

The high resolution infrared spectroscopy of cyanogen di-N-oxide (ONCCNO)

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The high-resolution infrared absorption spectrum of the oxalodinitrile di-N-oxide (ONCCNO) molecule has been recorded in the gas phase with a Fourier transform spectrometer at a resolution of 0.003 cm^{-1} . No previous high-resolution spectra have been recorded for this semistable palindromic molecule. On the basis of the 2:1 intensity alternation in the rotational lines caused by nitrogen nuclear spin statistics, the ONCCNO molecule appears to be linear. A quasilinear structure, however, cannot be ruled out at this stage of the analysis. The ν_4 and ν_5 fundamental modes at $2246.040\ 55(23)\text{ cm}^{-1}$ and $1258.475\ 30(11)\text{ cm}^{-1}$ have been analyzed to give ground state rotational constants of $B_0=0.042\ 202\ 10(96)\text{ cm}^{-1}$ and $D_0=8.77(70)\times 10^{-10}\text{ cm}^{-1}$. By fixing the CN and NO bond lengths to 1.1923 and 1.1730 Å, respectively, the C–C bond length was determined to be 1.3329 Å using the B_0 value. This short C–C bond length is thus similar to that observed for a carbon–carbon double bond. © 1995 American Institute of Physics.

INTRODUCTION

The cyanogen di-N-oxide (oxalodinitrile di-N-oxide, ONCCNO) molecule was first prepared at the beginning of this century.¹ However, its chemical formula and isolation were not achieved until the early 1960s by Grundmann.^{2,3} The ONCCNO molecule was prepared in organic solutions by HCl elimination from the stable dichloroglyoxime (HON=C(Cl)–(Cl)C=NOH) precursor. Two strong infrared absorption peaks at 2190 and 1235 cm^{-1} were observed in CCl_4 solution. The ultraviolet spectrum, which contains maxima at 312, 295, and 262 nm, can be obtained with a

freshly prepared solution of ONCCNO in *n*-hexane before polymerization occurs to make polyfuroxan.³ Since dilute solutions are stable at 0°C for several hours, ONCCNO has been widely used in organic chemistry for 1,3-dipolar cycloaddition reactions.⁴

The ONCCNO molecule is a candidate for astrophysical observation since it contains only the relatively abundant elements C, N, and O. The symmetric CNO dimer structure is also of spectroscopic and structural interest since there is the possibility of quasilinear behavior as found in HCNO.⁵ The symmetric linear CNO dimer ONCCNO has no dipole moment so that pure rotational spectra will be very weak and infrared or ultraviolet observations will be necessary.

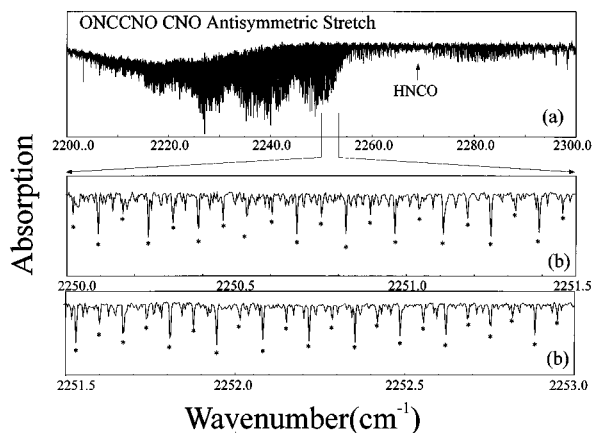


FIG. 1. (a) An overview of the $\nu_4\ \sigma_u$ CNO antisymmetric stretching mode of the ONCCNO molecule. Note the lines due to the HNCO molecule near 2270 cm^{-1} . (b) An expanded portion of the R branch 2:1 intensity alternation caused by the nuclear spin statistics of two equivalent nitrogen nuclei in a linear molecule.

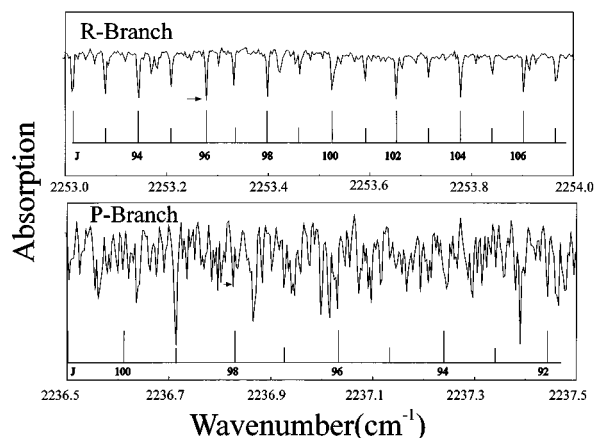


FIG. 2. Portions of R and P branches of the ν_4 mode of the ONCCNO molecule. The J quantum numbers are for the fundamental band and the perturbed R(96) and P(98) lines are marked by arrows.

