Density Functional Study of Systems with Nondynamical Electron Correlation: The S_3, Se_3, and Te_3 Potential Energy Surfaces

John D. Goddard,* Xiaoqing Chen, and Galina Orlova[†]

Department of Chemistry and Biochemistry, University of Guelph, Guelph, Ontario, Canada N1G2W1

Received: December 10, 1998; In Final Form: February 22, 1999

Critical points on the C_{2v} to D_{3h} interconversion pathway on the ground $^1A_1$ state potential energy surfaces of the S_3, Se_3, and Te_3 molecules were studied using pure (BLYP, BP86) and hybrid (B3LYP, B3P86) density functionals and double-ζ plus polarization (DZP) level or larger basis sets. True transition states near the crossing of the C_{2v} HOMO (b_2^2) and D_{3h} HOMO (b_1^2, orbital assigned as in C_{2v} symmetry) configurations were determined using fractionally occupied orbitals. Near the saddle points the orbital occupancy of the b_1 (HOMO in D_{3h}) decreases and the occupancy of b_2 (LUMO in D_{3h}) increases smoothly on proceeding from S_3 to Te_3. The average DFT barrier heights relative to the C_{2v} minima are 26, 17, and 10 kcal/mol for S_3, Se_3, and Te_3, respectively. For S_3, DFT predicts that the C_{2v} open structure is ca. 10 kcal/mol more stable than the D_{3h} ring. For Se_3 and Te_3 the total energies of the open and ring forms were predicted to be nearly degenerate. The correct ordering and reasonable values of the harmonic vibrational frequencies were obtained for all equilibrium structures. The accuracy of the predicted values depends on the nature of the exchange corrections: for S_3 and Se_3 hybrid Becke-3 (B3) yields the best energetics, whereas pure Becke-88 (B) predicts the best geometries and vibrational frequencies. For Te_3, the pure B functional is recommended on the basis of the present results. A change in the correlation functional plays a relatively minor role in computations on these systems. For all systems reasonable values may be obtained using basis sets beginning at the DZP level.

Introduction

The potential energy surfaces (PES) of the X_3 systems (X = O, S, Se, Te, Po) with strong nondynamical electron correlation have challenged theory and experiment for the last two decades.[1−4,8] It has been established by Ruedenberg et al.[3] at a multireference level of theory that on the 1^1A_1 ground-state PES of O_3 and, very likely, S_3[3c] there exist one D_{3h} minimum corresponding to the ring structure and, due to the total symmetry of X_3, three equivalent C_{2v} minima corresponding to the more stable bent structures. Consequently, three equivalent transition states (TS) exist for three possible symmetry equivalent C_{2v} to D_{3h} interconversions. Each TS lies on a very sharp ridge between the basins of the D_{3h} and C_{2v} minima. In the immediate vicinity of the TS, a second electronic state (2^1A_1) has a minimum in C_{2v} symmetry. Not far from each pair of TS and this 2^1A_1 minimum, the upper and lower states intersect conically in a point on the local ridge. These three intersection points lie on one intersection seam, which is a closed curve in a C_s region of coordinate space. In addition, this C_s intersection seam crosses each C_{2v} subspace at a second point were it connects with a further independent intersection seam (which lies entirely in a C_{2v} subspace) in an intersection-seam node.

The present work studies that part of the global PES of X_3 that corresponds to the C_{2v} to D_{3h} rearrangement and appears to be the result of an avoided crossing of the $(..4b_2^2 2b_1^0)$ and the $(..2b_1^2\ 4b_2^0)$ leading configurations of the global and secondary minima. Near the TS region along the reaction coordinate the leading configuration of the ground-state wave function must change, if C_{2v} symmetry is enforced. Post-Hartree−Fock methods such as CISD or coupled cluster can recover the avoided crossing but overestimate significantly the relative stability of the ring with respect to the open structure.[1j,m,n,o,q]

Reasonably accurate and low-cost density functional theory (DFT) methods have shown promise in describing systems with strong dynamic electron correlation.[5] However, conventional DFT methods are generally not applicable to the case of strongly nondynamical electron correlation effects. DFT as a single-determinant approach might violate the noncrossing rule and the Aufbau principle. This problem may be ameliorated using the fractional occupation number (FON) algorithm. Originally, the FON approach was implemented by Slater et al.[6a] into the DFT-Xα method for the study of transition metal compounds. Recently, the idea to simulate nondynamical correlations in small molecules[6b,c] by the FON procedure in the standard DFT approximation was successfully applied by Wang and Schwarz[7a] to the O_3 and SO_2 systems. The DFT FON approximation allows the lowering of the spin and spatial symmetries of the HOMO and LUMO and consequently can recover the avoided crossing in the TS region of the C_{2v} to D_{3h} pathway. Moreover, since DFT also includes dynamic correlation effects, the DFT FON calculations conceivably could produce even more reliable results than post-Hartree−Fock methods.[7a] Schipper et al.[7b] using the Kohn−Sham potential generated directly from an accurate correlated ab initio electron density confirmed the applicability of local and gradient-corrected DFT functionals with FON in the cases where the Aufbau principle is violated with the standard DFT procedure.

We investigate further the applicability of the DFT FON approach for the determination of the TS critical points for the

---

[†] Permanent address: Institute of Physical and Organic Chemistry, Rostov University, Rostov-on-Don, 344090, Russian Federation.

10.1021/jp9847134 CCC: $18.00

next members of the X_3 series: S_3, Se_3, and Te_3. To the best of our knowledge, the TS critical point has not been found correctly[2c,3c] except for S_3. There is a practical need to estimate the correct barrier heights and, consequently, the kinetic stabilities of the D_{3h} equilibrium structures of Se_3 and Te_3. The possible existence of ring isomers for both molecules has been proposed by the number of ab initio[1b,d,i,h,2c,3c] and DFT[1e,p,g,2b] studies. However, all attempts to locate the small ring clusters experimentally were unsuccessful.[8] Since the structural parameters for the X_3 are unknown from experiment and the spectroscopic study of these small clusters is not an easily tractable problem,[8] scrutiny of the equilibrium structures of X_3 is also important. Multireference ab initio methods have indicated that the equilibrium structures of X_3 have a true multiconfigurational nature, making the prediction of the properties of the X_3 more difficult.[1q,2a,2c,26] The applicability of the density functional approach for such an "internal" type of nondynamical correlation also was examined herein.

