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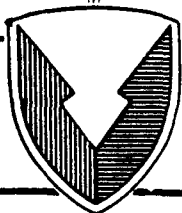


**SELECTIVE NITRATIONS: THE LASER-INDUCED NITRATION OF THREE CYCLOALKANES: I**

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The Army uses nitrated compounds as explosives and propellants. There is a special need for propellants with the chemical composition necessary to burn exactly with a minimum of side products which create smoke, but with high energy production. An important part of this process is the ability to selectively nitrate materials. Laser-induced chemistry possesses the potential to drive some reactions in an efficient and selective manner, and may be useful in driving nitration reactions toward specific products. Reported herein are the results of several successful attempts to laser-induce the reaction of nitrogen dioxide with three cycloalkanes. Specifically, the carbon dioxide infrared laser was used to drive the reaction between cyclopropane, cyclobutane, and cyclopentane under a variety of reaction conditions. The major products resulted from either ring cleavage or product dissociation, nitration or oxidation. Presented here is the qualitative spectrochemical analysis of the product mixtures. Optimal conditions were found for producing products. The array of products was found to be highly sensitive to the specific reaction conditions.

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## I. INTRODUCTION

Nitro compounds are important components of many high energy fuels, propellants, and explosives. Their reactions produce large volumes of hot gases upon proper initiation, and because the nitro compounds generally have low activation energies and high exothermicities, once initiated their reactions become self-sustaining. Characteristics of suitability are that the nitro compounds resist premature detonation upon handling, that they meet cost and production-scale standards and requirements for safety in transportation, and that they have storage stability. The ability to design, selectively, the molecular structures of these nitro compounds is critical for meeting more subtle performance requirements such as smokeless combustion. Current nitration procedures involving reactions with nitrogen dioxide or mixed acids result in low yields of complex mixtures of nitrated products. The commercial techniques are inconvenient and require high-temperature, high-pressure reactors that hold the reaction mixture at 200 - 400 °C and 8 - 12 atmospheres of pressure for hours.

Laser-induced nitration shows the promise of being an efficient and selective alternative to traditional synthetic methods. Lasers have been used recently in the nitration of several hydrocarbons. Umstead and co-workers [1] reported the nitration of isobutane using an argon-ion laser to excite nitrogen dioxide (NO<sub>2</sub>) molecules which then reacted with the isobutane by abstracting hydrogen atoms. In this reaction system both low yields of nitration production (2.5 percent 2-methyl-2-nitropropane) and significant product fragmentation resulted. Recently, Stanley and Godbey [2] reported the successful nitration of several alkanes by NO<sub>2</sub> using a tunable, continuous wave (CW), carbon dioxide (CO<sub>2</sub>) infrared laser to excite the hydrocarbon molecules. With propane, *n*-butane, isobutane or *n*-pentane, the major products of the reactions were secondary (tertiary for isobutane) nitroalkanes of the same chain length as the parent hydrocarbons. Nitration occurred to a lesser extent at the primary carbon atom. Some short chain nitrated compounds also resulted. Yields of nitroalkanes were based on the depletion of the limiting reagent NO<sub>2</sub>. The yield of 2-nitrobutane from butane was about 20 percent, 2-nitropropane from propane was 9 percent, 2-methyl-2-nitropropane from isobutane was 10 percent, and 2-nitropentane from pentane was about 9 percent. These yields are significantly higher than those reported using the argon-ion laser [1], and may be competitive with yields from thermal nitration.

In this work we have extended the use of the tunable, CW, CO<sub>2</sub> infrared laser to the successful nitration of the series of cyclic hydrocarbons: cyclopropane, cyclobutane, and cyclopentane. Cyclic alkanes have equivalent carbons. Nitration at any position on the rings should yield identical nitrocycloalkanes, unlike straight chain alkanes in which both primary and secondary carbon atoms are nitrated. Our objectives in this study were to optimize the experimental conditions for selective nitration yielding the nitrocycloalkanes and to identify the interesting array of products resulting from oxidation and fragmentation pathways that compete with nitration under certain irradiation conditions. We report these results here in a qualitative fashion.

## II. EXPERIMENTAL

Samples of cyclopropane, cyclopentane, 2,2-dimethylbutane, nitromethane, nitroethane, 1-nitropropane, 2-nitropropane, 2-methyl-2-nitropropane, 1-nitrobutane, 1-nitropentane, nitrocyclopentane, and nitrogen dioxide were obtained from Aldrich Chemical Company, Milwaukee, WI. The samples were of 98 percent or greater stated purity, except for 2-nitropropane, which was 94 percent stated purity, and cyclopentane which was 95 percent stated purity. The cyclobutane sample was provided by Dr. S. P. McManus, Department of Chemistry, University of Alabama in Huntsville, AL. The purity of the samples was monitored with gas chromatography-mass spectrometry (GC-MS), and the infrared spectra were compared with published spectra where literature spectra were available [3] - [8]. No further purification of the compounds was undertaken, with the exception of nitrogen dioxide and cyclobutane which were purified by trap-to-trap separation at  $-78.5\text{ }^{\circ}\text{C}$ . Nitrocyclopropane was prepared by the method of Gilkut and Borden [9]. After distillation, the sample was sent to the University of Alabama in Huntsville where its identity was verified by nuclear magnetic resonance (NMR) analysis. All compounds were degassed at  $-196.8\text{ }^{\circ}\text{C}$ .

A stainless steel cell of exterior dimensions  $5 \times 5 \times 10\text{ cm}$  was used to hold reactants during irradiation. This cell was equipped with zinc selenide or potassium chloride windows on the long path through which the laser was directed, and AMTIR-1 windows on the short path for collecting the infrared spectra of reactants and products. The optical pathlengths were 10.5 cm for the long path and 5 cm for the short path.

The infrared spectra were recorded on a Bomem DA3.002 interferometer equipped with a vacuum bench, a deuterated TGS detector and a KBr beamsplitter. The effective resolution was  $1\text{ cm}^{-1}$ . Thirty two scans were taken for each sample and reference. A medium apodization function was used [10].

The initial sample pressures were measured with a MKS Baratron electronic manometer, consisting of a Type 222B transducer and a Type PDR-5B power supply/digital readout.

A Coherent Radiation Model 41 CW,  $\text{CO}_2$  tunable laser provided the energy to drive the reactions, and it was operated in a single mode at various selected wavelengths and powers. The wavelength was verified with an Optical Engineering  $\text{CO}_2$  spectrum analyzer. The powers were measured by a Coherent Radiation Model 213 water-cooled power meter.

The reaction cell was positioned on a movable stage which could be translated along the laser path. All samples were irradiated with the cell positioned behind the focal point where the beam was slightly diverging. The zinc selenide window allowed a beam transmittance of about 70 percent through to the sample. The reported laser powers do not correct for this window absorption, nor for the difference in beam diameter at the sample, as opposed to the diameter at the power meter, where the beam is larger. The beam diameter was approximately 2 mm at the point of entry to the reaction cell.

The separation and analysis of the reaction products were accomplished using a Hewlett-Packard (HP) 5890 gas chromatograph equipped with a gas sampling loop and interfaced to an HP 5970 series mass selective detector. The chromatographic column was an HP Ultra 2 (crosslinked 5 percent phenyl methyl silicone) of about 40 m length, having a 0.2-mm interior diameter and 0.22- $\mu\text{m}$  film thickness. The volumetric flow rate was 1.6  $\text{cm}^3/\text{min}$  (linear flow rate 10  $\text{m}/\text{min}$ ); the split ratio was 47:1; and the column head pressure was 10 psi. For chromatographic analysis, two different temperature programs were used. With cyclopropane and cyclobutane mixtures, the oven temperature was programmed to 140  $^\circ\text{C}$  (10  $^\circ\text{C}/\text{min}$ ) following 5 minutes at the initial temperature of 40  $^\circ\text{C}$ . For the cyclopentane reaction mixture, the initial oven temperature was 60  $^\circ\text{C}$  and programming to 160  $^\circ\text{C}$  (10  $^\circ\text{C}/\text{min}$ ) began immediately. Identification of the components of the chromatographic peaks was attempted using the computer search routine and the NBS43k Mass Spectra Library. Whenever possible, component identities were verified by comparing the gas chromatographic retention times and the mass spectra to those of known samples. The separation of some highly volatile components was not possible with the chromatographic conditions used.

### III. RESULTS AND DISCUSSION

The CW,  $\text{CO}_2$  infrared laser emits several intense bands of radiation in the region between 900 and 1100  $\text{cm}^{-1}$ . Table 1 shows selected infrared laser transitions, their frequencies, and the relative powers available from each. Absorbance spectra for the three cycloalkanes recorded at approximately the same pressures are collected in Figure 1. The figure shows the differences in the absorptivity of the hydrocarbons in this region, and reveals vibrational bands for each compound accessible by the output of the  $\text{CO}_2$  laser. These bands, in common, indicate why we believed it would be possible to propel, by laser excitation, the reaction of the hydrocarbons with nitrogen dioxide. In instances where the power output of the laser transition is low or the hydrocarbon absorbs only weakly at that frequency, we used an infrared sensitizer, sulfur hexafluoride, to initiate the reaction indirectly.

We have irradiated about 60 mixtures of each cyclic hydrocarbon with nitrogen dioxide under conditions of varying laser powers, irradiation frequencies and times, and pressures of reactants and sensitizer. For each hydrocarbon, we will present results which illustrate the array of products forming under some of the different irradiation conditions.

#### A. Cyclopropane

Cyclopropane has two infrared absorption bands that are accessible to the laser, one at 866  $\text{cm}^{-1}$ , the other at 1027  $\text{cm}^{-1}$ . The band centered at 866  $\text{cm}^{-1}$  is nearly outside the laser range but irradiation on the shoulder of the R branch is possible using either the P(48) or the P(46) line of the  $(00^0 1) - (10^0 0)$  transition at 918.6  $\text{cm}^{-1}$  and 918.7  $\text{cm}^{-1}$ , respectively. These lines, in addition to being on the periphery of cyclopropane's absorbance, also afford limited laser power. The

power output from the P(18) line of the  $(00^{\circ}1) - (02^{\circ}0)$  transition at  $1048.7 \text{ cm}^{-1}$  could be varied easily from 20 – 50  $\text{W/cm}^2$ . Although the frequency is not at the absorption maximum of cyclopropane, it is located on a somewhat broad portion of the R branch of the band at  $1027 \text{ cm}^{-1}$  which may make its successful use less dependent on variations in the frequency settings. Overall, therefore, using this irradiation band was more desirable. A set of typical infrared spectra for reaction mixtures before and after irradiation using the P(18) laser line is shown in Figure 2 and the assignment of frequencies is summarized in Table 2. The laser excitation was for 60 s at  $30 \text{ W/cm}^2$ . The products identified from the infrared spectrum include  $\text{H}_2\text{O}$ , HCN,  $\text{CO}_2$ , NNO, CO, NO, formic acid, nitrocyclopropane, and ethene. The GC-MS analysis of this product mixture, summarized in Table 3, reveals the presence of a number of other components. No nitroalkanes except nitrocyclopropane were detected under these conditions. However, in other experiments, nitromethane was produced. For example, when cyclopropane (2.0 Torr) and  $\text{NO}_2$  (50 Torr) were irradiated at  $30 \text{ W/cm}^2$  for 30 s, nitromethane was observed at a retention time of 5.3 min by GC-MS analysis of the product mixture.