TABLE I. The line list for the ν_4 vibrational mode of ONCCNO (cm^{-1}).

Line	OBS	OMC ^a $\times 10^4$	Line	OBS	OMC $\times 10^4$	Line	OBS	OMC $\times 10^4$
P(101)	2236.5060	-8	P(53)	2241.3072	27	P(5)	2245.6118	-49
P(100)	2236.6118	-1	P(52)	2241.4013	22	P(4)	2245.6935	-83
P(99)	2236.7160	-9	P(51)	2241.4966	32	P(3)	2245.7812	-56
P(98)	2236.8269	53	P(50)	2241.5893	17	P(2)	2245.8638	-77
P(97)	2236.9284	23	P(49)	2241.6858	43	R(1)	2246.2950	-54
P(96)	2237.0320	17	P(48)	2241.7782	30	R(2)	2246.2950	24
P(95)	2237.1364	19	P(47)	2241.8715	28	R(3)	2246.3702	-61
P(94)	2237.2421	39	P(46)	2241.9647	27	R(4)	2246.4529	-69
P(93)	2237.3436	17	P(45)	2242.0581	30	R(5)	2246.5382	-49
P(92)	2237.4446	-8	P(44)	2242.1510	31	R(6)	2246.6200	-61
P(91)	2237.5485	0	P(43)	2242.2427	21	R(7)	2246.7011	-80
P(90)	2237.6514	-1	P(42)	2242.3361	30	R(8)	2246.7855	-63
P(89)	2237.7516	-26	P(41)	2242.4287	33	R(9)	2246.8691	-53
P(88)	2237.8557	-11	P(40)	2242.5205	31	R(10)	2246.9513	-54
P(87)	2237.9575	-16	P(39)	2242.6120	27	R(11)	2247.0333	-56
P(86)	2238.0600	-12	P(38)	2242.7041	31	R(12)	2247.1181	-28
P(85)	2238.1623	-7	P(37)	2242.7953	29	R(13)	2247.1974	-53
P(84)	2238.2651	4	P(36)	2242.8852	16	R(14)	2247.2806	-37
P(83)	2238.3634	-27	P(35)	2242.9770	23	R(15)	2247.3624	-33
P(82)	2238.4667	-6	P(34)	2243.0666	10	R(16)	2247.4447	-22
P(81)	2238.5661	-22	P(33)	2243.1527	-36	R(17)	2247.5253	-27
P(80)	2238.6689	-1	P(32)	2243.2526	59	R(18)	2247.6062	-26
P(79)	2238.7669	-26	P(31)	2243.3397	27	R(19)	2247.6881	-14
P(78)	2238.8686	-12	P(30)	2243.4298	28	R(20)	2247.7683	-17
P(77)	2238.9684	-15	P(29)	2243.5196	27	R(21)	2247.8501	-1
P(76)	2239.0690	-7	P(28)	2243.6081	15	R(22)	2247.9302	-1
P(75)	2239.1677	-16	P(27)	2243.6979	18	R(23)	2248.0123	21
P(74)	2239.2681	-6	P(26)	2243.7865	11	R(24)	2248.0898	-1
P(73)	2239.3673	-5	P(25)	2243.8740	-5	R(25)	2248.1665	-29
P(72)	2239.4666	-1	P(24)	2243.9639	5	R(26)	2248.2514	27
P(71)	2239.5654	0	P(23)	2244.0515	-7	R(27)	2248.3291	13
P(70)	2239.6629	-10	P(22)	2244.1396	-10	R(28)	2248.4094	27
P(69)	2239.7629	7	P(21)	2244.2282	-8	R(29)	2248.4895	41
P(68)	2239.8599	-3	P(20)	2244.3156	-15	R(30)	2248.5708	68
P(67)	2239.9585	4	P(19)	2244.4029	-22	R(31)	2248.6387	-36
P(66)	2240.0548	-8	P(18)	2244.4907	-22	R(32)	2248.7207	3
P(65)	2240.1539	8	P(17)	2244.5765	-39	R(33)	2248.7988	5
P(64)	2240.2507	5	P(16)	2244.6640	-38	R(34)	2248.8785	25
P(63)	2240.3482	11	P(15)	2244.7505	-45	R(35)	2248.9567	31
P(62)	2240.4448	9	P(14)	2244.8374	-46	R(36)	2249.0333	24
P(61)	2240.5415	11	P(13)	2244.9236	-52	R(37)	2249.1097	17
P(60)	2240.6367	1	P(12)	2245.0107	-48	R(38)	2249.1880	30
P(59)	2240.7338	11	P(11)	2245.0969	-50	R(39)	2249.2650	33
P(58)	2240.8287	2	P(10)	2245.1795	-87	R(40)	2249.3414	33
P(57)	2240.9276	35	P(9)	2245.2674	-68	R(41)	2249.4181	36
P(56)	2241.0207	11	P(8)	2245.3533	-68	R(42)	2249.4935	29
P(55)	2241.1168	21	P(7)	2245.4385	-73	R(43)	2249.5689	25
P(54)	2241.2121	23	P(6)	2245.5231	-83	R(44)	2249.6450	29
R(45)	2249.7211	35	R(73)	2251.7420	-6	R(101)	2253.5926	14
R(46)	2249.7967	38	R(74)	2251.8111	-6	R(102)	2253.6543	3
R(47)	2249.8708	29	R(75)	2251.8792	-13	R(103)	2253.7177	11
R(48)	2249.9443	16	R(76)	2251.9475	-16	R(104)	2253.7804	14
R(49)	2250.0198	24	R(77)	2252.0167	-9	R(105)	2253.8425	13
R(50)	2250.0941	24	R(78)	2252.0846	-11	R(106)	2253.9047	15
R(51)	2250.1678	18	R(79)	2252.1528	-8	R(107)	2253.9687	37
R(52)	2250.2425	26	R(80)	2252.2202	-11	R(108)	2254.0281	15
R(53)	2250.3149	12	R(81)	2252.2873	-15	R(109)	2254.0896	16
R(54)	2250.3890	18	R(82)	2252.3550	-11	R(110)	2254.1513	21
R(55)	2250.4622	16	R(83)	2252.4212	-19	R(111)	2254.2115	12
R(56)	2250.5334	-3	R(84)	2252.4884	-15	R(112)	2254.2727	16
R(57)	2250.6075	9	R(85)	2252.5563	-2	R(113)	2254.3330	12
R(58)	2250.6802	10	R(86)	2252.6224	-4	R(114)	2254.3936	14
R(59)	2250.7532	15	R(87)	2252.6876	-14	R(115)	2254.4542	17
R(60)	2250.8248	9	R(88)	2252.7542	-6	R(116)	2254.5137	10
R(61)	2250.8970	10	R(89)	2252.8202	-3	R(117)	2254.5730	4
R(62)	2250.9681	3	R(90)	2252.8850	-9	R(118)	2254.6332	8

