

The Gas-Phase Structure of the Asymmetric, Trans Dinitrogen Tetroxide (N₂O₄), formed by dimerization of Nitrogen Dioxide (NO₂), from Rotational Spectroscopy and *Ab Initio* Quantum Chemistry

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Abstract

We report the first experimental gas-phase observation of an asymmetric, trans N₂O₄ formed by the dimerization of NO₂. In addition to the dominant ¹⁴N₂¹⁶O₄ species, rotational transitions have been observed for all species with single ¹⁵N and ¹⁸O substitutions, as well as several multiply substituted isotopologues. These transitions were used to determine a complete substitution structure as well as an *r*₀ structure from the fitted zero-point averaged rotational constants. The determined structure is found to be that of an ON—O—NO₂ linkage with the shared oxygen atom closer to the NO₂ than the NO (1.42 vs 1.61 Å). The structure is found to be nearly planar with a *trans* O—N—O—N linkage. From the spectra of the ¹⁴N¹⁵N¹⁶O₄ species, we were able to determine the nuclear quadrupole coupling constants for each specific nitrogen atom. The equilibrium structure determined by *ab initio* quantum chemistry calculations is in excellent agreement with the experimentally determined structure. No spectral evidence of the predicted asymmetric, *cis* N₂O₄ was found in the spectra.

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Introduction

There is a rich chemistry of compounds formed from nitrogen and oxygen,^{1,2} which have the general chemical formula N_xO_y , and for each such formula, there are often multiple isomers; the spectroscopic literature on these compounds has been summarized in reviews by Melen and Herman³ and by Laane and Ohlsen.⁴ This class includes many molecules with unusual chemical bonding – two of the most common stable free radicals, NO and NO₂, are of this family. The nature of the chemical bonding in many N_xO_y molecules is a challenge to both elementary chemical models as well as quantum chemistry due to the strong electron correlation effects often found in these molecules and the symmetry-breaking problems that plague NO₂ and NO₃.⁵⁻⁸ In addition to their intrinsic chemical interest, these molecules play important roles in combustion,⁹ atmospheric chemistry,^{10,11} and biology.¹²

The equilibrium between NO₂ and its covalently bound dimer, N₂O₄, is well known to most chemistry undergraduate students from lecture demonstrations or laboratory exercises.¹³ This is one of the few equilibria between common gases that has an equilibrium constant at ambient temperature ($K_p = 4.7 \text{ bar}^{-1} @ 30^\circ\text{C}$)¹⁴ such that both species are present in sizable concentrations. In addition, the fact that the NO₂ monomer is a brown gas and N₂O₄ colorless makes qualitative shifts in concentrations easily observable. The most stable form of nitric dioxide dimer, *s*-N₂O₄, is planar with D_{2h} symmetry.¹⁵ This structure has a center of inversion symmetry and thus is nonpolar; no pure rotational spectrum is expected. Accurate gas phase structural parameters for this dimer are known from electron diffraction¹⁶ and from high resolution IR spectroscopy.¹⁷ The NO bond length, 1.190(1) Å, and ONO bond angle, 135.4(5)°, are close to those of the NO₂

monomer and the N-N bond length, 1.782(8)Å, is long for a covalent bond.¹⁶ A crystal structure, as a function of temperature, is also known.^{15, 18}

Fateley, Brent, and Crawford¹⁹ reported the first IR matrix spectrum of N₂O₄ in 1959. In addition to transitions assigned to the *D*_{2h} structure, they assigned features to higher energy isomers. Three bands, labeled C, were assigned to a structure of *D*_{2d} symmetry for which the planes of the two NO₂ groups are rotated by 90° to one another. They also assigned four peaks, labeled D, to an asymmetric structure with O-N-O-NO₂ bonding. St. Louis and Crawford²⁰ extended this work and assigned eight transitions to the *cis* form of ONO-NO₂ (which they labeled D) and seven to the *trans* form, which they labeled D', with D → D' observed as the matrix was warmed. The structure for the D' form, optimized at the B3LYP-D3/aug-cc-pVTZ level of theory, is shown in Figure 1. Smith and Guillory²¹ observed the formation of “D” peaks when a NO/O₂ matrix was warmed. Bolduan and Jodl^{22, 23} reported Raman spectra and assigned peaks to N₂O₄ structures C, D, and D', as well as four peaks to a NO⁺-NO₃⁻ complex formed in the matrix. There have been subsequent IR²⁴⁻²⁶ and Raman²⁷⁻²⁹ matrix isolation studies, including temperature annealing and photochemistry experiments of NO₂ doped in multiple matrix hosts. Isomers of a peroxide form, ONOONO, have also been predicted.^{30, 31} The asymmetric forms of N₂O₄ have been proposed as intermediates in the oxidation of NO to NO₂²⁶ and conversion of NO₂ to HNO₃.³² In polar solutions, the asymmetric N₂O₄ has been predicted to lead to the formation of NO₃⁻ and NO⁺.³³ There has not been, up to the present work, any gas phase experimental evidence for any of the asymmetric N₂O₄ species, despite earlier assignments in matrix spectroscopy and their important predicted chemical roles. In this work, we report the microwave spectrum of the

trans (D') asymmetric N_2O_4 and derive its structure from isotopic substitution. We did not observe transitions that could be assigned to the predicted *cis* asymmetric N_2O_4 species.