Conditions of higher laser power ( $50 \text{ W/cm}^2$ ) promote the fragmentation of reactants and products. The infrared spectrum in Figure 3B shows additional products, including methane, acetylene, and perhaps formaldehyde. The assignment of frequencies is presented in Table 4. Propene and 2-propanol can now be identified in the infrared spectrum of the product mixture, whereas in the preceding experiment, these products could not be detected in the infrared spectrum, though they were present in the GC trace. In the  $50 \text{ W/cm}^2$ -mixture, no nitrocyclopropane nor any other nitroalkane could be detected in the infrared or in the GC-MS analysis.

By careful selection of conditions we found it possible to produce nitrocyclopropane without making detectable amounts of any other nitrated products. Figure 4 shows the gas chromatogram from the analysis of a mixture of cyclopropane (191.1 Torr) and  $\text{NO}_2$  (40.0 Torr) which had been irradiated at  $30 \text{ W/cm}^2$  for 60 s. Nitrocyclopropane, at a retention time of 10.8 min, is the only nitroalkane present; any nitroalkane should appear in the GC trace at a retention time of greater than 5 min under these GC conditions.

## B. Cyclobutane

The infrared spectrum of cyclobutane shows a single, weak absorption centered at  $900 \text{ cm}^{-1}$  accessible to the CW,  $\text{CO}_2$  laser. Irradiation using the P(42) laser line of the  $(00^{\circ}1) - (10^{\circ}0)$  transition at  $922.9 \text{ cm}^{-1}$  was on the R branch near the maximum at  $922 \text{ cm}^{-1}$ . Because of the weak absorption and the limited laser power available, longer irradiation times were necessary to induce the nitration reaction. Figure 5 shows typical infrared spectra for reaction mixtures before and after irradiation of 199.9 Torr of cyclobutane and 40.0 Torr of  $\text{NO}_2$  on the P(42) line at  $60 \text{ W/cm}^2$  for 60 s. A number of products have been identified by infrared analysis, as shown by the frequency assignments in Table 5. The products were  $\text{H}_2\text{O}$ ,  $\text{CO}_2$ , CO, NO, formic acid, and ethene. We have tentatively attributed other absorbances at  $1560$  and  $1376 \text{ cm}^{-1}$  to nitrocyclobutane.

A sharp Q branch at  $1745\text{ cm}^{-1}$  may be due to formaldehyde. Table 2 shows a summary of the GC-MS analysis with the nitrated products, nitrocyclobutane at 13.6 min, and 1-nitropropane at 9.4 min. We did not identify conditions in which nitrocyclobutane could be produced without also making detectable amounts of 1-nitropropane, but under favorable conditions the 1-nitropropane could be minimized. Figure 6 shows the GC trace from the product mixture when 179.3 Torr of cyclobutane and 40.0 Torr of  $\text{NO}_2$  were irradiated at  $50\text{ W/cm}^2$  for 60 s.

### C. Cyclopentane

The commercial cyclopentane we used contained the impurity 2,2-dimethylbutane. The ratio of total ion areas in the GC-MS analyses indicated approximately 10 percent of the impurity, though this may be in error due to differing response factors for these two compounds. The supplier claimed 95 percent purity for the cyclopentane. Irradiation of 2,2-dimethylbutane,  $\text{NO}_2$ , and  $\text{SF}_6$  mixtures at the infrared frequencies we used for the cyclopentane studies described below, resulted in no nitration reactions for 2,2-dimethylbutane. However, a more extensive investigation is needed to rule out 2,2-dimethylbutane's participation in the nitration of cyclopentane.

Cyclopentane has a single, weak infrared absorption centered at  $897\text{ cm}^{-1}$ , which lies on the edge of the usable range of the  $\text{CO}_2$  laser. Thus, irradiation was possible only on the R-branch shoulder of the absorption band. Irradiation of a mixture of cyclopentane and nitrogen dioxide using the P(46) line of the  $(00^11) - (10^00)$  band ( $918.7\text{ cm}^{-1}$ ) with high laser power ( $50\text{--}70\text{ W/cm}^2$ ) produced small amounts of nitrocyclopentane and 1-nitrobutane.

Because of the inefficiency of the direct irradiation of the cyclopentane, an infrared sensitizer, sulfur hexafluoride, was introduced into the system. Figure 7 shows the strong infrared absorption of  $\text{SF}_6$  (maximum at  $945\text{ cm}^{-1}$ ) which permits irradiation at  $946.0\text{ cm}^{-1}$ , corresponding to the frequency of the P(18) line of the  $(00^11) - (10^00)$  band, an intense output line of the  $\text{CO}_2$  laser. With  $\text{SF}_6$  present in small amounts ( $0.2 - 0.5$  Torr), irradiation at this frequency produced significant quantities of the product nitrocyclopropane, as well as 1-nitropropane and 1-nitrobutane. Pressures of  $\text{SF}_6$  greater than about 1 Torr resulted in extensive fragmentation of cyclopentane and little nitrocyclopentane, making irradiation via the  $946.0\text{ cm}^{-1}$  line less useful than we had hoped. The high absorptivity of the  $\text{SF}_6$  band near the  $946.0\text{ cm}^{-1}$  laser line coupled with the difficulty in controlling the laser power below about  $25\text{ W/cm}^2$ , causes the reaction system to be too sensitive to small changes in the  $\text{SF}_6$  pressures. We, therefore, sought conditions which would allow the use of higher  $\text{SF}_6$  pressures.

The  $\text{SF}_6$  absorption is narrow (Fig. 7) but extremely intense, so that significant laser power is absorbed by  $\text{SF}_6$  even at frequencies offset from its maximum absorbance by more than  $25\text{ cm}^{-1}$ . The P(46) line of the  $(00^11) - (10^00)$  transition at  $918.7\text{ cm}^{-1}$  provides access to the overlapping absorptions of  $\text{SF}_6$  and cyclopentane, both of which absorb weakly at  $918.7\text{ cm}^{-1}$ . Using the P(46) laser line with sulfur hexafluoride at  $1.0 - 2.0$  Torr facilitated the production of nitrocyclopentane. The infrared spectra shown in Figure 8 are typical spectra

taken before and after irradiation. The irradiation conditions were 176 Torr of cyclopentane, 32 Torr of  $\text{NO}_2$ , and 1.5 Torr of  $\text{SF}_6$  at  $46 \text{ W/cm}^2$  for 60 s. As shown by the frequency assignments in Table 7, the products identified from the infrared spectrum were  $\text{H}_2\text{O}$ ,  $\text{CO}_2$ ,  $\text{CO}$ ,  $\text{NO}$ , formic acid, and a small amount of  $\text{C}\delta\text{NO}$  that arose from reaction of  $\text{NO}_2$  with the  $\text{KCl}$  windows. The formation of the  $\text{C}\delta\text{NO}$  seems to depend on the condition of the  $\text{KCl}$  window surface; we did not observe it in cases in which the windows had been "conditioned" by several nitration reactions. Other products, from GC-MS analysis, Table 8, included nitrocyclopentane, 1-nitropropane, and 1-nitrobutane, and small amounts of several unidentified products as well. For comparison, Figure 9 and Table 9 feature the infrared spectra from an irradiation using a larger amount of  $\text{SF}_6$  (2.0 Torr) with 168 Torr of cyclopentane and 32 Torr of  $\text{NO}_2$  at  $45 \text{ W/cm}^2$  for 60 s. Additional products resulting from the higher energy absorbed in this experiment and identified in the infrared were  $\text{HCN}$ , ethene, methane, and, tentatively, formaldehyde and  $\text{NNO}$ . Table 10 summarizes the GC-MS analysis of the 2.0 Torr,  $\text{SF}_6$  experiment: a larger proportion of mixed gases and relatively less nitrocyclopentane formed than in the 1.5 Torr,  $\text{SF}_6$  experiment summarized in Table 9.

We managed to find conditions under which nitrocyclopentane could be produced without making detectable amounts of other nitrated products. For example, Figure 10 shows the gas chromatogram of the product mixture resulting when 168.9 Torr of cyclopentane, 30.9 Torr of  $\text{NO}_2$ , and 0.4 Torr of  $\text{SF}_6$  were irradiated at  $45 \text{ W/cm}^2$  laser power for 60 s. Nitrocyclopentane, at a retention time of 9.6 min, was the only nitroalkane detected.

#### IV. CONCLUSIONS

We have successfully carried out the nitration reactions between nitrogen dioxide and cyclopropane, cyclobutane, and cyclopentane, using the CW,  $\text{CO}_2$  infrared laser to drive the reactions. By careful selection of irradiation conditions and reactant pressures, we were able to make nitrocycloalkanes as the major nitrated products from the cycloalkanes. For cyclopropane and cyclopentane we found conditions for producing nitrocyclopropane and nitrocyclopentane without forming detectable amounts of other nitroalkanes. We were unable to identify conditions for producing only nitrocyclobutane from cyclobutane without also forming other nitration products. It is uncertain whether this was due to a fundamental difference in the reactions that can occur in the butane nitration, or if further variations would have established the favorable conditions for producing solely this nitrocycloalkane. We were able to minimize the amounts of other nitration products in the cyclobutane system.

The fact that conditions were identified for producing nitrocyclopropane and nitrocyclopentane without also forming detectable amounts of nitrated fragments is in contrast to results from studies of straight chain homologues [2]. For the straight chain alkanes, the laser-induced nitration products include both primary and secondary nitroalkanes having the same chain length as the parent hydrocarbon, and, invariably, nitroalkanes of shorter chain length. Due to the equivalence of the carbon atoms in the cycloalkanes, one expects a single

nitrocycloalkane from each hydrocarbon; however, the absence, under some conditions, of an array of isomeric, ring-opened nitroalkanes and small chain nitrohydrocarbons, gives evidence that laser-induced nitration can be a highly selective process.

We have identified a variety of products from each cycloalkane mixture. As Table 11 shows, most of the products can be grouped into one of three categories: nitration, fragmentation/ring-opening, and oxidation. The diversity of products forming depends on the reaction conditions. Irradiation conditions can be selected to optimize the yields of desired nitroalkanes while minimizing the amounts of unwanted nitroalkanes, or in some cases, eliminating them entirely. The product mixtures consist of the reasonably nonvolatile nitroalkanes, along with a number of highly volatile components that could be easily separated from the less volatile nitroalkanes. The reactions are fast, can be conducted without high temperature reactors, and are probably adaptable to continuous processing near atmospheric pressures. These features make laser-induced nitration attractive as an alternative to current nitration methods.

In this report we have discussed, in a qualitative way, how the reaction systems respond to changing irradiation conditions. The topic of a future communication will be the quantitative dependence of the product mixtures on variations in the energy absorbed by the system and changes in the pressures of cyclic hydrocarbon and  $\text{NO}_2$ .

