

# Characterization of the Asymmetric Nitric Oxide Dimer $\text{O}=\text{N}=\text{O}=\text{N}$ by Resonance Raman and Infrared Spectroscopy

J. R. Ohlsen and J. Laane\*

Contribution from the Department of Chemistry, Texas A&M University, College Station, Texas 77843. Received May 9, 1978

**Abstract:** Nitric oxide reacts with Lewis acids ( $\text{BF}_3$ ,  $\text{BCl}_3$ ,  $\text{BBr}_3$ ,  $\text{SnCl}_4$ ,  $\text{SiF}_4$ ,  $\text{TiCl}_4$ ),  $\text{HCl}$ , or  $\text{SO}_2$  to form a red species at 77 K. This species absorbs in the visible region near 500 nm and, thus, can be examined using resonance Raman spectroscopy when laser excitation lines near the absorption maximum are utilized. Both Raman and infrared spectra of the red species formed from four different isotopic forms of nitric oxide ( $^{14}\text{N}^{16}\text{O}$ ,  $^{15}\text{N}^{16}\text{O}$ ,  $^{14}\text{N}^{18}\text{O}$ , and  $^{15}\text{N}^{18}\text{O}$ ) were recorded in order to ascertain the nature of the bonding. The results demonstrated that the asymmetric dimer  $\text{O}=\text{N}-\text{O}=\text{N}$  was formed. The vibrational frequencies assigned to the normal isotopic species were  $\nu_1(\text{N}=\text{O}$  stretch) at 1778,  $\nu_2(\text{N}=\text{O}$  stretch) at 1690,  $\nu_3(\text{N}-\text{O}$  stretch) at 482,  $\nu_4$ (in-plane bend) at 184, and  $\nu_5$ (in-plane bend) at 116  $\text{cm}^{-1}$ . In addition, also observed were  $2\nu_4$ ,  $3\nu_4$ ,  $4\nu_4$ ,  $5\nu_4$ ,  $2\nu_3$ ,  $2\nu_2$ ,  $\nu_3 + \nu_4$ ,  $\nu_3 + 2\nu_4$ ,  $2\nu_3 - \nu_4$ ,  $2\nu_3 - 2\nu_4$ ,  $2\nu_3 - \nu_4$ ,  $\nu_2 + \nu_4$ ,  $\nu_2 + 2\nu_4$ ,  $\nu_2 + 3\nu_4$ , and  $\nu_1 + \nu_4$ , as well as other overtones and combinations. In infrared spectra only bands corresponding to  $\nu_1$ ,  $\nu_2$ ,  $2\nu_2$ , and  $\nu_1 + \nu_2$  were detected. No frequency shifts for the acid molecules were detected. The isotopic shifts observed for the  $\nu_3$  mode indicated that an O-N linkage was present. Force constant calculations showed that in this molecular species both  $\text{N}=\text{O}$  groups retain strong multiple bond character and are joined by a weak N-O single bond.

## Introduction

For more than 50 years nitric oxide has been known to form colored mixtures with various Lewis acids and hydrogen chloride at liquid nitrogen temperature. In 1923 Rodebush and Yntema<sup>1</sup> reported that a mixture of nitric oxide and hydrogen chloride formed an intense purple color which, upon warming, dissociated into the original constituents. Based upon specific conductivity measurements between 120 and 130 K they suggested the complex to be of the ionic form  $(\text{NOH})^+\text{Cl}^-$ . Unstable, colored mixtures have also been observed between nitric oxide and the group 3A and group 5A halides. Finlay,<sup>2</sup> in a letter to the editor, noted the formation of a bright orange solid between nitric oxide and boron trifluoride and a dark purple solid between nitric oxide and boron trichloride at 77 K. In both cases the colored mixtures dissociated upon warming into the original constituents. Jolly has also cited the existence of red  $\text{NO}-\text{HCl}$  and  $\text{NO}-\text{BF}_3$  complexes.<sup>3</sup> Peacock and Wilson<sup>4</sup> reported red mixtures formed between nitric oxide and the pentafluorides of phosphorus and arsenic. In all the cases cited above no spectroscopic characterizations were made of these low-temperature mixtures.

In 1963 Hisatsune and Miller<sup>5</sup> reported the infrared spectra of nitrosyl chloride ( $\text{ONCl}$ ) and nitrosyl bromide ( $\text{ONBr}$ ) for the solid state. The  $\text{ONCl}$ , prepared from mixing nitric oxide with chlorine, exhibited its characteristic yellow-orange color in the vapor state, a dark red color in the liquid phase, and generally a yellow color in the solid state. However, it was observed that when nitric oxide gas first came in contact with solid chlorine at 77 K, a dark purple solid formed immediately. This color disappeared when the solid was vaporized, but it appeared again on refreezing the mixture. The substance that gave the purple color had a lower sublimation temperature than  $\text{ONCl}$  since it could be readily dispelled by warming the solid. Based upon infrared and mass spectrometric measurements the purple color was attributed to nitric oxide existing as a trapped or adsorbed monomeric species. A more extensive study based on these observations has never appeared.

The purpose of the present study was to identify and characterize the nature of these unstable species by means of various types of low-temperature spectroscopy. Since all the nitric oxide acid mixtures are colored and, therefore, are expected to produce resonance Raman spectra, such spectra were utilized extensively. In addition, infrared, visible, and EPR spectra

were utilized to aid in the characterization. Four isotopic forms of nitric oxide ( $^{14}\text{N}^{16}\text{O}$ ,  $^{15}\text{N}^{16}\text{O}$ ,  $^{14}\text{N}^{18}\text{O}$ , and  $^{15}\text{N}^{18}\text{O}$ ) were used to provide confirming evidence for the structural configuration of the colored species formed in the various reaction systems.

## Experimental Section

**Materials.** All preparations and purification were carried out in a standard high-vacuum system<sup>6</sup> employing both silicone-lubricated and greaseless stopcocks. Boron trifluoride (Matheson Gas Products, 99.5%), boron trichloride (M. G. P., 99.0%), hydrogen chloride (M. G. P., 99.0%), sulfur dioxide (M. G. P., 99.9%), silicon tetrafluoride (M. G. P., 99.6%), and chlorine (M. G. P., 99.5%) were transferred to the high-vacuum system by means of pressurized gas cylinders and were purified by low-temperature vacuum distillations.<sup>6</sup> All gases were stored in 1-L gas bulbs equipped with greaseless stopcocks. Tin tetrachloride,  $\text{SnCl}_4$  (Allied Chemical, 99.0%), and titanium tetrachloride,  $\text{TiCl}_4$  (Alfa Inorganics, 99.9%), were transferred in an inert atmosphere of nitrogen or argon to 25-mL vials equipped with greaseless stopcocks. The above liquids were purified by low-temperature vacuum distillations.<sup>6</sup>

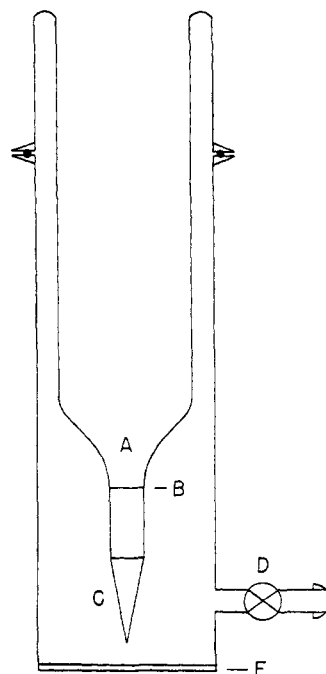
Nitric oxide,  $^{14}\text{N}^{16}\text{O}$  (Matheson Gas Products, 99.0%), was degassed at 77 K and then warmed to 87 K. The fraction volatile at this temperature was collected and used. In this way trace amounts of nitrous oxide,  $\text{N}_2\text{O}$ , and nitrogen dioxide,  $\text{NO}_2$ , were removed.<sup>7</sup> Nitrogen-15 enriched nitric oxide,  $^{15}\text{N}^{16}\text{O}$  (Stohler Isotopic Chemicals, 99.0%), oxygen-18 enriched nitric oxide,  $^{14}\text{N}^{18}\text{O}$  (Mound Laboratories, Miamisburg, Ohio), and nitrogen-15-oxygen-18 enriched nitric oxide,  $^{15}\text{N}^{18}\text{O}$  (Mound Laboratories), were treated in a similar fashion. The latter two enriched species were reported and confirmed to have  $^{18}\text{O}$  enrichment of better than 91%.

