Electronic Structure Study of the N_2O Isomers Using Post-Hartree–Fock and Density Functional Theory Calculations

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Multilocal minima on the potential energy surface (PES) of the electronic ground state ($X^1\Sigma^+$) of the N_2O molecule are predicted by various ab initio methods. The calculations confirm that the global minimum of the molecule possesses an N–N–O linear structure with $C_{\infty v}$ symmetry, as experiment and other theoretical calculations have recognized. The present calculations also predict other local minima on the energy surface: a less stable cyclic isomer with a C_{2v} symmetry and a least stable linear N–O–N isomer with a $D_{\infty h}$ symmetry. The electronic structures of the local minima indicate that the energy of the system increases if the N–N bond of the molecule becomes weak (the cyclic C_{2v} case) or breaks (the linear $D_{\infty h}$ case). The electronic structure and stabilities of the local minima of the N_2O molecule are also discussed and analyzed using DFT calculations and wave functions, and a qualitative valence bond representation for the $C_{\infty v} \rightarrow C_{2v} \rightarrow D_{\infty h}$ isomerization is provided.

Introduction

One of the fundamental tasks in computational chemistry is the accurate and efficient prediction of molecular geometries, energies, and potential energy surfaces. Traditional quantum mechanical methods, such as Hartree–Fock (HF) and its extensions including electron correlation and perturbation theory, together with appropriate basis sets for the molecular systems under study have been well developed and have been proved to be accurate and reliable. However, the post-HF methods, which take into account electron correlation, are computationally demanding and are not readily extended into larger systems with strong electron correlation. Originally developed from the study of solids, surfaces, and interfaces, density functional theory (DFT)[1,2] offers a promising alternative to the HF approach, since DFT includes electron correlation in a form that does not lead to the scaling problem of the HF-based methods. As a result, DFT has the potential to be applicable to large systems.

There is an opportunity for molecular DFT methods to become a useful and accurate tool in the study of the molecular structure and potential energy surfaces. The practical implementation of DFT leads to effective one-electron Kohn–Sham (KS) equations, which are similar to the HF equations except that in the KS equations the orbital-dependent exchange-correlation (XC) operator of the HF equations are replaced by an XC operator that depends only on the total electron density. This leads to a simpler form of the matrix elements, and the one-particle wave functions can be represented not only by Gaussian-type orbitals but also by a variety of other functions.[3] In the DFT, it is well-known that a significant improvement to the local spin density (LSD) method can be obtained by using functionals that depend on the gradient of the charge density (e.g., refs 4–6). The generalized gradient approximation (GGA) methods are developed as the nonlocal XC corrections to the LSD approximation. Hence, the GGA functionals have revo-

lutionized quantum chemistry, with the best ones working systematically better than LSD approximation and, in some calculations, approaching the accuracy of traditional quantum chemical methods (e.g., configuration interaction) at a fraction of the cost.[5]

Nitrous oxide, N_2O, has been an important subject for a number of scientific fields such as life science,[7] earth science,[8] atmospheric science,[9] and fuel industry.[10] It is also a subject of theoretical[11–15] and experimental studies.[16–18] However, the nature of even the primary structural description for N_2O still brings challenges to both theoreticians and the experimentalists. For the potential energy surface of the N_2O molecule, the majority of structural studies[12,17,19–22] focus on its global minimum.[19,21] For example, more complete IR spectroscopic properties[17,20] were obtained using the potential energy surface of N_2O from either the inversion of the limited available experimental rovibrational data[12,17,23–25] or ab initio calculations. The design of the grid points on the surface in the ab initio calculations is usually limited to the vicinity of the known potential well of the linear $C_{\infty v}$ isomer.[20] In the most recent ab initio calculations for the PES of N_2O, Nakamura and Kato[22] obtained some points that cover a broader N–N–O angle region than many previous studies. However, no other minima were reported in this recent ab initio study as well as in the most recent review regarding its mechanisms of formation.[26] Therefore, there is a need for a comprehensive potential energy surface (PES) of the electronic ground state of N_2O, which covers a sufficiently large angular area and is sufficiently accurate for the study of chemical reactions. In this paper we intend to study the electronic structure of the isomers on the PES for the ground electronic state of N_2O ($X^1\Sigma^+$) using post-HF methods combined with the DFT methods.