There have been many quantum chemical calculations published on the lowest singlet N_2O_4 potential energy surface, done at a wide range of theoretical methods. In one of the first, Liu and Zhou³⁴ found that the D_{2d} structure is unstable and corresponds to the barrier for internal rotation around the N-N bond of the D_{2h} structure; this has been confirmed by later calculations^{30, 35, 36} and experiments.^{37, 38} The most thorough previous calculation is a determination of the minima and transition states between them published by Liu and Goddard⁵ using a range of models. Stationary points were located using UB3LYP/G-311G** calculations, and they examined the stationary points at various levels of theory, including basis set size extrapolation. They report that two NO_2 molecules can come together on the ground, singlet, electronic surface with no barrier to form the symmetric dimer, with $D_e = 16.5$ kcal/mol at the RCCSD(T)/CBS level. They predict $\Delta G^0_{298} = -1.2$ kcal/mol for the dimerization reaction, compared to an experimentally determined value of -1.14 kcal/mol.¹⁴ The *trans*-asymmetric dimer was found to be the second most stable structure with $D_e = 7.9$ kcal/mol ($\Delta G^0_{298} = 5.3$ kcal/mol), followed by the *cis* asymmetric dimer with $D_e = 5.9$ kcal/mol ($\Delta G^0_{298} = 7.6$ kcal/mol). The *trans*-ONONO₂ form has been proposed as an intermediate in the gas phase hydrolysis reaction $2NO_2 + H_2O \rightarrow HONO + HNO_3$.³⁹ Liu and Goddard also found a weakly bound C_{2v} van der Waals minimum with $D_e = 1.6$ kcal/mol. In this structure, the two NO_2 monomer dipole moments are parallel and their planes 90° to one another, as in the earlier reported D_{2d} structure, but with favorable interaction energy for the two monomer electric dipole moments. Starting with McKee,³⁰ several theoretical studies have found minima

corresponding to peroxide structures (i.e. with an O-N-O-O-N-O chain), one of which is proposed as an intermediate in the reaction $\text{NO} + \text{NO} + \text{O}_2 \rightarrow 2 \text{NO}_2$.

Chirped-pulse Fourier transform microwave (CP-FTMW) spectroscopy is a powerful tool for detection of multiple isomers, and provides rotational transition frequencies that can be used to determine molecular structures.⁴⁰ The initial goal of the present project was to detect novel singlet and triplet isomers of N_2O_4 . Given that the most stable isomer does not have a rotational spectrum and that the NO_2 monomer has only a few low frequency rotational transitions, most of the transitions, sans those of compounds formed from impurities, should be from novel $(\text{NO}_2)_n$ isomers. The ONONO_2 isomers had been predicted to be highly polar which should facilitate their detection. Dipole moments for the *trans* and *cis* forms have been calculated as 3.6 and 4.5 D respectively at the MP2/6-311G* level,⁴¹ and 2.58 and 2.50 D respectively at the higher CCSD(T)/ANO1 level reported herein. While a rich spectrum was observed, the only new gas phase species whose rotational spectrum was assigned is the *trans*-asymmetric dimer. We had access to $^{18}\text{O}_2$ and $^{15}\text{N}^{18}\text{O}_2$ samples, and these were used to prepare isotopically enriched samples, which allowed determination of a complete substitution structure. This work was extended by measurements done on a Balle-Flygare (cavity) Fourier transform microwave spectrometer that covered a lower frequency region and also provided improved spectral resolution, allowing the analysis of the nuclear quadrupole hyperfine structure. This spectrometer was used to observe the spectra N_2O_4 formed from of an ^{15}N enriched sample of NO_2 . This allowed the complete structure to be determined by Kraitchman's equations as well as an unambiguous assignment of the nuclear quadrupole coupling constants for the two distinct N atoms in the structure.

