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SOME LASER PHOTOCHEMICAL REACTIONS OF
NITROGEN-CONTAINING COMPOUNDS
WITH ETHYLENES

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Some laser-induced reactions of tetrafluorohydrazine (N_2F_4) or nitrogen trifluoride (NF_3) with 1,1-difluoroethylene ($C_2H_2F_2$) or ethylene (C_2H_4) have been studied. Multiphoton absorption of infrared radiation from a cw CO_2 laser initiates each of these reactions, and the major products have been identified as hydrogen fluoride (HF), CF_4, CF_3CN, CF_3H, C_2F_4, and C_2F_6. The

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20. Abstract - Continued

visible emission which accompanies the reactions has been shown to be due, in part, to transient C_2 and CN. Possible mechanisms for these reactions are discussed. A reaction between ammonia (NH_3) and $C_2H_2F_2$ has also been studied, and it probably proceeds through a non-equilibrium thermal process rather than by multiphoton dissociation as in the other cases. The main products have been identified as acetylene (C_2H_2) and hydrogen cyanide (HCN). The role of infrared laser-induced chemistry in general as a viable alternative to pyrolytic reactions is also discussed.

CONTENTS

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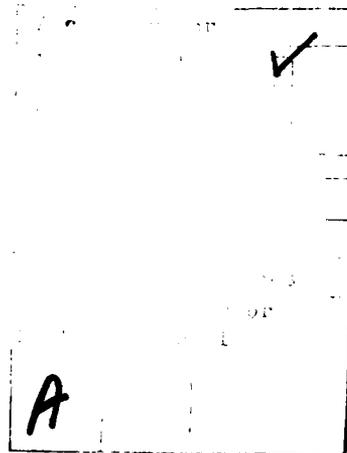
I. INTRODUCTION

The advent of discretely tunable infrared lasers has opened many new areas for research in chemical physics. Important among these is 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_2) 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.

Many laser-induced unimolecular reactions have been studied[1-3] primarily using pulsed-laser techniques, and a large amount of effort has been directed toward the possibility of isotope separations which take advantage of the differences in vibrational frequencies of molecules containing different isotopic modifications of an atom.[4] Molecular ionization can be accomplished using laser excitation,[5] and, in another area, considerable work has been concerned with bimolecular and other, more complicated reactions[6-8] which otherwise would not be favorable at ambient temperatures.

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.[9] 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.[10] This implies that the absorption of monochromatic infrared laser photons can result in a non-equilibrium 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. To fully assess the potential of laser-induced chemistry (LIC) it has been necessary to continue to pursue a number of experiments. The results of and the conculsions derived from these experiments are reported herein.

II. EXPERIMENTAL SECTION

Commercially available tetrafluorohydrazine, nitrogen trifluoride (Air Products), ammonia, ethylene, and 1,1-difluoroethylene (Matheson) were employed in the studies. Their infrared spectra[11-15] showed no detectable impurities, and the samples were used without further purification.

The reactions were carried out in stainless steel cells (5 × 10 cm) equipped with O-ring seals for securing windows (5 cm diameter) onto the cells. Windows fashioned from a number of materials were used, but best results were obtained when the infrared beams were directed through ZnSe windows and the visible emission was observed through a sapphire window. Evidence of side reactions was observed when KCl and Pyrex windows were used. Additionally, the windows were configured in such a way that the infrared beams traversed a 5 cm path.

Infrared laser excitation in the range of 10.4 or 9.4 μm was provided by a Coherent Radiation Laboratories Model 41 continuous-wave CO_2 laser. The exact laser frequencies were verified using an Optical Engineering CO_2 Spectrum Analyzer. In single-line operation, output powers between 50 and 150w could be obtained by varying the CO_2-N_2-He gas mixture in the laser. The beam size was measured from burn patterns and was found to be approximately circular with a 4mm diameter.

The visible emission which accompanied the reactions was focussed onto the entrance slit of a one meter Czerny-Turner monochromator. Standard photographic detection was generally employed, but an OMA-2 Optical Multi-channel Analyzer (Princeton Applied Research) could be mounted at the exit slit of the monochromator if experimental conditions warranted.

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, and typically the effective spectral resolution was 1.0 cm^{-1}.

III. RESULTS

The unique structural and chemical properties of N_2F_4 have been of considerable interest.[11,16,17] At ambient temperatures tetrafluorohydrazine consists of approximately one percent $\cdot NF_2$ radicals[17] as a result of the equilibrium,

$$N_2F_4 \rightleftharpoons 2 \cdot NF_2 \quad . \tag{1}$$

The stability of N_2N_4 when it is exposed to intense infrared fields has also been investigated. One study reports that the following reaction takes place,

$$N_2F_4 \rightleftharpoons N_2F_3\cdot + \cdot F \quad , \tag{2}$$

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while others suggest the non-equilibrium formation of $\cdot NF_2$ radicals.[18] The latter studies of the laser-induced chemistry of pure N_2F_4 are more fully supported.

A related compound is nitrogen trifluoride (NF_3), and the study of its laser-induced chemistry has recently been initiated. The selective production of silicon nitride (Si_3N_4) or pure silicon from the reactions of silane (SiH_4) and NF_3 in the gas phase has been reported.[7] Interestingly enough, similar reaction products can be obtained by mixing SiH_4 and N_2F_4. (NF_3 is also a product of this reaction.) The implication is that the same reactive intermediate initiates both reactions, and the most likely species is the $\cdot NF_2$ radical.[19]

The production of $\cdot NF_2$ using laser irradiation should provide a means of efficiently preparing nitrogen-containing compounds and, in particular, non-metal nitrides and other refractory materials. Initial experiments have dealt with the reactivities of N_2F_4 and NF_3 with olefinic compounds, since radical reactions are expected to be favorable for such a system.