Computational Details

The calculations, which identify the structures of the N_2O isomers, have been conducted using various quantum mechanical methods including Hartree–Fock based methods, such as

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N₂O Isomers

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TABLE 1: Comparison of Optimized Global Minimum ($C_{\infty v}$) for the Ground Electronic State ($X^1\Sigma^+$) of N₂O Using Different Quantum Mechanics Methods

method	R_{NN}/Å	Δ/%	R_{NO}/Å	Δ/%	E/E_h	ω_1/cm⁻¹	ω_2/cm⁻¹	ω_3/cm⁻¹	ref
SCF/TZ2P	1.0815	−4.06	1.1723	−1.08		706.9	1355.6	2588.7	19
CISD/TZ2P	1.1073	−1.77	1.1809	−0.35		645.5	1345.9	2419.5	19
CCSD(T)/TZ2P	1.1505	2.06	1.2068	1.83		579	1256	2221	19
CCSD(T)/cc-pVDZ	1.1478	1.82	1.1953	0.86	−184.233 981	601.1	1297.2	2282.8	20, 21
CCSD(T)/cc-pVTZ	1.1329	0.50	1.1896	0.38	−184.407 184	601.1	1297.2	2282.8	20,21
CCSD(T)/cc-pVQZ	1.1291	0.16	1.1870	0.16	−184.461 624	602.1	1303.5	2287.9	20, 21
MP2/6-311++G(d)	1.163	3.12	1.181	0.34	−184.290 030	538	1286	2243	43
CCSD(T)/6-31G*	1.147	1.75	1.208	1.95	−184.222 649 2	546.95	1275.74	2254.89	36
MCSCF/ANO	1.1197	−0.67	1.1864	0.11	−183.937 968 3				this work
CCSD(T)/ANO	1.1303	0.27	1.1896	0.38	−184.443 468 1				this work
VWN/TZVP	1.1375	0.90	1.1855	0.03	−183.348 474 6	618.67	1339.72	2338.12	this work
GGA-BP/TZVP	1.1453	1.60	1.2004	1.29	−184.754 084 4	589.70	1280.65	2253.07	this work
expt[a]	1.1273		1.1851			596.3	1298.3	2282.1	17

[a] The anharmonic vibrational fundamentals of ν for the N₂O molecule were measured with exceptionally high precision,[16,17,40] giving 588.8, 1271.4, and 2223.8 cm⁻¹.

multiconfiguration self-consistent field (MCSCF) and coupled-cluster CCSD(T) methods, as well as density functional theory (DFT) methods with the local spin density (LSD) approximation and generalized gradient approximation (GGA) methods. The LSD calculations invoke an LSD approximation using the Dirac exchange energy functional and the Vosko−Wilk−Nusair (VWN)[27] correlation energy functional. The GGA method uses a gradient-corrected functional based on the BP XC functionals-Becke 88[4,28] for exchange (X)/Perdew 86[29] for the correlation (C) in the calculations.

The Hartree−Fock based (MCSCF and CCSD(T)) calculations were performed using the Roos[30] augmented triple-ζ (TZ) atomic natural orbital (ANO) basis set. For nitrogen and oxygen atoms, the basis functions are thus a well-balanced (14s9p4d3f) basis set contracted to [5s4p3d2f]. The TZ-ANO basis set has been proven[31] to predict adequately the properties of NO with spectroscopic accuracy. In the DFT calculations a triple-ζ valence basis set with polarization (TZVP) is used. Such a basis set is especially designed for DFT calculations of molecules,[3,32] giving the contraction schemes of (7111/411/1). Corresponding to the orbital basis set is an auxiliary basis set called A2[33] to represent the electron density and the XC potential and energy. In the A2 basis set, s-, p-, and d-orbital exponentials were determined separately from optimization that reproduces as accurately as possible the energy from an atomic DFT calculation. The contraction schemes of A2 basis sets for N and O are (8/4/4), respectively.

The MCSCF and CCSD(T) calculations were performed using the MOLPRO96 suite of programs[34] on a Cray J916 computer. The DFT calculations were performed using the UNICHEM4.0 package[35] applying the DGAUSS suite of programs on an SGI-2 workstation and a Cray J90se/82048 computer, employing the computer distribution technique.

Results and Discussion

(a) N−N−O Global Minimum. Table 1 summaries the results of the predicted global minimum for the N₂O molecule from various quantum mechanical methods, including variational methods, perturbation theory, density functional theory, etc. The experimental equilibrium geometry is also given in this table for comparison. The ground state of N₂O is a linear $C_{\infty v}$ symmetry $X^1\Sigma^+$ state. The primary electronic configuration is

$$(1\sigma)^2(2\sigma)^2(3\sigma)^2(4\sigma)^2(5\sigma)^2(6\sigma)^2(1\pi)^4(7\sigma)^2(2\pi)^4$$

and this has been confirmed by experiments and various

theoretical predictions regardless of the levels of theory applied in the calculations. Because both various variational and nonvariational methods are used in the calculations, the total energy is not an appropriate property to make a comparison between those methods; that is, in Table 1 a method that gives a lower total energy of the molecule does not have a direct connection with the better quality of the corresponding calculations. Moreover, we are not aware of any experimental total energy for the N₂O molecule. Therefore, the geometric properties (i.e., R_{NN} and R_{NO}) become the appropriate properties for comparison purposes.