Nitrosyl chloride,  $\text{ONCl}$ ,<sup>8</sup> was prepared by mixing two parts of nitric oxide with one part of chlorine.

All materials were checked for purity by comparing their infrared gas-phase spectra with those reported in the literature.<sup>9</sup> All were found to be satisfactory.

**Sample Preparation.** Nitric oxide was mixed with the various acids in ratios ranging from 1:1 to 5:1. In all cases the mixtures were allowed to stand overnight in gas bulbs prior to spectroscopic analysis. A mixture of  $\text{NO}$  and  $\text{BF}_3$  produced an orange-colored solid at 77 K and a colorless, gaseous mixture at room temperature. Nitric oxide and  $\text{BCl}_3$  also produced a colorless mixture at 298 K but cooling to 77 K produced a purple-colored solid. A similar purple-colored solid was observed when  $\text{NO}$  was mixed with  $\text{HCl}$ ,  $\text{SnCl}_4$ , or  $\text{TiCl}_4$  and cooled to 77 K. Mixtures of  $\text{NO}$  with  $\text{BBr}_3$  and  $\text{NO}$  with  $\text{SO}_2$  produced brown- and white-colored solids, respectively, at 77 K.

**Spectroscopic Measurements.** Raman spectra were recorded on a



**Figure 1.** Low-temperature Raman cell: (A) liquid nitrogen reservoir; (B) copper to glass seal; (C) brass wedge silver soldered to the copper cold finger; (D) gas deposition line; (E) quartz window.

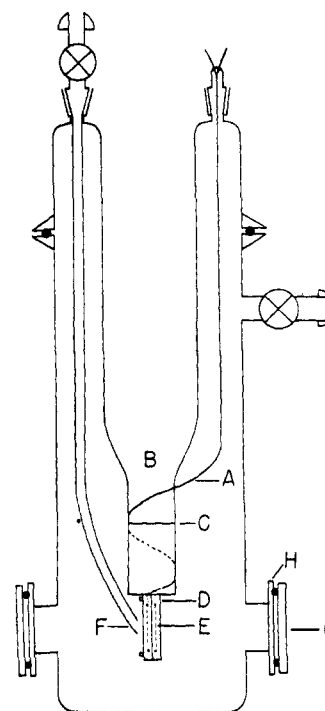
Cary Model 82 spectrophotometer equipped with a Coherent Radiation Model 52 krypton ion laser and a Coherent Radiation Model 53 argon ion laser. Krypton ion laser lines at 5209, 5682, and 6471 Å and argon ion laser lines at 5145 and 4880 Å were used extensively in this study. Laser power at the sample ranged from 100 to 200 mW. Typical spectra were recorded at a sensitivity of 1000 counts/s full scale and a constant spectral bandwidth of  $5\text{ cm}^{-1}$ .

The low-temperature Raman cell used in this study is shown in Figure 1. A mixture of nitric oxide and the acid was sprayed onto a highly polished brass wedge maintained at 77 K by liquid nitrogen. The rate of deposition ranged from 4 to 6 mM/h. The same deposition rates were also used prior to recording infrared and visible spectra. After completion of deposition, the brass wedge was rotated  $90^\circ$  and the Raman spectrum was recorded.

A Beckman IR-4260 spectrophotometer was used for recording mid-infrared spectra from 4000 to  $200\text{ cm}^{-1}$ . The low-temperature infrared cell is shown in Figure 2. The nitric oxide-acid mixtures were deposited as polycrystalline films onto a 1-in. diameter by  $\frac{3}{16}$ -in. thick CsI window maintained at 77 K by liquid nitrogen. The CsI window was sandwiched between two indium washers to ensure good thermal contact with the brass window holder. The outer windows were 55-mm diameter CsI. A chromel-alumel thermocouple was placed between the CsI window and the brass window holder. Variable-temperature studies were also performed with this cell by directing a stream of cold nitrogen gas onto the copper cold finger in the bottom of the cryostat Dewar. Cold nitrogen was produced by passing nitrogen gas through a copper coil immersed in liquid nitrogen. The temperature at the CsI window was readily controlled by regulating the rate of gas flow. This technique allowed any temperature between 77 and 273 K to be maintained over considerable periods of time to within a few degrees.

Far-infrared spectra from 80 to  $400\text{ cm}^{-1}$  were recorded using a Digilab FTS-20 high-resolution vacuum spectrophotometer. A 6.25- $\mu\text{m}$  Mylar beam splitter was used to cover this spectral range. The low-temperature cell was the same as that used to record mid-infrared spectra. The cold window was 1-in. diameter by  $\frac{1}{16}$ -in. thick single crystal silicon. The outer windows of the cell were polyethylene of 20-mil thickness. A Plexiglas flange, which could be bolted to the instrument sample chamber, was vacuum sealed to the cryostat using Apiezon Q. This arrangement permitted the entire spectrometer body to be evacuated, providing maximum signal throughput by requiring the source radiation to pass through only three cryostat windows.

A Cary 14 spectrophotometer was used for recording visible spectra from 700 to 400 nm. The low-temperature cell was the same as that



**Figure 2.** Low-temperature infrared cell: (A) chromel-alumel thermocouples; (B) liquid nitrogen reservoir; (C) copper to glass seal; (D) brass window holder silver soldered to copper cold finger; (E) CsI window sandwiched between two indium washers; (F) gas deposition line; (G) CsI windows; (H) aluminum O-ring flange vacuum sealed (Torr seal, Varian) to cryostat.

used to record infrared spectra. The cold window was 1-in. diameter by  $\frac{3}{16}$ -in. thick NaCl and the outer windows were 55 mm diameter quartz.

EPR spectra were recorded using a Varian E-6S spectrometer. The nitric oxide-acid mixtures were prepared for spectroscopic analysis by condensing them into a 4-mm o.d. by 20-cm long Pyrex tube equipped with a greaseless stopcock.

## Results

Reaction of nitric oxide at 77 K with any one of the acids listed above resulted in the formation of a reddish solid. The visible absorption spectra for three of the combinations are shown in Figure 3. Table I lists the absorption maxima for the colored species resulting from several different nitric oxide-acid combinations. No color was formed when pure nitric oxide was condensed or when it was mixed with unreactive compounds such as carbon tetrachloride or carbon dioxide.

Figure 3 also shows the wavelengths of six argon ion and krypton ion laser lines used for excitation for Raman spectroscopy. Since these all fall within the absorption region of the red species, resonance enhancement leads to stronger Raman signals as well as the observation of numerous overtone and combination bands. Figure 4 shows the resonance Raman spectrum of the red species resulting from mixing NO with HCl at liquid nitrogen temperature. The observed frequencies, relative intensities, and assignments are listed in Table II (refer to later discussion and Table XI for definition of the  $\nu_i$ ). It is evident from the spectrum that numerous overtones and combination bands with substantial intensity are present and that only five Raman lines, which are not combinations of others, can be found. For example, bands at 1684 and  $1773\text{ cm}^{-1}$  are fundamentals, but the one at  $1868\text{ cm}^{-1}$ , which is more intense than that at  $1773\text{ cm}^{-1}$ , is a combination of  $1684 + 183\text{ cm}^{-1}$ . In order to demonstrate that resonance enhancement was occurring, the spectra were recorded using different laser lines for excitation. As expected, the relative intensity of the overtones  $2\nu_3$  and  $2\nu_4$  dropped off as the laser

**Table I.** Absorption Maxima (nm) for Nitric Oxide + Acid at 77 K

combination	$\lambda_{\max}$	obsd color
NO + HCl	500	dark red
NO + BF <sub>3</sub>	470	dark orange
NO + BCl <sub>3</sub>	495	dark red
NO + TiCl <sub>4</sub>	495	dark red
NO + SnCl <sub>4</sub>	509	red