TABLE I. (Continued.)

Line	OBS	OMC ^a ×10 ⁴	Line	OBS	OMC ×10 ⁴	Line	OBS	OMC ×10 ⁴
R(63)	2251.0405	12	R(91)	2252.9512	0	R(119)	2254.6923	3
R(64)	2251.1115	9	R(92)	2253.0164	2	R(120)	2254.7497	-19
R(65)	2251.1820	2	R(93)	2253.0807	-2	R(121)	2254.8104	-4
R(66)	2251.2515	-12	R(94)	2253.1465	10	R(122)	2254.8690	-10
R(67)	2251.3233	0	R(95)	2253.2110	13	R(123)	2254.9284	-6
R(68)	2251.3940	3	R(96)	2253.2800	61	R(124)	2254.9856	-23
R(69)	2251.4636	-4	R(97)	2253.3339	-39			
R(70)	2251.5333	-7	R(98)	2253.4004	-10			
R(71)	2251.6030	-8	R(99)	2253.4645	-4			
R(72)	2251.6724	-9	R(100)	2253.5281	0			

^aObserved minus calculated line positions.

Pure samples of ONCCNO are difficult to handle. Crystalline, monomeric ONCCNO is stable at -78 °C but begins to visibly decompose near -45 °C and explodes a few minutes later at that temperature.⁶ Maier and Teles⁷ have reported the formation of ONCCNO by flash vacuum pyrolysis of dichloroglyoxime followed by condensation of the pyrolysis products diluted with argon on a cold (10 K) window, although they published no spectroscopic data. Until very recently no gas phase measurements have been made. Pasinszki and Westwood⁸ have successfully studied gaseous ONCCNO by He I photoelectron spectroscopy, photoionization mass spectrometry, low-resolution midinfrared spectroscopy as well as *ab initio* calculations. The strong IR absorption bands at 2226 and 1260 cm^{-1} correspond to the antisymmetric ($\nu_4 \sigma_u$) and symmetric ($\nu_5 \sigma_u$) CNO group stretching vibrations, respectively, which were reported earlier at 2190 cm^{-1} and 1235 cm^{-1} in CCl_4 solution.² Unfortunately, the *ab initio* calculations did not provide a solid conclusion as to whether the ONCCNO molecule was linear or bent although a linear or quasilinear structure was preferred. High-resolution gas phase spectroscopy can supply additional information on the molecular geometry.