In Table 1, when the same basis set, such as TV2P,[20] is employed in the calculations, the predicted N−N and N−O bond lengths increase slightly as the theory includes more electron correlation. Such a tendency for bond length increase in the calculations can also be seen in the present variational calculations using the ANO basis set. For example, the N−N and N−O bond lengths of 1.1197 and 1.1864 Å are obtained from the MCSCF/ANO calculations, whereas these bond lengths increase by 0.0106 and 0.0032 Å, respectively, when the CCSD-(T)/ANO calculations are conducted. As discussed by Wang and Larkins[31] earlier, this is perhaps due to the fact that the configurations contributing to the wave functions of the configuration interaction (CI) calculations correspond to the CI vectors associated with larger bond distances than that of the primary configuration given by a single determinant SCF calculation.

The coupled-cluster CCSD(T) "variational" calculations using different basis sets, such as TZ2P,[20] cc-pVDZ, cc-pVTZ, cc-pVQZ,[21] 6-31G*,[36] and the ANO basis set in the present work, provide useful information with respect to the goodness of the basis sets employed in this respect. It is apparent that the calculations using TZ2P,[20] cc-pVDZ,[21] and 6-31G*[36] do not give sufficiently accurate predictions of bond lengths and the harmonic vibrational frequencies of the molecule. Though the calculations using a large cc-pVQZ basis set give good predictions of bond lengths and total energy[21] (see Table 1), the shape of the potential well obtained from the corresponding calculations indicates that the cc-pVQZ basis set, which is computationally more demanding, does not guarantee a better description of the curvature of the potential well than does the cc-pVTZ basis set.[21] For a systematic study of the molecular geometry and harmonic vibrational fundamental frequencies of the NNO global minimum with respect to various basis sets at the CISD level of theory, see refs 21 and 37; at the HF level of theory refer to ref 21.

TABLE 2: Properties of the Local Minimum Structures of N_2O Using Various Methods[b]

structure	symmetry	method	R_{NN}/Å	R_{NO}/Å	A_{NON}/(deg)	A_{NNO}/(deg)	E/E_h
linear (N−N−O)	$C_{\infty v}$	CCSD(T)/ANO	1.130	1.190		180.0	−184.443 468
		MCSCF/ANO	1.120	1.186		180.0	−183.937 968
		BP/TZVP	1.145	1.200		180.0	−184.754 084
		VWN/TZVP	1.138	1.186		180.0	−183.348 475
		MP2/6-311++G(d)[a]	1.163	1.181		180.0	−184.290 030
cyclic	C_{2v}	CCSD(T)/ANO	1.188	1.536		67.3	−184.340 025
		MCSCF/ANO	1.163	1.563		68.2	−183.821 393
		BP/TZVP	1.197	1.551		67.3	−184.643 038
		VWN/TZVP	1.188	1.549		67.4	−183.228 979
		MP2(Full)/6-31G*[c]	1.224	1.525		66.3	−184.109 331
		MP2/6-311++G(d)[a]	1.214	1.511		66.4	−184.169 359
linear (N−O−N)	$D_{\infty h}$	CCSD(T)/ANO		1.202	180.0		−184.267 093
		MCSCF/ANO		1.183	180.0		−183.669 661
		BP/TZVP		1.211	180.0		−184.584 744
		VWN/TZVP		1.192	180.0		−183.175 740
		MP2/6-311++G(d)[a]		1.341	180.0		−184.183 851

[a] Reference 43. [b] For experimental results, see ref 17. [c] Recent calculations of Schulz (private communication, 1998).

The predictions obtained from density functional theory (DFT) methods such as BP/TZVP and VWN/TZVP are in reasonable agreement with the experimental observations. The calculations using DFT methods become very attractive if the computer resources requested by the calculation are also taken into account. Moreover, it is interesting to note that the quality of the equilibrium geometry and the vibrational frequencies of N_2O obtained using the BP/TZVP method in the present work competes well with those obtained by the CCSD(T)/6-31G* method of Schulz.[36] Perhaps the apparent difference between the two sets of calculations is that the former is less computer resource demanding.