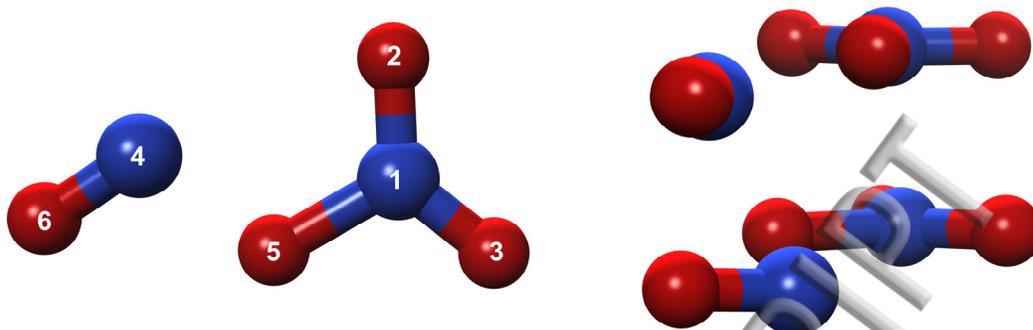


Figure 1. The *trans*-N₂O₄ dimer, optimized at the B3LYP-D3/aug-cc-pVTZ level of theory, shown at various angles. The numbers indicated in the figure will be used to identify different atoms in the structure.

Experimental

The initial experiments were performed on a 18 – 26.5 GHz CP-FTMW spectrometer that was developed by the Pate group at the University of Virginia.⁴² The gas sample used in this phase of the work was made using an isotopically labeled NO₂ mixture containing N¹⁶O¹⁶O, N¹⁸O¹⁶O and N¹⁸O¹⁸O with approximate ratios of 4:3:2, which was prepared by reaction of ¹⁴N¹⁶O gas with O₂ gas that was enriched in ¹⁸O. The reaction product was collected in a liquid N₂ cooled trap, which allowed unreacted O₂ and NO gas to be pumped away. The sample was trap-to-trap distilled (between 77 and 195 K) to reduce low vapor pressure contaminants. This NO₂ gas was then diluted with Ne to form a 0.2% mixture and was supersonically expanded into vacuum through 3 pulsed nozzles with a backing pressure of 1 bar. The sample free induction decay (FID) following chirped-pulse excitation was signal averaged for 200,000 microwave pulses, with 10 microwave pulses per 700 μs long valve pulse, with a valve a repetition rate of 3.3 Hz. Transitions had a 200 kHz full width half maximum.

The N_2O_4 spectrum was also observed with the Balle-Flygare FTMW instrument at Amherst College.⁴³⁻⁴⁶ This allowed extension down to lower frequency transitions and increased resolution, which was useful for assignment of the N-14 hyperfine structure. A gas mixture of 0.2% NO_2 in 1.7 bar of Ar gas was expanded through a 0.8 mm diameter nozzle. The FID after each microwave excitation pulse was digitized at 10 MHz and sampled for 2048 points. The FID was zero-filled to 4096 points and then Fourier transformed, giving a resolution element of 2.44 kHz. Since the molecular beam is parallel to the mirror axis, each transition appears as a Doppler doublet. The rest frequency of the transition is the mean frequency of the two Doppler components. The observed transitions had a FWHM linewidth of approximately 8 – 10 kHz. Due to the complexity of the spectrum of an asymmetric top with two unique quadrupole moments, it was decided to study the spectrum of singly ^{15}N -substituted species. We were no longer able to purchase $^{15}\text{NO}_2$, but Prof. Lester Andrews kindly supplied a $^{15}\text{N}^{18}\text{O}_2$ sample (Isotec) that he had in his chemical inventory. This was mixed with NO_2 gas of normal isotopic composition (supplied by Aldrich) in a ratio of 1:5 and then diluted to 0.2% in Ar.

Calculations

Equilibrium structures, force constants and properties were calculated for the *cis* and *trans* dimer structures as well as the symmetric D_{2h} isomer with coupled-cluster theory in the singles, doubles and perturbative triples (CCSD(T)) approximation.⁴⁷ All isomers were studied with the polarized double-zeta atomic natural orbital basis designated as ANO0,^{48, 49} the *trans* structure featured in this work and the symmetric dimer were also studied with the polarized triple zeta basis ANO1. Equilibrium structures and first order properties (dipole moments and quadrupole hyperfine

coupling constants) were determined using analytic energy gradients,⁵⁰ and numerical differentiation of energy gradients were used to determine the harmonic and anharmonic force fields. Efforts to determine a so-called “semi-experimental” (equilibrium) structure via correction of measured ground state constants (A_0 , B_0 and C_0) to the corresponding equilibrium values (A_e , B_e and C_e) through use of calculated vibrational corrections – a fairly standard procedure⁵¹ – were not satisfactory. This clearly implicates a shortcoming of second-order vibrational theory⁵² (which is used to calculate the vibrational corrections) to treat the large-amplitude motions in the asymmetric dimer. All quantum chemical calculations were done with the CFOUR program package,⁵³ using the frozen-core approximation.