The infrared absorptions of N_2F_4 and NF_3 which overlap the output of a CO_2 laser are shown in Figure 1. Specific laser frequencies which were used in various experiments are labeled in the figure. Additionally, the absorption spectra of $C_2H_2F_2$ (1,1-difluoroethylene) and C_2H_4 in this region are shown. It is clear that these species are suitable for studies of laser-induced chemistry and provide flexibility in designing experiments.

The infrared spectrum of a mixture of N_2F_4 and $C_2H_2F_2$ gases (1:1 molar ratio) is shown in Figure 2. Also shown is a spectrum of the products after such a mixture is irradiated with 30 W (240 W/cm^2) of infrared radiation at 914.42 cm^{-1}, P(50)[00°1-10°0]. The P($\Delta J = -1$) and R($\Delta J = +1$) branches between 4300 and 3600 cm^{-1} in the lower spectrum are characteristic of a linear diatomic molecule, and in this case they are due to hydrogen fluoride, HF.[20] The region between 1400 and 850 cm^{-1} is displayed in expanded form in Figure 3, and the fine structure associated with some of the bands is visible. These and other bands have been used to confidently identify CF_4,[21] CF_2CN,[22] CF_3H,[23] C_2F_4,[24] and C_2F_6[25] as reaction products, and the exact frequencies are given in Table 1.

N₂F₄

NF₃

C₂H₂F₂

C₂H₄

P(48)   R(20)   P(24)   P(50)
 ‖   ‖ ‖   ‖ ‖ ‖   ‖
P(42)   R(36)   P(14) P(34)

1100   1050   1000   950   900   850

WAVENUMBER
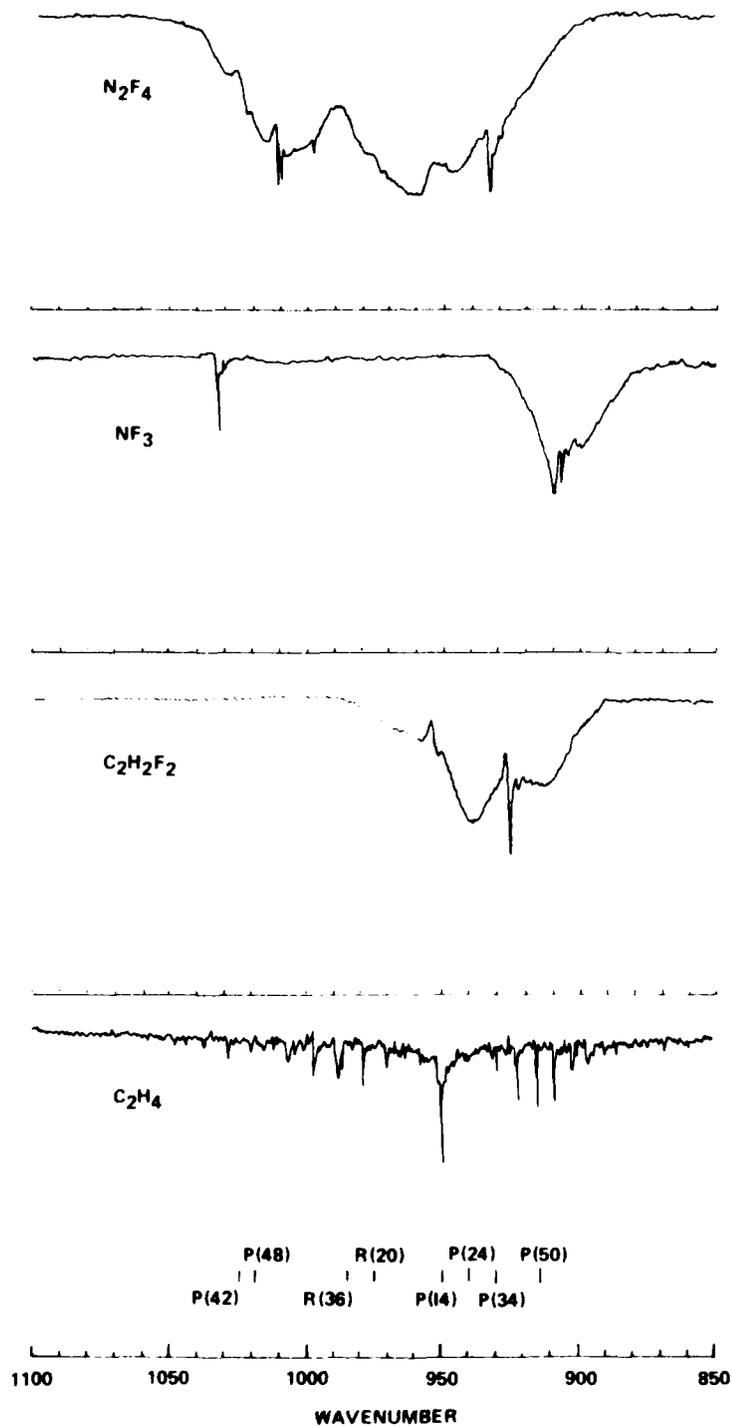
Figure 1.   Infrared spectra of N_2F_4, NF_3, $C_2H_2F_2$, and C_2H_4 in the region which is resonant with the output of the CO_2 laser.