**Table II.** Observed Raman Frequencies (cm<sup>-1</sup>) for NO + HCl at 77 K

Raman shift	rel intensity	assignment
120	21	$\nu_5$
183	1000	$\nu_4$
301	40	$\nu_4 + \nu_5 = 303$ or $\nu_3 - \nu_4 = 300$
373	247	$2\nu_4 = 366$
483	271	$\nu_3$
560	73	$3\nu_4 = 549$ or $183 + 373 = 556$
595	21	$2\nu_3 - 2\nu_4 = 593$ or $965 - 373 = 592$
669	126	$\nu_3 + \nu_4 = 666$
744	18	$4\nu_4 = 732$ or $183 + 560 = 743$
778	29	$2\nu_3 - \nu_4 = 783$ or $965 - 183 = 782$
853	52	$\nu_3 + 2\nu_4 = 849$ or $483 + 373 = 856$
931	8	$5\nu_4 = 916$ or $183 + 744 = 927$
965	48	$2\nu_3 = 966$
1038	18	$\nu_3 + 3\nu_4 = 1032$ or $483 + 560 = 1043$
1151	29	$2\nu_3 + \nu_4 = 1149$ or $965 + 183 = 1148$
1197	11	$\nu_2 - \nu_3 = 1201$
1342	18	$2\nu_3 + 2\nu_4 = 1332$ or $965 + 373 = 1338$
1684	147	$\nu_2$
1773	37	$\nu_1$
1868	68	$\nu_2 + \nu_4 = 1867$
1952	18	$\nu_1 + \nu_4 = 1956$
1982	19	$\nu_2 + (\nu_4 + \nu_5) = 1987$ or $\nu_2 + (\nu_3 - \nu_4) = 1984$
2052	19	$\nu_2 + 2\nu_4 = 2050$ or $1684 + 373 = 2057$
2137	11	$\nu_1 + 2\nu_4 = 2139$ or $1773 + 373 = 2146$
2162	23	$\nu_2 + \nu_3 = 2167$
2238	10	$\nu_2 + 3\nu_4 = 2233$ or $1684 + 560 = 2244$
2345	18	$\nu_2 + (\nu_3 + \nu_4) = 2350$

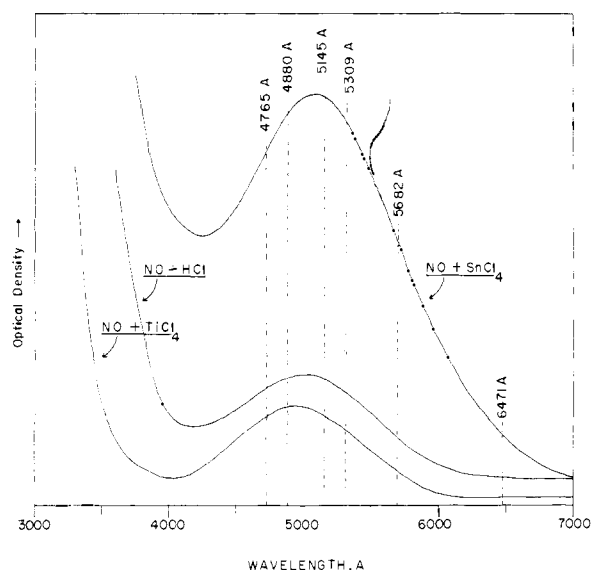
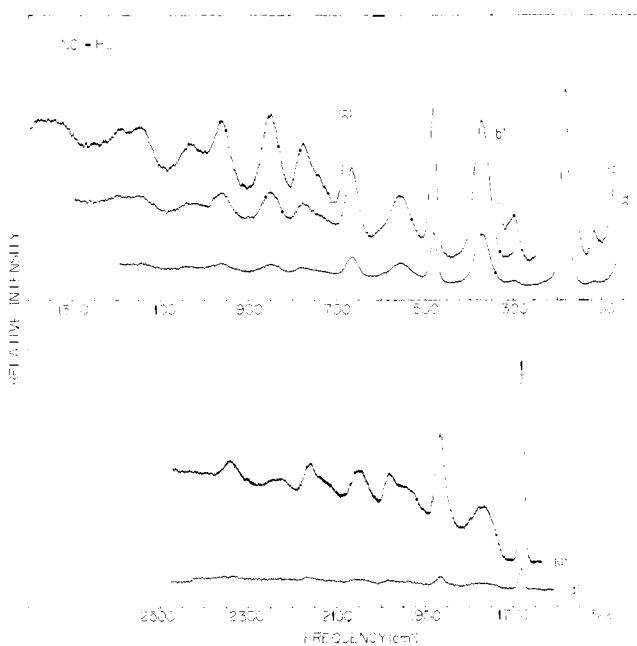
**Table III.** Relative Raman Intensities of the  $2\nu_3$  and  $\nu_3$  Bands and the  $2\nu_4$  and  $\nu_4$  Bands in NO + HCl as a Function of Exciting Frequency

exciting line, Å	$2\nu_3$ (965 cm <sup>-1</sup> ) / $\nu_3$ (483 cm <sup>-1</sup> )	$2\nu_4$ (373 cm <sup>-1</sup> ) / $\nu_4$ (183 cm <sup>-1</sup> )
4765	0.13	0.24
5145	0.18	0.25
6471	0.09	0.12

**Table IV.** Observed Infrared Frequencies (cm<sup>-1</sup>) for NO + HCl at 77 K

frequency	intensity <sup>a</sup>	assignment
3738	mw	$2\nu_1 + \nu_4$ or $2\nu_2 + 2\nu_4$
3450	mw	$\nu_1 + \nu_2$
3370	w	$2\nu_2$
2757	m	HCl <sup>b</sup>
2715	w	HCl
2481 (broad)	m	
1990	mw	
1770	vvs	$\nu_1$
1685	ms	$\nu_2$
~450 (broad)	w	$\nu_3$
280	mw	

<sup>a</sup> s, strong; m, medium; w, weak; v, very. <sup>b</sup> HCl assignments from R. Savoie and A. Anderson, *J. Chem. Phys.*, **44**, 548 (1966).

**Figure 3.** Visible spectra of NO + HCl, NO + TiCl<sub>4</sub>, and NO + SnCl<sub>4</sub> at 77 K in relation to the exciting wavelengths of the argon ion and krypton ion laser lines.**Figure 4.** Resonance Raman spectrum of NO + HCl at 77 K using 10 mW of 5145-Å radiation. Spectra (a), (b), (c), and (d) are recorded at different sensitivities.

line frequency was moved further away from the absorption band maximum. This can be seen in Table III.

The infrared spectrum of NO + HCl at 77 K is shown in Figure 5 and the frequencies with assignments are listed in Table IV. It is significant that  $\nu_1$  and  $\nu_2$  are confirmed as fundamental vibrational frequencies and that the combination  $\nu_1 + \nu_2$  demonstrates that both frequencies result from the same molecule.

The observation that both the 1684- and 1773-cm<sup>-1</sup> bands arise from the same molecule shows that two (at least) N=O groups must be present in the species. The spectral locations of these bands clearly indicate that they cannot be assigned to monomeric NO (1883 cm<sup>-1</sup>),<sup>10</sup> NO<sup>+</sup> (2150–2400 cm<sup>-1</sup>),<sup>9</sup> NO<sup>-</sup> (1350–1375 cm<sup>-1</sup>),<sup>11</sup> *cis*-O=N–N=O (both 1870 and 1776 cm<sup>-1</sup>),<sup>12</sup> *cis*-N<sub>2</sub>O<sub>2</sub><sup>2-</sup> (both 830–857 and 1042–1057

**Table V.** Fundamental Vibrational Frequencies ( $\text{cm}^{-1}$ ) of the Molecular Species Present in Various NO + Acid Mixtures and ONCl

	$\nu_1$	$\nu_2$	$\nu_3$	$\nu_4$	$\nu_5$
NO + HCl	1773	1684	483	183	120
NO + $\text{BF}_3$	1804	1694	484	184	114
NO + $\text{BCl}_3$	1778	1690	482	184	116
NO + $\text{SiF}_4$	1783	1685	486	186	115
NO + $\text{TiCl}_4$	1770	1686	480	185	115
NO + $\text{SnCl}_4$	1777	1684	481	181	113
NO + $\text{SO}_2$	1784	1686	488	190	118
ONCl <sup>a</sup>	1777	1688	486	188	120