Results

Looking at the full chirped-pulse spectrum, various features of known species including several isotopic forms of N_2O_3 , HNO_2 , and HNO_3 were assigned.⁵⁴⁻⁵⁹ These species, formed from impurities in the sample, accounted for the strongest lines in the spectrum. A rotational temperature of ~ 1 K is estimated based upon the relative intensities of these transitions. Using the *ab initio* rotational constants as a starting point, transitions were assigned to the trans-ONONO₂ structure, including singly and doubly ¹⁸O-substituted forms of this dimer. Transitions of the ¹⁴N₂¹⁶O₄ parent and singly substituted isotopologues are identified in Figure 2. The numbering for the oxygen and nitrogen atoms in the complex are indicated Figure 1. All observed transitions are a-type, which is expected given that *ab initio* calculations at the CCSD(T)/ANO1 (B3LYP-D3/aug-cc-pVTZ) level predict transition electric dipole projections of $\mu_a = 2.383$ (2.724), $\mu_b = 0.191$ (0.239), and $\mu_c = 0.113$ (0.108) Debye for the trans dimer. The observed transitions for each isotopic species were fit to the Watson asymmetric top A reduction Hamiltonian using the SPFIT

program.^{60, 61} Table 1 gives the fitted spectroscopic constants for $t\text{-}^{14}\text{N}_2^{16}\text{O}_4$ as well comparing these constants with two levels of *ab initio* theory. Table 2 gives the fitted spectroscopic constants for the 11 observed isotopically substituted species. A complete listing of assigned transitions is given in Supplementary materials for this paper.

Transitions were observed in the cavity machine in the 12-18 GHz region for $t\text{-}^{14}\text{N}_2^{16}\text{O}_4$ as well as the three species with one or both nitrogen replaced by ^{15}N . The ^{14}N hyperfine structure was resolved and fit and the resulting constants are given in tables 1 and 2.

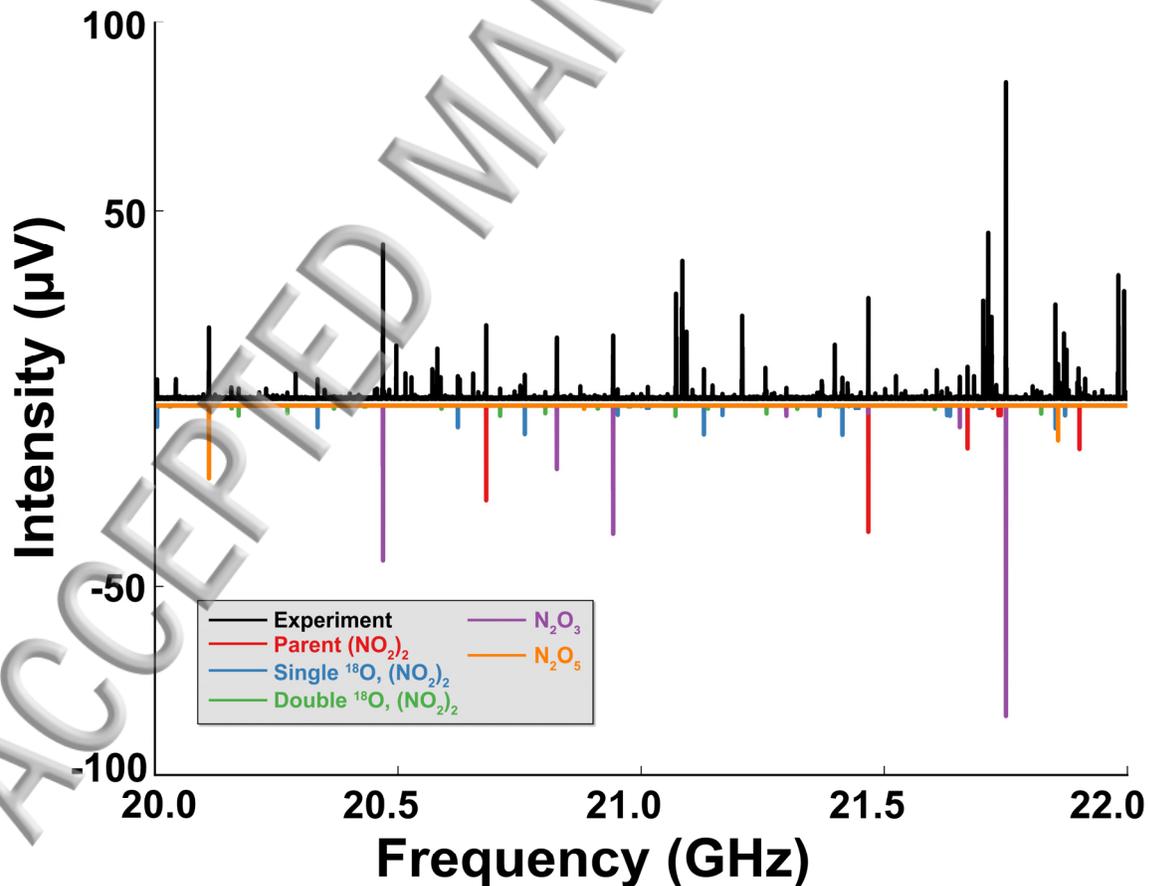


Figure 2. A 2 GHz section of the 18-26.5 GHz spectrum obtained using the chirped-pulse microwave spectrometer. The colored transitions are inverted to show the positions of the predicted transitions given fitted parameters for the given species. Parent refers to the parent isotopic species of the *trans*-N₂O₄ dimer. The predictions for the singly (blue) and doubly (green) substituted ¹⁸O are combined into single composite predictions for simplicity.

