J. Phys. Chem. A **2004,** *108,* 2871−2873

What is the Ground State of $Ni(O_2)$?[†]

Charles W. Bauschlicher, Jr.*

Space Technology Division, NASA Ames Research Center, Moffett Field, California 94035

Received: August 6, 2003; In Final Form: October 17, 2003

The separation between the $^3B_1$ and $^1A_1$ states of $Ni(O_2)$ is computed using density functional theory (DFT), internally contracted multireference configuration interaction with the multireference analogue of the Davidson correction (IC-MRCI+Q), and coupled-cluster with single and double (and perturbative) triple excitations (CCSD(T)) approaches. Although IC-MRCI+Q and DFT both predict a $^3B_1$ ground state, the CCSD(T) predicts a $^1A_1$ ground state. We suggest that the true separation lies between the IC-MRCI+Q and CCSD(T) values, and that the ground state is likely $^1A_1$, despite the IC-MRCI+Q result. We also show that $Ni(O_2)^-$ has a quartet ground state and, therefore, the $^1A_1$ state of $Ni(O_2)$ is probably not observed in the anion photoelectron spectra.

1. Introduction

In 1993,[1] we assigned the ground state of $Ni(O_2)$ as $^1A_1$, where $Ni(O_2)$ means nickel bonded to the side of O_2, i.e., a cyclic structure. More recent work,[2−4] using density functional theory (DFT), yields a $^3B_1$ ground state, with the $^1A_1$ state being slightly higher in energy. The results of matrix isolation infrared studies[2] are more consistent with the DFT vibrational frequencies of the $^1A_1$ state than with those of the $^3B_1$ state, thus suggesting that the $^1A_1$ state is the species present in the matrix and, therefore, possibly the ground state of $Ni(O_2)$.

Anion photoelectron spectroscopy of $Ni(O_2)^-$ yields two peaks:[5] the first peak has a threshold of 0.86 eV, and the higher peak starts at ∼1.8 eV and is very broad. The two closely spaced states of $Ni(O_2)$ predicted from the DFT calculations are not observed in the anion photoelectron spectra. However, the calculations of Gutsev et al.[3] show that the ground state of $Ni(O_2)^-$ is $^4B_1$; therefore, although the observation of the $^3B_1$ state of $Ni(O_2)$ is highly likely in the anion photoelectron spectra, the observation of the $^1A_1$ state of $Ni(O_2)$ is unlikely, because it is not produced by a one-electron process. (The recent manuscript of Deng et al.[4] reports a $^4B_2$ ground state of $Ni(O_2)^-$, however, the conclusion that only the $^3B_1$ state of neutral will be observed in the anion photoelectron spectra is still valid.) Thus, if the ground state of $Ni(O_2)^-$ is a quartet, then the anion photoelectron spectra does not appear to offer much hope in determining the ground state of the neutral.

Given the difference between the DFT work and our previous calculations on the identification of ground state and the fact the $^1A_1$ state is observed in the matrix experiments, we have performed new high-level calculations on the $^1A_1$ and $^3B_1$ states of $Ni(O_2)$ and on the doublet and quartet states of $Ni(O_2)^-$.

II. Methods

We have performed three types of high-level calculations: (i) coupled cluster singles and doubles calculations,[6,7] including the effect of connected triples determined using perturbation theory[8,9] (which is denoted UCCSD(T) in Molpro), (ii) internally contracted[10,11] multireference configuration interaction (IC-MRCI) calculations, and (iii) internally contracted averaged coupled pair functional[12] (IC-ACPF) calculations. For the IC-MRCI calculations, the effect of higher excitations is estimated using the multireference analogue of the Davidson correction (denoted IC-MRCI+Q). In these high-level calculations, the Ni 3d and 4s and the O 2s and 2p electrons are correlated. In the CCSD(T) calculations, the orbitals are determined using the self-consistent-field (SCF) approach, whereas in the IC-MRCI and IC-ACPF calculations, the orbitals are determined using the complete-active-space SCF (CASSCF) approach. The final inactive/active spaces are picked based on full-valence CASSCF calculations and are described below for each state; the inactive/active space is denoted by the number of a_1, b_1, b_2, and a_2 inactive orbitals, followed by a slash and the number of active orbitals in each symmetry. Note that the core space is (6,2,3,0) and is the same in all calculations. All configurations from the CASSCF calculations are used as references in the IC-MRCI and IC-ACPF calculations. Scalar relativistic effects are included in some calculations using the Douglas−Kroll−Hess[13,14] (DKH) approach. In addition to the high-level calculation, some calculations are performed using DFT. The Becke-Perdue86[15,16] (BP86) and hybrid[17] B3LYP[18] functionals are used.