Although different DFT potentials have been used for studying the O_3 and S_3 molecules,[2b,d,7] there are insufficient data to favor pure or hybrid DFT functionals. The identification of the best available computational scheme for the X_3 systems is another goal of this work. Since the O_3 molecule has been studied intensively both theoretically and experimentally, the DFT FON computations on O_3 were performed for the purposes of comparison.

Methods

All calculations were carried out with the GAUSSIAN94,[10] and GAUSSIAN98[11] packages. Becke's 1988 (B)[12] functional with gradient correction of the density and Becke's three-parameter hybrid functional (B3)[13] that incorporates a contribution for Hartree–Fock exchange were used to model the exchange. Correlation was included via the functionals of Lee, Yang, and Parr (LYP)[14] with local and nonlocal terms and Perdew-1986 (P86)[15] gradient corrections. Thus the exchange-correlation combinations used were BLYP, BP86, B3LYP, and B3P86.

Several basis sets were used to assess their effects. For computations on the O_3 molecule the valence triple-ζ (TZ) 6-311[18] basis set was augmented with polarization functions (P) 2d (two sets of d-type polarization functions), 2df (two sets of d-type and one set of f-type polarization functions), and 3d2f (three sets of d-type and 2 sets of f-type polarization functions). The basis sets were augmented with diffuse functions (+) to enhance the descriptions of the outer valence regions primarily to improve the computed results for frontier orbital mixing. The 6-311+G(2d) and 6-311+G(2df) basis sets also were used for predictions on the S_3 and Se_3 molecules. Valence basis sets with the effective core potentials incorporated in the GAUSSIAN packages also were employed for the chalcogens. The Stephens–Basch–Krauss effective core potential (ECP) triple-split basis CEP-121G[19] was used for S_3. The Los Almos ECP of double-ζ (DZ) quality LanL2DZ[20] was employed for S_3, Se_3, and Te_3. This basis set also was augmented with one set of polarization functions (LanL2DZ G(d)). The 3-21G[21] basis extended with diffuse and polarization functions (3-21+G and 3-21+G(d), with α_d (Te) $= 0.22$) also were used for predictions on Te_3. Computations on the Te compounds present some difficulties with respect to the choice of basis sets. Several additional basis sets beyond conventional ECP and split-valence types were used: the Christiansen relativistic ECP (RECP)[22a] basis sets GIN, with the DiLabio s/p/d (511/511/5111) contraction for 16 valence electrons,[22b] and the large (18s14p8d) all-electron basis set of Huzinaga,[22c] HD.

To determine correctly the transition states, unrestricted solutions (UDFT) for formally closed shell species were found according to Pulay's method.[16] With the GAUSSIAN series, the computational scheme involves the guess equals mix option to destroy $\alpha-\beta$ orbital pairing and symmetries. For all systems the nature of the TS point has been verified by the existence of a single negative eigenvalue in its Hessian matrix ($\lambda = 1$). To confirm the connection of this saddle point to the minima on the C_{2v} to D_{3h} pathway, Minyaev's[17] gradient reaction line approach was used. For all molecules considered, the C_{2v} or D_{3h} minima were reached from the corresponding saddle point by moving along the gradient line defined by the direction of the transition state vector. Harmonic vibrational frequencies, with all eigenvalues positive ($\lambda = 0$) were obtained for all equilibrium structures. Since in the relatively high D_{3h} symmetry a pseudo-Jahn–Teller distortion is possible, the stabilities of the DFT solutions were confirmed for the D_{3h} structures using the tests for instabilities implemented in the GAUSSIAN packages.

Results and Discussion

The predicted properties from the DFT approaches for the O_3, S_3, Se_3, and Te_3 molecules (relative energies, geometries, frequencies) are given separately in Tables 1–11. Each table also contains the available experimental data and/or the most accurate ab initio results for comparison. To illustrate the contribution of Hartree–Fock (HF) exchange to the hybrid B3 potential, HF results for the X_3 species also are presented.

1. Relative Energies. Earlier correlated methods predict a preference for the C_{2v} structure of 8–15 kcal/mol for S_3 but much closer to degeneracy for the isomers of Se_3, Te_3, and Po_3. It has been pointed out that the stability of the ring isomer increases and the barrier to interconversion decreases with increasing atomic number.[1k] Distinct from the correlated methods, HF theory overestimates the relative stability of the ring structures significantly, with a preference for the closed structure over the open isomer even for S_3.[1d] Thus, the B3 hybrid functional that includes approximately 20% of the HF exchange would be expected to overestimate the relative stability of the D_{3h} structure compared to pure DFT B-exchange.

The relative energies from DFT of the D_{3h} structures and TS with respect to the C_{2v} form along with the zero-point vibrational energy corrected values are listed in Tables 1–3. The pure DFT B functional underestimates the relative stability of the closed form for all systems considered by 5–6 kcal/mol compared to the earlier ab initio results. For Te_3, the B functional results are in the best agreement with the IMRCDCI+Q predictions. The better performance of a pure DFT functional as opposed to a hybrid one has been noted by Brabson et al.[27] in their study of the S_2...O_2 complex with quite long intermolecular distances. The increasing accuracy of energetics with the pure DFT B functional with increasing bond lengths on going from the F_2 to the I_2 molecules was noted previously by Salahub et al.[5d] Probably, the description of the pure B potential is more accurate in the region of longer interatomic distances. Thus there is no necessity to include HF exchange in the DFT potential to improve the energetics at such distances.