The vibrational frequencies of the molecule generated by static methods are usually obtained from second derivative calculations under the harmonic oscillator approximation rather than from the "exact" dynamical solutions of the corresponding nuclear Schrödinger equations. In general, the frequencies calculated at the HF level of theory are about 10−12% too high in many cases.[38] This is due to the fact that the electron correlation effects, which are not included in the HF theory, become increasingly important as the molecule is distorted from its ground state geometry under vibrations. Consequently, the curvature of the energy hypersurface at the minimum is overestimated in HF theory.[19] Post-HF and DFT methods are expected to improve the calculations, which has been confirmed in the results presented in Table 1. Therefore, the harmonic vibrational frequencies can assist the understanding of the curvature of the potential well for the molecule. The harmonicity of the fundamental vibrations of a molecule can be indicated by the differences between the two sets of experimentally available vibrational frequencies of the N_2O molecule, that is, the experimental harmonic vibrational fundamental frequencies (ω's)[17,39] and the experimental anharmonic vibrational fundamental frequencies (ν's).[16,17,40] For example, the bending mode of the N−N−O isomer, which is a doubly degenerate bending motion for the linear configuration, exhibits a considerable degree of harmonicity at the vicinity of the potential well, since the harmonic bending frequency ω_1 only has approximately 8 cm^{-1} deviation from its anharmonic bending frequency ν_1 of 588.8 cm^{-1}. Hence, the harmonic oscillator approximation can be considered as a good approximation for the bending motion of the molecule. However, the symmetric stretch mode (ω_2 or ν_2) is not so harmonic because the frequency deviation gives ca. 27 cm^{-1}, and the asymmetric stretch mode (ω_3 or ν_3) is very anharmonic (the frequency deviation is ca. 59 cm^{-1}). As a result, the degree of agreement between the calculations and experiments also reveals the anharmonicity of the vibrations.

(b) N_2O Isomers on the Potential Energy Surface. Perhaps the first local minimum on the N_2O PES reported in the literature is the cyclic isomer obtained by Klapötke and Schulz[41,42] in a study of the dissociation of the N_4O molecule using the MP2/6-31+G* level of theory. This cyclic isomer structure was then confirmed and studied by Galbraith and Schaefer[37] using various ab initio methods. A linear isomer N−O−N with a $D_{\infty h}$ symmetry is reported in the present work as a less stable isomer than the cyclic isomer on the PES of N_2O. As pointed out by Klapötke et al.,[42] searching for the energy minima on a multidimensional potential energy hypersurface is one of the most difficult problems in computational chemistry and it largely depends on experience and on the initial guesses of the molecular geometry. In the previous studies, the majority of initial geometry guesses of the NNO ground-state structural optimizations focused on NNO's global minimum in the vicinity of the experimental geometry of the molecule. For example, the initial guesses were set for the N−N−O angle $\theta \geq 120°$, knowing the fact that the molecule has a $C_{\infty v}$ symmetry. As a result, the optimization with such an initial geometry will always result in the global minimum with a linear $C_{\infty v}$ symmetry for the NNO ground state, since most of the optimization approaches use second derivatives to find minima. In these cases, there is little probability for the optimization to overcome or tunnel through the energy barrier of the transition state at the N−N−O angle of ca. 101.5°.[42]

Table 2 reports the results of the search for N_2O isomers on the potential energy surface of the ground electronic state. Three isomers have been identified by various quantum mechanical methods in this work. They are the N−N−O linear isomer of $C_{\infty v}$ symmetry as the global minimum, the cyclic isomer with a C_{2v} symmetry as a local minimum, and the N−O−N linear isomer with a $D_{\infty h}$ symmetry as the most shallow local minimum on the PES of N_2O molecule. A search for the cyclic C_{2v} isomer was designed to begin with a smaller N−N−O angle (the left side of the transition state at 101.5°[42]). As a result, a stable cyclic isomer of N_2O was predicted as a local minimum on the potential energy surface. This isomer was also predicted as one of the products when the *trans,trans*-nitrosyl azide molecule, N_4O, dissociates.[41] Our CCSD(T)/TZ-ANO calculation predicts that the cyclic C_{2v} isomer lies 2.81 eV (64.80 kcal mol^{-1}) above the N−N−O global minimum. This isomer ($^1A'$) has the electronic configuration[37b]

$$'(1a_1)^2(2a_1)^2(3a_1)^2(4a_1)^2(5a_1)^2(6a_1)^2(7a_1)^2(8a_1)^2(1b_1)^2(1b_2)^2$$
$$(2b_1)^2(2b_2)^2$$