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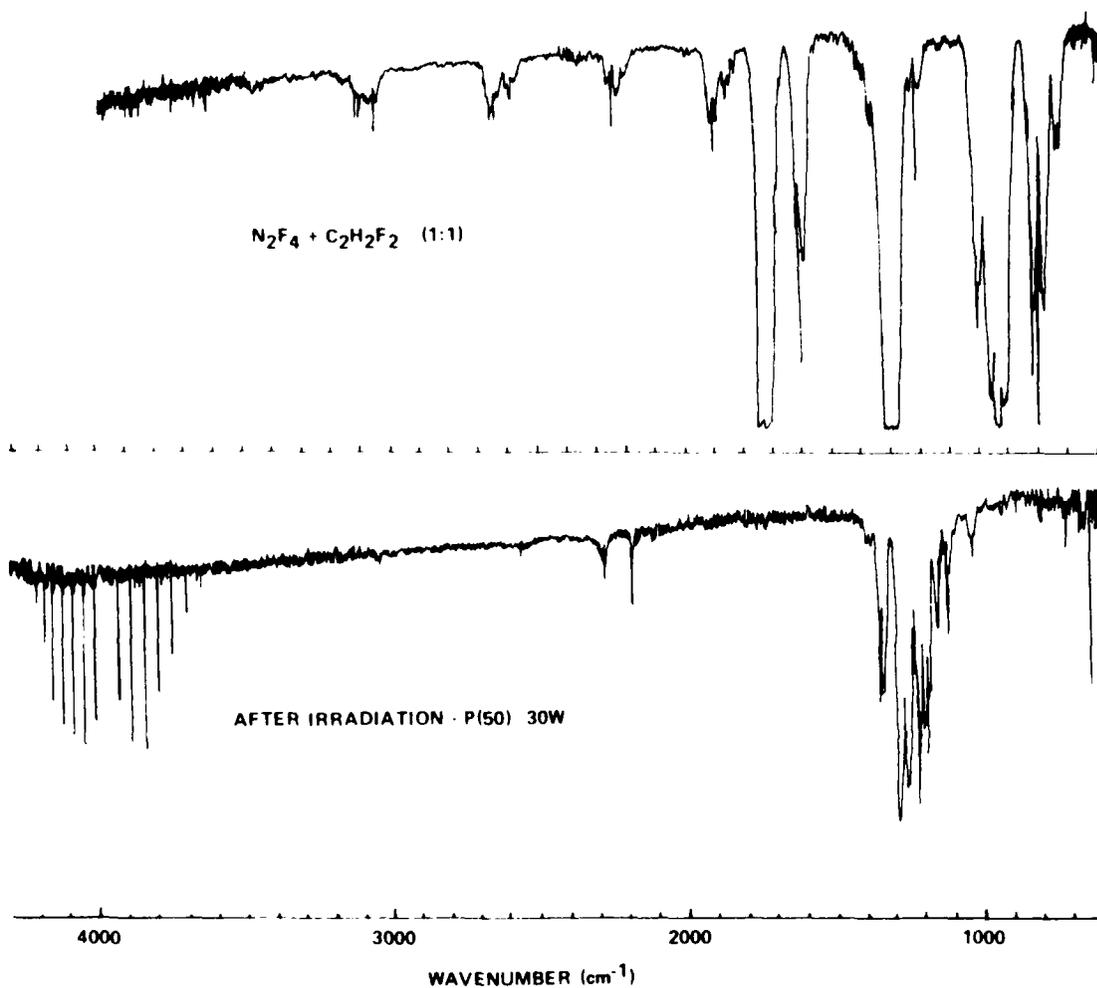
Figure 2. Infrared spectra of (upper) a 1:1 mixture of N_2F_4 and $C_2H_2F_2$ and (lower) a mixture of products formed as a result of laser radiation.

For all the laser-induced reactions it was necessary to control a number of experimental variables. Extremely critical is the choice of reaction cell and cell window materials. There were no apparent reactions with the stainless steel cell bodies, but the HF which was invariably produced reacted with certain of the window materials. If KCl or Pyrex windows were used, large quantities of HCl[13] or SiF_4,[26] respectively, were produced, and no HF was observed. These problems were solved by using ZnSe and sapphire windows.

Table 1. *Frequencies and assignments for the infrared bands observed in the laser-induced chemical reactions of N_2F_4 and $C_2H_2F_2$ and similar reaction systems.*

Frequency/Band Type			Assignment
2278	Q		CF_3CN
2274			
2271			
2268			
1342	R		C_2F_4
(1338)	center	B-type	
1331	P		
1286	R		CF_4
1283	Q	vs	
1281	Q		
1279	sh		
1250	(perpendicular)		C_2F_6
1241	Q		$^{13}CF_4$
1239			
1227			CF_3CN
1214	Q		CF_3CN
1194	R		
1187	Q	A-type	C_2F_4
1180	P		
1152	(broad)		CF_3H
1122	R		
1116	Q	(parallel)	C_2F_6
1108	P		
1031	Q		SiF_4
729	Q		C_2H_2
714	Q		C_2F_6
712	Q		HCN
631	Q		CF_4

The mole ratios of the reactants and the choice of laser frequency also affected the outcome of the reactions. For N_2F_4 and $C_2H_2F_2$ the reactions were carried out either with equal partial pressures or with 2:1 pressure ratios, with one or the other in excess. Spectra of the products of reactions in which the N_2F_4:$C_2H_2F_2$ concentration ratios were 1:1 and 2:1 are shown in the middle and lower frames of Figure 3. In the latter reaction the only observed products were HF, CF_4 and a trace of N, (907 cm^{-1}). The concentration of CF_4 was considerably greater in the reaction of the 2:1 mixture than in the case of the 1:1 mixture. In fact the band structure attributable to $^{13}CF_4$ in natural abundance is prominent (1241 cm^{-1}). On the other hand, for a 1:2 ratio (N_2F_4:$C_2H_2F_2$), HF, CF_3CN, CF_3H, C_2F_4 and C_2F_6 were produced along with only traces of CF_4. Other products included HCN and C_2H_2.