	¹⁴ N ₂ ¹⁶ O ₂	ANO0/CCSD(T)		ANO1/CCSD(T)		B3LYP-D3 / aug-cc-pVTZ
	Exp.	equilibrium	Zero pt.	equilibrium	Zero pt.	
<i>A</i> / MHz	11789.49(13)	11682.351	11514.7315	11725.842	11753.5928	11820.3
<i>B</i>	2363.23731(20)	2314.5964	2311.569	2375.5631	2353.6764	2322.4
<i>C</i>	1976.30177(21)	1931.8447	1938.811	1989.9236	1959.2976	1951
Δ_1 / u Å ²	-0.998(33)	0	-1.8556	-1.8712	0.222	-1.33
Δ_J / kHz	0.4020(48)	0.348		0.59		0.62
Δ_{JK}	3.856(70)	3.636		21.5		21.3
Δ_K	[0]	5.889		1.47		1.65
δ_J	0.0313(42)	0.0578		-0.013		-0.00056
δ_K	[0]	2.452		4.92		4.94
χ_{aa} (N1) / MHz	0.6095(13)	0.571		0.6376		0.6
χ_{bb}	-0.5307(17)	-0.309		-0.5537		-0.68
χ_{cc}	-0.0788(18)	-0.262		-0.839		0.086
χ_{aa} (N4) / MHz	-0.1003(12)	0.057		-0.0225		-0.38
χ_{bb}	-2.8854(10)	-3.667		-2.812		-3.05
χ_{cc}	2.9857(10)	3.301		2.8352		3.43
<i>N</i>	128					
σ / kHz	7.2					

Table 1. Fit and predicted rotational constants, distortion constants, and nuclear quadrupole hyperfine coupling constants for *trans*-¹⁴N₂¹⁶O₄. The constants are the result of a combined fit of all transitions from the cavity and chirped-pulse measurements, which include 10 distinct rotational transitions with *J* spanning 1 – 4 and *K* spanning 0 – 2.

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	¹⁵ N-1	¹⁵ N-4	¹⁵ N-1/ ¹⁵ N-4	
A / MHz	11790.63(15)	11747.29(12)	11748.038(31)	
B	2351.86586(39)	2341.15011(25)	2329.654628(41)	
C	1968.36911(37)	1959.92085(26)	1951.884276(39)	
Δ_J / kHz	0.4081(74)	0.4172(50)	0.40629(93)	
Δ_{JK}	3.667(62)	3.585(47)	3.730(29)	
Δ_K	[0]	[0]	[0]	
δ_J	0.0360(76)	0.0341(51)	0.03499(65)	
δ_K	[0]	[0]	[0]	
χ_{aa} (N1) / MHz	--	-0.0995(14)	--	
χ_{bb}	--	-2.8835(23)	--	
χ_{cc}	--	2.9829(23)	--	
χ_{aa} (N4) / MHz	0.6061(10)	--	--	
χ_{bb}	-0.5258(22)	--	--	
χ_{cc}	-0.08033(22)	--	--	
N	46	40	9	
σ / kHz	1.9	1.2	0.9	
	¹⁸ O-2	¹⁸ O-3	¹⁸ O-5	¹⁸ O-6
A / MHz	11033.66(31)	11518.21(40)	11561.13(46)	11770.81(37)
B	2340.9720(21)	2282.8351(22)	2362.1296(25)	2244.9686(16)
C	1938.5594(19)	1912.4629(20)	1969.2519(23)	1892.3680(16)
N	12.4	12.8	12.9	11
σ / kHz	11	10	10	12
	¹⁸ O-6/ ¹⁸ O-2	¹⁸ O-6/ ¹⁸ O-3	¹⁸ O-5/ ¹⁸ O-2	¹⁸ O-5/ ¹⁸ O-3
A / MHz	11015.88(54)	11494.55(50)	10817.57(50)	11306.94(58)
B	2222.5547(26)	2168.8394(16)	2339.5734(36)	2281.4791(24)
C	1856.1647(26)	1831.1803(16)	1931.1367(32)	1905.8610(24)
N	13.1	7.9	10.5	12.5
σ / kHz	9	9	8	9

Table 2. Fit of observed transitions of the isotopically substituted *trans*-N₂O₄ species. The spectroscopic constants distortion constants, and nuclear quadrupole hyperfine coupling constants for *trans*-N₂O₄ are given. The ¹⁵N-substituted isotopologues were only observed with the cavity instrument. All ¹⁸O isotopologue measurements were taken from the chirped-pulse data, and all have their centrifugal distortion constants fixed to those of the parent isotopic species.