In this work, we report on our high-resolution Fourier transform infrared spectra of the cyanogen di-N-oxide molecule. The ν_4 and ν_5 vibrational modes have been recorded in the gas phase and these two fundamental bands have been rotationally analyzed.

EXPERIMENT

The ONCCNO molecule was generated *in situ* using the same method as described by Pasinszki and Westwood.⁸ Briefly, the thermolysis of dichloroglyoxime in a quartz tube (8 mm i.d. by 15 cm) heated to 550 °C gives a good yield of ONCCNO plus HCl with only trace amounts of the side products, NO, CO, CO_2 , and HNCO. The experimental setup is typical for absorption spectroscopic work using a cell and a glower external to the spectrometer. The infrared glower was collimated by a parabolic mirror and passed through a 20 cm long absorption cell equipped with KBr windows and entered the spectrometer through the emission port. The thermolysis products were pumped slowly through the gas cell at a pressure of about 250 mTorr.

The high-resolution absorption spectra were recorded with a Bruker FTS 120 HR spectrometer at the University of Waterloo with a resolution of 0.003 cm^{-1} . The ν_4 mode, near 2250 cm^{-1} , was recorded with an InSb detector and 46 scans were coadded in the 1800–2900 cm^{-1} region. A redpass filter with a cutoff at 2900 cm^{-1} set the upper wave number limit while the lower wave number limit was set by the band gap of the InSb detector. A HgCdTe detector was used to record the ν_5 mode at 1260 cm^{-1} and the spectrum was obtained by coadding 55 scans. Another redpass filter (cutoff at 1672 cm^{-1}) set the high wave number limit and the HgCdTe detector response set the lower limit. A KBr beam-splitter was used for both spectra.

ANALYSIS

The spectral analysis program PC-DECOMP, developed by J. W. Brault, was used for the spectral line measurements. Using this program, the line profiles were fitted with Voigt lineshape functions. The signal-to-noise ratio for the strongest lines in the spectrum was about 5:1 and the precision of the line position measurement is better than ± 0.0006 cm^{-1} .

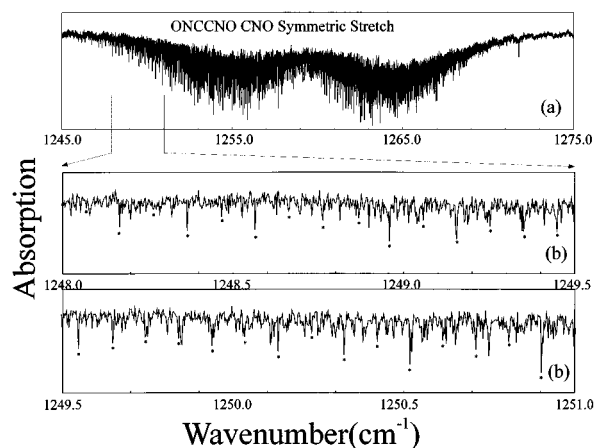


FIG. 3. (a) An overview of the $\nu_5 \sigma_u$ CNO symmetric stretching mode of the ONCCNO molecule. (b) An expanded portion of the P branch of the ν_5 mode. The marked lines are for the fundamental band and show the 2:1 intensity alternation caused by nuclear spin statistics.

TABLE II. The line list for the ν_5 vibrational mode of ONCCNO (cm^{-1}).