The DFT calculations use the 6-311+G* basis sets.[19−22] Excluding one basis set test, in the nonrelativistic CCSD(T), IC-MRCI, and IC-ACPF calculations, we use the Ni (20s15p10d6f4g)/[7s6p4d3f2g] averaged atomic natural orbital set[23] and oxygen augmented correlation-consistent polarized valence triple-ζ (aug-cc-pVTZ) set.[24,25] In the DKH calculations, the same oxygen primitive set is used; however, the contraction coefficients are taken from atomic DKH calculations. For nickel, the primitive set is supplemented with diffuse s and p functions and the form of the contraction is changed somewhat (see ref 26 for a complete description of the Ni basis set). To investigate the effect of basis set limitations, one set of CCSD(T) calculations is performed using a larger basis set. The larger oxygen basis is the aug-cc-pV quadruple-ζ set.[24,25] The larger Ni set is derived from the (20s15p10d6f4g) primitive set, which is supplemented with 3 h functions with exponents of 4.55, 1.82, and 0.73. The valence basis set is contracted for the $^3D(3d^94s^1)$ state of Ni. Using a general contraction, the first 16 s primitives

---

* E-mail: bauschli@pegasus.arc.nasa.gov.

[†] Part of the special issue “Fritz Schaefer Festschrift”.

10.1021/jp030960i

TABLE 1: Summary of Computed $^1A_1-^3B_1$ Separation of $Ni(O_2)$

method	ΔE^a (kcal/mol)	ΔE (DKH) (kcal/mol)
SCF[b]	+47.72	
CCSD[b]	+8.77	
CCSD(T)[b]	−8.17	
CCSD(T) (big basis set)[b]	−8.16	
B3LYP	+10.03	
BP86	+7.57	
BPW91[c]	+7.29	
CASSCF[d]	+8.25	+8.35
IC-MRCI[d]	+11.77	+11.86
IC-MRCI+Q[d]	+12.78	+12.82
IC-ACPF[d]	+12.31	
IC-ACPF (big)[d]	+12.17	

[a] A plus sign indicates that the ground state is $^3B_1$. [b] Computed at CCSD(T) equilibrium geometries. [c] From ref 29. [d] Computed at nonrelativistic IC-MRCI+Q equilibrium geometries.

are contracted to three functions, the first 10 p primitives are contracted to two functions, and the first 5 d primitives are contracted to one function; all the remaining primitives are uncontracted. The polarization functions are contracted using the natural orbitals from an singles and double CI calculation on the ^3D state. The final basis set is [7s7p6d3f2g1h].

The CCSD(T), IC-MRCI, and IC-ACPF calculations are performed using Molpro,[27] whereas the DFT calculations are performed using Gaussian98.[28]

III. Results

A. $Ni(O_2)$. The geometries of the $^3B_1$ and $^1A_1$ states of $Ni(O_2)$ are optimized at the CCSD(T) level. The Ni−O and O−O distances are 1.862 and 1.415 Å, respectively, for the $^1A_1$ state. The analogous values for the $^3B_1$ state are 1.887 and 1.362 Å, respectively. At this geometry, the SCF method places the $^3B_1$ state ~48 kcal/mol below the $^1A_1$ state (see Table 1). Accounting for electron correlation at the CCSD level reduces the separation to ~9 kcal/mol, and only with the inclusion of the triples estimate is the $^1A_1$ state lower in energy. Expanding the basis set has almost no effect on the CCSD(T) separation; therefore, basis set incompleteness should not contribute significantly to the uncertainty in the computed separation.