Since the pure B functional underestimates but the HF method overestimates the stability of the closed forms for the O_3, S_3, and Se_3, the inclusion of the HF exchange into the DFT functional may improve their predicted energetics. Indeed, for O_3 and S_3 the B3 functional results in a preference for the open

TABLE 1: Relative Stability of D_{3h} Minima with Respect to the C_{2v} Forms for O_3, S_3, and Se_3 (in kcal/mol)[a]

method	O_3	S_3	Se_3
BLYP/			
CEP-121+G(2d)			13.8 (13.8)
6-311+G(2d)	36.4 (36.2)	14.0 (14.0)	7.6 (7.7)
6-311+G(2df)	35.7 (35.5)	13.1 (13.1)	5.4 (5.5)
6-311+G(3d2f)	35.5 (35.3)		
BP86/			
6-311+G(2d)	36.7 (36.5)	11.9 (11.9)	5.5 (5.6)
6-311+G(2df)	35.8 (35.6)	11.5 (11.6)	3.0 (3.1)
6-311+G(3d2f)	35.6 (35.4)		
B3LYP/			
6-31G(d)		9.3 (9.3)	−2.6 (−2.6)
6-311+G(2d)	31.4 (30.9)	8.8 (8.4)	1.6 (1.6)
6-311+G(2df)	30.6 (30.2)	7.6 (7.6)	−0.7 (−0.6)
LanL2DZ		4.3 (4.4)	0.4 (0.4)
LanL2DZ G(d)		7.9 (7.9)	−0.3 (−0.2)
CEP-121+G(2d)		8.6 (8.6)	
B3P86/			
6-311+G(2d)	31.4 (31.0)	6.6 (6.6)	−0.4 (−0.4)
6-311+G(2df)	30.6 (30.2)	5.4 (5.3)	−2.9 (−2.8)
HF/*6-311+G(2d)*	*14.0*	*−6.7*	*−14.0*
FORS[3c]	30.5	8.5	
MRCI[2c]		5−6	
MRSDCI+Q[2a]			3.5

[a] Zero-point vibrational energy corrected values are in parentheses.

TABLE 2: Relative energies of the D_{3h} Structures and Rearrangement Barrier Heights[a] with Respect to the C_{2v} Isomer for Te_3 (in kcal/mol)[b]

	Te_3	
method	D_{3h}	TS
BLYP/		
GIN	2.9 (2.9)	12.1 (12.0)
HD	0.6 (0.7)	10.5 (10.4)
3-21+G	3.0 (3.1)	9.6 (*c*)
3-21+G(d)	−1.1 (−0.9)	*c*
BP86/		
HD	−1.7 (−1.6)	10.0 (9.9)
3-21+G	1.7 (1.7)	9.3 (9.2)
B3LYP/		
LanL2DZ	−1.1 (−1.1)	7.7 (7.5)
LanL2DZ G(d)	−4.4 (−4.4)	9.6 (9.4)
HD	−5.6 (−5.5)	8.5 (8.3)
3-21+G	−4.0 (−3.9)	6.7 (6.5)
3-21+G(d)	−7.2 (−7.2)	9.3 (10.2)
B3P86/		
HD	−7.8 (−7.8)	8.1 (8.0)
3-21+G	−5.3 (−5.2)	6.6 (6.8)
3-21+G(d)	−9.5 (−9.5)	9.0 (6.6)
HF/*HD*	*−18.0*	
MRSDCI+Q[2a]	∼0.0	∼15.0

[a] Barrier heights were computed with UDFT. [b] The values with zero-point vibrational energy corrections are in parentheses. [c] Values were not obtained due to SCF convergence problem.

structures in excellent agreement with FORS[3c] computations. For Se_3, B3 calculations predict nearly degenerate total energies for the open and ring isomers, which is in good agreement with the earlier MRCDCI+Q results.[2a] For Te_3, the B3 functionals result in a preference for the ring structure of 3−9 kcal/mol depending on the basis set. This result is not unexpected given the HF component in B3; our HF computation with the large all-electron HD basis shows a preference for the Te_3 ring structure of 18 kcal/mol.

Changes in the correlation potential and inclusion of the zero-point vibrational energy corrections play relatively minor roles in the energetics.

TABLE 3: Rearrangement Barrier Heights with Respect to the C_{2v} Minima for O_3, S_3, and Se_3 (kcal/mol)[a]

method	O_3	S_3	Se_3
UBLYP/			
CEP-121+G(2d)		26.9 (26.4)	
6-311+G(2d)	46.9 (45.5)	27.7 (27.1)	18.6 (18.3)
6-311+G(2df)	46.7 (45.3)	27.8 (27.2)	18.0 (17.8)
6-311+G(3d2f)	46.5 (45.1)		
UBP86/			
6-311+G(2d)	48.5 (47.0)	27.6 (27.1)	18.4 (18.1)
6-311+G(2df)	48.2 (46.8)	28.4 (27.8)	17.7 (17.4)
6-311+G(3d2f)	48.0 (46.5)		
UB3LYP/			
6-31G(d)		27.4 (26.7)	15.6 (15.2)
6-311+G(2d)	47.5 (45.7)	27.0 (26.3)	16.9 (16.6)
6-311+G(2df)	47.5 (45.7)	27.3 (26.6)	16.6 (16.3)
LanL2DZ		13.6 (13.1)	9.9 (9.7)
LanL2DZ G(d)		25.4 (24.8)	15.1 (14.9)
CEP-121+G(2d)		26.2 (25.6)	
UB3P86/			
6-311+G(2d)	49.0 (47.2)	27.1 (26.4)	16.9 (16.6)
6-311+G(2df)	49.0 (47.2)	27.2 (26.6)	16.4 (16.1)
FORS[3c]	52.7	36.1	
MRSDCI+Q[2a]			16.0

[a] Zero-point vibrational energy corrected values are in parentheses.

For the ring closure reaction from the C_{2v} to the D_{3h} isomer, the barrier height is correlated with the relative energy of the LUMO.[1j] A significant underestimation of gaps between the Kohn−Sham HOMO and LUMO is typical of DFT approaches and is not sensitive to any corrections.[26] For the S_3 bent structure, HF yields a gap of 0.32 eV. B3LYP and BLYP predict nearly equal gaps of 0.07 and 0.05 eV, respectively. Many-body Green's function methods predict a gap of ca. 3 eV for Se_3 and ca. 2 eV for Te_3.[1j] The predicted values with B3 (B) are 0.07 (0.03) eV and 0.06 (0.02) eV for Se_3 and Te_3, respectively. Thus, it is expected that the B and B3 potentials will yield similar barrier heights. Tables 2 and 3 a show that all DFT methods reveal quantitatively similar results. UDFT underestimates the barriers by about 5 kcal/mol for O_3 and Te_3 and 10 kcal/mol for S_3 compared to earlier ab initio results. Calculated values for Se_3 are in agreement with the earlier MRCDCI+Q extrapolated value.

