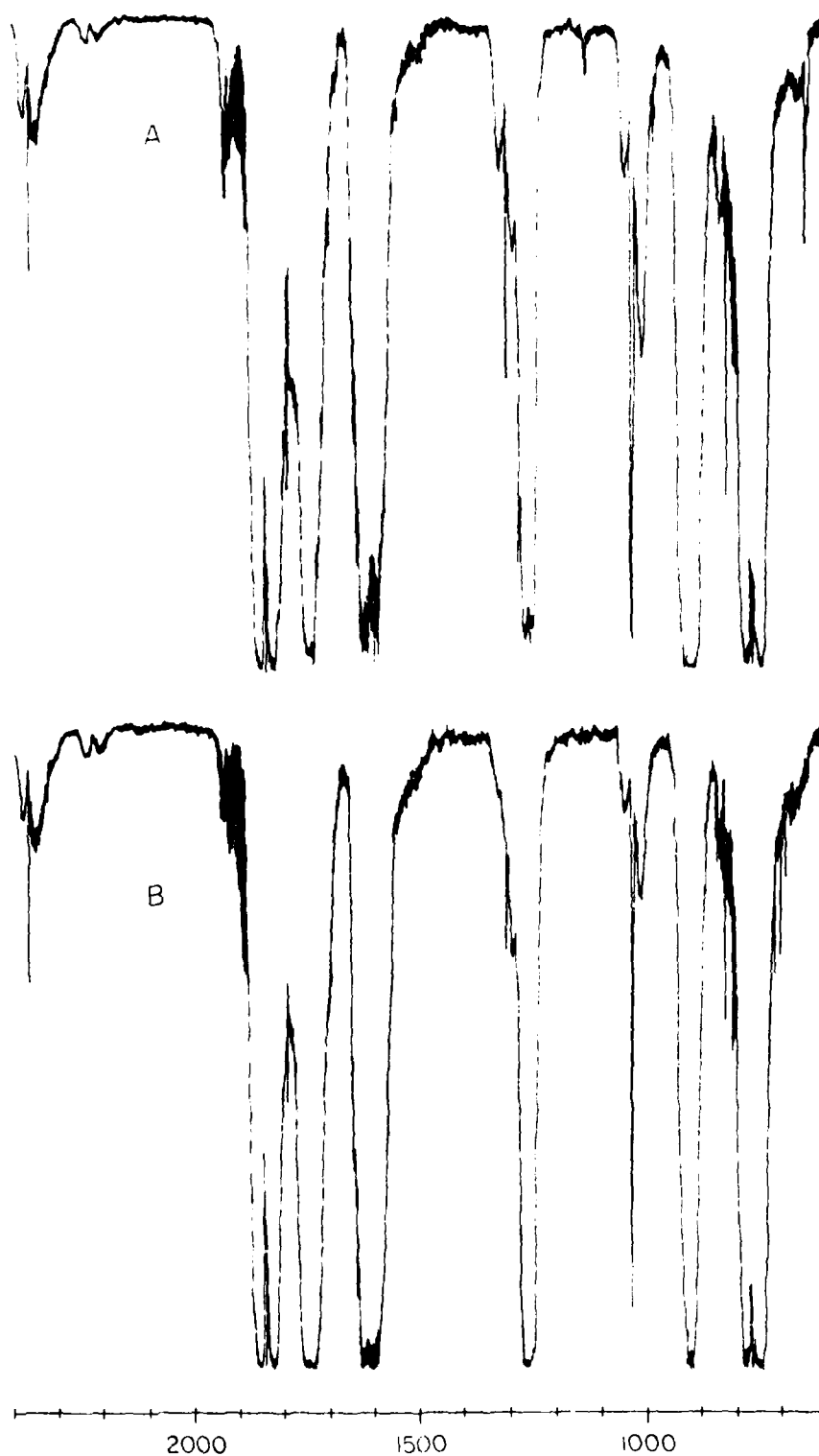


Figure 10. Spectra of the products of the laser-induced reaction of  $\text{NO}_2$  and  $\text{NF}_3$  using P(36)  $[0001 - 1000]$ ; (A) 45 torr, 50W, 25 sec (B) 60 torr  $\text{NO}_2$ , 30 torr  $\text{NF}_3$ , 50W, 25 sec, followed by 130W, 10 sec.