In addition to the gaseous products in these reactions, varying amounts of solid carbon were deposited on the cell walls and windows. Enough carbon was formed in the reactions of 1:2 mixtures that the infrared beam was severely attenuated, and it was necessary to clean the cell after each reaction. Far less carbon was produced when the relative amount of hydrocarbon reactant was decreased, as, for example, in the cases of the 1:1 or 2:1 reaction mixtures. Also it was noted that the formation of HCN and C_2H_2 accompanied the production of large amounts of carbon.

Rather surprisingly, the production of carbon was also dependent upon the laser frequency. For example, in reactions initiated by the P(24)[00°1 – 10°0] laser line at 940.55 cm^{-1}, large amounts of carbon were produced regardless of the relative concentrations of reactants. This problem was minimized by using the P(50) [00°1 – 10°0] line at 914.42 cm^{-1}, and only traces of carbon were deposited in the reactions of equal molar concentrations of reactants.

Other laser lines were also used in the experiments. The R(20)[00°1 – 10°0] line at 975.93 cm^{-1} successfully initiated the reaction of 1:1 mixtures of N_2F_4 and $C_2H_2F_2$, and HF and the "normal" collection of fluorocarbons were produced with virtually no carbon deposits. Irradiation of mixtures at 985.49 cm^{-1}, R(36)[00°1 – 10°0], and 1025.30 cm^{-1}, P(42)[00°1 – 02°0], with powers as high as 60 W (480 W/cm^2), however, did not initiate reaction. The positions of these laser lines relative to the absorptions of the reactants have been presented in Figure 1, and it can be seen that while the latter two frequencies are resonant with a band in N_2F_4, they are not resonant with the strong N–F stretch centered at 933 cm^{-1} or either of the bands in $C_2H_2F_2$.

The data indicated that, for excitation with a given laser line, the types of products depend upon the relative amounts of starting materials. In further efforts to characterize the reactions, buffer gases were added to the reaction mixtures. The addition of He to the system (with irradiation at 914.42 cm^{-1})
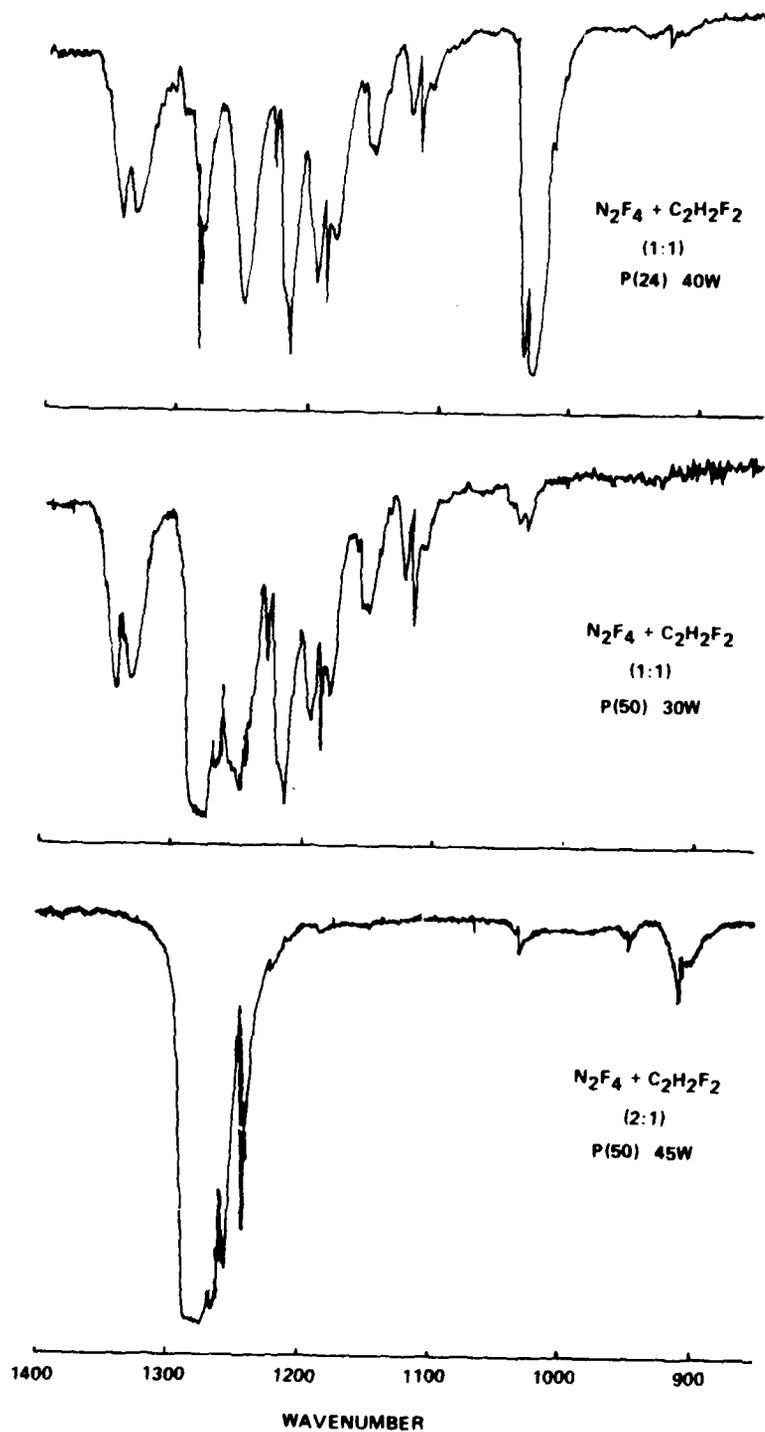
Figure 3. Infrared spectra of the products of laser-induced chemical reactions of N_2F_4 and $C_2H_2F_2$.