TABLE 1. Laser Transitions, Frequencies, and Relative Powers

Transition - Band	Frequency ( $\text{cm}^{-1}$ )	Relative Power
P(18) (00 <sup>1</sup> ) - (02 <sup>0</sup> )	1048.7	0.75
P(40) (00 <sup>1</sup> ) - (02 <sup>0</sup> )	1027.4	0.65
P(6) (00 <sup>1</sup> ) - (10 <sup>0</sup> )	956.2	0.75
P(18) (00 <sup>1</sup> ) - (10 <sup>0</sup> )	946.0	1.0
P(42) (00 <sup>1</sup> ) - (10 <sup>0</sup> )	922.9	0.7
P(46) (00 <sup>1</sup> ) - (10 <sup>0</sup> )	918.7	0.55
P(48) (00 <sup>1</sup> ) - (10 <sup>0</sup> )	916.6	0.55

TABLE 2. Infrared Frequencies ( $\text{cm}^{-1}$ ) of Cyclopropane (247.7 Torr) and  $\text{NO}_2$  (40.0 Torr) Before Irradiation and After Irradiation for 60 s at  $30 \text{ W/cm}^2$  Laser Power on Laser Line P(18) of the  $(00^1) - (02^0)$  Transition.

<u>BEFORE</u>	<u>AFTER*</u>	<u>IDENTITY</u>	<u>REF</u>
4600	4599	Cyclopropane <sup>†</sup>	
4550	4550		
4530R	4528R		
4506Q	4505Q		
4478P	4479P		
4299R	4299R		
4288Q	4289Q		
4277P	4278P		
4223	4223		
4217	4217		
4195	4197		
4110	4110		
3889			
	3335R	HCN	3
	3309Ctr		
	3281P		
3129R	3127R	Cyclopropane	
3117	3117		
3109	3110		
3100Q	3100Q		
3047	3045		
3021	3022		
3004	3002		
2955	2953		
2946	2946		
2934	2934		
2930	2930		
2925	2926		
2918	2921		
2892			
2892	2892	$\text{NO}_2$	6
2870	2870	Cyclopropane	
2636R	2635R		
2625Ctr	2625Ctr		
2617P	2618P		
2479	2480		
2464	2467		
2360Q			

TABLE 2. Infrared Frequencies (cm<sup>-1</sup>) of Cyclopropane (247.7 Torr) and NO<sub>2</sub> (40.0 Torr) Before Irradiation and After Irradiation for 60 s at 30 W/cm<sup>2</sup> Laser Power on Laser Line P(18) of the (00<sup>1</sup>) - (02<sup>0</sup>) Transition. (cont'd)

<u>BEFORE</u>	<u>AFTER*</u>	<u>IDENTITY</u>	<u>REF</u>
	2360R 2348Ctr 2335P	CO <sub>2</sub>	3
2310Q	2310	Cyclopropane	
	2234	NNO ?	11
2223? 2200R? 2186Q 2160P	2186Q	Cyclopropane	
	2171R 2142Ctr 2110P	CO	12
2109R 2090Q 2086 2069P 2054Q 2040Q 1931Q 1891 1862Q	2090Q  2069P  2041Q 1931Q	Cyclopropane	
	1893R 1876Q 1857P	NO	13
	1786R 1776Q	Formic Acid	3
~ 1749 offscale	~ 1745 bd	N <sub>2</sub> O <sub>4</sub>	7
1629 1611? 1594	1628  1595	NO <sub>2</sub>	6
1450R 1438Q 1419P	1438Q 1419P	Cyclopropane	
	1381R 1374Q 1368P	Nitrocyclopropane	8
	1323 ? 1311 ?	?	

TABLE 2. Infrared Frequencies ( $\text{cm}^{-1}$ ) of Cyclopropane (247.7 Torr) and  $\text{NO}_2$  (40.0 Torr) Before Irradiation and After Irradiation for 60 s at  $30 \text{ W/cm}^2$  Laser Power on Laser Line P(18) of the  $(00^{\circ}1) - (02^{\circ}0)$  Transition. (cont'd)

<u>BEFORE</u>	<u>AFTER*</u>	<u>IDENTITY</u>	<u>REF</u>
1269R 1260Q 1253P	1272R 1263Q 1250P	$\text{N}_2\text{O}_4$	7
	1119R 1105Q	Formic Acid	3
1048R 1029 1027Q 1018 1008P	1049R 1029 1027Q 1020 1006P	Cyclopropane	
	987 978 970 949	Ethene†	
896R 870 865Q 852 839P	897R 870 865Q 853 839P	Cyclopropane	
755 748		$\text{NO}_2 + \text{N}_2\text{O}_4$	6,7
	712	HCN	3
	667	$\text{CO}_2$	3

\* Individual water lines are not listed but were observed in the  $3500 - 400 \text{ cm}^{-1}$  region and in the  $1350 - 1810 \text{ cm}^{-1}$  region.

† The spectral assignments for cyclopropane and ethene were made by comparison to the spectra of known samples of these compounds.

TABLE 3. Summary of GC-MS Data from the Analysis of the Products of the CO<sub>2</sub> Laser Irradiation of Cyclopropane (247.7 Torr) and NO<sub>2</sub> (40.0 Torr) for 60 s at 30 W/cm<sup>2</sup> Laser Power on Laser Line P(18) of the (00<sup>1</sup>) - (02<sup>0</sup>) Transition.

Retention Time	Area	Area %	Ratio %	Probable Identification
3.584	44152257	14.49	17.95	Mixed gases
3.651	2297870	0.75	0.93	Propene
3.729	2.5E8	80.76	100	Cyclopropane
3.884	7463196	2.45	3.03	??
4.300	475158	0.16	0.19	2-propenal
4.371	141370	0.05	0.06	Acetonitrile (?)
10.787	3410593	1.12	1.39	Nitrocyclopropane

TABLE 4. Infrared Frequencies ( $\text{cm}^{-1}$ ) of Cyclopropane (170.4 Torr) and  $\text{NO}_2$  (30.0 Torr) Before Irradiation and After Irradiation for 20 s at  $50 \text{ W/cm}^2$  Laser Power on Laser Line P(18) of the  $(00^1) - (02^0)$  Transition.

<u>BEFORE</u>	<u>AFTER*</u>	<u>IDENTITY</u>	<u>REF</u>
4601	4599		
4551	4550		
4530R	4525R		
4505Q	4504Q		
4480P	4477P		
4298R	4297R		
4289Q	4287Q	Cyclopropane <sup>†</sup>	
4277P	4276P		
4223	4222		
4217	4217		
4199	4296		
4110	4110		
3890			
	3335R		
	3321 Ctr	HCN	3
	3280P		
3127R	~ 3124		
3117			
3109	3109	Cyclopropane	
3101Q	3101Q		
- 3071R?			
	3091?	Propene ? <sup>†</sup>	
	3086?		
	3076	Methane <sup>†</sup>	
	3067		
	3058		
3047	3047		
3023	3023	Cyclopropane	
	3017	Methane	
3005	3003	Cyclopropane	
	2988	Methane	
2953		Cyclopropane	
	2954		
	2951	Propene	
	2938	Methane	
2934			
2930		Cyclopropane	
2926			

TABLE 4. Infrared Frequencies ( $\text{cm}^{-1}$ ) of Cyclopropane (170.4 Torr) and  $\text{NO}_2$  (30.0 Torr) Before Irradiation and After Irradiation for 20 s at  $50 \text{ W/cm}^2$  Laser Power on Laser Line P(18) of the  $(00^1_1) - (02^0_0)$  Transition. (cont'd)

<u>BEFORE</u>	<u>AFTER*</u>	<u>IDENTITY</u>	<u>REF</u>
	2931		
	2918	Propene	
2918			
2900		$\text{NO}_2$	
2894			
	2890	Propene	
2870		Cyclopropane	
	2868		
	2855	Propene	
	2801		
	2780	Formaldehyde ?	3
	2778		
	2766		
2636			
2617	2618		
2483		Cyclopropane	
2464			
2359			
	2362		
	2349 Ctr	$\text{CO}_2$	3
	2335P		
2310		Cyclopropane	
	2278 ? vvw		
	2235 bd,w	$\text{NNO ?}$	11
2186		Cyclopropane	
	2175R		
	2143 Ctr	$\text{CO}$	12
	2102P		
2108R			
2090Q			
2086			
2067P			
2054		Cyclopropane	
2040			
1931			
1891			
1862			

TABLE 4. Infrared Frequencies ( $\text{cm}^{-1}$ ) of Cyclopropane (170.4 Torr) and  $\text{NO}_2$  (30.0 Torr) Before Irradiation and After Irradiation for 20 s at  $50 \text{ W/cm}^2$  Laser Power on Laser Line P(18) of the  $(00^0 1) - (02^0 0)$  Transition. (cont'd)

<u>BEFORE</u>	<u>AFTER*</u>	<u>IDENTITY</u>	<u>REF</u>
	1899R 1876Q 1849P	NO	13
	1776	Formic Acid	3
1755		$\text{N}_2\text{O}_4$	7
1744	1745	Formaldehyde ?	3
	1729 bd 1714 bd	2-propenal ?	3
	1664R 1652Q 1635P	Propene	
1630 1621 1611 1595		$\text{NO}_2$	6
1472 vw 1457 1401R 1439Q 1419P		Cyclopropane	
	1470 bd 1446 bd 1442	Propene	
	1347 1342 1337 1332 1327 1322 1305	Methane	
1270R 1261Q 1255P		$\text{N}_2\text{O}_4$	7
	1158	?	
	1119R 1105Q	Formic Acid	3

TABLE 4. Infrared Frequencies ( $\text{cm}^{-1}$ ) of Cyclopropane (170.4 Torr) and  $\text{NC}_2$  (30.0 Torr) Before Irradiation and After Irradiation for 20 s at  $50 \text{ W/cm}^2$  Laser Power on Laser Line P(18) of the  $(00^1_1) - (02^0_0)$  Transition. (cont'd)

<u>BEFORE</u>	<u>AFTER*</u>	<u>IDENTITY</u>	<u>REF</u>
1045			
1051R			
1030	1030		
1027Q	1027Q	Propene	
1019			
1008P	1006P		
	997	Ethene <sup>†</sup>	
	991	Propene	
	987		
	978		
	970	Ethene	
	949		
	922		
	912	Propene	
899R			
871	870		
866Q	866Q	Cyclopropane	
853	853		
840P	840P		
755			
750			
748		$\text{N}_2\text{O}_4 + \text{NO}_2$	6,7
742			
	730	Acetylene	3
	712	HCN	3
	667	$\text{CO}_2$	3

\* Individual water lines are not listed but were observed in the  $3550 - 4000 \text{ cm}^{-1}$  region and in the  $1350 - 1810 \text{ cm}^{-1}$  region.

† The spectral assignments for cyclopropane, propene, methane, and ethene were made by comparison to the spectra of known samples of these compounds.