Consistent with previous DFT calculations,[2,3] the $^3B_1$ state is below the $^1A_1$ state at both the B3LYP and BP86 levels. Although the DFT order of the states differs from the CCSD(T) results, the DFT and CCSD(T) geometries are similar; the BP86 (B3LYP) values for the $^3B_1$ state are 1.861 (1.906) and 1.381 (1.343) Å, and the values for the $^1A_1$ state are 1.801 (1.790) and 1.401 (1.385) Å. Computation of the frequencies is very easy at the DFT level: we take one-half the sum of the harmonic frequencies as the zero-point energy (ZPE). At the B3LYP (BP86) level, the ZPE of the singlet state is 0.41 (0.52) kcal/mol larger than that of the triplet state.

At the BP86 geometries, full-valence CASSCF calculations are performed for the $^1A_1$ and $^3B_1$ states. On the basis of these calculations, the inactive/active spaces are picked to be (4,1,2,0/2,2,2,2) for the $^1A_1$ state and (4,1,1,0/2,2,3,2) for the $^3B_1$ state. Using these inactive/active spaces, the geometries of these two states are optimized at the IC-MRCI+Q level of theory. The geometries are similar to CCSD(T) and DFT results; the Ni−O and O−O distances for the $^1A_1$ state are 1.995 and 1.379 Å, respectively, whereas the analogous values for the $^3B_1$ state are 1.922 and 1.375 Å, respectively. The computed separation between the two states is given in Table 1. The CASSCF value is much smaller than the SCF result, which actually agrees reasonably with the CCSD and DFT values. The addition of more-extensive correlation at the IC-MRCI or IC-MRCI+Q levels favors the $^3B_1$ state, increasing the separation. The IC-ACPF result, using the same active space as that used in the IC-MRCI treatment, yields a value between the IC-MRCI and IC-MRCI+Q results. One concern is that the $^3B_1$ state uses a larger active space than the $^1A_1$ state; to test if this has an effect on the separation, an IC-ACPF calculation with the larger active space for the $^1A_1$ state was performed, which is listed as "IC-ACPF (big)" in Table 1. Using the larger active space for the $^1A_1$ state makes a small reduction in the separation. The inclusion of scalar relativistic effects leads to a small increase in the separation.

TABLE 2: Computed Separations for the Low-Lying States of $Ni(O_2)^-$

state	Computed Separation (kcal/mol)		
	BP86	CCSD(T)	IC-MRCI+Q
$^4B_1$	0.0	0.0[a]	0.0
$^4A_2$	15.4	4.3	
$^4B_2$	16.4	5.5	
$^2B_2$	9.8	10.3	5.8

[a] Computed at BP86 equilibrium geometry.

B. $Ni(O_2)^-$. At the BP86 level, we find four low-lying states: three quartets and one doublet. The computed separations are given in Table 2. We find a $^4B_1$ ground state, with the $^4B_2$ state being 16.4 kcal/mol higher in energy. Thus, our ground state is consistent with the assignment of Gutsev et al.[3] Our lowest doublet state is $^2B_2$, in contrast to the $^2A_1$ state reported by Deng et al.[4] We have studied the same four states at the CCSD(T) level. We are able to optimize the geometry of three of the states but not the $^4B_1$ state. The $^4B_1$ state has a $11a_1^2 12a_1^1 4b_1^2 5b_2^2 6b_2^1 1a_2^2 2a_2^1$ occupation, and we are able to find two SCF solutions: in one solution, the $1a_2$ orbital is Ni 3d-like and the $2a_2$ orbital is the O_2 out-of-plane π orbital, and in the second solution, the orbital character is reversed. Unfortunately, the switch in SCF solutions occurs near the equilibrium geometry, making it impossible to optimize the geometry for this state. Therefore, we compute the separation between the states of $Ni(O_2)^-$ using the BP86 geometry for the $^4B_1$ state and the CCSD(T) geometries for the other three states. At the CCSD(T) level, the separation between the quartet states is reduced, but the position of the $^2B_2$ state remains approximately the same.