Labels within the figure:

$N_2F_4 + C_2H_2F_2$
(1:1)
P(24) 40W

$N_2F_4 + C_2H_2F_2$
(1:1)
P(50) 30W

$N_2F_4 + C_2H_2F_2$
(2:1)
P(50) 45W

1400 1300 1200 1100 1000 900

WAVENUMBER

did not affect the outcome of the reaction. However, the presence of N_2 gas in the 1:1 mixtures of N_2F_4 and $C_2H_2F_2$ altered the laser-induced reactions such that HF, CF_4 and NF_3 were the only products. It is interesting to note that these are also the products obtained when excess N_2F_4 is used in the absence of a buffer gas. These data are summarized in Table 2.

Table 2. Summary of products formed in the laser-induced chemical reactions.

Reactants (mole ratios)	Major products*
N_2F_4; $C_2H_2F_2$ (1:1)	HF, CF_4, CF_3CN, CF_3H, C_2F_4, C_2F_6
N_2F_4; $C_2H_2F_2$ (2:1)	HF, CF_4, (NF_3)
N_2F_4; $C_2H_2F_2$ (1:2)	HF, (CF_4), CF_3CN, CF_3H, C_2F_4, C_2F_6, HCN, C_2H_2
N_2F_4; $C_2H_2F_2$; He (1:1:1), (1:1:2)	HF, CF_4, CF_3CN, CF_3H, C_2F_4, C_2F_6
N_2F_4; $C_2H_2F_2$; N_2 (1:1:1), (1:1:2)	HF, CF_4, NF_3
N_2F_4; C_2H_4 (1:1)	HF, CF_4, CF_3CN, CF_3H, C_2F_4, C_2F_6
NF_3; $C_2H_2F_2$ (2:1)	HF, CF_4, CF_3CN, CF_3H, C_2F_4, C_2F_6
NF_3; $C_2H_2F_2$ (1:1)	(HCN), CF_4, CF_3CN, CF_3H, C_2F_4, C_2F_6
NF_3; C_2H_4 (2:1)	HF, CF_4, CF_3CN, CF_3H, C_2F_4, C_2F_6
NF_3; C_2H_4 (1:1)	HF, HCN, (CF_4), (CF_3H)

*Compounds in parentheses were produced in very small amounts.

As mentioned previously, a bright visible emission accompanies each of the reactions mentioned thus far, and, in fact, all of those listed in Table 2. A representative spectrum, recorded photographically in first-order, is shown in Figure 4. The location of the band heads and their assignments are given for the C_2 Swan bands and the CN red and violet emission.[27] Also indicated are the mercury lines which were used for calibration. The C_2 and CN emissions were also observed with an optical multichannel analyzer (OMA), but most of the pertinent features are displayed clearly enough on the photograph. Missing from the photograph, as a result of the lack of sensitivity of

NF$_3$ + C$_2$H$_4$ P(50)

Figure 4.   Visible emission spectra of C$_2$ and CN formed during CO$_2$
            laser irradiation of mixtures of N$_2$F$_4$ or NF$_3$ with C$_2$H$_2$F$_2$
            or C$_2$H$_4$. (Mercury calibration lines are indicated.)

of the film, is an indication that a near-continuum exists beyond ∿6500Å,
but this emission was apparent when the OMA was used.

Tetrafluorohydrazine (N$_2$F$_4$) was also mixed with ethylene (C$_2$H$_4$) and
exposed to the P(50)[00°1 -10°0], 914.42 cm^{-1}, radiation of the laser. It
was observed that the laser power required to initiate a reaction was lower
in each case than that required for the corresponding reactions involving
C$_2$H$_2$F$_2$ (see Table 3). If a slight excess of C$_2$H$_4$ was used, the gaseous
products (which give rise to infrared spectra) were HF and traces of HCN and
and CF$_3$H. For approximately a 1:1 mode ratio of reactants (very slight
excess of N$_2$F$_4$) the products were HF, CF$_4$, CF$_3$CN, CF$_3$H, C$_2$F$_4$ and C$_2$F$_6$, and
for a 2:1 ratio the same products were observed. Spectra from 1400 to 850
cm^{-1} for the latter two cases are shown in Figure 5. The primary difference
is clearly the amount of CF$_4$ (1283 cm^{-1}) which is formed. The relative
amounts of the other products are the same in the two portions of the figure.

Table 3.   Laser power required to initiate reaction.