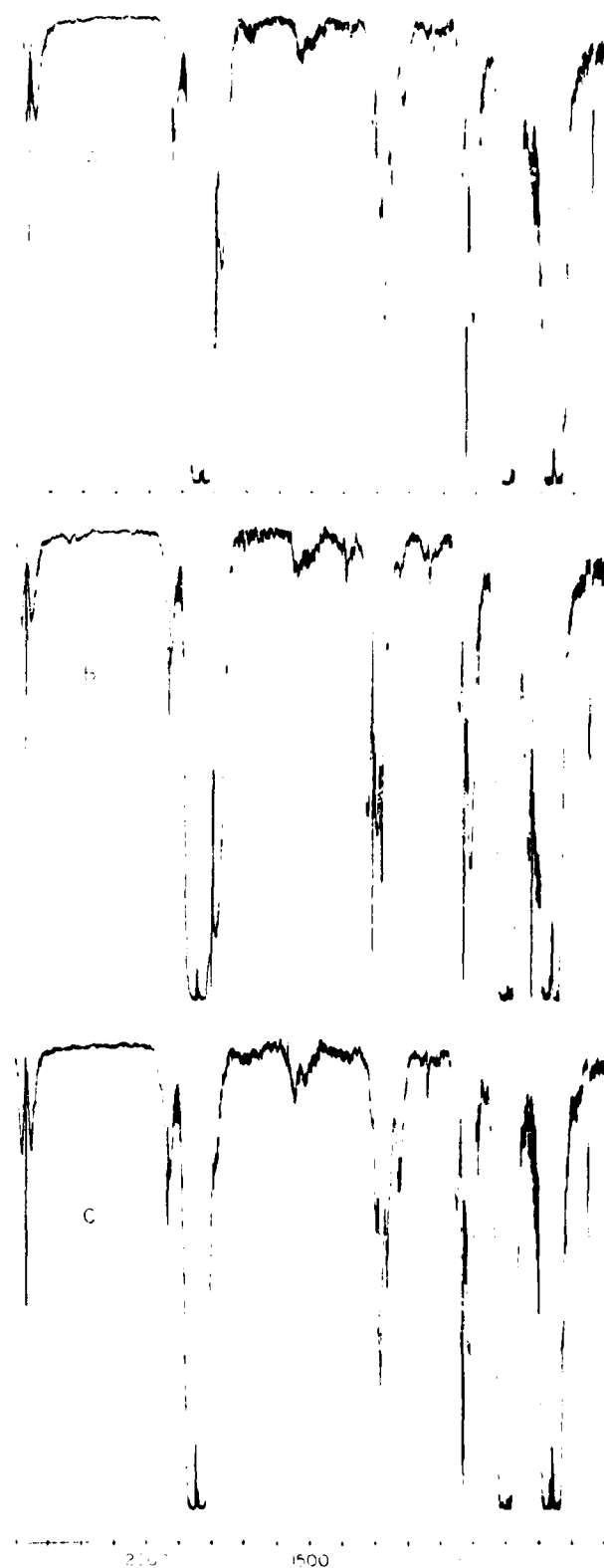


Figure 11. Spectra of the products of the laser-induced reaction of  $\text{NO}_2$  (30 torr) and  $\text{NF}_3$  (60 torr) using P(36)  $[0001 - 10^\circ 0]$ ; (A) 140W, 10 sec, (B) 50W, 20 sec, (C) 140W, additional 20 sec.