With respect to the choice of the basis set for X_3, polarization functions must be included. The addition of diffuse functions is not as significant. Zero-point vibrational energy corrections flatten the PES's slightly, thus decreasing the barrier heights by approximately 0.5 kcal/mol.

Our DFT computations confirm once more that the Se_3 and Te_3 ring isomers are sufficiently kinetically stable to be trapped experimentally at low temperature.

2. Geometries of Equilibrium Structures. Analysis of the DFT geometries for the X_3 molecules is hindered by a lack of experimental data and the existence of a range of computed values. The DFT-optimized geometries of the C_{2v} structures are reported in Tables 4 and 5 . In contrast to the situation regarding relative energies, the geometries calculated with the B functional are in better agreement than the B3 with the most accurate ab initio and experimental results. The underestimation of bond length values with hybrid B3 is probably due to the HF exchange component. The HF method itself predicts bond lengths that are too short for S_3 and Se_3. For Te_3, HF reproduces the interatomic distances reasonably well, and thus hybrid and pure functionals would be expected to produce similar results.

For the open isomer of O_3, the BP86 computed bond lengths are in quite good agreement with experiment. The largest triple-ζ

TABLE 4: Geometries of the C_{2v} Structures of O_3, S_3, and Se_3[a]

	O_3		S_3		Se_3	
method	*R*	α	*R*	α	*R*	α
BLYP/						
CEP-121+G(2d)			1.985	118.6		
6-311+G(2d)	1.291	118.2	1.976	118.6	2.269	117.2
6-311+G(2df)	1.288	118.2	1.961	118.5	2.257	117.2
6-311+G(3d2f)	1.287	118.1				
BP86/						
6-311+G(2d)	1.280	118.2	1.958	118.6	2.245	117.2
6-311+G(2df)	1.276	118.2	1.938	118.6	2.233	117.0
6-311+G(3d2f)	1.275	118.1				
B3LYP/						
6-31G(d)			1.952	118.3	2.219	115.4
6-311+G(2d)	1.257	118.3	1.943	118.1	2.231	116.3
6-311+G(2df)	1.253	118.4	1.930	118.1	2.219	116.2
LanL2DZ			2.139	115.0	2.375	114.1
LanL2DZ G(d)			1.956	117.5	2.246	116.1
CEP-121+G(2d)			1.955	118.1		
B3P86/						
6-311+G(2d)	1.247	118.3	1.927	118.1	2.209	116.3
6-311+G(2df)	1.244	118.4	1.916	118.0	2.197	116.2
HF/*6-311+G(2df)*	*1.96*	*119.3*	*1.897*	*117.6*	*2.175*	*115.1*
experiment[b]	1.272	116.8	1.90 ± 0.05			
FORS[3c]		1.283	116.8	1.963	117.4	
MRSDCI+Q[2c]			1.937	117.8		
MRSDCI+Q[2a]					2.253	114.2

[a] Distances (*R*) in Å, angles α in degrees. [b] Reference 22 for O_3. Reference 8c for S_3.

TABLE 5: Geometries of the C_{2v}, D_{3h}, and rearrangement TS[a] Structures of Te_3[b]

	C_{2v}		D_{3h}	TS	
method	*R*	α	*R*	*R*	α
BLYP/					
GIN	2.736	118.1	2.90	2.822	77.3
HD	2.694	116.5	2.850	2.774	77.8
3-21+G	2.805	115.3	3.001	2.921	74.9
3-21+G(d)	2.683	116.9	2.833		
BP86/					
HD	2.674	116.4	2.822	2.746	79.1
3-21+G	2.776	115.3	2.967	2.881	75.9
B3LYP/					
HD	2.657	115.2	2.819	2.736	80.4
3-21+G	2.765	113.4	2.963	2.870	78.3
3-21+G(d)	2.641	115.1	2.800	2.718	80.3
LanL2DZ	2.723	113.4	2.930	2.838	77.0
LanL2DZ G(d)	2.621	115.1	2.786	2.705	79.8
B3P86/					
HD	2.639	115.1	2.796	2.710	81.3
3-21+G	2.737	113.5	2.931	2.835	79.2
3-21+G(d)	2.613	114.7	2.770	2.685	81.7
HF/*HD*	*2.668*	*111.8*	*2.869*		
MRSDCI+Q[2a]	2.637	111.5	2.775		
CASSCF[2a]	2.673	113.2	2.827	∼2.76	∼81.0

[a] TS geometries were computed with UDFT. [b] Distances (*R*) in Å, angles α in degrees.

TABLE 6: Geometries of the D_{3h} Structures of O_3, S_3, and Se_3[a]

method	O_3	S_3	Se_3
BLYP/			
CEP-121+G(2d)		2.157	
6-311+G(2d)	1.466	2.148	2.435
6-311+G(2df)	1.466	2.129	2.414
6-311+G(3d2f)	1.465		
BP86/			
6-311+G(2d)	1.453	2.123	2.404
6-311+G(2df)	1.448	2.099	2.383
6-311+G(3d2f)	1.447		
B3LYP/			
6-31G(d)		2.116	2.377
6-311+G(2d)	1.433	2.119	2.400
6-311+G(2df)	1.429	2.099	2.377
LanL2DZ		2.354	2.577
LanL2DZ G(d)		2.130	2.412
CEP-121+G(2d)		2.130	
B3P86/			
6-311+G(2d)	1.419	2.097	2.373
6-311+G(2df)	1.415	2.079	2.352
HF/*6-311+G(2df)*	*1.365*	*2.084*	*2.353*
FORS[3c]	1.461	2.131	
MRSDCI+Q[2a]			2.402
CASSCF[1k]		2.10	2.43

[a] Distances (*R*) in Å.

basis set with the additional 3d2f polarization functions yields the best result. It has been shown[23] that for O_3 f-type functions are essential for obtaining quantitative accuracy for this structure. For chalcogens the experimental structural parameters are unknown (the bond length was estimated for S_3[8c]). In comparison with the FORS[3c] and MRCI+Q/ANO6532[2c] computations, the BLYP functional wielded the best bond lengths with any basis set of triple-ζ quality that included diffuse and polarization functions. For Se_3, according to earlier ab initio results, all computational schemes that include polarization functions give reasonable values. For the Te_3 molecule, the computed bond distances depend on the precise mixture of exchange and correlation components and basis sets but all lie in the narrow range of 2.6−2.7 Å. These results are in good agreement with multireference ab initio computations that reveal the same range of distances. When comparing the LYP and P86 correlation corrections, P86 predicts shorter bond lengths by ∼0.02 Å.