TABLE 5. Infrared Frequencies ( $\text{cm}^{-1}$ ) of Cyclobutane (199.9 Torr) and  $\text{NO}_2$  (40.0 Torr) Before Irradiation and After Irradiation for 60 s at  $60 \text{ W/cm}^2$  Laser Power on Laser Line P(42) of  $(00^1_1) - (10^0_0)$  Transition

<u>BEFORE</u>	<u>AFTER*</u>	<u>IDENTITY</u>	<u>REF</u>
4455	4455		
4410	4410		
4404	4404		
4392	4392		
4385	4386		
4295	4295		
4228	4229		
4203	4203		
4168	4168		
4140	4140		
4126	4122		
4117	4117	Cyclobutane <sup>†</sup>	
4102	4102		
4088	4088		
4063	4063		
4026	4026		
3992	3992		
3840 bd			
3698 bd			
3606 bd	3184		
3184			
3169	3969		
3147	3147		
3066	3068		
OFFSCALE		Cyclobutane + $\text{NO}_2$	6
2782	2781		
2755			
2741	2742		
2730	2730		
2709	2710	Cyclobutane	
2693	2694		
2457	2457		
2453	2454		
2358			
	2360R		
	2348Ctr	$\text{CO}_2$	3
	2335P		
2280R?	2277R?		
2260Q?	2262Q?	Cyclobutane	

TABLE 5. Infrared Frequencies ( $\text{cm}^{-1}$ ) of Cyclobutane (199.9 Torr) and  $\text{NO}_2$  (40.0 Torr) Before Irradiation and After Irradiation for 60 s at  $60 \text{ W/cm}^2$  Laser Power on Laser Line P(42) of (00<sup>1</sup>) - (10<sup>0</sup>) Transition (cont'd)

<u>BEFORE</u>	<u>AFTER*</u>	<u>IDENTITY</u>	<u>REF</u>
2201 2198 2189 2177 2173 2151		Cyclobutane	
	2171P 2143Ctr 2112R	CO	12
2134 2107 2096 2046 2034 1890 1875	2134 2107  2045 2035	Cyclobutane	
	1897R 1875Q 1845P	NO	13
1850		Cyclobutane	
	~ 1789R 1776Q	Formic Acid	3
1749	1749	$\text{N}_2\text{O}_4$	7
	1745	Formaldehyde ?	3
1674		Cyclobutane	
1629 1621 1609 1593	1627 1620 1610 1595	$\text{NO}_2$	6
	1560 sh	Possibly Nitrocyclobutane	
1550 1548 1528 1470 1465R 1453Q 1434P 1430	1528 1470 1466R 1453Q 1434P 1430	Cyclobutane	
	1376 broad	Possibly Nitrocyclobutane	

TABLE 5. Infrared Frequencies ( $\text{cm}^{-1}$ ) of Cyclobutane (199.9 Torr) and  $\text{NO}_2$  (40.0 Torr) Before Irradiation and After Irradiation for 60 s at  $60 \text{ W/cm}^2$  Laser Power on Laser Line P(42) of  $(00^1) - (10^0)$  Transition (cont'd)

<u>BEFORE</u>	<u>AFTER*</u>	<u>IDENTITY</u>	<u>REF</u>
1373	1373	Cyclobutane	
1353	1353		
1325	1325 1310R 1302Q	?	
1270	1270	Cyclobutane + $\text{NO}_2$	6
1261Q	1260		
1255			
1223	1223		
	1119R 1105Q 1090P	Formic Acid	3
1074		Cyclobutane	
	1006 997 987 978 949 922 915 908	Ethene <sup>†</sup>	
951		Cyclobutane	
922R	~ 920R		
904	904		
901Q	901Q		
880P	878P		
755	755	$\text{NO}_2 + \text{N}_2\text{O}_4$	6,7
750	750		
747	748		
743			
741	741		
	667	$\text{CO}_2$	3
638	638	Cyclobutane	
625	625		

\* Individual water lines are not listed but were observed in the  $3550 - 4000 \text{ cm}^{-1}$  region and in the  $1810 - 1350 \text{ cm}^{-1}$  region.

† The spectral assignments for cyclobutane and ethene were made by comparison to the spectra of known samples of these compounds.

TABLE 6. Summary of GC-MS Data from the Analysis of the Products of the CO<sub>2</sub> Laser Irradiation of Cyclobutane (199.9 Torr) and NO<sub>2</sub> (40.0 Torr) for 60 s at 60 W/cm<sup>2</sup> Laser Power on Laser Line P(42) of the (00<sup>1</sup>) - (10<sup>0</sup>) Transition

Retention Time	Area	Area Percent	Ratio Percent	Probable Identification
3.559	77403802	9.39	9.99	Mixed Gases
3.736	2698312	0.29	0.35	??
3.831	5914799	0.64	0.75	2-butene (?)
3.938	1261231	.14	0.16	??
4.109	7.7E8	84.04	100	Cyclobutane
4.195	43934866	4.75	5.57	Butene (?)
6.841	3238722	0.35	0.42	??
7.019	585503	0.06	0.08	??
9.358	1144587	0.12	0.15	1-nitropropane
13.596	5404590	0.59	0.70	Nitrocyclobutane

TABLE 7. Infrared Frequencies ( $\text{cm}^{-1}$ ) of Cyclopentane (176 Torr),  $\text{NO}_2$  (32 Torr), and  $\text{SF}_6$  (1.5 Torr) Before Irradiation and After Irradiation for 60 s at  $46 \text{ W/cm}^2$  Laser Power on Laser Line P(46) of the  $(00^01) - (10^00)$  Transition

<u>BEFORE</u>	<u>AFTER*</u>	<u>IDENTITY</u>	<u>REF</u>
4369	4367	Cyclopentane <sup>†</sup>	
4296	4294		
4147	4135		
4070	4069		
3805	3805 under water bands		
3559	3553		
3493	3493		
3197	3199		
3107		??	
Offscale	Offscale	Cyclopentane + $\text{NO}_2$	6
2749	2754	Cyclopentane	
2629	2628		
2600	2599		
2480	2481		
2405	2406		
	2360R 2348 Ctr, B 2337P	$\text{CO}_2$	3
2350 2264 2189R 2178Q		Cyclopentane	
	2175R 2142 Ctr, B 2112P	$\text{CO}$	12
2103 2033 1892	2030	Cyclopentane	
	1896R 1875Q 1857P	$\text{NO}$	13
1797	1807R 1798Q 1790P	$\text{C}\&\text{NO}$	14
	1776Q	Formic Acid	3

TABLE 7. Infrared Frequencies ( $\text{cm}^{-1}$ ) of Cyclopentane (176 Torr),  $\text{NO}_2$  (32 Torr), and  $\text{SF}_6$  (1.5 Torr) Before Irradiation and After Irradiation for 60 s at  $46 \text{ W/cm}^2$  Laser Power on Laser Line P(46) of the  $(00^11) - (10^00)$  Transition (cont'd)

<u>BEFORE</u>	<u>AFTER*</u>	<u>IDENTITY</u>	<u>REF</u>
1754 1745	1744	$\text{N}_2\text{O}_4$	7
1628 1621 1611 1595	1628   1597	$\text{NO}_2$	6
1471 1460 1450 1369	1471 1460 1450 1369	Cyclopentane	
1270R 1261Q 1255P	1273R 1263Q 1252P	$\text{N}_2\text{O}_4$	7
1221	1223	Cyclopentane	
	1120R 1105Q 1091P	Formic Acid ??	3
985	983		
945	946	$\text{SF}_6$	
930	930		
909R 896Q 880P 826	908R 896Q 880P	Cyclopentane	
808		?	
758R 755Q 751Q 748Q 743P		$\text{NO}_2 + \text{N}_2\text{O}_4$	6,7
	667Q	$\text{CO}_2$	3

\* Individual water lines are not listed but were observed in the  $3550 - 4000 \text{ cm}^{-1}$  region and in the  $1810 - 1350 \text{ cm}^{-1}$  region.

† The spectral assignments for cyclopentane and  $\text{SF}_6$  were made by comparison to the spectra of known samples of these compounds.

TABLE 8. Summary of GC-MS Data from the Analysis of the Products of the CO<sub>2</sub> Laser Irradiation of Cyclopentane (176 Torr), NO<sub>2</sub> (32 Torr), and SF<sub>6</sub> (1.5 Torr) for 60 s at 46 W/cm<sup>2</sup> Laser Power on Laser Line P(46) of the (00<sup>1</sup>) - (10<sup>1</sup>) Transition

Retention Time	Area	Area Percent	Ratio Percent	Probable Identification
3.546	48423958	7.58	9.74	Mixed Gases
3.980	1085286	0.17	0.22	??
4.033	1906393	0.30	0.38	??
4.170	856603	0.13	0.17	??
4.280	73551452	11.51	14.80	2,2-dimethylbutane
4.424	5.0E8	77.77	100.	Cyclopentane
4.600	11220998	1.75	2.26	??
4.939	642796	0.10	0.18	??
5.388	281163	0.04	0.06	??
5.718	949553	0.15	0.19	1-nitropropane
6.970	1241373	0.19	0.25	1-nitrobutane
9.490	1873318	0.29	0.38	Nitrocyclopentane

TABLE 9. Infrared Frequencies ( $\text{cm}^{-1}$ ) of Cyclopentane (168 Torr),  $\text{NO}_2$  (32 Torr), and  $\text{SF}_6$  (2.0 Torr) Before Irradiation and After Irradiation for 60 s at  $45 \text{ W/cm}^2$  Laser Power on Laser Line P(46) of the  $(00^1) - (10^0)$  Transition

<u>BEFORE</u>	<u>AFTER*</u>	<u>IDENTITY</u>	<u>REF</u>
4383	4381	Cyclopentane <sup>†</sup>	
4368	4368		
4299	4299		
4143	4140		
4074	4075		
3849			
3492	3498		
	3335R	HCN	3
	3311 Ctr		
	3283P		
3195		Cyclopentane	
	3170	Ethene	
	3162		
	3154		
	3147		
	3139		
	3131		
	3124		
	3122		
3119	3119	Cyclopentane + Ethene	
	3115	Ethene	
	3104		
	3094		
	3085		
	3069		
	3067		
	3060		
Offscale		Cyclopentane + $\text{NO}_2$	6
	2781	Formaldehyde	3
	2778		
	2766		
	2747		
2638		Cyclopentane	
2597	2597		
2484	2484		
2350			
	2359R	$\text{CO}_2$	3
	2349 Ctr		
	2338P		

TABLE 9. Infrared Frequencies ( $\text{cm}^{-1}$ ) of Cyclopentane (168 Torr),  $\text{NO}_2$  (32 Torr), and  $\text{SF}_6$  (2.0 Torr) Before Irradiation and After Irradiation for 60 s at  $45 \text{ W/cm}^2$  Laser Power on Laser Line P(46) of the  $(00^1) - (10^0)$  Transition (cont'd)

<u>BEFORE</u>	<u>AFTER*</u>	<u>IDENTITY</u>	<u>REF</u>
2263	2263	Cyclopentane	
	~ 2237	NNO	11
2190R 2177Q 2163P		Cyclopentane	
	2170R 2143 Ctr 2110P	CO	12
2033	2033	Cyclopentane	
1876Q	1900R 1875Q 1853P	NO	13
1806R 1798Q 1790P		$\text{ClNO}$	14
	1790R 1776Q	Formic Acid	3
~ 1750		$\text{N}_2\text{O}_4$	7
	1745	Formaldehyde ??	3
1629 1621 1610 1595	1629 bd	$\text{NO}_2$	6
	1565 bd		
1463 1460 1369	1463 1460 1369	Cyclopentane	
1326		?	
	1306	Methane <sup>†</sup>	
1270R 1261Q 1254P	1264 ??	$\text{N}_2\text{O}_4$	7
1222	1218	Cyclopentane	
	1120R 1105Q 1092P	Formic Acid	3
984		?	

TABLE 9. Infrared Frequencies ( $\text{cm}^{-1}$ ) of Cyclopentane (168 Torr),  $\text{NO}_2$  (32 Torr), and  $\text{SF}_6$  (2.0 Torr) Before Irradiation and After Irradiation for 60 s at  $45 \text{ W/cm}^2$  Laser Power on Laser Line P(46) of the  $(00^0 1) - (10^0 0)$  Transition (cont'd)

<u>BEFORE</u>	<u>AFTER</u>	<u>IDENTITY*</u>	<u>REF</u>
	1048	?	
	1027		
	1019		
	1006		
	996	Ethene	
	987		
	978		
	970		
946	945	$\text{SF}_6^\dagger$	
930	938		
	922		
	915	Ethene	
	908		
	902		
911			
909?			
897Q	896	Cyclopentane	
882P	880		
755			
750			
748		$\text{NO}_2$	6
743			
	712	$\text{HCN}$	3
	697	?	
	667	$\text{CO}_2$	3
627R?	624R?	?	
615Q?	614Q?	?	