Kraitchman's equations express the squares of the distance of an atom from the inertial axes in the coordinate system of a reference isotopic form, $t\text{-}^{14}\text{N}_2^{16}\text{O}_4$ in the present case, in terms of the rotational constants of the reference isotopic form and those of the molecule where that atom has been isotopically substituted.^{62, 63} The set of internal coordinates calculated from these Cartesian coordinates is called the substitution structure (r_s). As is well known, when an atom is nearly on one of the axes, Kraitchman's equations will often determine a negative value for the square of the distance, due to the neglect of vibration-rotation interactions. An alternative procedure is to directly fit a set of internal coordinates to all the moments of inertia calculated from the ground state rotational constants of the twelve observed isotopic forms, neglecting vibration-rotation interactions, which gives what is known as the r_0 structure. We used a program by Z. Kisiel to do this nonlinear least squares fit.^{63, 64} In the case of $t\text{-N}_2\text{O}_4$, we fit five bond lengths, four bond angles, and three dihedral angles, which completely define the structure and then these were used to calculate Cartesian coordinates. The rms of the fit of the moments of inertia was $0.0070 \text{ u}\text{\AA}^2$, which can be compared to the predicted experimental uncertainties of 0.0015, 0.00017, and $0.00024 \text{ u}\text{\AA}^2$ for I_A , I_B , and I_C calculated from standard errors of the spectroscopic fits to the observed transitions. Table 3 compares the equilibrium internal coordinates and Table 4 lists the equilibrium Cartesian coordinates calculated by B3LYP-D2, and CCSD(T)/ANO1 with the values determined from Kraitchman's equation and the r_0 fit. All four sets of structural parameters are in excellent agreement. The r_0 structure is shown in Figure 3. The CCSD(T)/ANO1 structure agrees better with the experimentally determined structures than the B3LYP-D2 structure. The r_0 structure is also in better agreement with the theoretical r_e structure

than the substitution structure. While the overall structure is slightly nonplanar, the NO_3 unit is very nearly planar. It should be noted that the experimentally derived structures, both r_s and r_0 , are effected by vibrational-rotation interactions. The differences of the r_0 and the CCDD(T) r_e structures are within differences expected due to zero point motion.

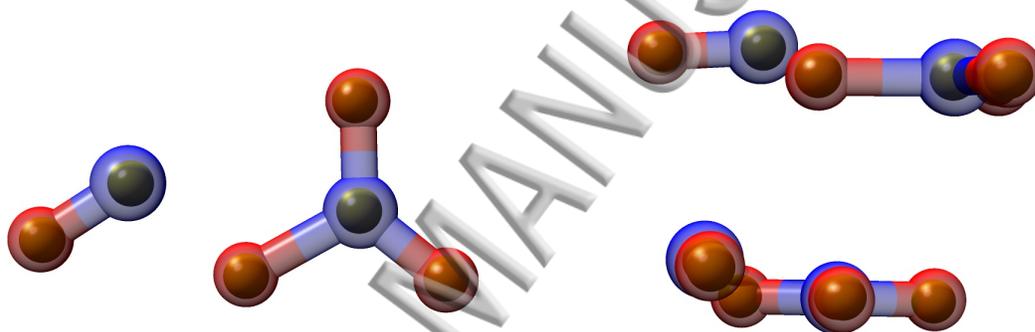


Figure 3 The *trans*- N_2O_4 dimer structure as determined by r_0 analysis. As in Figure 1, the solid spheres are the experimentally determined positions while the semitransparent refer to the B3LYP-D3 calculated geometry.

Parameter	B3LYP-D3	CCSD(T)/ANO1	Kraitchman	r_0
Bond Length / Å				
N1-O2	1.201	1.2053	1.2318(12)	1.2043(29)
N1-O3	1.198	1.2015	1.1836(23)	1.2015(33)
N1-O5	1.424	1.4245	1.3956(68)	1.4202(37)
N4-O5	1.624	1.5908	1.6069(69)	1.6075(30)
N4-O6	1.129	1.1456	1.1368(47)	1.1276(19)
Angle / °				
O2-N1-O5	117.56	117.40	117.12(20)	117.76(33)
O3-N1-O5	112.33	112.22	113.97(21)	110.05(29)
N1-O5-N4	111.77	109.61	111.17(28)	110.05(34)
O5-N4-O6	107.51	107.24	108.1(5)	107.01(30)
Dihedral / °				
O6-N4-O5-N1	175.57	176.57	177.4(10)	176.4(16)
N4-O5-N1-O2	-15.91	-18.86	-12.0(13)	-13.75(35)
N4-O5-N1-O3	164.90	162.25	169.6(22)	167.5(20)