The geometries of the $^4B_1$ and $^2B_2$ states of $Ni(O_2)^-$ are optimized at the IC-MRCI+Q level of theory, using inactive/active spaces of (3,1,1,0/3,2,3,2) and (3,1,2,0/3,2,2,2), respectively. Although the separation between the two states is smaller than that at the CCSD(T) or BP86 levels, the IC-MRCI+Q approach also yields a $^4B_1$ ground state for $Ni(O_2)^-$.

IV. Discussion

The IC-MRCI+Q, CCSD(T), and BP86 levels all predict a $^4B_1$ ground state for $Ni(O_2)^-$, which is consistent with the results of Gutsev et al.,[3] who used the DFT approach but with a functional that was different from that used in our work. Given the consistency of the results for $Ni(O_2)^-$, we conclude that $Ni(O_2)^-$ has a quartet ground state and, therefore, the singlet state of $Ni(O_2)$ is probably not observed in the anion photoelectron spectra. Thus, the anion photoelectron spectra cannot help in the assignment of the $Ni(O_2)$ ground state.

The assignment of the ground state of $Ni(O_2)$ based solely on the calculations is not easy, because the two highest levels of theory—the CCSD(T) and IC-MRCI+Q—yield different assignments. We can probably rule out scalar relativistic or basis set effects as being sources of uncertainty in the computed separation. The largest uncertainty is probably in the treatment of the electron correlation. In principle, the IC-MRCI+Q approach should be superior to the CCSD(T) approach, because it can address the multireference character of the $^1A_1$ state; however, the size of the active space is small, because of restrictions on the size of the CI expansion. Thus, it is not clear if the IC-MRCI accounts for, relative to a single reference, the effect of higher excitations as well as the CCSD(T). In this regard, we note that the IC-MRCI+Q total energies are much closer to the CCSD values than the CCSD(T) values, which are significantly lower. Because the IC-MRCI+Q and CCSD separations are similar, we speculate that the IC-MRCI expansion is too small to include all of the important higher excitation effects that are included in the CCSD(T) approach. An upper bound to missing higher excitations in the IC-MRCI+Q calculation could be obtained by adding the effect of the triplets computed at the CCSD(T) level, thus yielding a separation of -4.2 kcal/mol. This value could be an overestimate; therefore, a conservative view would place the separation between this value and the 12.78 kcal/mol value that was obtained at the IC-MRCI+Q level. Because the matrix observations are more consistent with the $^1A_1$ state, we believe that the ground state of Ni(O_2) is probably $^1A_1$, despite the IC-MRCI+Q result. Clearly, a gas-phase experimental determination of the ground state or at least a determination of the gas-phase Ni(O_2) frequencies could be very useful.

V. Conclusions

We have studied Ni(O_2) and Ni(O_2)$^-$ at several levels of theory. The results of all methods used show that Ni(O_2)$^-$ has a quartet ground state. This suggests that the anion photoelectron spectra will not observe the $^1A_1$ state of Ni(O_2). Although the density functional theory (DFT) and IC-MRCI+Q levels yield a $^3B_1$ ground state for Ni(O_2), the CCSD(T) approach yields a $^1A_1$ state. The IC-MRCI approach can better account for the multireference character of the $^1A_1$ state, whereas the CCSD(T) approach is probably better in regard to accounting for the higher excitations. Thus, the assignment of the ground state is not easy. We suggest that the true separation lies between the IC-MRCI+Q and CCSD(T) values, and that the ground state is likely $^1A_1$, despite the IC-MRCI+Q result.