\* Individual water lines are not listed but were observed in the  $3550 - 4000 \text{ cm}^{-1}$  region and in the  $1810 - 1350 \text{ cm}^{-1}$  region.

† The spectral assignments for cyclopentane, ethene, methane, and  $\text{SF}_6$  were made by comparison to the spectra of known samples of these compounds.

TABLE 10. Summary of GC-MS Data from the Analysis of the Products of the CO<sub>2</sub> Laser Irradiation of Cyclopentane (168 Torr), NO<sub>2</sub> (32 Torr), and SF<sub>6</sub> (2.0 Torr) for 60 s at 45 W/cm<sup>2</sup> Laser Power on Laser Line P(46) of the (00<sup>0</sup>1) - (10<sup>0</sup>0) Transition

Retention Time	Area	Area Percent	Ratio Percent	Probable Identification
3.895	63899961	11.06	14.58	Mixed gases
4.026	3474227	0.60	0.79	??
4.079	1785007	0.31	0.41	??
4.209	3372496	0.58	0.77	??
4.334	62018559	10.73	14.15	2,2-dimethylbutane
4.476	4.4E8	75.84	100.	Cyclopentane
4.577	1860163	0.32	0.42	??
4.989	532777	0.09	0.12	??
5.831	746879	0.13	0.17	1-nitropropane
7.027	781958	0.14	0.18	1-nitrobutane
9.556	1131510	0.20	0.26	Nitrocyclopentane

TABLE 11. Summary of Products Formed in the CW CO<sub>2</sub> Laser-induced Nitration of Cyclic Alkanes Using NO<sub>2</sub>

	Cyclopropane	Cyclobutane	Cyclopentane
Nitration Products	Nitrocyclopropane Nitromethane	Nitrocyclobutane 1-nitropropane	Nitrocyclopentane 1-nitrobutane 1-nitropropane
Fragmentation/ Ring-Opening Products	Ethene Propene Acetylene Methane	Ethene 2-butene	Ethene Methane
Oxidation Products	H <sub>2</sub> O HCN CO <sub>2</sub> CO Formic Acid 2-propanol Acetonitrile? Formaldehyde?	H <sub>2</sub> O CO <sub>2</sub> CO Formic Acid Formaldehyde?	H <sub>2</sub> O CO <sub>2</sub> CO Formic Acid HCN Formaldehyde?
Other Products	NNO NO	NO	NNO NO

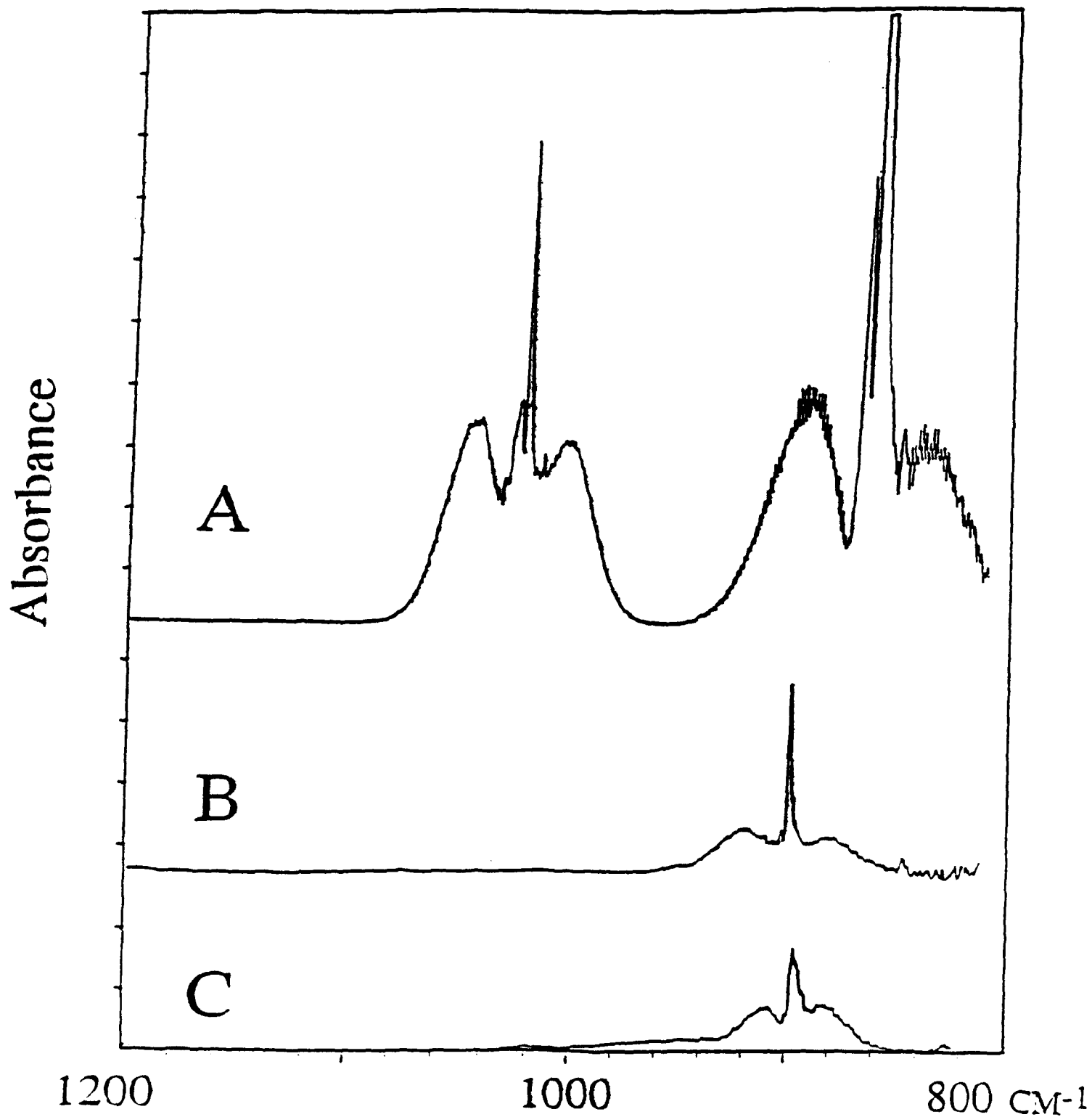


Figure 1. Gas-phase infrared spectra of cyclic hydrocarbons: (A) cyclopropane (110 Torr), (B) cyclobutane (100 Torr), and (C) cyclopentane (100 Torr).

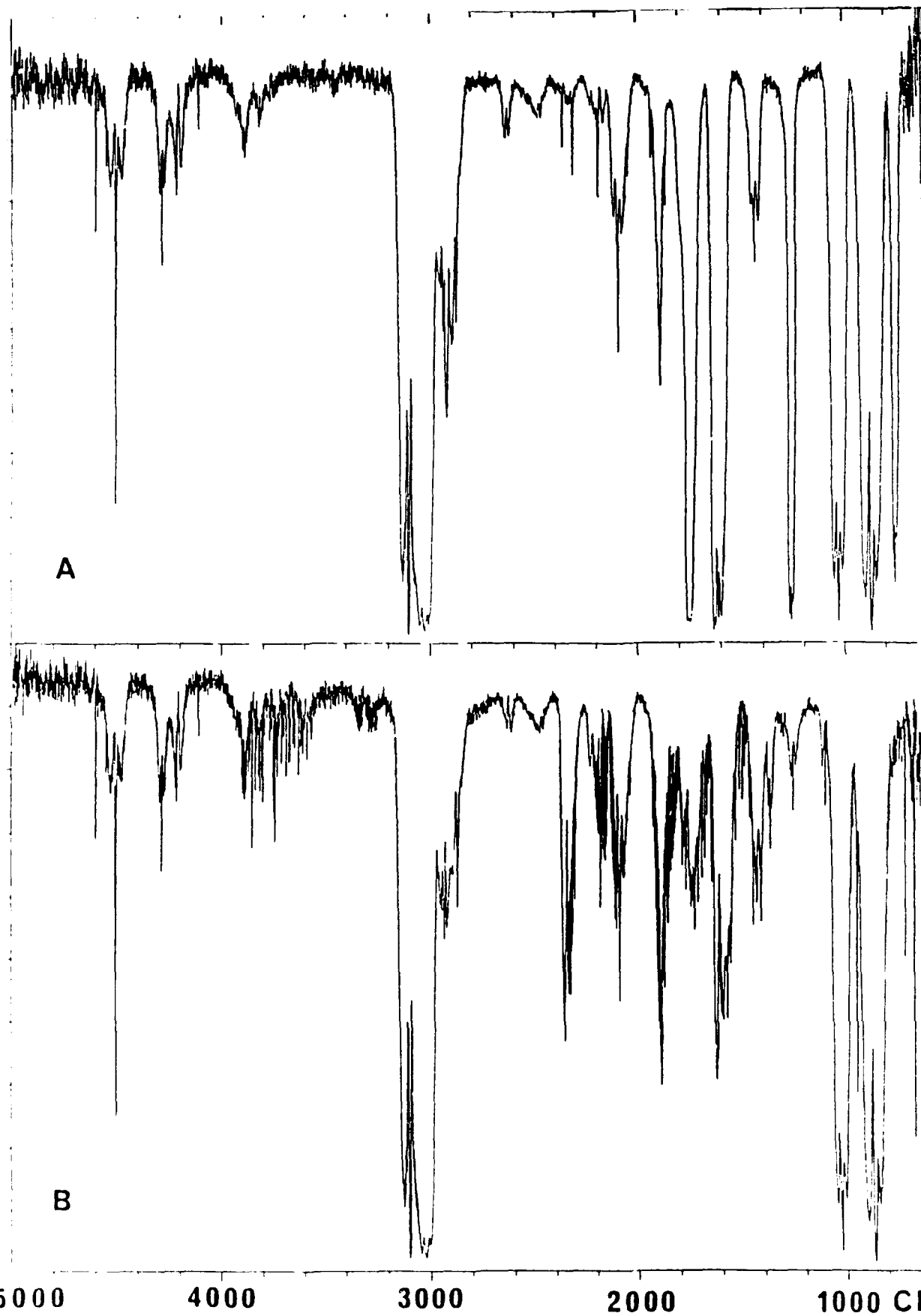


Figure 2. Gas-phase infrared spectra of cyclopropane-NO<sub>2</sub> mixture before excitation and products resulting from the CO<sub>2</sub> laser excitation of the mixture. (A) spectrum of cyclopropane, 247.7 Torr, and NO<sub>2</sub>, 40 Torr. (B) Spectrum of products formed from the CO<sub>2</sub> laser excitation of the mixture in (A) under the conditions P(18) of (00°1) - (02°0), 1048.7 cm<sup>-1</sup>, 30 W/cm<sup>2</sup>, 60 s.