Table 3. Internal coordinates for *trans*-N₂O₄. Calculation from Kraitchman coordinates used signs from B3LYP-D2 calculation and took 0.0 for imaginary coordinates. The r_0 values were determined by the fit of the ground vibrational state rotational constants of all twelve observed isotopologues, using the program STRFIT written by Zbigniew Kisiel.⁶⁴ That fit used the above internal coordinates. The B3LYP-D3 and CCSD(T)/ANO1 values are the calculated equilibrium internal coordinates.

		B3LYP-D3/aVTZ	CCSD(T)/ANO1	Kraitchman	r_0 fit
N1	a (Å)	1.040	1.0247	1.0241(15)	1.0267(16)
	b	0.0268	0.0280	[0.0620]	0.0285(28)
	c	-0.0144	-0.0170	[0.0193]	-0.0099(294)
O2	a	1.039	1.0122	1.0105(15)	1.0105(8)
	b	1.227	1.2325	1.2317(12)	1.2323(7)
	c	-0.050	-0.0608	[0.0476]	-0.0481(99)
O3	a	1.953	1.9435	1.95341(78)	1.9538(5)
	b	-0.742	-0.7370	0.7320(21)	-0.7315(13)
	c	0.087	0.1012	0.038(39)	0.0649(12)
N4	a	-1.457	-1.4116	1.4235(11)	-1.4279(13)
	b	0.380	0.3673	0.3746(41)	0.3798(30)
	c	0.133	0.1599	0.133(11)	0.1244(63)
O5	a	-0.216	-0.2239	0.2071(73)	-0.2162(22)
	b	-0.636	-0.6456	0.6509(23)	-0.6529(13)
	c	-0.125	-0.1469	0.091(17)	-0.0981(83)
O6	a	-2.412	-2.3930	2.39652(63)	-2.3968(3)
	b	-0.205	-0.1960	0.1979(76)	-0.2053(18)
	c	-0.016	-0.0187	[0.047]	-0.0234(84)

Table 4. Coordinates of atoms in the principal axis system of *trans*- $^{14}\text{N}_2^{16}\text{O}_4$. Distances are in Å. Kraitchman's equations give values for the square of coordinates, and thus not signs. Entries given as [...] indicate imaginary results, i.e. negative values returned by Kraitchman's equations. The entries given as [...] need to be replaced with zeros to reproduce the calculated internal coordinates given in Table 3. The r_0 values come from a fit of all twelve observed isotopic forms, using the program STRFIT written by Zbigniew Kisiel.⁶⁴ The r_0 values are unique up to an inversion of all signs for any of the a, b, or c coordinates.

Discussion

As can be seen in Figure 3, the *trans*-NO₂ dimer is better described as NO-NO₃. The N4-O6 bond length, 1.1276(19) Å, is intermediate between the bond lengths of 1.151 Å of NO⁶⁵ and 1.063 Å of NO⁺⁶⁶ and significantly less than the 1.1934 Å bond length in NO₂.⁶⁷ The terminal N1-O2 and N1-O3 bond lengths, ca. 1.20 Å, are intermediate between those of NO₂ and NO₃, 1.24 Å.⁶⁷ The bridging oxygen, O(5), is closer to the triply bound nitrogen atom, (N1-O5), 1.4202(37) Å, than it is to the doubly bound nitrogen atom (N4-O5), 1.6075(30) Å. The N1-O5 bond length is similar to the N-OH single bond lengths found in *t*-HONO, 1.432(5) Å; *c*-HONO,⁵⁶ 1.392(5) Å; HNO₃,⁶⁸ 1.406(5) Å; and H₂NOH,⁶⁹ 1.453(3) Å. The N4-O(5) bond length is longer than for other known covalent N-O bonds and is similar to the N-N bond lengths found in *s*-N₂O₄,¹⁶ 1.782(8) Å, and N₂O₃,⁵⁴ 1.864(7) Å. For comparison, the nitrogen – oxygen bond lengths are 1.24 Å in NO₃,⁷⁰ and 1.155 Å in (NO)₂.⁷¹ One isomer of dinitrogen trioxide has the ON-NO₂ structure, with a NO bond length of 1.139(4) Å for the NO unit, and N-O bond lengths of 1.188(4) Å (*cis*) and 1.217(8) Å (*trans*) on the NO₂ unit.⁷² The symmetric, C_{2v} isomer, ONONO has terminal NO bond lengths calculated [B3LYP/6-311++G(3df)] as 1.153 Å and interior NO bond lengths of 1.484 Å.⁷³ The N₂O₅ molecule has two symmetric NO₂ groups bound by a central O atom. McClelland *et al.* fit electron diffraction data on this molecule to determine that the interior N-O bond lengths are 1.492(4) Å and the terminal ones are 1.183(2) Å.⁷⁴ The interior N-O bond lengths of *trans*-N₂O₄ bracket those of N₂O₅ and the terminal bond lengths are slightly longer.