N₂O Isomers

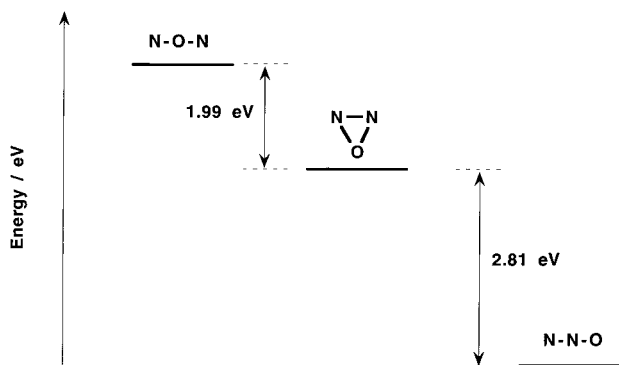*J. Phys. Chem. A, Vol. 104, No. 6, 2000* **1307**

Figure 1. Relative energy diagram for the three isomers of the N₂O based on the CCSD(T)/ANO calculations.

An N−O−N local minimum with a $D_{\infty h}$ symmetry was discovered in the present work from a completely different search for minimum/local minima on the PES of N₂O as the least stable isomer among the three N₂O isomers on the PES. The N−O−N isomer ($X^1\Sigma^+$) is calculated to lie 4.80 eV (110.69 kcal mol⁻¹) above the N−N−O global minimum and 1.99 eV (45.89 kcal mol⁻¹) above the N₂O cyclic isomer and has the electronic configuration

$$(1\sigma_g)^2(2\sigma_g)^2(3\sigma_g)^2(4\sigma_g)^2(1\sigma_u)^2(2\sigma_u)^2(3\sigma_u)^2(1\pi_u)^4(1\pi_g)^4$$

The location of the N−O−N isomer on the PES of N₂O cannot be discovered assuming the N−N−O connectivity, since the N−O−N isomer does not have a direct N−N bond.

Independently, this N−O−N linear isomer was reported by Crawford and Klapötke in their most recent note[43] using the MP2/6-311++G(d) method. However, their conclusion that the N−O−N isomer is more stable than the cyclic isomer (by 9.1 kcal mol⁻¹) is the reverse of the prediction in the present work. The contribution of the core orbitals to the binding energy is structure-dependent. It is noted that the MP2/6-311++G(d) method with a frozen core approximation and with a minimal polarized basis set does not allow sufficient variational freedom in the calculations in order to determine correctly the energy of the isomers. Moreover, the MP2/6-311++G(d) method itself would introduce an estimated error of ca. 39.2 kcal mol⁻¹,[38] which is too large to ensure valid calculations. A comprehensive discussion of the core orbital wave function contributions of the three N₂O isomers in momentum space will be presented elsewhere.[44]

(c) Stability of the N₂O Isomers. Potential energy surfaces and the minimum/local minima as well as transition states on the surface are critical in the study of chemical reaction pathways. For this reason, it is important to study further the electronic structures and bonding mechanisms of the minima on the potential hypersurface. Compared to the experimental N−O bond length of 1.151 Å for the NO diatomic molecule,[45] the N−O bond is stretched in the N−N−O $C_{\infty v}$ isomer because of the formation of the N−N bond on the nitrogen atom of the NO molecule. On the other hand, the N−O bond of the NO diatomic molecule is stretched to a similar extent if a nitrogen atom is attached to an oxygen atom to form an N−O bond. However, when either the N−N−O isomer bends to form a second N−O bond or the N−O−N isomer bends to form an N−N bond, the cyclic isomer with C_{2v} symmetry is obtained. The difference between these possible reaction pathways is that the former causes an energy increase whereas the latter results in an energy decrease. The relative energies of the three isomers

are displayed in Figure 1. In this figure, either an energy increase of 2.81 eV [CCSD(T)/ANO] is obtained if the N−N−O isomer becomes bent to form the cyclic C_{2v} isomer or the energy will decrease 1.99 eV from the N−O−N isomer to form the cyclic isomer. Therefore, the stability of the N₂O isomers seems to correlate with the strength of the N−N bond.