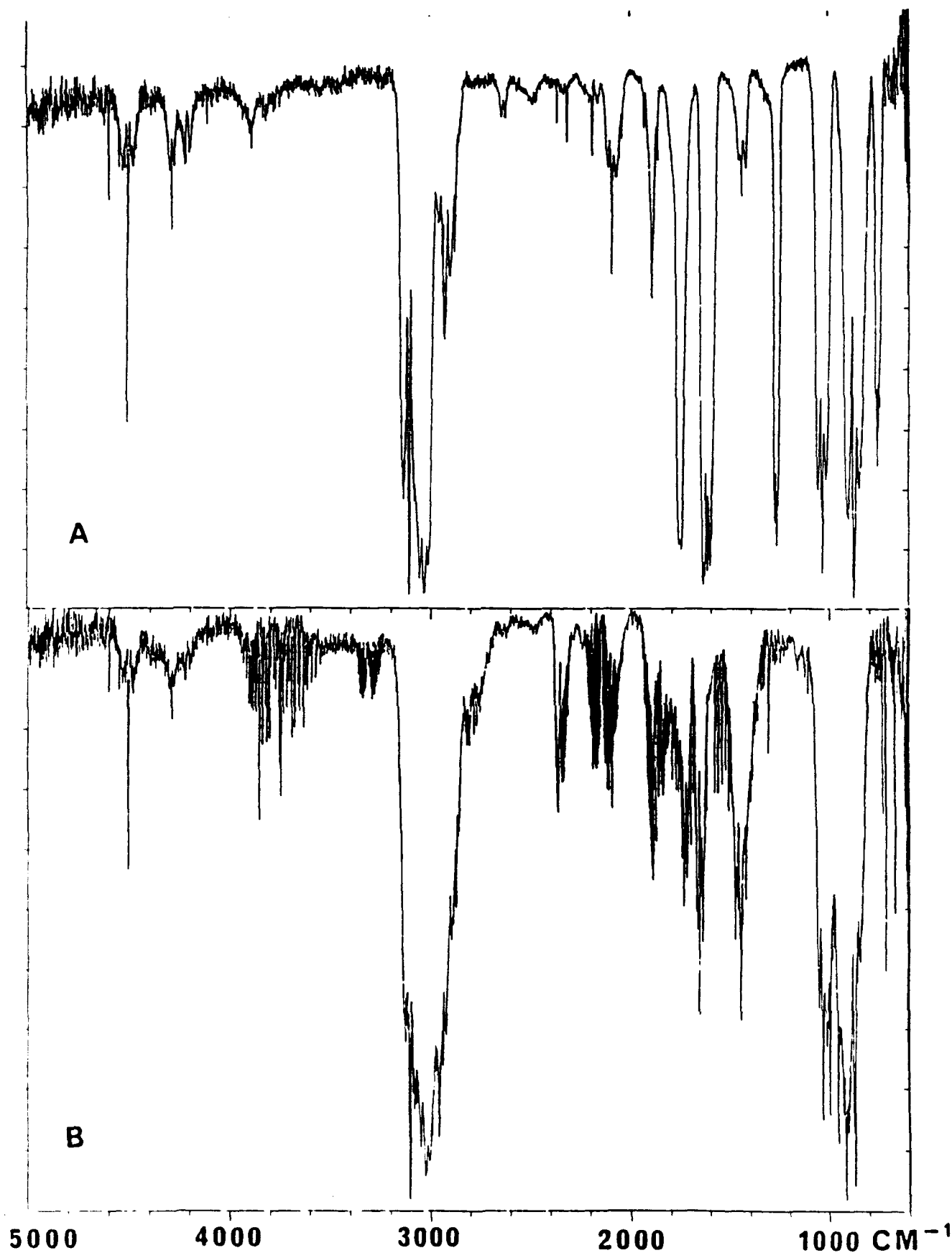


Figure 3. Gas-phase mid-infrared spectra of cyclopropane- $\text{NO}_2$  mixture before excitation and products resulting from the  $\text{CO}_2$  laser excitation of the mixture. (A) Spectrum of cyclopropane, 170.4 Torr, and  $\text{NO}_2$ , 30.0 Torr. (B) Spectrum of products formed from the  $\text{CO}_2$  laser excitation of the mixture in (A) under the conditions P(18) of  $(00^1)-(02^0)$ ,  $1048.7 \text{ cm}^{-1}$ ,  $50 \text{ W/cm}^2$ , 20 s.

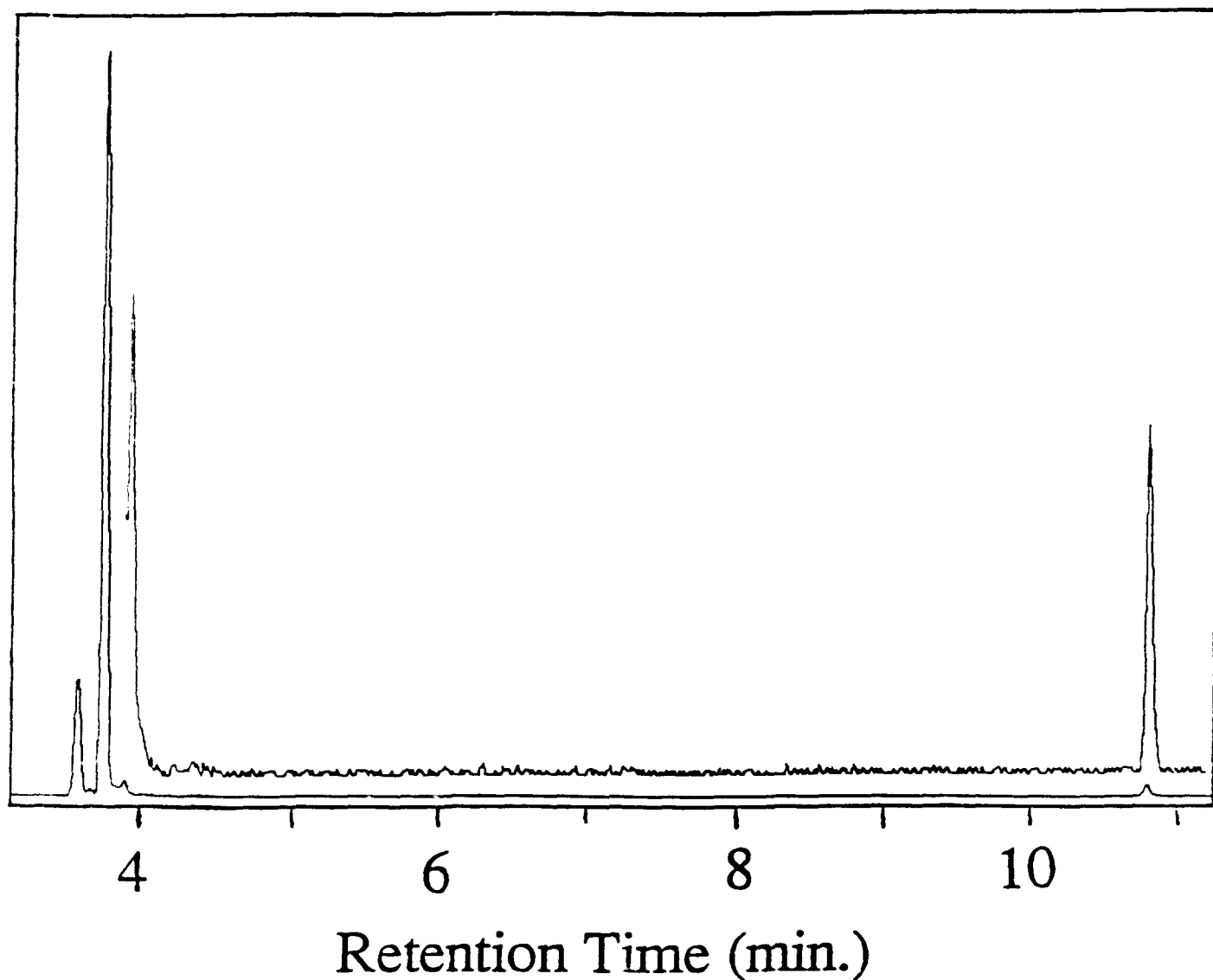


Figure 4. Gas chromatogram from the analysis of the product mixture from the CO<sub>2</sub> laser excitation of 1.1 Torr of cyclopropane and 40.0 Torr of NO<sub>2</sub> for 60 s at 30 W/cm<sup>2</sup> laser power on the P(18) line of the (00<sup>1</sup>) – (02<sup>0</sup>) transition (1048.7 cm<sup>-1</sup>).

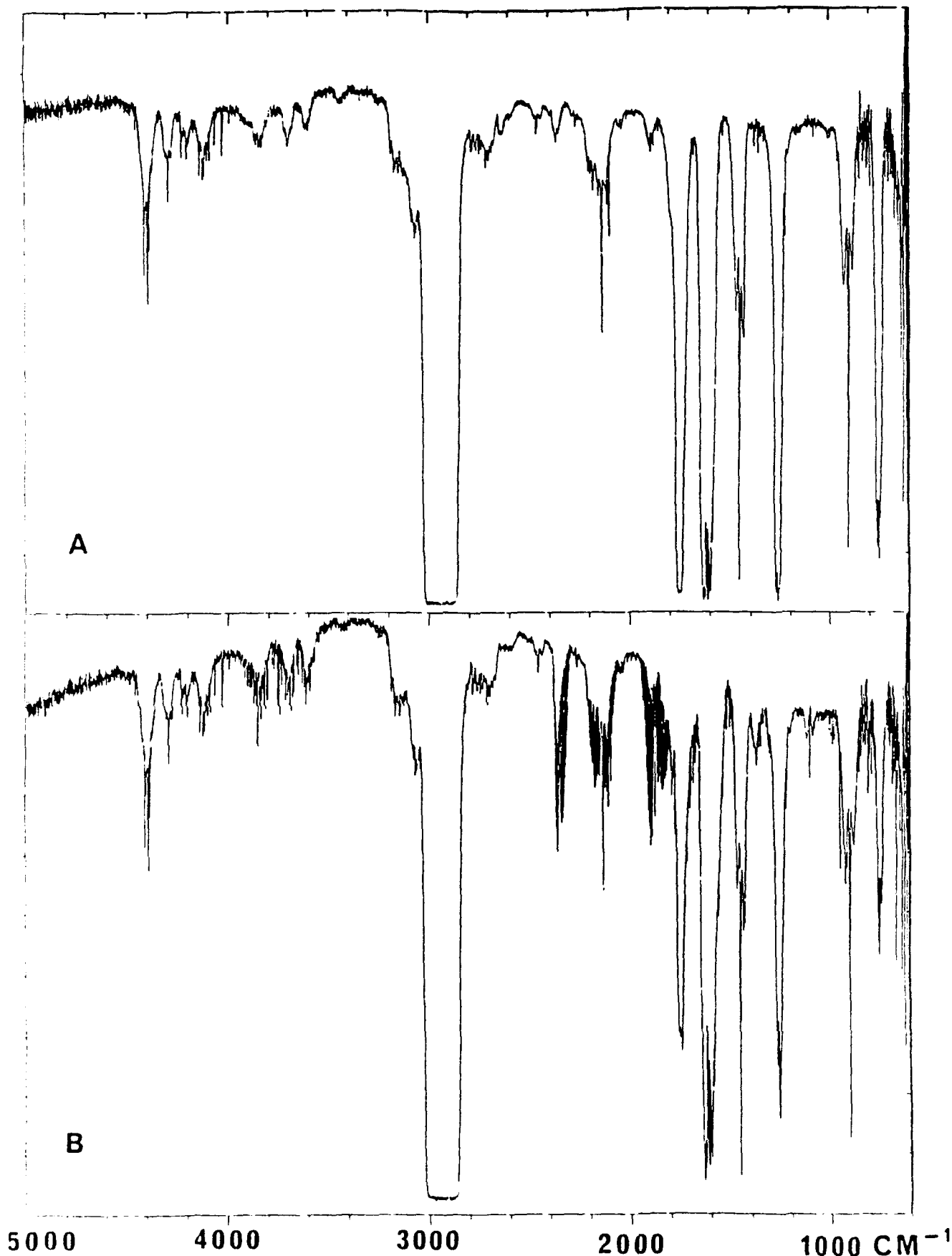


Figure 5. Gas-phase, mid-infrared spectra of cyclobutane-NO<sub>2</sub> mixture before excitation and products resulting from the CO<sub>2</sub> laser excitation of the mixture. (A) Spectrum of cyclobutane, 199.9 Torr, and NO<sub>2</sub>, 40.0 Torr. (B) Spectrum of products formed from the CO<sub>2</sub> laser excitation of the mixture in (A) under the conditions, P(42) of (00<sup>1</sup>) - (10<sup>0</sup>), 922.9 cm<sup>-1</sup>, 60 W/cm<sup>2</sup>, 60 s.