Line	OBS	OMC ^a $\times 10^4$	Line	OBS	OMC $\times 10^4$	Line	OBS	OMC $\times 10^4$
P(141)	1245.2485	-8	P(91)	1250.2297	-3	P(43)	1254.7237	17
P(140)	1245.3501	-8	P(90)	1250.3266	-2	P(42)	1254.8133	11
P(139)	1245.4511	-14	P(89)	1250.4230	-5	P(41)	1254.9029	6
P(138)	1245.5539	-1	P(88)	1250.5197	-3	P(40)	1254.9938	17
P(137)	1245.6538	-18	P(87)	1250.6146	-18	P(39)	1255.0824	5
P(136)	1245.7571	2	P(86)	1250.7119	-8	P(38)	1255.1724	9
P(135)	1245.8595	12	P(85)	1250.8084	-3	P(37)	1255.2619	9
P(134)	1245.9588	-9	P(84)	1250.9041	-6	P(36)	1255.3495	-8
P(132)	1246.1625	3	P(83)	1251.0000	-6	P(35)	1255.4401	5
P(131)	1246.2639	7	P(82)	1251.0954	-9	P(34)	1255.5297	10
P(130)	1246.3645	1	P(81)	1251.1900	-19	P(33)	1255.6180	4
P(129)	1246.4661	8	P(80)	1251.2861	-12	P(32)	1255.7068	4
P(128)	1246.5682	20	P(79)	1251.3782	-45	P(31)	1255.7953	2
P(127)	1246.6675	5	P(78)	1251.4765	-13	P(30)	1255.8839	3
P(126)	1246.7681	3	P(77)	1251.5712	-17	P(29)	1255.9785	66
P(125)	1246.8691	6	P(76)	1251.6663	-15	P(28)	1256.0604	2
P(124)	1246.9693	2	P(75)	1251.7599	-26	P(27)	1256.1479	-4
P(122)	1247.1692	-8	P(74)	1251.8548	-24	P(26)	1256.2365	2
P(121)	1247.2708	5	P(73)	1251.9529	12	P(25)	1256.3248	7
P(120)	1247.3707	2	P(72)	1252.0471	11	P(24)	1256.4110	-8
P(119)	1247.4702	-5	P(71)	1252.1422	19	P(23)	1256.4993	-1
P(118)	1247.5708	1	P(70)	1252.2388	45	P(22)	1256.5858	-10
P(117)	1247.6710	3	P(69)	1252.3308	25	P(21)	1256.6706	-35
P(116)	1247.7707	2	P(68)	1252.4228	7	P(20)	1256.7611	-1
P(115)	1247.8707	4	P(67)	1252.5177	20	P(19)	1256.8483	1
P(114)	1247.9705	6	P(66)	1252.6103	10	P(18)	1256.9351	0
P(113)	1248.0706	11	P(65)	1252.7040	13	P(17)	1257.0212	-6
P(112)	1248.1694	5	P(64)	1252.7963	4	P(16)	1257.1077	-7
P(111)	1248.2683	1	P(63)	1252.8893	2	P(15)	1257.1935	-14
P(110)	1248.3675	1	P(62)	1252.9827	7	P(14)	1257.2815	3
P(109)	1248.4676	10	P(61)	1253.0757	8	P(13)	1257.3661	-13
P(108)	1248.5659	4	P(60)	1253.1677	1	P(12)	1257.4531	-3
P(107)	1248.6640	-4	P(59)	1253.2602	2	P(11)	1257.5348	-45
P(106)	1248.7631	0	P(58)	1253.3528	3	P(10)	1257.6248	-3
P(105)	1248.8620	2	P(57)	1253.4454	6	P(9)	1257.7121	13
P(104)	1248.9600	-4	P(56)	1253.5368	-2	P(8)	1257.7955	-7
P(103)	1249.0583	-5	P(55)	1253.6289	0	P(7)	1257.8792	-24
P(102)	1249.1552	-19	P(54)	1253.7215	7	P(6)	1257.9625	-43
P(101)	1249.2539	-13	P(53)	1253.8108	-17	P(5)	1258.0506	-14
P(100)	1249.3526	-6	P(52)	1253.9049	9	P(4)	1258.1367	-2
P(99)	1249.4490	-21	P(51)	1253.9938	-17	P(3)	1258.2158	-59
P(98)	1249.5476	-14	P(50)	1254.0868	0	P(2)	1258.3060	-4
P(97)	1249.6489	23	P(49)	1254.1764	-16	R(0)	1258.5586	-10
P(96)	1249.7448	6	P(48)	1254.2649	-41	R(1)	1258.6400	-37
P(95)	1249.8409	-7	P(47)	1254.3594	-5	R(2)	1258.7253	-24
P(94)	1249.9385	-4	P(46)	1254.4502	-4	R(3)	1258.8090	-26
P(93)	1250.0344	-17	P(45)	1254.5420	8	R(4)	1258.8938	-15
P(92)	1250.1328	4	P(44)	1254.6334	18	R(5)	1258.9819	31
R(6)	1259.0618	-5	R(37)	1261.5807	1	R(68)	1263.9685	43
R(7)	1259.1431	-25	R(38)	1261.6610	14	R(69)	1264.0432	44
R(8)	1259.2277	-10	R(39)	1261.7395	10	R(70)	1264.1157	24
R(9)	1259.3120	2	R(40)	1261.8182	10	R(71)	1264.1925	48
R(10)	1259.3933	-15	R(41)	1261.8965	7	R(72)	1264.2650	31
R(11)	1259.4753	-22	R(42)	1261.9743	1	R(74)	1264.4080	-18
R(12)	1259.5590	-11	R(43)	1262.0541	16	R(75)	1264.4821	-15
R(13)	1259.6425	-1	R(44)	1262.1311	4	R(76)	1264.5557	-15
R(14)	1259.7250	1	R(45)	1262.2068	-20	R(77)	1264.6317	10
R(15)	1259.8069	-3	R(46)	1262.2844	-22	R(78)	1264.7058	17
R(16)	1259.8887	-5	R(47)	1262.3642	-2	R(79)	1264.7775	2
R(17)	1259.9706	-5	R(48)	1262.4413	-6	R(80)	1264.8526	22
R(18)	1260.0534	5	R(49)	1262.5188	-7	R(81)	1264.9215	-19
R(19)	1260.1345	-1	R(50)	1262.5973	6	R(82)	1264.9950	-12
R(20)	1260.2168	7	R(51)	1262.6726	-13	R(83)	1265.0673	-16
R(21)	1260.2981	6	R(52)	1262.7506	-4	R(84)	1265.1411	-3
R(22)	1260.3788	1	R(53)	1262.8277	-2	R(85)	1265.2183	46
R(23)	1260.4605	7	R(54)	1262.9042	-4	R(86)	1265.2838	-22