<sup>a</sup> Red species present in ONCl.**Table VI.** Observed Raman Frequencies ( $\text{cm}^{-1}$ ) for  $^{14}\text{NO}$ ,  $^{15}\text{NO}$ , and  $^{15}\text{N}^{18}\text{O}$  with  $\text{BF}_3$  at 77 K

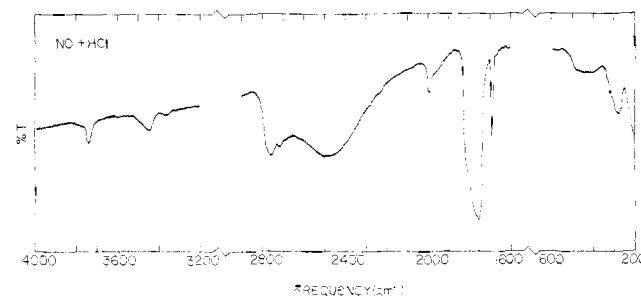
assignment	$^{14}\text{N}^{16}\text{O}$	$^{15}\text{N}^{16}\text{O}$	$^{15}\text{N}^{18}\text{O}$
$\nu_5$	114	114	114
$\nu_4$	184	184	179
	259	252	253
$\nu_4 + \nu_5$ or $\nu_3 - \nu_4$	298	297	289
$2\nu_4$	373	373	360
$\nu_3$	484	477	467
$3\nu_4$	557	555	538
$2\nu_3 - 2\nu_4$	592	581	572
$\nu_3 + \nu_4$	669	662	646
$4\nu_4$	741	742	722
$2\nu_3 - \nu_4$	782	767	759
$\nu_3 + 2\nu_4$	853	847	824
$5\nu_4$	928		
$2\nu_3$	964	953	932
$\nu_3 + 3\nu_4$	1039	1022	1004
$2\nu_3 + \nu_4$	1157	1142	1112
$\nu_2 - \nu_3$	1203	1183	1149
$2\nu_3 + 2\nu_4$			1296
$\nu_2 - \nu_4$			1432
$\nu_2$	1694	1666	1619
$\nu_1$	1804	1775	1727
$\nu_2 + \nu_4$	1880	1851	1797
$\nu_1 + \nu_4$	1991	1954	1902
$\nu_2 + 2\nu_4$	2063	2036	1977
$\nu_2 + \nu_3$	2174	2140	2081
$\nu_2 + 3\nu_4$	2253	2217	2152
$\nu_2 + (\nu_3 + \nu_4)$	2360	2324	2260
$2\nu_2$	3376	3319	3224
$2\nu_2 + \nu_5$		3431	3332
$2\nu_2 + \nu_4$		3515	3407

$\text{cm}^{-1}$ ),<sup>13</sup> or *trans*- $\text{N}_2\text{O}_2^{2-}$  (both 1031 and 1115  $\text{cm}^{-1}$ ).<sup>14,15</sup> Nor can they be assigned to any other previously reported nitrogen oxides.

In addition to the two fundamentals observed in the  $\text{N}=\text{O}$  stretching region three bands in the low-frequency region at 483, 183, and 120  $\text{cm}^{-1}$  were assigned as  $\nu_3$ ,  $\nu_4$ , and  $\nu_5$ . The assignment of the 483- and 183- $\text{cm}^{-1}$  bands as fundamentals was rather straightforward in that they are the most intense bands in the low-frequency region and they also show overtone progressions. Furthermore, the majority of bands in the spectrum could be assigned as combination and/or difference bands involving  $\nu_3$  and  $\nu_4$ . The assignment of the 120- $\text{cm}^{-1}$  band as a fundamental ( $\nu_5$ ) is more ambiguous. The band is very weak and, unlike the other fundamentals, no overtone progressions associated with it were observed. Its combination band,  $\nu_4 + \nu_5 = 303 \text{ cm}^{-1}$ , is nearly coincident with the difference band  $\nu_3 - \nu_4 = 300 \text{ cm}^{-1}$ . Furthermore, the difference band  $\nu_3 - 2\nu_4 = 110 \text{ cm}^{-1}$  is close to this region. Nonetheless, since the isotopic data, which are to be discussed later, support the assignment of 120  $\text{cm}^{-1}$  to a fundamental rather than a difference band, it was assigned as such.

**Table VII.** Observed Infrared Frequencies ( $\text{cm}^{-1}$ ) for NO +  $\text{BF}_3$  at 77 K

frequency	assignment	frequency	assignment
1805 m	$\nu_1$ (red species)	870 m	$\nu_1$ ( $^{11}\text{BF}_3$ )
1695 w	$\nu_2$ (red species)	830 s	
1450 vs, broad	$\nu_3$ ( $\text{BF}_3$ ) <sup>a</sup>	790 w	
1350 s	$\nu_1 + \nu_4$ ( $\text{BF}_3$ )	650 vs, broad	$\nu_2$ ( $\text{BF}_3$ )
1272 s		520 vw	
1020 mw		480 vs	$\nu_4$ ( $\text{BF}_3$ )
900 s	$\nu_1$ ( $^{10}\text{BF}_3$ )	335 s	

<sup>a</sup>  $\text{BF}_3$  assignments from D. A. Davis, *J. Chem. Phys.*, **31**, 1637 (1959).**Figure 5.** Infrared spectrum of NO + HCl at 77 K.

When nitric oxide was reacted at 77 K with a number of other acids, the resonance Raman spectra were virtually identical showing the same fundamentals, overtones, and combination bands. Table V summarizes the fundamental frequencies recorded for several of these systems. The only combination which resulted in a noticeably different spectrum was that of the orange NO +  $\text{BF}_3$ . In this case,  $\nu_1$  was shifted up about 30  $\text{cm}^{-1}$  relative to NO + HCl and  $\nu_2$  was slightly shifted up by 10  $\text{cm}^{-1}$ . Observed Raman frequencies for the NO +  $\text{BF}_3$  system are shown in Table VI. The differences between this and the NO + HCl system were useful for confirming the combination band assignments. For example,  $\nu_1 + \nu_4$  for the  $\text{BF}_3$  system is at 1991  $\text{cm}^{-1}$  but at 1952  $\text{cm}^{-1}$  for the HCl combination. Figure 5 shows the infrared spectrum observed for NO +  $\text{BF}_3$  and Table VII lists the frequencies. In addition to  $\nu_1$  and  $\nu_2$  of the colored species at 1805 and 1695  $\text{cm}^{-1}$ , the spectrum shows a number of bands due to  $\text{BF}_3$ . These appear to be unshifted relative to free  $\text{BF}_3$ . It is noteworthy that in most cases bands due to acids were only observed in infrared spectra. In Raman spectra the resonance enhancement of the bands due to the red species was sufficient to obscure any acid bands which were not resonantly enhanced.

The red species with the type of spectrum described above could also be obtained from nitrosyl chloride using trap to trap vacuum distillation, without the use of any acids. Initially, freshly prepared ONCl was condensed into a trap at 189 K (ethyl acetate slush) and the uncondensed vapors at this temperature were condensed in a trap at 143 K (*n*-pentane slush). The uncondensed vapors at this temperature were condensed as a red solid into a third trap at 77 K. This solid was warmed to room temperature and then condensed onto the Raman cold tip at 77 K as a red film. The spectrum obtained was virtually identical with that obtained from NO + HCl. No bands due to ONCl were observed. When a Raman spectrum of the yellow "pure" ONCl was recorded at 77 K, frequencies due to the red species at 116, 186, 480, 1685, and 1777  $\text{cm}^{-1}$  were observed. In addition, ONCl fundamentals at 230 (with overtone at 456), at 493 and 511 (doublet), and at 1908  $\text{cm}^{-1}$  were observed. Finally, bands were observed at 202, 266, and 1853

**Table VIII.** Raman Frequencies ( $\text{cm}^{-1}$ ) for  $\text{O}=\text{N}-\text{N}=\text{O}$  in Various Chemical Environments

assignment		liquid <sup>a</sup>	$\text{NO} + \text{CO}_2$	$\text{NO} + \text{CCl}_4$
$\nu_1$	$\text{N}=\text{O}$ sym str	1861	1858	1857
$\nu_2$	$\text{N}-\text{N}$ str	262	262	263
$\nu_3$	$\text{N}-\text{N}=\text{O}$ sym bend	196	202	198
$\nu_4$	out of plane bend	487		
$\nu_5$	$\text{N}=\text{O}$ antisym str	1760		
$\nu_6$	$\text{N}-\text{N}=\text{O}$ antisym bend	167	161	169

<sup>a</sup> A. L. Smith, W. E. Keller, and H. L. Johnston, *J. Chem. Phys.*, **19**, 189 (1951); D. M. Eshelman, F. J. Torre, and J. Bigeleisen, *ibid.*, **60**, 420 (1974). Gas-phase frequencies of 1860 and 1788  $\text{cm}^{-1}$  have also been reported: C. E. Dinerman and G. E. Ewing, *ibid.*, **53**, 626 (1970).