References and Notes

(1) Bauschlicher, C. W.; Langhoff, S. R.; Partridge, H.; Sodupe, M. *J. Phys. Chem.* **1993**, *97*, 856.

(2) Citra, A.; Chertihin, G. V.; Andrews, L.; Neurock, M. *J. Phys. Chem. A* **1997**, *101*, 3109.

(3) Gutsev, G. L.; Rao, B. K.; Jena, P. *J. Phys. Chem. A* **2000**, *104*, 11961.

(4) Deng, K.; Yang, J.; Zhu, Q. *J. Chem. Phys.* **2003**, *115*, 6868.

(5) Wu, H.; Wang, L.-S. *J. Chem. Phys.* **1997**, *107*, 16.

(6) Bartlett, R. J. *Annu. Rev. Phys. Chem.* **1981**, *32*, 359.

(7) Knowles, P. J.; Hampel, C.; Werner, H.-J. *J. Chem. Phys.* **1993**, *99*, 5219.

(8) Raghavachari, K.; Trucks, G. W.; Pople, J. A.; Head-Gordon, M. *Chem. Phys. Lett.* **1989**, *157*, 479.

(9) Watts, J. D.; Gauss, J.; Bartlett, R. J. *J. Chem. Phys.* **1993**, *98*, 8718.

(10) Werner, H.-J.; Knowles, P. J. *J. Chem. Phys.* **1988**, *89*, 5803.

(11) Knowles, P. J.; Werner, H.-J. *Chem. Phys. Lett.* **1988**, *145*, 514.

(12) Gdanitz, R. J.; Ahlrichs, R. *Chem. Phys. Lett.* **1988**, *143*, 413.

(13) Douglas, M.; Kroll, N. M. *Ann. Phys. (N.Y.)* **1974**, *82*, 89.

(14) Hess, B. A. *Phys. Rev. A* **1986**, *33*, 3742.

(15) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098.

(16) Perdew, J. P. *Phys. Rev. B* **1983**, *33*, 8822.

(17) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(18) Stephens, P. J.; Devlin, F. J.; Chabalowski, C. F.; Frisch, M. J. *J. Phys. Chem.* **1994**, *98*, 11623.

(19) Frisch, M. J.; Pople, J. A.; Binkley, J. S. *J. Chem. Phys.* **1984**, *80*, 3265 and references therein.

(20) Wachters, A. J. H. *J. Chem. Phys.* **1970**, *52*, 1033.

(21) Hay, P. J. *J. Chem. Phys.* **1977**, *66*, 4377.

(22) Raghavachari, K.; Trucks, G. W. *J. Chem. Phys.* **1989**, *91*, 1062.

(23) Bauschlicher, C. W. *Theor. Chim. Acta* **1995**, *92*, 183.

(24) Dunning, T. H. *J. Chem. Phys.* **1989**, *90*, 1007.

(25) Kendall, R. A.; Dunning, T. H.; Harrison, R. J. *J. Chem. Phys.* **1992**, *96*, 6796.

(26) Bauschlicher, C. W.; Gutsev, G. L. *Theor. Chem. Acc.* **2002**, *108*, 27.

(27) MOLPRO is a package of ab initio programs written by H.-J. Werner, and P. J. Knowles, with contributions from J. Almlöf, R. D. Amos, A. Berning, D. L. Cooper, M. J. O. Deegan, A. J. Dobbyn, F. Eckert, S. T. Elbert, C. Hampel, R. Lindh, A. W. Llyod, W. Meyer, A. Nicklass, K. Peterson, R. Pitzer, A. J. Stone, P. R. Taylor, M. E. Mura, P. Pulay, M. Schütz, H. Stoll, and T. Thorseinsson.

(28) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Salvador, P.; Dannenberg, J. J.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.11; Gaussian, Inc.: Pittsburgh, PA, 2001.

(29) Gustev, G. L., personal communication, 2003.