TABLE II. (Continued.)

Line	OBS	OMC ^a ×10 ⁴	Line	OBS	OMC ×10 ⁴	Line	OBS	OMC ×10 ⁴
R(24)	1260.5413	5	R(55)	1262.9810	-2	R(87)	1265.3573	-9
R(25)	1260.6240	24	R(56)	1263.0565	-12	R(88)	1265.4311	10
R(26)	1260.7024	1	R(57)	1263.1349	9	R(89)	1265.5064	44
R(27)	1260.7838	10	R(58)	1263.2101	-1	R(90)	1265.5734	-3
R(28)	1260.8644	11	R(59)	1263.2857	-5	R(91)	1265.6459	7
R(29)	1260.9450	15	R(60)	1263.3637	16	R(92)	1265.7157	-10
R(30)	1261.0247	10	R(61)	1263.4382	3	R(93)	1265.7862	-18
R(31)	1261.1037	0	R(62)	1263.5143	9	R(94)	1265.8591	-2
R(32)	1261.1837	3	R(63)	1263.5893	4	R(95)	1265.9321	18
R(33)	1261.2644	12	R(64)	1263.6646	3	R(96)	1266.0000	-13
R(34)	1261.3437	9	R(65)	1263.7410	16	R(97)	1266.0745	24
R(35)	1261.4228	6	R(66)	1263.8161	15	R(98)	1266.1414	-14
R(36)	1261.5028	13	R(67)	1263.8925	31	R(99)	1266.2132	-1

^aObserved minus calculated line positions.

for these lines. However, many of the weaker lines and the blended features were determined only to a precision of about $\pm 0.005 \text{ cm}^{-1}$.

An interactive color Loomis–Wood computer program was used to pick out the branches and helped to assign the spectra. The CO molecule was present in the cell as a side product of the thermolysis. The measured spectral lines of the ν_4 vibrational mode were calibrated with the CO lines using line positions taken from the literature.⁹ For the ν_5 vibrational mode, we used the water absorption for calibration.¹⁰

The ν_4 fundamental mode

Figure 1 shows the high-resolution spectrum of the CNO antisymmetric stretching mode ($\nu_4 \sigma_u$) of ONCCNO. The HNCO molecule is present on the high wave number side of the overview spectrum [Fig. 1(a)]. Figure 1(b) is an expanded portion of the *R* branch of the ν_4 fundamental. The alternation in intensities is caused by the nuclear spin statistics of two equivalent ($I=1$) nitrogen atoms. The symmetrically located nitrogen atoms cause an intensity alternation of 2:1 with the even J'' values being stronger.

The main problem in the analysis was the presence of a large number of hot bands which causes a line density as high as 100 lines/cm⁻¹. It was impossible to locate the band origin because of the overlapping hot bands. The final J assignments were achieved with the help of a small local perturbation at $J'=97$ in the upper level. Figure 2 shows the perturbed *R*(96) and *P*(98) lines. The *R*(96) line was shifted by 0.005 cm^{-1} to higher wave numbers while the *P*(98) line was shifted by the same amount. There are several other small local perturbations in this band which also confirm the assignments. In total, 230 rotational lines were assigned for the ν_4 band and they are listed in Table I.