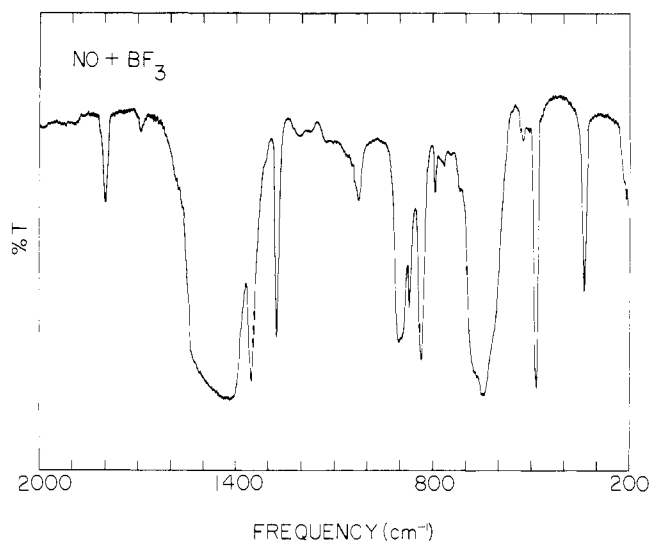
**Table IX.** Observed Raman Frequencies ( $\text{cm}^{-1}$ ) for Four Isotopic Species of  $\text{NO}$  with  $\text{BCl}_3$  at 77 K

assignment	$^{14}\text{N}^{16}\text{O}$	$^{15}\text{N}^{16}\text{O}$	$^{14}\text{N}^{18}\text{O}$	$^{15}\text{N}^{18}\text{O}$
$\nu_5$	116	115	115	114
$\nu_4$	184	183	180	179
	255			245
$\nu_4 + \nu_5$ or $\nu_3 - \nu_4$	296	300	295	291
$2\nu_4$	371	370	359	360
$\nu_3$	482	475	472	466
$3\nu_4$	552	550	540	535
$2\nu_3 - 2\nu_4$	593	573		567
$\nu_3 + \nu_4$	672	655	653	642
$4\nu_4$	744	730		707
$2\nu_3 - \nu_4$	778	760	~766	755
$\nu_3 + 2\nu_4$	849	841	831	817
$5\nu_4$	925			
$2\nu_3$	962	943	940	929
$\nu_3 + 3\nu_4$			1016	998
$2\nu_3 + 2\nu_4$			1120	1110
$\nu_2 - \nu_3$			~1170	1147
$\nu_2$	1690	1661	1641	1610
$\nu_1$	1778	1750	1726	1695
$\nu_2 + \nu_4$	1873	1843	1816	1786
$\nu_1 + \nu_4$	1957	1928	~1900	1868
$\nu_2 + (\nu_4 + \nu_5)$ or $\nu_2 + (\nu_3 - \nu_4)$	1994	1962	~1930	1901
$\nu_2 + 2\nu_4$	2061	2027	1996	1965
$\nu_2 + \nu_3$	2176	2130	2105	2067
$\nu_2 + 3\nu_4$	2237			2139
$\nu_2 + (\nu_3 + \nu_4)$				2241
$2\nu_2$	3363			3202
$2\nu_2 + \nu_5$	3469			3310
$2\nu_2 + \nu_4$	3541			3378

$\text{cm}^{-1}$ . These are presumably due to the symmetric nitric oxide dimer  $\text{O}=\text{N}-\text{N}=\text{O}$ .

In order to test whether the red species would form in the presence of more inert molecules, the spectra of  $\text{NO} + \text{CCl}_4$  and  $\text{NO} + \text{CO}_2$  were recorded. The result was that no red species was formed, and the spectra corresponded only to symmetric  $\text{O}=\text{N}-\text{N}=\text{O}$ , as can be seen in Table VIII.

It was, therefore, clear that the same red species was formed when nitric oxide was reacted with any one of the acids, but that this was different from symmetric  $\text{O}=\text{N}-\text{N}=\text{O}$ , which is formed when no acid is present. Furthermore, the observation of two fundamental  $\text{N}=\text{O}$  stretching frequencies and of three other fundamental frequencies made it clear that at least four atoms and two  $\text{N}=\text{O}$  groups were present in the molecule. In order to ascertain how the  $\text{N}=\text{O}$  groups were bonded to each other, three additional isotopic forms of nitric oxide ( $^{15}\text{N}^{16}\text{O}$ ,  $^{14}\text{N}^{18}\text{O}$ , and  $^{15}\text{N}^{18}\text{O}$ ) were used for the experiment. Table VI has already shown some of the results for the  $\text{BF}_3$  system. Table IX shows the results for all four isotopic forms

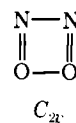
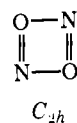
**Figure 6.** Infrared spectrum of  $\text{NO} + \text{BF}_3$  at 77 K.**Table X.** Observed and Calculated Isotopic Shifts ( $\text{cm}^{-1}$ )<sup>a</sup> for  $\nu_1$ ,  $\nu_2$ , and  $\nu_3$  of the  $\text{NO} + \text{BCl}_3$  Red Species

	obsd	$\text{O}=\text{N}-\text{O}=\text{N}$	$\text{O}=\text{N}-\text{N}=\text{O}$	$\text{N}=\text{O}-\text{O}=\text{N}$	$\text{O}=\text{N} \cdots \text{N}$
			$^{15}\text{N}^{16}\text{O}$		
$\nu_1$	28	32	32	32	32
$\nu_2$	29	30	30	30	33
$\nu_3$	7	9	16	0	7
			$^{14}\text{N}^{18}\text{O}$		
$\nu_1$	52	47	47	47	47
$\nu_2$	49	45	45	45	45
$\nu_3$	10	12	0	28	13
			$^{15}\text{N}^{18}\text{O}$		
$\nu_1$	83	79	79	79	79
$\nu_2$	80	76	76	76	73
$\nu_3$	16	21	16	28	22

<sup>a</sup> Relative to the  $^{14}\text{N}^{16}\text{O}$  system; calculations based on the harmonic oscillator approximation except for the T-shaped structure, for which the Wilson FG method was used.

of  $\text{NO}$  reacted with  $\text{BCl}_3$ . In addition to confirming the previous assignment of fundamentals, overtones, and combination bands, the isotopic study was important for discriminating between various possible structures for the red species. The observed frequency shifts for  $\nu_1$ ,  $\nu_2$ , and  $\nu_3$  as well as the calculated shifts for four possible structures of the red species are shown in Table X. It is evident from the shifts that  $\nu_1$  and  $\nu_2$  do indeed arise from  $\text{N}=\text{O}$  stretchings and that  $\nu_3$  is most likely due to a nitrogen-oxygen linkage. Clearly, no  $\text{N}-\text{N}$  or  $\text{O}-\text{O}$  bonds are present. However, the isotopic shift calculations do not exclude the possibility of a T-shaped molecule. Preliminary molecular orbital calculations on this structure, however, suggest that this configuration would be considerably less stable than a chain structure  $\text{O}=\text{N}-\text{O}=\text{N}$ .<sup>16</sup> A different T configuration, with the positions of the nitrogen and oxygen atoms reversed so that an oxygen is closest to the top of the T, was excluded owing to incompatibility with the observed shifts.