(d) Electron Deformation Density of the Isomers. To understand the bonding mechanism of the N₂O isomers, we conducted VWN/TZVP calculations of their deformation electron densities (electron density differences between the molecule and its component atoms). Figure 2 gives the deformation electron energy density contour plots of (a) the N−N−O linear isomer, (b) the cyclic isomer, and (c) the N−O−N isomer. In Figure 2a, the electron density is intense in the region of the N−N bond and it is apparently more intense than in the N−O bond region. And the electron deformation densities of the terminal atoms exhibit the electron clouds of nonbonding electrons, which is in agreement with the conclusion drawn by valence bond (VB) theory[15] (structures **I** and **II**). When the N−N−O linear molecule bends, the terminal N and O atoms join together to give the second N−O bond. Figure 2b presents the electron deformation density of the cyclic N₂O isomer. As is shown in this figure, the electron clouds are concentrated in the region of the N−N bond. The dilute electron density between the N−O regions is evidence of the existence of weak N−O bonds in the cyclic isomer of N₂O. Moreover, the very asymmetric electron density distribution along the N−O bonds implies that the N−O internuclear axis has some degree of bent character. Because of the stress on the N−O bent bonds of the cyclic isomer, the most probable tendency is to break one of the N−O bonds in order to reduce the energy (by 2.81 eV) to result in the N−N−O linear structure. However, if the cyclic N₂O isomer obtains sufficient energy to break the N−N bond, the bent N₂O will stretch to form an N−O−N linear isomer (Figure 2c) accompanying the shrinkage of the N−O bond length by 0.35 Å.

(e) Valence Bond Description of the Isomerization of N₂O. To conclude this discussion, we provide a qualitative valence bond representation for the electronic reorganization that may be associated with a $C_{\infty v} \rightarrow C_{2v} \rightarrow D_{\infty h}$ isomerization when we assume that a unimolecular process is involved. On many occasions,[14,15,42,46] it has been indicated that the primary VB structure for linear NNO is the increased-valence structure **II**,
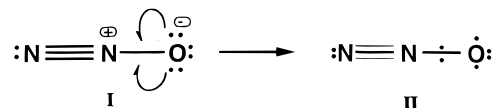
with fractional π_x(NN) and π_y(NN) bonds and one-electron π_x-(NO) and π_y(NO) bonds. This VB structure may be constructed from the familiar standard Lewis structure **I** via the one-electron delocalizations of oxygen 2p π_x and 2p π_y electrons into π_x(NO) and π_y(NO) bonding molecule orbitals (MO), as indicated in **I**. These delocalizations lead to a stabilization of the Lewis structure **I**[14,15,46] and weakening of the π_x(NN) and π_y(NN) bonds. The primary feature of the electronic reorganization that may occur as one proceeds from the linear $C_{\infty v}$ NNO (structure **II**) to the cyclic C_{2v} and the linear $D_{\infty h}$ NON isomers is indicated in structures **III−IX** in Figure 3. The singlet diradical structure **VII** for the $D_{\infty h}$ isomer is stabilized via one-electron delocalizations to generate the equivalent increased-valence structures **VIII** and **IX**. For the $C_{\infty v} \rightarrow C_{2v}$ isomerization, reasons for preferring **III** → **IV** → **V** (Figure 3) over the
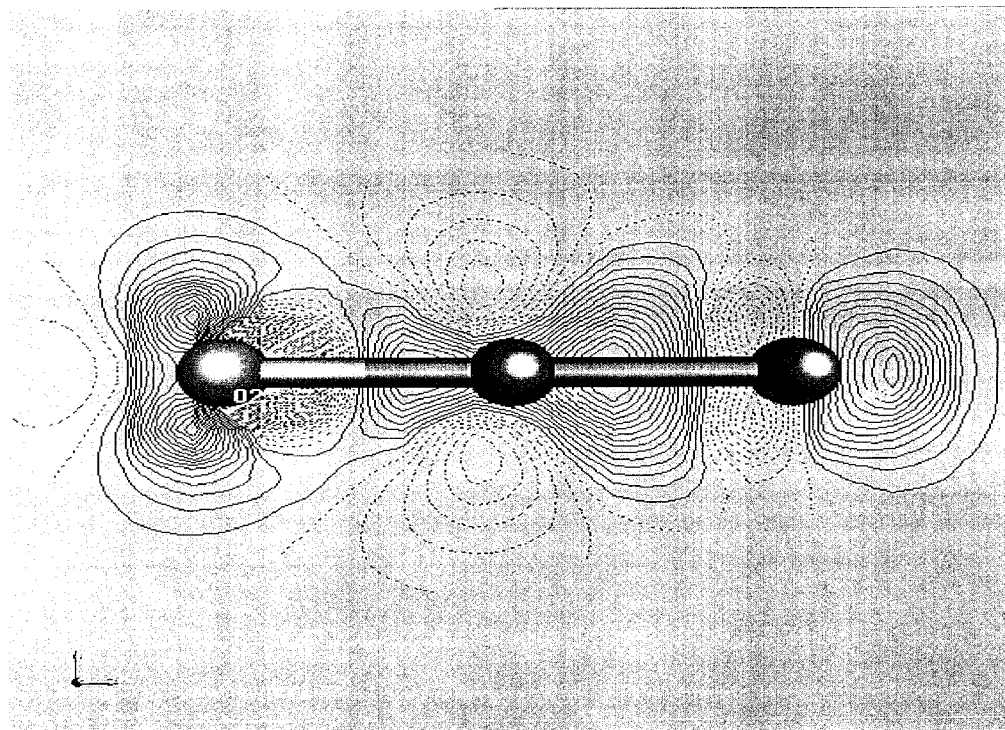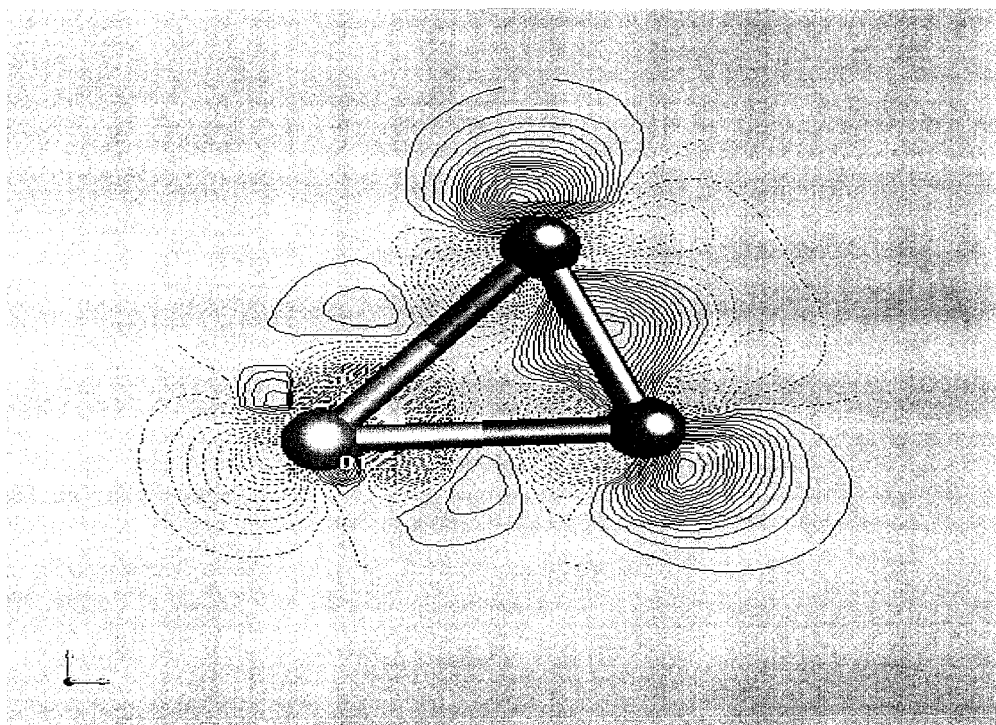
a