The ν_5 fundamental mode

The high-resolution spectrum of the CNO symmetric stretching mode ($\nu_5 \sigma_u$) is shown in Fig. 3(a). An expanded portion of the *P* branch is shown in Fig. 3(b), again demonstrating the 2:1 intensity alternation due to nitrogen nuclear spin statistics. The measurement and assignment of ν_5 pro-

ceeded in the same way as for ν_4 . The ν_5 mode also had a high line density but no perturbations were present to help the assignment. The rotational assignment of ν_5 was made by changing the relative assignment of the *P* and *R* branches until the ground state combination differences matched those of ν_4 . About 200 lines were assigned and the complete line list is shown in Table II.

The rotational constants

The line positions (Tables I and II) of the two fundamental bands were fitted together in a global least-squares fit. The energy level expression

$$F(J) = \nu_0 + BJ(J+1) - D[J(J+1)]^2 + H[J(J+1)]^3$$

was used in the fit and the resulting rotational constants are listed in Table III. The ground state B_0 constant, $0.042\,202\,10 \text{ cm}^{-1}$ (1.265 187 GHz), is in good agreement with the *ab initio* prediction⁸ of 1.24–1.25 GHz. The centrifugal distortion constants of the excited ν_4 vibrational level may be perturbed by interaction with other modes.

DISCUSSION AND CONCLUSION

The semistable cyanogen di-N-oxide (ONCCNO) molecule can be generated *in situ* with a good yield in the gas phase from the precursor molecule dichloroglyoxime by thermolysis. The high-resolution spectra of the ONCCNO molecule have been obtained for the two strongest vibrational modes ν_4 and ν_5 . The rotational analysis of these two modes and the intensity alternation of the lines indicates that the ONCCNO molecule is not bent.

TABLE III. The rotational constants for ONCCNO (in cm⁻¹). One standard deviation is in parentheses.

Level	ν_0	B	10^9D	$10^{14}H$
Ground	0.0	0.042 202 10(96)	0.877(70)	...
ν_4	1258.475 30(11)	0.042 133 64(98)	1.071(74)	1.196(38)
ν_5	2246.040 55(23)	0.042 109 39(97)	1.978(73)	3.503(96)

TABLE IV. Estimated geometry of ONCCNO.^a

Parameter	Structure I	Structure II
$r_{\text{NO}}/\text{\AA}$	1.1994 ^b	1.1923 ^c
$r_{\text{CN}}/\text{\AA}$	1.1679 ^b	1.1730 ^c
$r_{\text{CC}}/\text{\AA}$	1.3337 ^d	1.3329 ^d
$\angle\text{ONC}$	180.0°	180.0°
$\angle\text{NCC}$	180.0°	180.0°

^aLinear framework assumed.^b r_s bond lengths from HCNO, Ref. 11.^cSee text for details.^dBond length calculated using experimental rotational constant.

Indications from the *ab initio* calculations, and comparisons with similar molecules, suggest that the important CC bond is quite short.⁸ The single B value obtained in this work is insufficient to provide this parameter without some assumptions about the CN and NO bond lengths. One approach to this problem is to use the known CN and NO bond lengths in the parent HCNO molecule,¹¹ and assuming a linear structure, extract the CC value from the rotational constant (B_0) determined in this work. Table IV, structure I, shows the structure of ONCCNO, predicted by this method. This, of course, assumes that the CN and NO bond lengths are transferable from HCNO.

A possible improvement on this method is to see how a computational method [MP3(full)/6-31G*]⁷ performs for both HCNO and ONCCNO, and then “correct” the CN and NO values and apply them to ONCCNO. With these “refined” CN and NO bond lengths, the mutual effect of back-to-back CNO groups should be taken into account, and, using the experimental rotational constant, a value for the CC bond length is obtained. This assumes that the differences between the CN and NO bond lengths in HCNO and ONCCNO are predicted correctly by the MP3 method. Table IV, structure II, shows the revised values for ONCCNO. This structure which takes into account the interaction of the two CNO groups, indicates that the NO bond length has slightly decreased, while the CN bond length has slightly increased, in accord with expectations based on a more delocalized framework.

Both the directly transferred CN and NO lengths, and the corrected values, lead to the result that the CC bond length is about 1.333 Å, approximately the same as that in ethylene, H₂CCH₂, a molecule of known double bond character. Table V shows CC bond lengths for a range of molecules. An important observation is that the experimental CC bond length in cyanogen, NC-CN is 1.389 Å,¹² already much shorter than a typical CC single bond and we anticipate that this will decrease upon adding terminal oxygen atoms (compare H₃CCN and H₃CCNO in Table V). We note that MP3(full)/6-31G* calculations for NCCN predict CC to be 1.393 Å, with similar calculations for ONCCNO predicting CC to be 1.361 Å.⁸ The inference from this is that the CC length in ONCCNO is at least 0.03 Å less than that in NCCN.