Two cyclical structures of formula  $\text{N}_2\text{O}_2$  were also considered. These, however, were eliminated after consideration of



**Table XI.** Vibrational Assignment for the Asymmetric ON-ON Molecule

	assignment <sup>a</sup>	frequency, cm <sup>-1</sup>
$\nu_1$	-O=N stretch	1778
$\nu_2$	-N=O stretch	1690
$\nu_3$	=N-O= stretch	482
$\nu_4$	-O=N-O= bend	184
$\nu_5$	-N=O-N= bend	116
$\nu_6$	torsion	not obsd

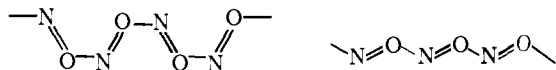
<sup>a</sup> Assignments for  $\nu_1$  and  $\nu_2$  may be reversed, and  $\nu_4$  and  $\nu_5$  may be reversed.

the spectroscopic data. The planar  $\overline{\text{O=N-O=N}}$  structure has  $C_{2h}$  symmetry and a center of symmetry. The mutual exclusion rule requires that such molecules have no infrared and Raman coincidences, but, in fact, both  $\nu_1$  and  $\nu_2$  were observed in both infrared and Raman spectra. Thus, this structure can be eliminated.

The second cyclic structure  $\overline{\text{O=N-N=O}}$  has  $C_{2v}$  symmetry in which both NO groups are equivalent. For this kind of structure, the two observed N=O stretches would correspond to symmetric and antisymmetric stretches. Since these two frequencies are separated by about 90 cm<sup>-1</sup>, a substantial interaction force constant would have to be present to give rise to this splitting. The consequence of this would be that in a mixing experiment (such as <sup>14</sup>N<sup>16</sup>O + <sup>15</sup>N<sup>16</sup>O) six separate N=O stretching frequencies should be observed: two each for the species <sup>14</sup>N=<sup>16</sup>O-<sup>14</sup>N=<sup>16</sup>O, <sup>15</sup>N=<sup>16</sup>O-<sup>15</sup>N=<sup>16</sup>O, and <sup>14</sup>N=<sup>16</sup>O-<sup>15</sup>N=<sup>16</sup>O. The frequencies for the first two species would be the same as those observed for the unmixed <sup>14</sup>N<sup>16</sup>O and <sup>15</sup>N<sup>16</sup>O studies, respectively. However, the species containing both <sup>14</sup>N and <sup>15</sup>N would show significantly shifted symmetric and antisymmetric frequencies relative to the unmixed systems, and in addition they should have approximately double the intensity. In the actual mixing experiment carried out, a 1:1 mixture of <sup>14</sup>N<sup>16</sup>O and <sup>15</sup>N<sup>16</sup>O was reacted with BCl<sub>3</sub>. In the N=O stretching region four bands were observed at 1774, 1754, 1685, and 1663 cm<sup>-1</sup>. For  $\nu_3$ , bands at 481 and 472 cm<sup>-1</sup> were observed and for  $\nu_4$  and  $\nu_5$  unresolved bands at 183 and 115 cm<sup>-1</sup> were recorded. For practical purposes, the spectrum appeared as an overlap of <sup>14</sup>N<sup>16</sup>O + BCl<sub>3</sub> and <sup>15</sup>N<sup>16</sup>O + BCl<sub>3</sub> spectra recorded separately. A similar mixing experiment using <sup>15</sup>N<sup>16</sup>O and <sup>15</sup>N<sup>18</sup>O resulted in bands at 1745, 1694, 1648, 1614, 473, 467, 182, 178, and 115 cm<sup>-1</sup>. These results led to the conclusion that the coupling between N=O groups in the red species is very small, and a structure such as the  $C_{2v}$   $\overline{\text{O=N-N=O}}$  is not compatible with the observations.

The conclusion from the isotopic data, therefore, is that the red species is in fact the asymmetric nitric oxide dimer O=N-O=N. Preliminary molecular orbital calculations suggest that this probably has a planar cis conformation.<sup>16</sup> The vibrations expected for this molecule are correlated with the observed frequencies for the BCl<sub>3</sub> + NO system in Table XI. It is not obvious whether the -N=O or -O=N stretching should be at a higher frequency. Consequently, the assignments for  $\nu_1$  and  $\nu_2$  may need to be reversed. Furthermore,  $\nu_4$  and  $\nu_5$  may also be reversed. The  $\nu_3$  band near 480 cm<sup>-1</sup>, however, clearly corresponds to an N-O stretching mode, and this is of great value in characterizing the molecule.

The possibility that the molecule is a polymer rather than a simple dimer has also been considered. For example, the following structures might be possible:



For either of these structures  $\nu_2$  near 1680 cm<sup>-1</sup> would correspond to the -N=O- stretch,  $\nu_3$  near 480 cm<sup>-1</sup> to the

**Table XII.** Harmonic Frequencies (cm<sup>-1</sup>)<sup>a</sup> and Anharmonicity Constants (cm<sup>-1</sup>)<sup>b</sup> for Isotopic Species of NO + BCl<sub>3</sub>

	<sup>14</sup> N <sup>16</sup> O	<sup>15</sup> N <sup>16</sup> O	<sup>14</sup> N <sup>18</sup> O	<sup>15</sup> N <sup>18</sup> O
$\omega_1$	1796	1767	1744	1712
$\omega_2$	1709	1679	1659	1627
$\omega_3$	486	479	476	470
$\omega_4$	185	184	181	180
$\omega_5$	117	116	116	115
$x_{11}$	[-9] <sup>c</sup>	[-9]	[-9]	[-9]
$x_{22}$	-9.3 (0.5)	-8.9 (0.5)	-8.7 (0.5)	-8.4 (0.5)
$x_{33}$	-2.1 (1.0)	-2.0 (1.0)	-2.0 (1.0)	-1.9 (1.0)
$x_{44}$	-0.3 (0.4)	-0.3 (0.4)	-0.3 (0.4)	-0.3 (0.4)
$x_{55}$	[-0.3] <sup>d</sup>	[-0.3]	[-0.3]	[-0.3]
$x_{23}$	-2.0 (2.8)	-1.9 (2.7)	-1.8 (2.6)	-1.8 (2.5)
$x_{24}$	-0.5 (0.5)	-0.5 (0.5)	-0.4 (0.5)	-0.4 (0.5)
$x_{34}$	-0.2 (1.1)	-0.2 (1.1)	-0.2 (1.0)	-0.2 (1.0)

<sup>a</sup> Uncertainties for the  $\omega_i$  are  $\pm 2$  cm<sup>-1</sup>. <sup>b</sup> Uncertainties calculated for the  $x_{ij}$  are given in parentheses. <sup>c</sup> Estimated from  $x_{22}$  values. <sup>d</sup> Estimated from  $x_{44}$  values.

=O-N= stretch, and  $\nu_4$  and  $\nu_5$  near 180 and 115 cm<sup>-1</sup> would represent bending motions. The  $\nu_1$  band would have to correspond to the stretching of a terminal -N=O or O=N-group.<sup>17</sup> The drawback to a polymer model is that  $\nu_1$  is very intense in the infrared spectra, much more so than would be expected from an end group.

It should again be reiterated that no changes in the spectral features of the acids were observed. This implies that at most a weak interaction between the acid and O=N-O=N is present, and the likelihood of species resulting from electron transfer, such as BF<sub>3</sub><sup>-</sup> and ONON<sup>+</sup>, is small. Nonetheless, the presence of an acid is necessary (except in the special ONCl case) for the creation of the red molecular species. EPR spectra were of little value in providing additional information about the electron pairing since the weak signal obtained may have been due to free NO.