Overall, for geometries, the sensitivity to the exchange-correlation functional, B or B3, decreases from O_3 to Te_3 (i.e., the applicability of the Hartree−Fock method increases on going to Te_3). The accuracy of the computed geometries for the tellurium species is determined mainly by the quality of the basis set.

TABLE 7: Harmonic Vibrational Frequencies (ω) of the C_{2v} Structures of O_3, S_3, and Se_3 (cm^{-1})

method	O_3			S_3			Se_3		
	ω_2	ω_3	ω_1	ω_2	ω_1	ω_3	ω_2	ω_1	ω_3
BLYP/									
CEP-121+G(2d)				238	536	608			
6-311+G(2d)	682	997	1135	241	536	605	111	294	328
6-311+G(2df)	686	997	1138	244	547	616	114	298	336
6-311+G(3d2f)	689	999	1140						
BP86/									
6-311+G(2d)	702	1059	1178	247	561	639	116	306	347
6-311+G(2df)	706	1060	1181	250	570	652	118	310	352
6-311+G(3d2f)	709	1061	1183						
B3LYP/									
6-31G(d)				258	578	661	123	328	377
6-311+G(2d)	744	1209	1257	258	581	668	121	315	358
6-311+G(2df)	748	1210	1260	260	593	681	122	319	363
LanL2DZ				197	458	503	104	268	298
LanL2DZ G(d)				253	578	656	120	312	354
CEP-121+G(2d)				253	578	665			
B3P86/									
6-311+G(2d)	761	1264	1296	263	604	698	123	325	370
6-311+G(2df)	766	1266	1300	265	615	710	124	330	375
experiment[a]	716	1089	1135	256	575	656	(350)		
CCSD(T)[1m]	718	1053	1153						
FORS[3f]	685	1044	1153						
BLYP/TZ(2df)[2b]				247	551	623			

[a] Reference 9 for O_3 (harmonic frequencies). Reference 8c for S_3 (fundamentals). Reference 8a for Se_3 (fundamentals). For Se_3 the reported value was not assigned to any mode.

For Te_3, all basis sets with polarization functions predict reasonable geometries. Note that for B3P86 the Te−Te distance with the smaller 3-21+G(d) is too short due to the sum of effects due to P86 and the polarization function both of which tend to shorten the bond lengths. The relativistic core potential plus valence basis sets give results in general agreement with the 3-21+G(d) predictions. However, the most accurate results were obtained with the largest all-electron HD basis set. These results with and without relativistic core potential agree with investigations[2a] of group 16 trimers which noted significant relativistic effects only for Po_3.

The D_{3h} ring minimum is characterized by significant lengthening of the X−X bonds compared to the open C_{2v} structure due to the occupancy of an antibonding b_1 (π*) orbital instead of a nonbonding b_2 orbital ($n\sigma$) in the open structure. Tables 5 and 6 demonstrate that, in general, all trends obtained with DFT for the C_{2v} structure also may be noted for the D_{3h} ring.

3. Harmonic Vibrational Frequencies. The ordering and the values of the O_3 stretching frequencies have proven difficult to predict theoretically. For most triatomic systems AB_2, the asymmetric stretch is higher than the two symmetric vibrations. For O_3, the asymmetric stretch (ω_3) lies between the lowest symmetric bend (ω_2) and the symmetric stretch (ω_1). It is known[25] that the C_{2v} global minimum of O_3 has its ground-state electron configuration mixed with a significant amount of a low-lying doubly excited electron configuration. These configurations differ by the double excitation from HOMO to LUMO. It has been pointed out by Stanton et al.[24] that predictions of the ordering and the value of ω_3 are very sensitive to the level of electron correlation included. Thus, MP2 and HF obtain the wrong order of ω_n, CCSD overestimates the values of ω_n considerably, but DFT and multireference ab initio results are in good agreement with experiment.[2d] The unconventional ordering of frequencies, usually is attributed to the multireference nature of O_3. In the case of the S_3 bent structure, it has the normal ordering of frequencies, as shown both experimentally[8c] and theoretically,[2b] despite the fact it has much the same multireference character [2c] as O_3.[25] Thus, the connection between the unusual ordering of frequencies and the degree of multireference character cannot be as simple as previously suggested.

Much less is known about the ordering and the values of the harmonic vibrational frequencies for Se_3 and Te_3. An IR band at 350 cm^{-1} was assigned to the C_{2v} structure of Se_3.[8a] For the Te_3 molecule the asymmetric stretch at 232 cm^{-1} was assigned to the bent form.[8b] Schnöckel[8d] reported the symmetric stretching in the range 206 to 203 cm^{-1}. It is proposed that Te_3 and, very likely, Se_3 have the conventional ordering of the frequencies as was predicted for S_3.

Harmonic vibrational frequencies for the C_{2v} structures are presented in Tables 7 and 8. The DFT approach reproduces the "nonintuitive" ordering of the vibrational frequencies in the case of O_3 and the conventional ordering for all the other members of the X_3 series. The absolute values of ω_n and the differences between the frequencies decrease on going from O_3 to Te_3 as reduced masses increase and the force constants decrease with lengthening of the X−X bonds.

In contrast to the open forms, the closed forms for both O_3 and S_3 have the same ordering of frequencies: a degenerate e′ (ω_2') mode and an A_1' symmetric stretch ω_1'.[2b,d] DFT predictions of the vibrational frequencies for the D_{3h} structures are given in Tables 8 and 9. All species have the same ordering of frequencies. The computed values for the D_{3h} structures obey trends similar to the C_{2v} species discussed above. For harmonic vibrations, the best values were obtained with the pure B functional. For the ring isomer of Te_3 the DFT computed frequencies are in agreement with an experimentally extrapolated fundamental of 153 cm^{-1} and, consequently, with the supposition[8b] that the fundamentals of the possible D_{3h} structure could not be observed experimentally owing to limitations of the spectrophotometer.