Clearly, experimental and theoretical studies on this molecule have a long way to go before a full characterization is

TABLE V. The C–C bond lengths (r_0) in simple organic molecules.

Molecule	Method	$r_{\text{C-C}}$ (Å)
H ₃ C–CH ₃	IR	1.536 ^a
H ₃ C–C≡N	MW	1.4582 ^b
H ₃ C–C≡NO	MW	1.442 ^c
N≡C–C≡N	IR	1.389 ^d
HC≡C–C≡N	MW	1.382 ^e
H ₂ C=CH ₂	IR	1.337 ^f
ONC–CNO	IR	1.3329 ^g
HC≡CH	IR	1.20862 ^h

^aReference 13.^bReference 14.^cReference 15.^dReference 12.^eReference 16.^fReference 17.^gThis work.^hReference 18.

achieved. For example, the possibility of quasilinear behavior cannot be ruled out at this stage of the analysis. We plan additional experiments to record spectra of the much weaker bending vibrational modes as well as combination bands. This work will help assign the numerous hot bands that we have measured and will provide information on the missing modes of gerade symmetry.

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¹W. Steinkopf and B. Jürgens, *J. Prakt. Chem.* **83**, 453 (1911).²Ch. Grundmann, *Angew. Chem.* **75**, 450 (1963); *Angew. Chem. Int. Ed. Engl.* **2**, 260 (1963).³Ch. Grundmann, V. Mini, J. M. Dean, and H.-D. Frommelt, *Justus Liebigs Ann. Chem.* **687**, 191 (1965).⁴(a) N. E. Alexandrou and D. N. Nicolaidis, *J. Chem. Soc. C*, 2319 (1969); (b) D. N. Nicolaidis and T. A. Kouimtzis, *Chem. Chron.* **3**, 63 (1974); (c) A. Gül, A. I. Okur, A. Cihan, N. Tan, and Ö. Bekaroglu, *J. Chem. Res. (S)*, 90 (1986); (d) S. Serin and Ö. Bekaroglu, *Z. Anorg. Allg. Chem.* **496**, 197 (1983); (e) Y. Gök and Ö. Bekaroglu, *Synth. React. Inorg. Met.-Org. Chem.* **11**, 621 (1981); (f) V. Ahsen, E. Musluoglu, A. Gürek, A. Gül, Ö. Bekaroglu, and M. Zehnder, *Helv. Chim. Acta* **73**, 174 (1990); (g) Y. Gök and S. Serin, *Synth. React. Inorg. Met.-Org. Chem.* **18**, 975 (1988); (h) Y. Gök and A. Demirbas, *ibid.* **19**, 681 (1989).⁵B. P. Winnewisser, *Molecular Spectroscopy: Modern Research*, edited by K. N. Rao (Academic, New York, 1985), Vol. 3.⁶Ch. Grundmann and P. Grünanger, *The Nitrile Oxides* (Springer-Verlag, New York, 1971).⁷G. Maier and J. H. Teles, *Angew. Chem.* **99**, 152 (1987); *Angew. Chem. Int. Ed. Engl.* **26**, 155 (1987).⁸T. Pasinszki and N. P. C. Westwood, *J. Am. Chem. Soc.* (to be published).⁹A. G. Maki and J. S. Wells, *Wavenumber Calibration Tables from Heterodyne Frequency Measurements* (NIST Special Publication 821, Washington DC, 1991).¹⁰R. A. Toth, *J. Opt. Soc. Am. B* **8**, 2236 (1991).¹¹(a) H. K. Bodenseh and M. F. Winnewisser, *Z. Naturforsch. A* **24**, 1973 (1969); (b) B. P. Winnewisser, M. F. Winnewisser, and F. Winther, *J. Mol. Spectrosc.* **51**, 65 (1974).¹²A. G. Maki, *J. Chem. Phys.* **3**, 3193 (1965).¹³W. J. Lafferty and E. K. Plyler, *J. Chem. Phys.* **37**, 2688 (1962).¹⁴C. C. Costain, *J. Chem. Phys.* **29**, 864 (1958).¹⁵H. K. Bodensen and K. Morgenstern, *Z. Naturforsch.* **25a**, 150 (1970).¹⁶A. A. Westenberg and E. B. Wilson, Jr., *J. Am. Chem. Soc.* **72**, 199 (1950).¹⁷H. C. Allen, Jr. and E. K. Plyler, *J. Am. Chem. Soc.* **80**, 2673 (1958).¹⁸A. Baldacci, S. Ghersetti, S. C. Hurlock, and K. N. Rao, *J. Mol. Spectrosc.* **59**, 116 (1976).