Reactants, 30 torr total (mole ratios)	Laser Power, P(50)
N_2F_4; $C_2H_2F_2$ (1:1)	30 W
N_2F_4; C_2H_4 (1:1)	10 W
NF_3; $C_2H_2F_2$ (2:1)	20 W
NF_3; C_2H_4 (2:1)	20 W
N_2F_4; $C_2H_2F_2$; He (1:1:1)	50 W
40 torr (1:1:2)	50 W
N_2F_4; $C_2H_2F_2$; N_2 (1:1:1)	45 W
40 torr (1:1:2)	45 W
N_2F_4; $C_2H_2F_2$ (2:1)	45 W
NF_3; $C_2H_2F_2$ 20 torr (1:1)	40 W
NF_3; C_2H_4 20 torr (1:1)	50 W

N₂F₄ + C₂H₄
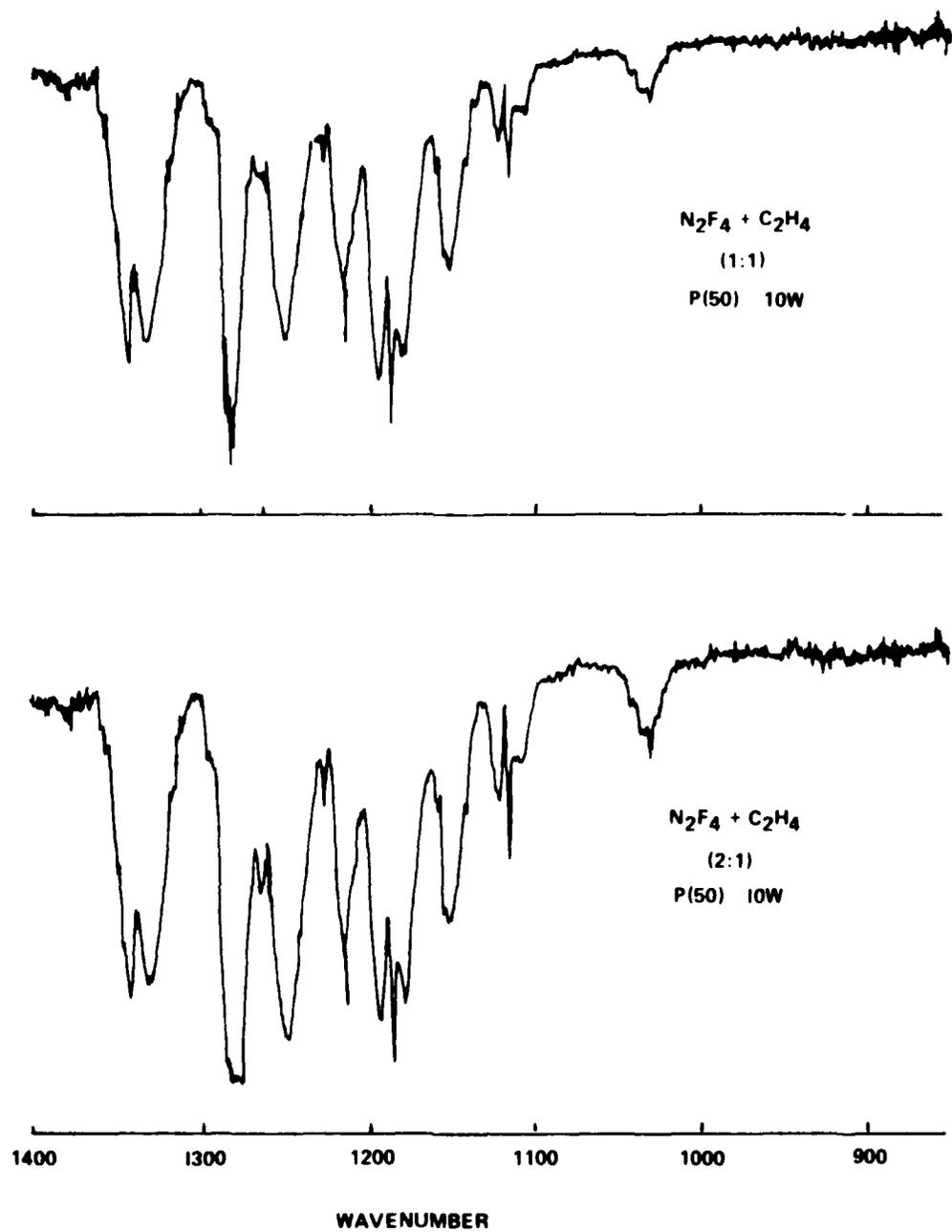(1:1)
P(50)   10W

N₂F₄ + C₂H₄
(2:1)
P(50)   10W

WAVENUMBER

Figure 5.   Infrared spectra of the products of the laser-induced
chemical reaction of N_2F_4 and C_2H_4.
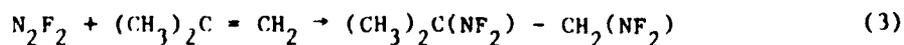
The reactions of NF_3 with $C_2H_2F_2$ and C_2H_4 have been investigated, and the results are summarized in Table 2 and Figure 6. For NF_3 and $C_2H_2F_2$ in a 2:1 mole ratio, the normal group of products was observed (HF, CF_4, CF_3CN, CF_3H, C_2F_4 and C_2F_6), while a 1:1 ratio gave, in addition to these, some HCN. However, when a large excess of NF_3 was used, HF and CF_4 (along with NF_3) remained after the reaction. The reaction of a 2:1 mixture of NF_3 and C_2H_4, induced by P(50)[00°1 - 10°0] radiation at 914.42 cm^{-1} gave HF, CF_4, CF_3CN, CF_3H, C_2F_4 and C_2F_6 as products. However, when a 1:1 mixture was irradiated, HF, HCN and traces of CF_4 and CF_3H were formed.