b

Figure 2. Continued.

N₂O Isomers

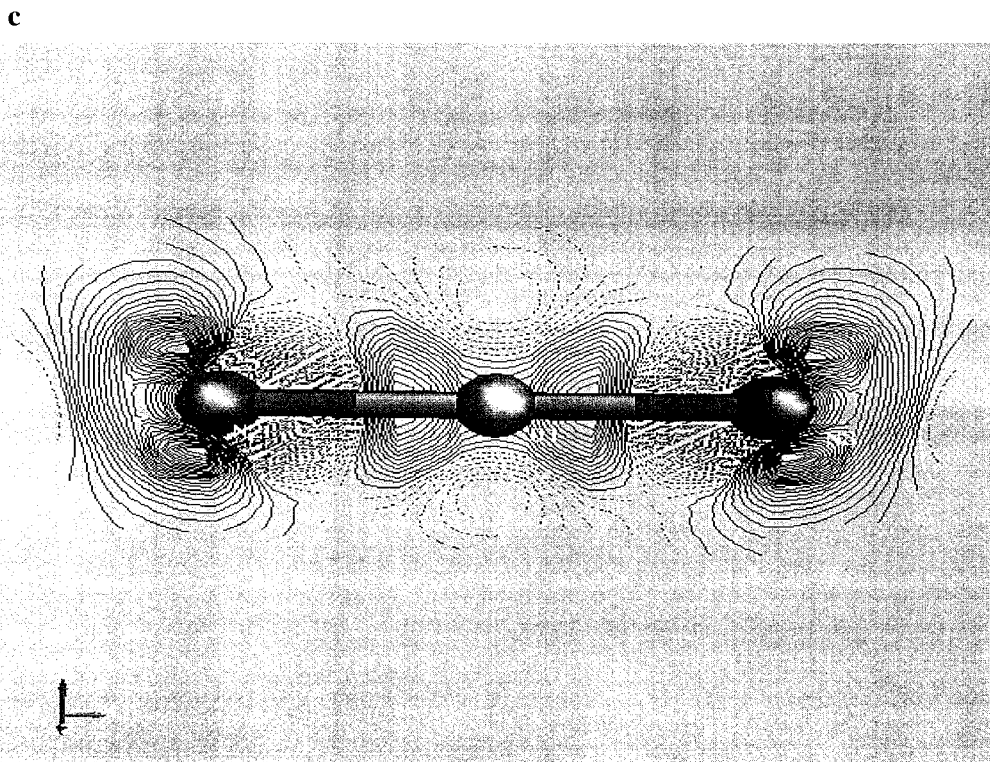*J. Phys. Chem. A, Vol. 104, No. 6, 2000* **1309**