More detail on the experiments described above and on related results can be found elsewhere.<sup>18</sup>

### Calculations

In order to verify that the spectral data for the four different isotopic forms of ONON was consistent with expectation and in order to better understand the bonding forces in the molecule, a force constant calculation was carried out. Since numerous overtone and combination bands were observed for the molecule, the harmonic frequencies and anharmonicity constants could be calculated.<sup>19</sup> These are shown in Table XII. The anharmonicity constants are small as can clearly be seen in the table. The harmonic frequencies were used for carrying out force constant calculations for *cis*-ONON, *trans*-ONON, skewed ONON, and the T-shaped ON<sub>2</sub>O. Results for the first of these, which is believed to be the most probable structure, will be presented here. Calculations for the other structures can be found elsewhere.<sup>18</sup>

The internal coordinates selected for the calculation were

**Table XIII.** Adjusted Force Constants<sup>a</sup> for Three Configurations of Asymmetric ON-ON

	cis	skewed	trans
$k_{\text{N-O}}$	1.029 (0.026) <sup>b</sup>	1.029 (0.008)	1.005 (0.008)
$k_{\text{O=N-}}$	12.770 (0.026)	12.774 (0.025)	12.768 (0.025)
$k_{\text{-O=N}}$	14.122 (0.027)	14.129 (0.026)	14.117 (0.026)
$k_{\text{ONO}}$	0.163 (0.092)	0.169 (0.006)	0.208 (0.004)
$k_{\text{NON}}$	0.122 (0.058)	0.096 (0.004)	0.076 (0.002)
$k_{\text{ONO,NON}}$	0.032 (0.023)	0.0 <sup>c</sup>	0.0 <sup>c</sup>

<sup>a</sup> Stretching constants in mdyn/Å; bending and bend-bend interaction constants in mdyn Å. <sup>b</sup> Uncertainty is given in parentheses. <sup>c</sup> Assumed.

Table XIV. Observed and Calculated Harmonic Frequencies ( $\text{cm}^{-1}$ ) of the Various Isotopic Species of *cis*-ONON

assignment	$^{16}\text{O}^{14}\text{N}^{16}\text{O}^{14}\text{N}$		$^{16}\text{O}^{15}\text{N}^{16}\text{O}^{15}\text{N}$		$^{18}\text{O}^{14}\text{N}^{18}\text{O}^{14}\text{N}$		$^{18}\text{O}^{15}\text{N}^{18}\text{O}^{15}\text{N}$	
	obsd	calcd	obsd	calcd	obsd	calcd	obsd	calcd
$\omega_1$ -O=N str	1796	1795	1767	1763	1744	1747	1712	1714
$\omega_2$ O=N- str	1709	1707	1679	1677	1659	1662	1627	1631
$\omega_3$ O-N str	486	488	479	480	476	476	470	467
$\omega_4$ ONO bend	185	186	184	184	181	180	180	178
$\omega_5$ NON bend	117	118	116	116	116	116	115	114

Table XV. Potential Energy Distribution for *cis*-ONON

	$k_{\text{N-O}}$	$k_{\text{O=N-}}$	$k_{\text{N=O-}}$	$k_{\text{ONO}}$	$k_{\text{NON}}$	$k_{\text{ONO,NON}}$
$\omega_1$	0.001	0.000	0.997	0.001	0.001	0.000
$\omega_2$	0.002	0.996	0.000	0.001	0.001	0.000
$\omega_3$	0.927	0.002	0.002	0.040	0.018	0.012
$\omega_4$	0.006	0.002	0.001	0.766	0.504	-0.278
$\omega_5$	0.064	0.000	0.000	0.246	0.529	0.162

Table XVI. Observed and Calculated Harmonic Frequencies ( $\text{cm}^{-1}$ ) for *cis*-ONON from  $^{14}\text{N}^{16}\text{O} + ^{15}\text{N}^{16}\text{O}$  Mixing and  $^{15}\text{N}^{16}\text{O} + ^{15}\text{N}^{18}\text{O}$  Mixing

	obsd		calcd			
	$^{15}\text{N}^{16}\text{O} + ^{15}\text{N}^{18}\text{O}$	$^{16}\text{O}^{14}\text{N}^{16}\text{O}^{14}\text{N}$	$^{16}\text{O}^{14}\text{N}^{16}\text{O}^{15}\text{N}$	$^{16}\text{O}^{15}\text{N}^{16}\text{O}^{14}\text{N}$	$^{16}\text{O}^{15}\text{N}^{16}\text{O}^{15}\text{N}$	
$\omega_1$	1792, 1770	1795	1763	1795	1763	
$\omega_2$	1704, 1681	1707	1707	1677	1677	
$\omega_3$	485, 476	488	488	479	479	
$\omega_4$	184	186	186	185	185	
$\omega_5$	116	118	116	118	116	
	$^{15}\text{N}^{16}\text{O} + ^{15}\text{N}^{18}\text{O}$	$^{16}\text{O}^{15}\text{N}^{16}\text{O}^{15}\text{N}$	$^{16}\text{O}^{15}\text{N}^{18}\text{O}^{15}\text{N}$	$^{18}\text{O}^{15}\text{N}^{16}\text{O}^{15}\text{N}$	$^{18}\text{O}^{15}\text{N}^{18}\text{O}^{15}\text{N}$	
$\omega_1$	1763, 1710 <sup>a</sup>	1763	1714	1763	1714	
$\omega_2$	1667, 1632 <sup>b</sup>	1677	1677	1631	1631	
$\omega_3$	477, 471	480	480	467	467	
$\omega_4$	183, 179	184	184	178	178	
$\omega_5$	116	116	114	116	114	

<sup>a</sup> The infrared values are 1761 and 1713  $\text{cm}^{-1}$ . <sup>b</sup> The infrared values are 1671 and 1635  $\text{cm}^{-1}$ .

the two N=O stretches, the N-O stretch, and the two angle bends. The sixth vibration, corresponding to a torsion, was neglected since this out of plane motion has different symmetry and does not mix in with the other modes. The geometrical parameters selected for the calculation were bond lengths  $r_{\text{N=O}} = 1.16 \text{ \AA}$ ,  $r_{\text{N-O}} = 1.74 \text{ \AA}$ , and bond angles  $\angle\text{ONO} = \angle\text{NON} = 107^\circ$ . Six nonzero force constants, five diagonal and one interaction constant, were used to obtain the best fit between the 20 calculated and observed frequency values using the Wilson FG method. The final values for the constants are shown for three structures of ONON in Table XIII. The observed and calculated frequencies are given in Table XIV and the potential energy distribution (PED) in terms of the force constants is presented in Table XV. The frequency fit is very good, giving substance to our conviction that the structure of the red species is indeed *cis*-ONON. The PED shows that except for the angle bending motions the vibrations are relatively uncoupled. This has already been noted as a fact necessary to explain the isotopic mixing experiments. In fact, the mixing data are reproduced well when the set of force constants in Table XIII is used to calculate frequencies for the mixed isotopic species. This is shown in Table XVI where the observed and calculated frequencies for the mixing experiment are shown. Owing to the broadness of peaks and some overlap resulting in apparent merging of peaks the observed frequencies are in somewhat poorer agreement with the calculated values, but the fit is still highly satisfactory. This is especially true in that the observed number of bands matches that expected from the calculation.

It is important to note that reversal of the assignment of the

O=N- stretch to 1794  $\text{cm}^{-1}$  and the -O=N stretch to 1709  $\text{cm}^{-1}$  would have no net adverse effect on the calculation. The values of  $k_{\text{N=O-}}$  and  $k_{\text{O=N-}}$  would simply need to be reversed. That is, the higher force constant corresponds to the higher frequency, no matter which N=O group gives rise to it. In similar fashion, the angle bending assignments and force constants may be reversed with no drastic effects.

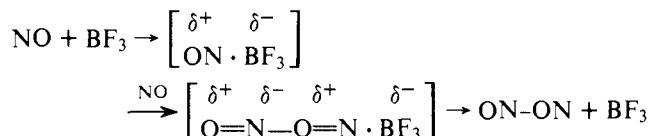
It is interesting to compare the force constants of asymmetric O=N-O=N to those reported<sup>20</sup> for symmetric O=N-N=O. For the latter molecule the values are  $k_{\text{N=O}} = 14.51$ ,  $k_{\text{N-N}} = 0.57$ , and  $k_{\text{ONN}} = 0.15$ . Thus, the red asymmetric dimer apparently has somewhat weaker N=O bonding but a significantly stronger bond joining the two NO groups (1.03 vs. 0.57  $\text{mdyn/\AA}$ ). The bending constants are all very similar.