4. Transition States on the C_{2v} to D_{3h} Interconversion Pathway. The transition states computed with DFT for X_3

TABLE 8: Harmonic vibrational frequencies (ω) of the C_{2v} and D_{3h} Structures of Te_3 (cm^{-1})

	C_{2v}			D_{3h}	
method	ω_2	ω_1	ω_3	(e) ω_2'	ω_1'
BLYP/					
GIN	60	180	208	145	197
HD	64	188	212	152	206
3-21+G	58	175	197	138	187
3-21+G(d)	65	194	223	161	220
BP86/					
HD	66	197	223	161	218
3-21+G	60	181	209	143	193
B3LYP/					
HD	69	203	230	161	220
3-21+G	62	185	231	144	195
3-21+G(d)	67	211	237	172	235
LanL2DZ	65	182	203	138	190
LanL2DZ.G(d)	71	208	236	163	221
B3P86/					
HD	70	210	240	169	230
3-21+G	63	187	216	149	201
3-21+G(d)	70	224	252	181	247
experiment[8b]	203 (206)	232[a]		(153)[b]	

[a] Fundamental values. [b] Extrapolated fundamental value.

TABLE 9: Harmonic Vibrational Frequencies (ω) of the D_{3h} Structures of O_3, S_3, and Se_3 (cm^{-1})

	O_3		S_3		Se_3	
method	(e) ω_2'	ω_1'	(e) ω_2'	ω_1'	(e) ω_2'	ω_1'
BLYP/						
CEP-121+G(2d)			416	555		
6-311+G(2d)	785	1100	417	556	228	306
6-311+G(2df)	795	1106	425	560	234	312
6-311+G(3d2f)	792	1105				
BP86/						
6-311+G(2d)	824	1144	442	586	240	321
6-311+G(2df)	835	1154	449	586	247	328
6-311+G(3d2f)	834	1153				
B3LYP/						
6-31G(d)			450	586	260	349
6-311+G(2d)	850	1205	445	595	242	326
6-311+G(2df)	858	1211	454	600	250	334
LanL2DZ			345	481	205	285
LanL2DZ G(d)			449	594	245	328
CEP-121+G(2d)			442	592		
B3P86/						
6-311+G(2d)	888	1248	467	622	254	340
6-311+G(2df)	897	1254	467	625	262	349
CCSD(T)[1m]	795	1114				
FORS[3f]	750	1046				
BLYP[2b]	792	1104	428	559		

TABLE 10: Geometries of the Rearrangement TS of O_3, S_3, and Se_3[a]

	O_3		S_3		Se_3	
method	R	α	R	α	R	α
UBLYP/						
CEP-121+G(2d)			2.094	77.3		
6-311+G(2d)	1.426	74.7	2.085	77.6	2.366	76.7
6-311+G(2df)	1.421	75.0	2.068	78.1	2.347	77.7
6-311+G(3d2f)	1.421	75.0				
UBP86/						
6-311+G(2d)	1.409	75.1	2.059	78.3	2.335	77.7
6-311+G(2df)	1.404	75.4	2.037	78.7	2.316	78.6
6-311+G(3d2f)	1.403	75.4				
UB3LYP/						
6-31G(d)			2.057	79.0	2.306	79.9
6-311+G(2d)	1.384	77.4	2.049	79.5	2.325	78.9
6-311+G(2df)	1.379	77.7	2.032	79.9	2.306	79.8
LanL2DZ			2.275	76.0	2.493	76.8
LanL2DZ G(d)			2.069	78.8	2.341	79.2
CEP-121+G(2d)			2.060	79.1		
UB3P86/						
6-311+G(2d)	1.369	77.7	2.027	80.0	2.298	79.6
6-311+G(2df)	1.365	78.0	2.011	80.4	2.279	80.5
FORS[3c]	1.426	83.9	2.089	83.6		
CAS-MCSCF[1k]	1.43	83.6	2.10	84.	2.37	83.9
MRSDCI+Q[2a]					2.33	80.0

[a] Distances (R) in Å, angles α in degrees.

TABLE 11: Fractional Orbital Occupancy Numbers [(2−n):n] for the Mixed Frontier Orbitals along the D_{3h} to C_{2v} Pathway as a Function of Bond Angle

	configuration $b_1^{2-n} \rightarrow b_2^{n}$ [a]		configuration $b_2^{2-n} \rightarrow b_1^{n}$ [a])		
structure	75°	TS	85°	90°	C_{2v} min
O_3	1.83:0.17	1.60:0.40	1.32:0.68[b]	1.45:0.55[b]	1.86:0.14[b]
S_3	1.77:0.23	1.35:0.65	1.08:0.92	1.40:0.60	2.00:0.0
Se_3	1.65:0.35	1.31:0.69	1.12:0.88	1.40:0.60	2.00:0.0
Te_3	1.58:0.42	1.12:0.88	1.13:0.87	1.39:0.61	2.00:0.0

[a] In the region from D_{3h} to the TS the b_1 orbital is more strongly occupied, while after the avoided crossing in the region of the TS the b_2 orbital is more strongly occupied. [b] The a_2^{2-n} orbital is the more occupied of the highest two orbitals in the region of the C_{2v} global minimum of O_3.

(X=O, S, Se, Te) were located with fractionally occupied HOMO and LUMO UDFT orbitals, $4b_1^2 \rightarrow 2b_2^2$. In this case, the PES avoids the crossing. Tables 5 and 10 show the computed geometries of the TS. For all systems considered, saddle points are situated closer to the ring than the open structure, with an X−X-X angle of approximately 80°, in accord with Hammond's postulate and with earlier multireference ab initio results. For O_3, S_3, and Se_3 the B functional gives the best agreement of the computed bond lengths with the literature. For Te_3, quantitatively similar results were obtained by all DFT methods.