c

Figure 2. Deformation electron density of the isomers of N_2O generated by VWN/TZVP calculations: (a) linear $C_{\infty v}$ global minimum; (b) cyclic C_{2v} isomer; (c) linear $D_{\infty h}$ isomer.
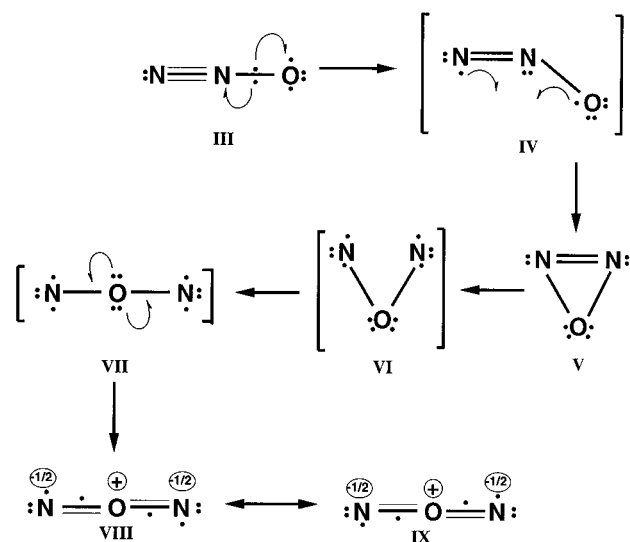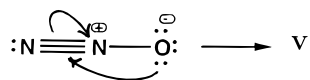

Figure 3. Valence bond formulation of $C_{\infty v} \rightarrow C_{2v} \rightarrow D_{\infty h}$ isomerization.

more familiar

formulation are similar to those described in ref 14 for VB representations of N_3NO and N_3NO_2 decompositions.

Although the mechanisms **III → V** and **V → VIII ↔ IX** are concerted, we have displayed structures **IV**, **VI**, and **VII** in order to indicate how the primary features of the geometrical and electronic reorganization may occur. Bimolecular mechanisms for the formation of the C_{2v} and $D_{\infty h}$ isomers could involve the decompositions of cyclic C_{2v} and D_{2h} dimers of the $C_{\infty v}$ isomer.

The above valence bond formulation of the unimolecular isomerization mechanism involves the initial formation of the C_{2v} isomer rather than the $D_{\infty h}$ isomer. This is in accord with the energies of the isomers that we have calculated (Table 2).

Conclusions

The geometry and energies of the three isomers on the potential energy surface of the ground electronic state of the N_2O molecule have been calculated using various quantum mechanical methods, which include post-Hartree−Fock and density functional theory methods employing different basis sets. The three isomers are a linear N−N−O as the global minimum with a $C_{\infty v}$ symmetry, a cyclic isomer with a C_{2v} symmetry as the local minimum with an energy of 2.81 eV above the N−N−O global minimum, and a linear N−O−N local minimum with a $D_{\infty h}$ symmetry and an energy of 4.80 eV above the N−N−O isomer but 1.99 eV above the cyclic C_{2v} isomer. The stabilization ordering of the three isomers of N_2O are given by $C_{\infty v} > C_{2v} > D_{\infty h}$. The bonding mechanisms and stability of these isomers have been analyzed using an energy diagram based on CCSD(T)/TZ-ANO calculations and the electron deformation density generated by the VWN/TZVP calculations. The isomerization has been formulated using valence-bond structures.

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