## Discussion

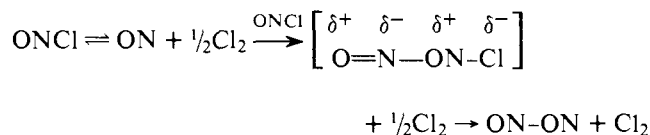
From the spectroscopic studies it is evident that the same molecular species is responsible for the red color whenever nitric oxide is reacted at 77 K with a Lewis acid, HCl, or  $\text{SO}_2$ . The same molecule can also be isolated from ONCl. Use of the various isotopic forms of nitric oxide demonstrated that a weak N-O linkage joins two N=O groups. The red species is thus most likely the dimer O=N-O=N, although a multimer or polymer cannot be ruled out with certainty. The weakness of the N-O bond is reflected by the fact that there is very little vibrational interaction between the two N=O groups, and by the small magnitudes of its vibrational frequency (482  $\text{cm}^{-1}$ ) and force constant (1.03  $\text{mdyn/\AA}$ ). For *cis*-HONO the N-O stretching constant has been calculated<sup>21</sup> to be 2.74  $\text{mdyn/\AA}$

and the N-O frequency was observed at 850 cm<sup>-1</sup>. Similarly, symmetric N<sub>2</sub>O<sub>3</sub> (O=N-O-N=O) has stronger N-O bonding as reflected by the observed<sup>22</sup> stretching frequency at 969 cm<sup>-1</sup>. Dinitrogen pentoxide<sup>23</sup> (O<sub>2</sub>N-O-NO<sub>2</sub>) has the two N-O stretching frequencies at 860 and 353 cm<sup>-1</sup>.

The stabilization of asymmetric ON-ON at low temperatures offers some insight into the reaction occurring between nitric oxide and the various acids. In the presence of an inert chemical environment nitric oxide readily dimerizes to form symmetric ON-NO, of which the cis form is most stable (see Table VIII). In the presence of various Lewis acids, SO<sub>2</sub>, or HCl at low temperatures a colored species is formed in which nitric oxide dimerizes to the asymmetric form ON-ON. Infrared and Raman spectra indicate that the various acids appear unaffected in the colored mixtures. A reasonable mechanism by which the ON-ON is formed is given below.



The initial intermediate is a donor-acceptor complex between the acid and nitric oxide. Similar intermediates have been proposed in the reaction of nitric oxide with tri-*n*-butylborane, BR<sub>3</sub>, to form R<sub>2</sub>NOBR<sub>2</sub>.<sup>24</sup> Further reaction with nitric oxide forms a second intermediate which leads to the observed products. An analogous reaction scheme can be rationalized using BCl<sub>3</sub>, SiF<sub>4</sub>, TiCl<sub>4</sub>, SnCl<sub>4</sub>, and SO<sub>2</sub>. For the red-colored species observed in excess ONCl the following mechanism is proposed:



Nitrosyl chloride exists in equilibrium with NO and Cl<sub>2</sub> and from this mixture an intermediate can be formed which leads to ON-ON and Cl<sub>2</sub>. The mechanism by which ON-ON is formed from NO and HCl is not immediately obvious, but an intermediate involving species such as (NOH)<sup>+</sup>, or (ONONH)<sup>+</sup>, or (ONON)<sup>+</sup> and (HCl)<sup>-</sup> or Cl<sup>-</sup>, is possible, leading to ON-ON and HCl.

The origin of the intense colors (λ<sub>max</sub> ~500 nm) observed in the various NO + acid mixtures is most likely a charge transfer process involving an electronic transition between ONON and the acid. This kind of process can tend to form a weak attraction between the ONON and free acid. The fact that ν<sub>1</sub> for the BF<sub>3</sub> system is about 30 cm<sup>-1</sup> higher than for the other systems suggests that at least some interaction between ONON and the acid is present.

An alternative explanation for the color (and λ<sub>max</sub> ~500 nm absorption) of the ON-ON species can be based on assigning the transition between π-type orbitals within the N<sub>2</sub>O<sub>2</sub> system itself. Some idea of possible orbitals can be obtained by examining the calculations by Gimarc on C<sub>2</sub>O<sub>2</sub><sup>2-</sup> and related systems (although the calculations were carried out for symmetric systems).<sup>25</sup>

Molecular orbital calculations are underway<sup>16</sup> in order to better understand the bonding in the O=N-O=N molecule. Other systems in which this same species (e.g., NO + catalytic surfaces) may be formed are also being investigated. In addition, the reactions of other nitrogen oxides with BF<sub>3</sub> (and other Lewis acids), which are known to form B<sub>2</sub>O<sub>3</sub> and NOBF<sub>4</sub> at room temperature,<sup>26,27</sup> will also be reinvestigated in light of the present study.

**Acknowledgment.** The authors wish to thank the Robert A. Welch Foundation for financial support. The valuable assistance of Dr. N. A. Matwiyoff of Los Alamos Scientific Laboratory in helping us obtain <sup>14</sup>N<sup>18</sup>O and <sup>15</sup>N<sup>18</sup>O samples is gratefully acknowledged.

## References and Notes

- (1) W. H. Rodebush and T. O. Yntema, *J. Am. Chem. Soc.*, **45**, 332 (1923).
- (2) G. R. Finlay, *J. Chem. Educ.*, **24**, 149 (1947).
- (3) W. L. Jolly, "The Inorganic Chemistry of Nitrogen", W. A. Benjamin, New York, N.Y., 1964, p 75.
- (4) R. D. Peacock and I. L. Wilson, *J. Chem. Soc. A* 2030 (1969).
- (5) I. C. Hisatsune and P. Miller, Jr., *J. Chem. Phys.*, **38**, 49 (1963).
- (6) D. F. Shiver, "The Manipulation of Air-Sensitive Compounds", McGraw-Hill, New York, N.Y., 1969.
- (7) J. Hecklen, *J. Phys. Chem.*, **70**, 112 (1966).
- (8) L. H. Jones, R. R. Ryan, and L. B. Asprey, *J. Chem. Phys.*, **49**, 581 (1968).
- (9) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds", 2nd ed., Wiley-Interscience, New York, N.Y., 1970.
- (10) W. G. Fateley, H. A. Bent, and B. L. Crawford, Jr., *J. Chem. Phys.*, **31**, 204 (1959).
- (11) D. E. Tevault and L. Andrews, *J. Phys. Chem.*, **77**, 1646 (1973).
- (12) W. A. Guillory and C. E. Hunter, *J. Chem. Phys.*, **50**, 3516 (1969).
- (13) N. Gee, D. Nicholls, and V. Vincent, *J. Chem. Soc.*, 5897 (1964).
- (14) J. E. Rauch and J. C. Decius, *Spectrochim. Acta*, **22**, 1963 (1966).
- (15) G. E. McGraw, D. L. Bernitt, and I. C. Hisatsune, *Spectrochim. Acta, Part A*, **23**, 25 (1967).
- (16) M. M. Strube and J. Laane, unpublished results.
- (17) The mixing experiment indicates that there is minimal coupling between adjacent N=O groups, whether the structure be a dimer or a polymer.
- (18) J. R. Ohlsen, Ph.D. thesis, Texas A&M University, 1977.
- (19) G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules", Van Nostrand, Princeton, N.J., 1945, p 205.
- (20) D. M. Eshelman, F. J. Torre, and J. Bigeleisen, *J. Chem. Phys.*, **60**, 420 (1974).
- (21) W. A. Guillory and C. E. Hunter, *J. Chem. Phys.*, **54**, 598 (1971).
- (22) E. L. Varetto and G. C. Pimentel, *J. Chem. Phys.*, **55**, 3813 (1971).
- (23) I. C. Hisatsune, J. P. Devlin, and Y. Wada, *Spectrochim. Acta*, **18**, 1641 (1962).
- (24) M. Inatome and L. R. Kuhn, *Adv. Chem. Ser.*, **42**, 183 (1964).
- (25) B. M. Gimarc, *J. Am. Chem. Soc.*, **92**, 266 (1970).
- (26) J. C. Evans, H. W. Rinn, S. J. Kuhn, and G. A. Olah, *Inorg. Chem.*, **3**, 857 (1964).
- (27) A. B. Ray, *Inorg. Chem.*, **6**, 110 (1967).