Some general trends of the electronic nature of the X_3 species were obtained using the DFT FON approach. Table 11 presents the UB3LYP occupancies of the mixed b_1 and b_2 orbitals as a function of bond angle computed with the 6-311+G(2d) basis set for O_3 to Se_3 and HD for Te_3. The DFT FON results appear quite reasonable. For all systems considered, the leading configuration at the TS has a greater occupancy of the b_1 orbital but a significant occupancy in the b_2 orbital. The b_2 occupancy number increases with increasing atomic number due to the decrease of the energies of the b_2^{LUMO} on proceeding from S_3 to Te_3. The b_1 configuration is dominant in the range 81° and below: this region includes both the TS and the D_{3h} critical points. In the range between 82° and 120° (C_{2v} minimum) the configuration with b_2 more occupied characterizes the lowest state. These general results are in very good agreement with multireference ab initio computations.[25] Any multireference character of the minima for S_3, Se_3, and Te_3 and the D_{3h} minimum for O_3 are not illustrated by the DFT FON determined by mixing the HOMO and LUMO. Mixed configurations $a_i^2 \rightarrow 2b_1^2$ for C_{2v} and $a_i^2 \rightarrow 2b_2^2$ for D_{3h} structures are determined by excitations from lower orbitals[2c,25] not modified by the mixing. Of the minima, only for the C_{2v} structure of O_3 does the leading b_2^2 configuration mix with $a_2^{2-n} \rightarrow 2b_1^n$, where a_2 appears to be the HOMO. It may be noted in Table 11 that the DFT FON method reflects the multireference character of the global minimum of ozone qualitatively well. In summary, for X_3 systems DFT FNO mirrors the multireference character of electronic states in any region determined by the mixing of frontier orbitals.

Conclusions

Critical points on the C_{2v} to D_{3h} interconversion pathways for the S_3, Se_3, and Te_3 molecules were determined correctly by DFT methods. Accurate results for the geometries of both the C_{2v} open and the D_{3h} closed equilibrium structures were obtained. For S_3, the C_{2v} structure is approximately 10 kcal/mol more stable than the D_{3h} one. Se_3 and Te_3 have almost degenerate C_{2v} and D_{3h} minima. The unusual ordering of vibrational frequencies for O_3 and the conventional ordering for the subsequent members of the X_3 series are reproduced well by DFT. The computed values of the harmonic vibrational frequencies with DFT are in good agreement with experiment or with earlier multireference ab initio computations.

The DFT FON approach recovers an avoided crossing in the TS region on the C_{2v} to D_{3h} interconversion pathways on the ground $^1A_1$ potential energy surfaces of S_3, Se_3, and Te_3. The true transition states were obtained by mixing the frontier UDFT orbitals for all species considered. The occupancy of the b_2 LUMO in the saddle point region increases with increasing atomic number. The DFT barriers of interconversion are ∼26, ∼17, and ∼10 kcal/mol for S_3, Se_3, and Te_3, respectively.

DFT predicts that the ring structures of Se_3 and Te_3 are stable and thus could be found experimentally. The very low harmonic frequencies of Te_3 may hinder any IR spectroscopic identification of this ring isomer.

Computational accuracy for these X_3 species depends mainly on the type of exchange correction and on the basis set. Correlation corrections play a more minor role. For S_3 and Se_3, hybrid B3 functional yields the best energetics, while the pure B functional provides the best geometries and frequencies. For Te_3 accurate relative energies and geometries were obtained with the pure B functional. Basis sets beginning with DZ quality may be used, provided polarization functions are included.

Density functional approaches may be applied to these systems with nondynamical electron correlation: the equilibrium structures of multireference character and saddle points with mixed state determined by frontier orbitals crossing. A given exchange potential produces reasonable results that may be improved by selection of a particular correlation functional.

Acknowledgment. Financial support of this research by the Natural Sciences and Engineering Research Council of Canada (NSERC) is gratefully acknowledged.

References and Notes

(1) (a) Goddard, W. A.; Dunning, T. H.; Hunt, W. J.; Hay, P. J. *Acc. Chem. Res.* **1973**, *6*, 368. (b) Luchesse, R. R.; Schaefer, H. F. *J. Chem. Phys.* **1977**, *67*, 848. (c) Harding, L. B.; Goddard, W. A. *J. Chem. Phys.* **1977**, *67*, 2377. (d) Carlsen, N. R.; Schaefer, H. F. *Chem. Phys. Lett.* **1977**, *48*, 390. (e) Morin, M.; Foti, A. E.; Salahub, D. R. *Can. J. Chem.* **1985**, *63*, 1982. (f) Laidlaw, W. G.; Trsic, M. *Can. J. Chem.* **1985,** *63*, 2044. (g) Jones, R. O. *J. Chem. Phys.* **1986**, *84*, 318. (h) Rice, J. E.; Amos, R. D.; Handy, N. C.; Lee, T. J.; Schaefer, H. F. *J. Chem. Phys.* **1986**, *85* (2), 963. (i) Fueno, T.; Buenker, R. J. *Theor. Chim. Acta* **1988**, *73*, 123, (j) von Niessen, W.; Cederbaum, L. S.; Tarantelli, F. *J. Chem. Phys.* **1989**, *91*, 3582. (k) Basch, H. *Chem. Phys. Lett*. **1989**, *157*, 129. (l) Raghavachari, K.; Rohlfing, C. M.; Binkley, J. S. *J. Chem. Phys.* **1990**, *93*, 5862. (m) Lee, T. J. *Chem. Phys. Lett.* **1990**, *169*, 529. (n) Shalabi, A. S.; El-Misiery, A. E. M. *J. Mol. Struct. (THEOCHEM)* **1993**, *281*, 1. (o) Raghavachari, K.; Trucks, G. W.; Pople, J. A.; Replogle, E. *Chem. Phys. Lett.* **1989**, *158*, 207. (p) Jones, R. O. *Chem. Phys. Lett.* **1986**, *125*, 221. (q) Scuseria, G. E.; Lee, T. J.; Scheiner, A. C.; Schaefer, H. F., III *J. Chem. Phys.* **1989**, *90*, 5635.

(2) (a) Balasubramanian, K.; Dai, D.*J. Chem. Phys.* **1993**, *99*, 5239. (b) Murray, C. W.; Handy, N. C.; Amos, R. D. *J. Chem. Phys.* **1993**, *98*, 7145. (c) Koch, W.; Natterer, J.; Heinemann, C. *J. Chem. Phys.* **1995**, *102*, 6159. (d) Tozer, D. *J. Chem. Phys.* **1996**, *104*, 4166. (e) Heinemann, C.; Koch, W.; Lindner, G.-G.; Reinen, D.; Widmark, P.-O. *Phys. Rev. A* **1996**, *54*, 1979.