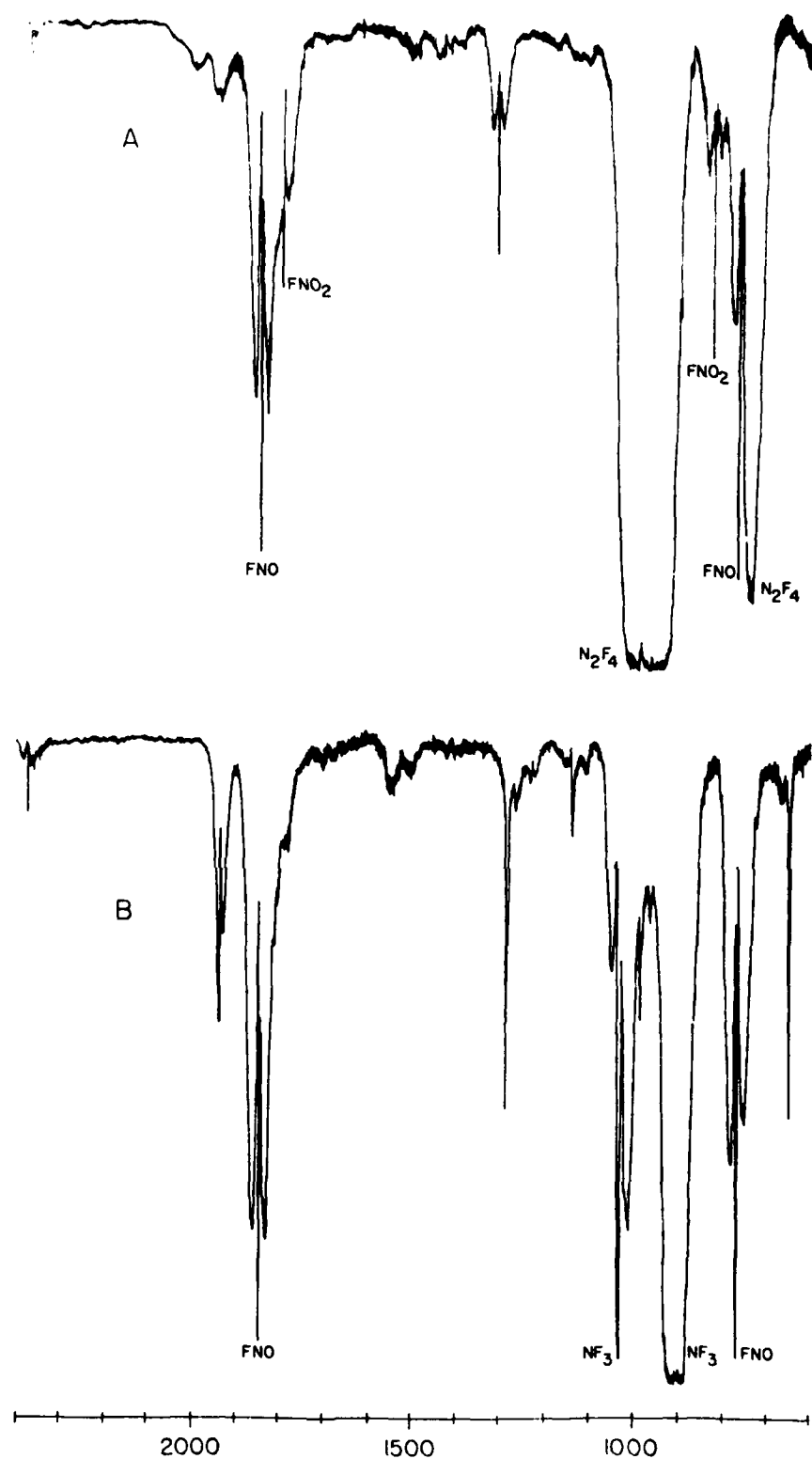


Figure 12. Infrared spectra of the products of the (A) spontaneous reaction of  $\text{NO}_2$  (10 torr) and  $\text{N}_2\text{F}_4$  (40 torr); (B) laser-induced reaction using P(36) [00<sup>0</sup>1 - 10<sup>0</sup>0] of the products of the spontaneous reaction, 140W, 10 sec.

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