The equilibrium structure is predicted to be planar at the ANO0/CCSD(T) level and nonplanar, but with a very lower barrier to planarity ($\sim 10 \text{ cm}^{-1}$), at the ANO1/CCSD(T) level. The zero point energy in the corresponding out-of-plane mode is likely above such a low barrier to planarity. There is a large difference in the zero point energy contribution of the inertial defect, Δ , for the two CCSD(T) calculations: For ANO0, Δ decreases by 1.8 u \AA^2 while for ANO1 it increases by 2.09 u \AA^2 . The experimental value is about midway between these two theoretical predictions. A low frequency out-of-plane vibration gives a negative contribution to Δ and a low frequency in-plane vibration a positive contribution. The change in Δ can be rationalized by the creation of a very low frequency out-of-plane mode by the very slightly nonplanar equilibrium in the ANO1 case. This mode is certainly very anharmonic, so the normal mode prediction of Δ is not reliable.

The ANO1/CCSD(T) calculated dipole moment, 2.39 D and pointing approximately from N1 to N4, indicates a contribution of resonance structures with electron transfer from $\text{NO} \rightarrow \text{NO}_3$. The change in the electronic structure upon forming the *t*- N_2O_4 from the NO_2 monomers is also evident from the changes in the quadrupole hyperfine constants. Since *t*- N_2O_4 is nearly planar, it is helpful to look at χ_{cc} values as these will not require correction for changes in orientation of the inertial axes. From table 1, we see that $\chi_{cc} = -0.0788(18)$ and $+2.9857(10)$ MHz for N1 and N4 respectively. For NO_2 , $\chi_{cc} = 1.26$ MHz, and for NO dimer $\chi_{cc} = 6.305$ MHz.⁷⁵ The χ values are nearly the same for the singly substituted species as for the parent, which is consistent with the small calculated rotation of the inertial axes (< 1 mrad) upon isotopic substitution.

An interesting observation is that we have not yet been able to assign any transitions to the *cis* dimer. Liu and Goddard's calculations⁵ predict this form to be less stable ($\Delta H_{298\text{K}}$) than the *trans* dimer by 2.0 kcal/mol, which in turn is predicted less stable than the symmetric dimer by 7.7 kcal/mol. The ANO0/CCSD(T) calculation predict $\Delta H_{0\text{K}} = 2.1$ and 6.8 kcal/mol for the enthalpy differences for the *trans-to-cis* and the symmetric-to-*trans* dimer isomerizations. Direct formation of the *trans* dimer from the monomers is predicted by Liu and Goddard to have an activation enthalpy barrier of 13.2 kcal/mol and 43.9 kcal/mol from the symmetric dimer, but only 2.4 kcal/mol from the *cis* dimer minimum. The transition state between *cis* and *trans* dimers has an enthalpy 1.8 kcal/mol, energy 1.2 kcal/mol, below the monomers. Formation of the *cis* dimer from monomers is calculated to have an activation enthalpy of 1.3 kcal/mol (energy barrier 1.9 kcal/mol), so an initially formed *cis* dimer is predicted to have sufficient internal energy to isomerize to the more stable *trans* dimer unless the third body in the recombination collision takes more than 43% of the energy released upon *cis* complex formation. At 298 K, the equilibrium for the reaction *cis* \rightarrow *trans* is predicted to have an equilibrium constant of 50 and can be expected to grow rapidly as the expansion cools the gas, so the lack of *cis* dimers is rationalized. Based upon the calculated free energy of the *trans* dimer, only about 0.3 ppm of the NO₂ molecules should be in the *trans* dimer well prior to the expansion, so we can presume that the signals we observe are not due to *trans* dimers already present in the gas prior to expansion. The 1.9 kcal/mol calculated energy barrier to formation of an asymmetric N₂O₄ from two isolated NO₂ molecules suggests that formation of this molecule is unlikely in a jet expansion since there is a $e^{-3.2}$ Boltzmann factor at the very beginning of the expansion. It is possible that t-N₂O₄ is formed by more complex

chemistry as was recently invoked by Nava *et al.* to explain the formation of HSNO from H₂S and NO in a similar pulsed supersonic jet instrument.⁷⁶

Supplementary Material

See supplementary material for a complete listing of all assigned rotational transitions, along with residuals of fits to the Spectroscopic constants given in Tables 1 and 2.

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