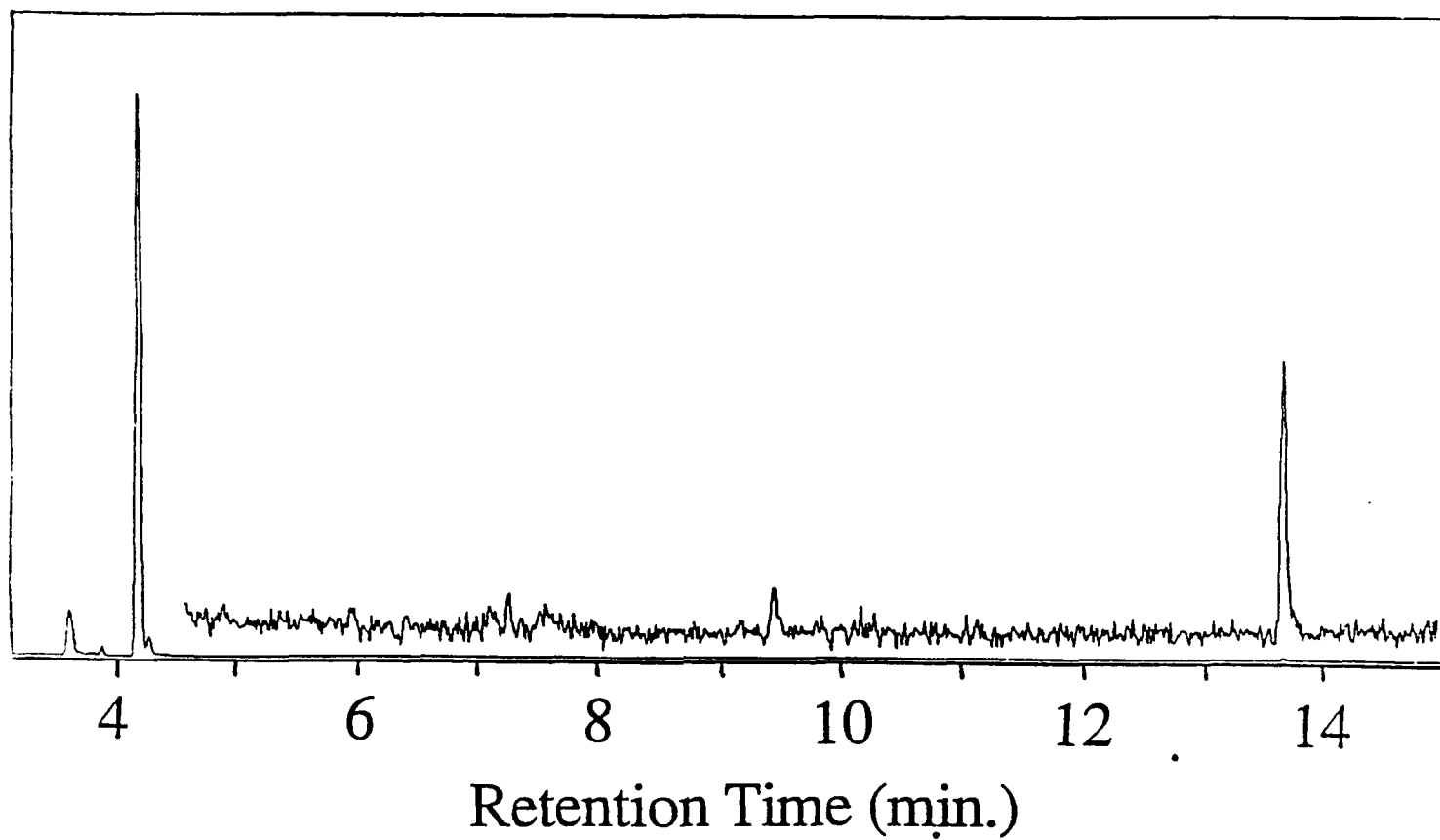


Figure 6. Gas chromatogram from the analysis of the product mixture from the  $\text{CO}_2$  laser excitation of 179.3 Torr of cyclobutane and 40.0 Torr of  $\text{NO}_2$  for 60 s at 50  $\text{W}/\text{cm}^2$  laser power on the P(42) line of the  $(00^1_1) - (10^0_0)$  transition ( $922.9 \text{ cm}^{-1}$ ).

Absorbance

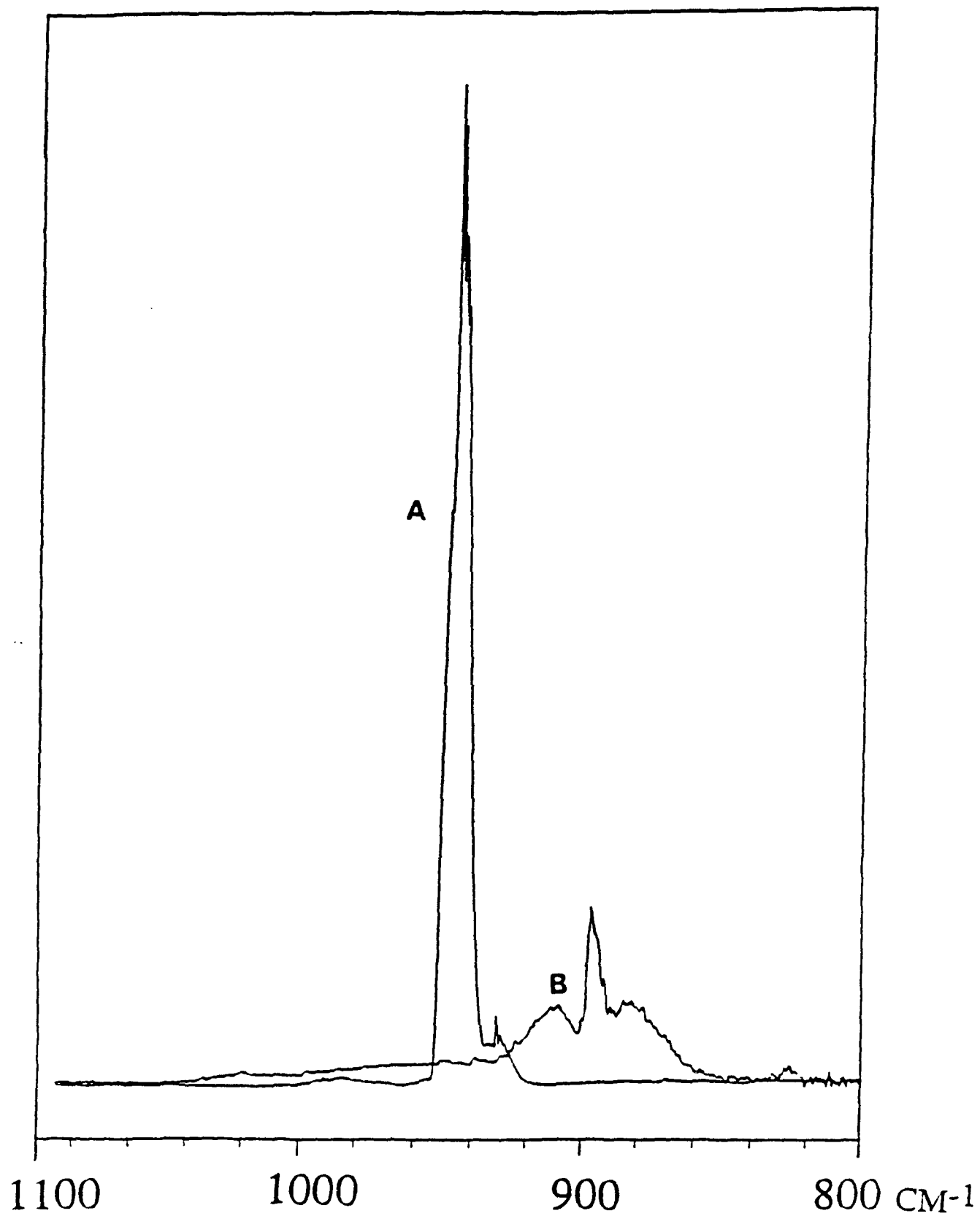


Figure 7. Gas-phase infrared spectra of (A) sulfur hexafluoride (0.9 Torr) and (B) cyclopentane (100 Torr).