(3) (a) Xantheas, S.; Atchity, G. J.; Elbert, S. T.; Ruedenberg, K. *J. Chem. Phys.* **1990**, *93*, 7519. (b) Atchity, G. J.; Ruedenberg, K.; Nanayakkara, A. *Theor. Chem. Acc.* **1997**, *96*, 195. (c) Ivanic, J.; Atchity, G. J.; Ruedenberg, K. *J. Chem. Phys.* **1997**, *107*, 4307. (d) Atchity, G. J.; Ruedenberg, K. *J. Chem. Phys.* **1993**, *99*, 3790. (e) Xantheas, S.; Atchity, G. J.; Elbert, S. T.; Ruedenberg, K. *J. Chem. Phys.*, **1991**, 94, 8054.

(4) Yarkony, D. R. *Acc. Chem. Res.*, **1998**, 31, 551.

(5) (a) Fan, L.; Ziegler, T. *J. Chem. Phys.* **1991**, *95*, 7401. (b) Appel, A.; Jäkle, F.; Priemeier, T.; Schmid, R.; Wagner, M. *Organometallics* **1996**, *15*, 1188. (c) Orlova, G.; Scheiner, S. *Organometallics* **1998**, *17*, 4362. (d) Ruiz, E.; Salahub, D. R.; Vela, A. *J. Am. Chem. Soc.* **1995**, *117*, 1141 and references therein.

(6) (a) Slater, J. C.; Mann, J. B.; Wilson, T. M.; Wood, J. H. *Phys. Rev.* **1969**, *184*, 672. (b) Dunlap, B. I.; Mei, W. N. *J. Chem. Phys.* **1983**, *78*, 4997. (c) Goursot, A.; Malrieu, J. P.; Salahub, D. R. *Theor. Chim. Acta* **1995,** *91*, 225.

(7) (a) Wang, S. G.; Schwarz, W. H. E. *J. Chem. Phys.* **1996**, *105*, 4641. (b) Schipper, P. R. T.; Gritsenko, O. V.; Baerends, E. J. *Theor. Chem. Acc.* **1998**, *99*, 329.

(8) (a) Brabson, G. D.; Andrews, L. *J. Chem. Phys.* **1992**, *96*, 9172. (b) Hassanzadeh, P.; Thompson C., Andrews, L. *J. Chem. Phys.* **1992**, *96*, 8246. (c) Lenain, P.; Picquenard, E.; Lesne, J. L.; Corset, J. *J. Mol. Struct.* **1986**, *142*, 355, (d) Schnöckel, H., *Z. Anorg. Allg. Chem.* **1984**, *72*, 510.

(9) Barbe, A.; Secroun, C.; Jouve, P. *J. Mol. Spectrosc.* **1974**, *49*, 171.

(10) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T. A.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortitz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian 94*; Gaussian, Inc.: Pittsburgh, PA, 1995.

(11) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A.; 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.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; 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.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A.; *Gaussian98*; Gaussian, Inc.: Pittsburgh, PA, 1998.

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

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

(14) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785. Miechlish, B.; Savin, A.; Stoll, H.; Preuss, H. *Chem. Phys. Lett.* **1989**, *157*, 200.

(15) Perdew, J. P. *Phys. Rev. A* **1988**, *38*, 3098.

(16) (a) Pulay, P.; Hamilton, T. P. *J. Chem. Phys.* **1988**, *88*, 4926. (b) Bofill, J. M.; Pulay, P. *J. Chem. Phys.*, **1989**, *90*, 3637. (c) Pulay, P.; Liu, R.-F. *J. Phys. Chem.*, **1990**, *94*, 5548.

(17) Minyaev, R. M. *Int. J. Quantum Chem.* **1994**, *49*, 105.

(18) Binning, R. C.; Curtiss, L. A. *J. Comput. Chem.*, **1990**, *11*, 1206. Curtiss, L. A., McGrath, M. P.; Blaudeau, J.-P.; Davis, N. E.; Binning, R. C.; Radom, L. *J. Chem. Phys.* **1995**, *103*, 6104. McGrath, M. P.; Radom, L. *J. Chem. Phys.* **1991**, *94*, 511.

(19) Stevens, W. J.; Basch, H.; Krauss, M. *J. Chem. Phys.* **1984**, *81*, 6026. Stevens, W. J.; Krauss, M.; Basch, H.; Jasien, P. G. *Can. J. Chem.* **1992**, *70*, 612. Cundari, T. R.; Stevens, W. J. *J. Chem. Phys.* **1993**, *98*, 5555.

(20) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 270. Wadt, W. R.; Hay, P. J. *J. Chem. Phys.* **1985**, *82*, 284. Hay, P. J.; Wadt, W. R., *J. Chem. Phys.* **1985**, *82*, 299.

(21) Pietro, W. J.; Francl, M. M.; Hehre, W. J.; Defrees, D. J.; Pople, J. A.; Binkley, J. S. *J. Am. Chem. Soc.* **1982**, *104*, 5039.

(22) (a) LaJohn, L. A.; Christiansen, P. A.; Ross, R. B.; Atashroo, T.; Ermler, W. C. *J. Chem. Phys.* **1987**, *87*, 2812. (b) G. DiLabio, private communication; (c) Poirier, R.; Kari, R.; Csizmadia, I. G. *Handbook of Gaussian Basis Sets*; Elsevier: New York, 1985.

(23) Lee, T. J.; Scuseria, G. E. *J. Chem. Phys.* **1990**, *93*, 489.

(24) Stanton, J. F.; Lipscomb, W. N.; Maggers, D. H.; Bartlett, R. J. *J. Chem. Phys.* **1989**, *90*, 1077.

(25) Banichevich, A.; Peyerimhoff, S. D. *Chem. Phys.* **1993**, *174*, 93.

(26) (a) Almbladh, C. O.; von Barth, U. *Phys. Rev. B* **1985**, *31*, 3231. (b) Van Leeuwen, R.; Baerends, E. J. *Phys. Rev. A* **1994**, *49*, 2421.

(27) Brabson, G. D.; Citra, A.; Andrews, L.; Davy, R. D.; Neurock, M. *J. Am. Chem. Soc.* **1996**, *118*, 5469.