Evident in Figure 6 is the fact that the relative concentrations of products are different for the two reaction systems. In the NF_3-$C_2H_2F_2$ reaction, CF_4 (1283 cm^{-1}) is produced in larger quantity. Also, relative to the C_2F_4 bands (1338, 1187 cm^{-1}), the amount of CF_3CN (1214 cm^{-1}) is larger and the amount of CF_3H (1152 cm^{-1}) is smaller for this reaction. It is interesting to note that laser powers of 20 W (160 W/cm^2) were required for both of the reaction systems involving NF_3 (2:1 mole ratios). This contrasts the results for the corresponding N_2F_4 reactions (1:1), where 30 W (240 W/cm^2) were required for the $C_2H_2F_2$ and C_2H_4 reactions, respectively. One might have expected similar trends for the thresholds in the reactions, and a consideration of the observed data should provide mechanistic information.

Finally the possible reaction of NH_3 and $C_2H_2F_2$ was investigated. Mole ratios of 2:1 and 1:1 were irradiated at 931.00 cm^{-1}, P934)[00°1 - 10°0], but there was no instantaneous visible emission as there had been in the reactions discussed above. Reactions could, however, be induced by exposing the gas mixtures to high laser powers for periods of a few seconds. During the exposure, a "glow" was visible along the path of the laser beam. As the reaction proceeded and the reactants were depleted, the intensity of the glow diminished. Among the products were C_2H_2, HCN, some NH_4^+ salts and some unidentified gases and solids. Further work is required in this area of study, but the initial results are encouraging insofar as solids have been prepared from the laser-induced chemistry of gaseous reactants. Also $C_2H_2F_2$ alone (40 torr) was subjected to 50 W (400 W/cm^2) of P(34)[00°1 - 10°0] radiation for 5 seconds. Again there was a glow, and some C_2H_2 and HF were produced.

IV. DISCUSSION

It has been reported that N_2F_4 and isobutylene react at 300°C according to the following reaction;
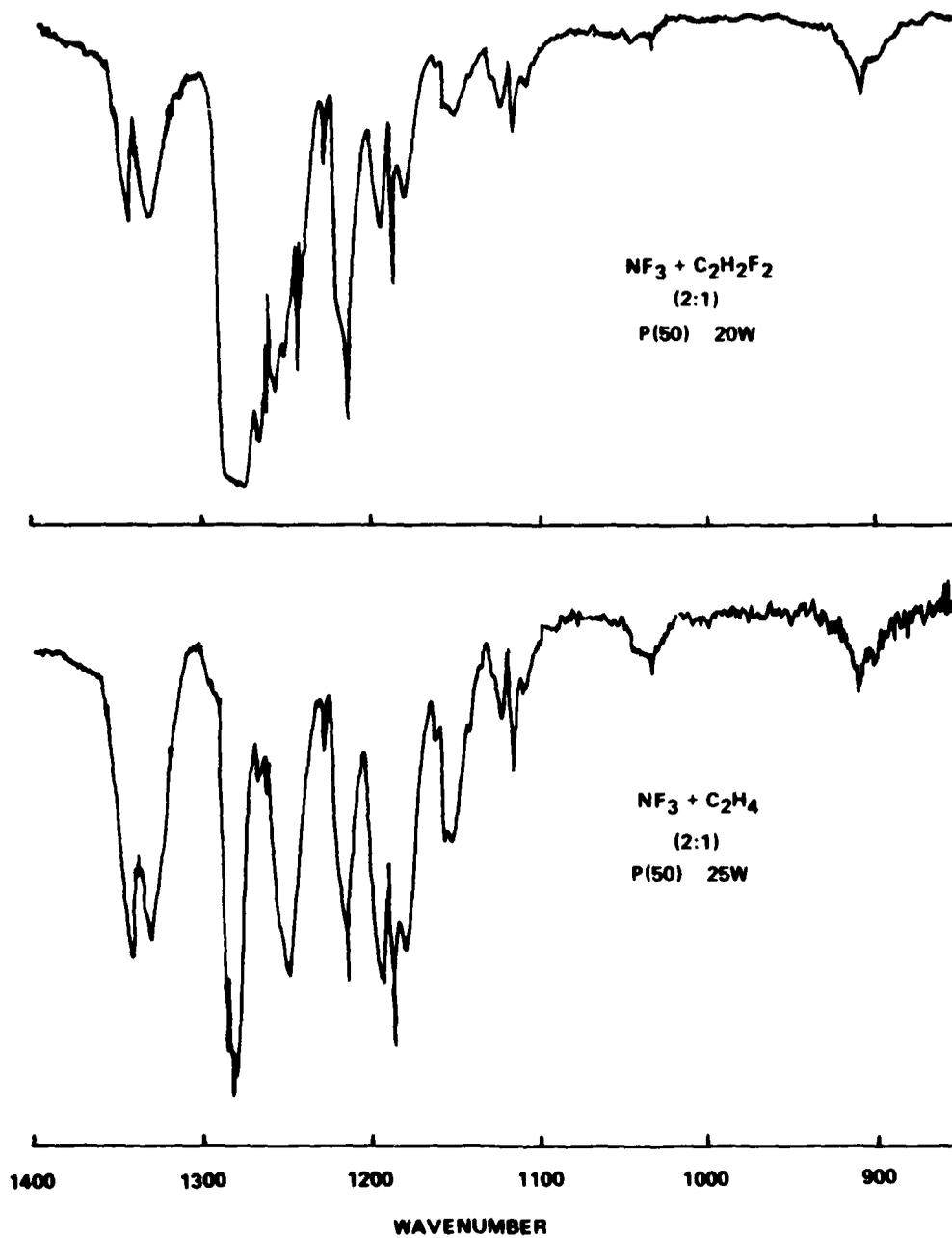
$$N_2F_2 + (CH_3)_2C = CH_2 \rightarrow (CH_3)_2C(NF_2) - CH_2(NF_2) \qquad (3)$$