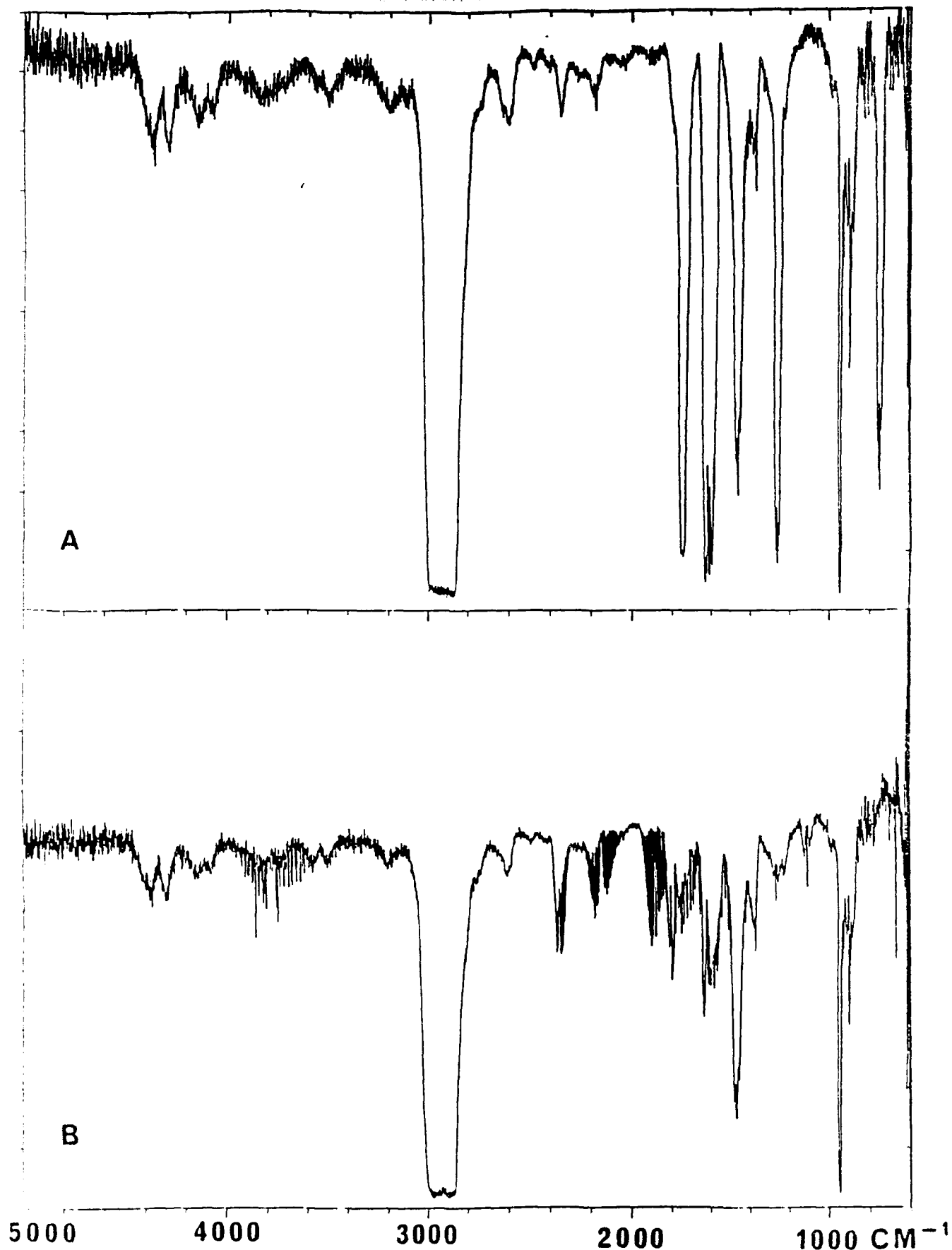


Figure 8. Gas-phase mid-infrared spectra of cyclopentane-NO<sub>2</sub> mixture before excitation and products resulting from the CO<sub>2</sub> laser excitation of the mixture. (A) Spectrum of cyclopentane, 176 Torr, NO<sub>2</sub>, 32 Torr, and SF<sub>6</sub>, 1.5 Torr. (B) Spectrum of products formed from the CO<sub>2</sub> laser excitation of the mixture in (A) under the conditions, P(46) of (00<sup>1</sup>) - (10<sup>0</sup>), 918.7 cm<sup>-1</sup>, 46 W/cm<sup>2</sup>, 60 s.

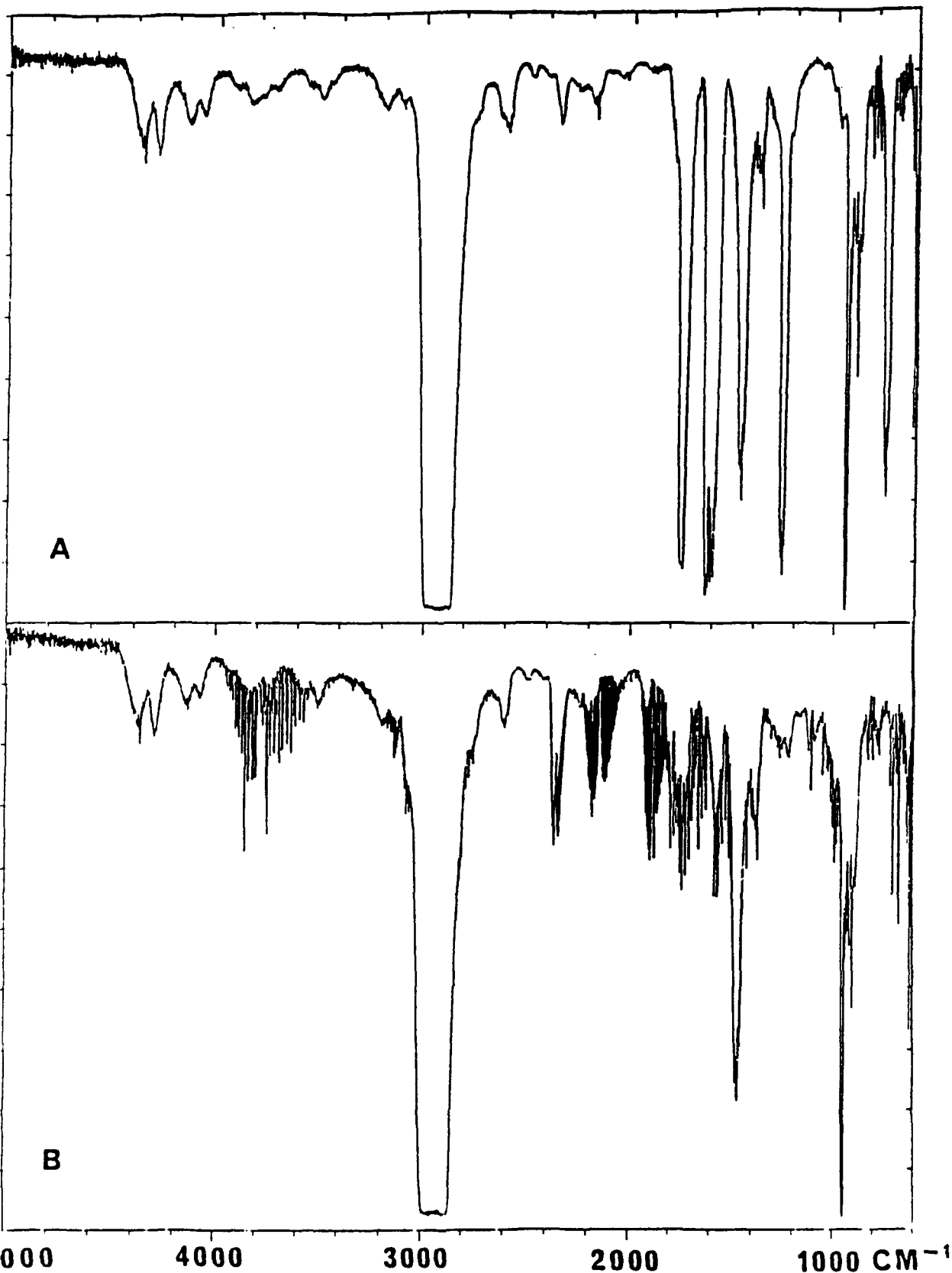


Figure 9. Gas-phase mid-infrared spectra of cyclopentane-NO<sub>2</sub> mixture before excitation and products resulting from the CO<sub>2</sub> laser excitation of the mixture. (A) Spectrum of cyclopentane, 168 Torr, NO<sub>2</sub>, 32 Torr, and SF<sub>6</sub>, 2.0 Torr. (B) Spectrum of products formed under the CO<sub>2</sub> laser excitation of the mixture in (A) under the conditions, P(46) of (00<sup>1</sup>) - (10<sup>0</sup>), 918.7 cm<sup>-1</sup>, 45 W/cm<sup>2</sup>, 60 s.

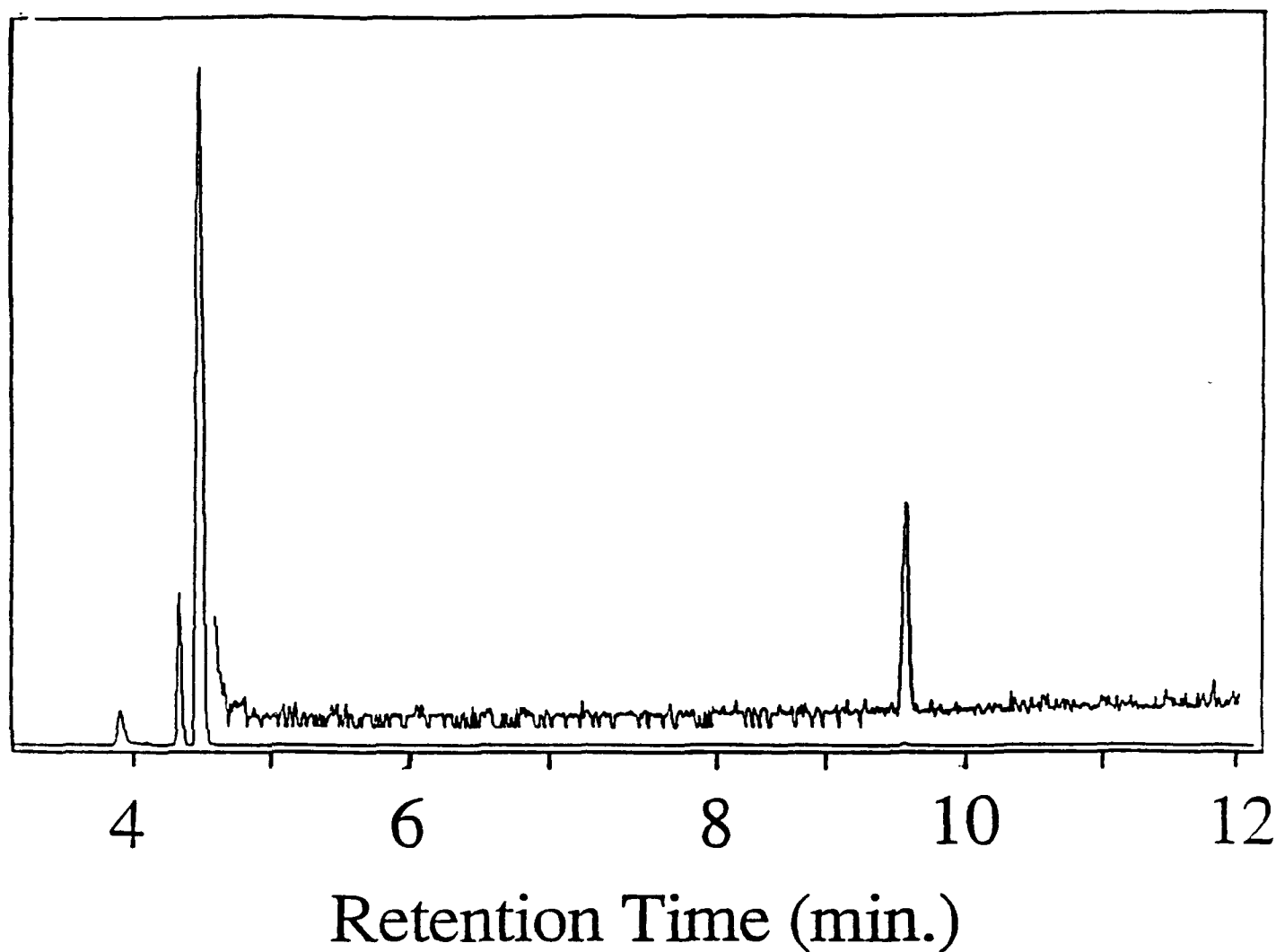


Figure 10. Gas chromatogram from the analysis of the product mixture from the  $\text{CO}_2$  laser excitation of 168.9 Torr of cyclopentane, 30.9 Torr of  $\text{NO}_2$ , and 0.4 Torr of  $\text{SF}_6$  for 60 s at  $45 \text{ W/cm}^2$  laser power on the P(46) line of the  $(00^1) - (10^0)$  transition ( $918.7 \text{ cm}^{-1}$ ).

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