NF₃ + C₂H₂F₂
(2:1)
P(50)   20W

NF₃ + C₂H₄
(2:1)
P(50)   25W

1400   1300   1200   1100   1000   900

WAVENUMBER

*Figure 6.   Infrared spectra of the products of the laser-induced
chemical reactions of NF₃ with C₂H₂F₂ or C₂H₄.*

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which represents simple addition across the double bond. When high pressure mixtures are exposed to intense infrared radiation, the following reaction takes place;[28]

$$6N_2F_4 + (CH_3)_2C = CH_2 \rightarrow 4CF_4 + 8HF + 6N_2 \quad . \tag{4}$$
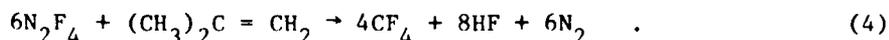
The reactions of N_2F_4 and NF_3 with $C_2H_2F_2$ and C_2H_4 appear to be rather more interesting and complicated than reactions (3) and (4) would indicate. Regardless of the mole ratios, in each of the four reaction systems described in Table 2, the visible emission which accompanies the reactions in due primarily to C_2 and CN. The composition of the products, however, depends directly upon the relative amounts of the reactants. For example, in the N_2F_4 - $C_2H_2F_2$ reaction system, with 1:1 mole ratios HF and fluorocarbons are produced. If an excess of nitrogen (supplied by N_2F_4 or N_2) is used, HF, CF_4 and NF_3 are formed, while if there is excess carbon, HCN and C_2H_2 are produced along with the other fluorocarbons. As noted previously, one of the major differences in the products for the various reactions is the amount of CF_4. In an approximate sense, there are larger amounts of CF_4 when large relative amounts of fluorine exist in the reactants.

A mechanistic explanation for the observed reactions is complicated. Obviously the reactions are initiated by the excitation in the N-F stretching and C-H bending or C-F stretching modes. The formation of C_2 from ethylenes has been carried out using multiphoton absorption, and studies of ^{13}C isotope effects have confirmed the initial interpretations.[29] The formation of CN indicates that a reactive nitrogen-containing species (presumably $\cdot NF_2$) is attacking the carbon-containing species, but it is impossible to conclude whether such a reaction involves C_2, $C_2H_2F_2$ (or C_2H_4) or some intermediate fragment. The formation of the fluorocarbons indicates that C_2 and CN are reacting with fluorine atoms, but any detailed description of the process would be speculative. Likewise, it is impossible to determine whether HF is formed as an elimination product (of a species like $F_2N-CH_2-CH_2-NF_2$) or as a result of recombination of hydrogen and fluorine atoms produced from the multiphoton reaction of the starting materials. In actual fact, all of these processes may be occurring simultaneously, but information such as this can only be obtained from carefully executed temporal studies using detectors which can be specific for the individual components of interest. Since so many intermediate reactions are possible, a detailed mechanism can be devised only after such data are available.

Bimolecular reactions initiated by laser radiation are necessarily more complicated than unimolecular reactions. With the increased number of possible reactions, the thermodynamic stabilities of the potential products must be considered. Very few CH-containing molecules were identified in the reaction products. The majority of the hydrogen was involved with HF formation, and the carbon was found almost exclusively as fluorocarbons and cyanides. Thermodynamically both the H-F and C-F bonds are more stable than C-H bonds,

and all three are more stable than N-F bonds. The observed reactions are thermodynamically favorable, but without the laser excitation, they are kinetically unfavorable. The multiphoton absorption which produces radicals and other reactive species obviously alters the system enough to overcome the kinetic barrier.

The apparent absence of a multiphoton reaction in the NH_3 systems may be due to the increased stability of NH_3 or to major differences in the kinetics of NH_3 reactions. The formation of NH_4^+ salts is an indication that reactions are proceeding, and it will be important to study the mechanisms of the formation of solids in general from laser-induced reactions.

V. CONCLUSIONS AND RECOMMENDATIONS

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 system. 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.

In going to completion, the laser-induced reactions give off considerable amounts of energy. As such, the possibilities of making use of stored chemical energy through laser-induced reactions exist. The net output of these reactions could be quite large since a relatively small amount of laser radiation is required to initiate the reactions.

The types of intermediates which have been identified suggest that the production of refractory materials is feasible. Ethylenes serve as a source of C_2, and presumably refractory carbides could form under the proper conditions. Silicon carbide, for example, might be expected in a reaction of silane and an ethylene derivative. The production of silicon nitride from laser-induced reactions of silane has been demonstrated, and the process appears to be broadly applicable.

In studying laser-induced chemical reactions it is imperative that short-lived species be identified. Species which emit visible light have been studied using a monochromator and either photographic detection or an optical multichannel analyzer. Similar studies to investigate the infrared emission should be initiated as well. In addition to identifying the intermediates, temporal studies are needed if mechanistic data are to be derived. 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 programs in laser-induced chemistry deserve continued attention and support. Many fundamental experiments have not been 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.

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