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Theoretical investigations of molecules composed only of fluorine, oxygen and nitrogen: determination of the equilibrium structures of FOOF, $(NO)_2$ and FNNF and the transition state structure for FNNF *cis–trans* isomerization

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The deficiencies of common *ab initio* methods for the reliable prediction of the equilibrium structures of compounds composed of only the fluorine, oxygen and nitrogen atoms are investigated. Specifically, the importance of using large one-particle basis sets with multiple sets of polarization functions has been studied. Additionally, the need for a set of *f* basis functions was investigated. Several different single reference electron correlation methods have been tested in order to determine whether it is possible for a single reference based method to be routinely used on such chemical systems. These electron correlation methods include second order Møller–Plesset perturbation theory (MP2), singles and doubles configuration interaction (CISD), the coupled pair functional (CPF) approach and singles and doubles coupled cluster (CCSD) theory. The molecular systems studied include difluoroperoxide (FOOF), the *cis* form of the NO dimer, *cis* and *trans* difluorodiazene (FNNF) and the transition state to interconversion of the *cis*

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and *trans* isomers of FNNF. To the best of our knowledge, this is the first time that the *cis-trans* isomerization transition state has been reported. At the highest level of theory employed, the equilibrium structures of *cis* and *trans* FNNF agree very well with the experimental structures. However, the barrier to interconversion is predicted to be 65 kcal/mole, which is substantially higher than the experimental activation energy of 32 kcal/mole. Potential sources of error are discussed. A new diagnostic method for determining *a priori* the reliability of single reference based electron correlation methods is suggested and discussed.

Key words: *Ab initio*-methods — Equilibrium structure — *Cis-trans* isomerization — Difluoroperoxide — NO dimer — Difluorodiazene

1. Introduction

Over the past twenty years *ab initio* quantum mechanical methods have become useful and important tools with which to investigate many physical and chemical problems. Indeed, in many instances experimental chemists will either delay the final analysis of experimental data until *ab initio* results are available to corroborate an assignment [1, 2], or even change an assignment if a high quality *ab initio* study demonstrates the need to do so [3–6]. There are, however, many chemical systems for which commonly used *ab initio* methods do not consistently provide reliable predictions. One such class of chemical systems are those which are composed only of fluorine, oxygen and nitrogen. For example, at the minimum basis set self-consistent-field (SCF) level of *ab initio* theory the equilibrium geometry of *cis* difluorodiazene [7] (*cis* FNNF) ($R_{N\text{-}F} = 1.277$ Å, $R_{N\text{-}N} = 1.373$ Å, $\angle NNF = 111.5°$) does not even resemble the experimental structure [8] ($R_{N\text{-}F} = 1.384$ Å, $R_{N\text{-}N} = 1.214$ Å, $\angle NNF = 114.5°$). Another example would be the equilibrium structure of difluoroperoxide (FOOF) where minimum basis SCF gives [7] $R_{O\text{-}F} = 1.358$ Å, $R_{O\text{-}O} = 1.392$ Å, $\angle OOF = 104.2°$, and $\tau = 88.1°$ and the experimentally observed structure as determined from microwave spectroscopy [9] is 1.575 Å, 1.217 Å, 109.5° and 87.5°, respectively.

Quantum chemists certainly do not expect to obtain highly accurate equilibrium structures at the minimum basis SCF level of theory. However, it is disconcerting that these structures are not even qualitatively correct. The structures of most hydrocarbon compounds are reproduced reasonably well at this level of theory [10] with typical errors for C–C bonds and C–H bonds being 0.02 Å and 0.01 Å, respectively. The *cis* FNNF and FOOF examples cited above are probably among the most extreme cases, though there are numerous other fluorine, oxygen and nitrogen compounds where the quality of results from low level *ab initio* methods is certainly less than desirable. Naturally, many quantum chemists have attempted to improve upon the minimum basis set SCF results by using much higher levels of theory. For the most part, higher levels of theory has meant that *ab initio* methods which incorporate a large fraction of the electron correlation energy have been investigated. In the present study we report the results of our investigations on difluoroperoxide, the NO dimer and difluorodiazene.

The FOOF molecule has been studied a few times in the last ten years [11-14]. In 1982, Ahlrichs and Taylor [12] (AT) performed a constrained geometry optimization (OOF bond angle and torsional angle fixed at the experimental values) of FOOF using the coupled electron pair approximation [16] (CEPA-1) in conjunction with a basis set of double zeta plus polarization (DZP) quality. The CEPA electron correlation methods are designed to include, in an approximate fashion, higher excitation effects which arise from unlinked clusters of singles and doubles. Therefore, the study by AT represents the first attempt to explicitly take into account higher than double excitations. The equilibrium structure obtained by AT was in fact the best theoretical result at that time. However, the error in the O-F bond distance was still 0.05 Å, which is not acceptable. AT did state a fundamentally important conclusion though, which is that the non size-extensive singles and doubles configuration interaction (CISD) method was incapable of properly describing the O-F bonds present in FOOF. In 1987, Clabo and Schaefer [13] reported the results of a study investigating the importance of including diffuse *p* functions in the one particle basis set. Their DZP plus diffuse *p*-function basis was used in conjunction with the SCF and CISD methods. Although the diffuse *p* functions did change the equilibrium geometry, this effect was very small. Also in 1987, Rohlfing and Hay [14] (RH) reported the results of an in depth study on FOOF. While RH did use two different basis sets (one including a diffuse set of *s* and *p* functions on each F), their primary concern was the improvement of the *n*-particle basis. They performed large complete active space SCF contracted CI (CASSCF-CCI) structural optimizations, again keeping the OOF bond and torsional angles fixed at the experimental values. The most accurate O-F bond distance obtained by RH is only 0.001 Å shorter than the experimental r_0 value, however, the O-O distance is not as accurate as that obtained by AT, being 0.022 Å longer than experiment.

Very recently a study has appeared [15] which claims to have solved the theoretical difficulties inherent in the study of the FOOF molecule. These workers used second order Møller-Plesset perturbation theory [17] (MP2) in conjunction with several different one particle basis sets. However, it seems that their approach involved the modification of the one particle basis in an unbalanced fashion (without regard for established procedures) in order to obtain the experimental structure. Two of the many problems with this approach is that (1) once a reasonable equilibrium structure has been found there is no guarantee that such an unbalanced basis set will yield accurate results for other molecular properties, and (2) "this end result" might not have been obtained without prior knowledge of the experimental studies and so the procedures used to obtain "the end result" will be of limited value in the study of similar, but as yet experimentally unknown compounds. Therefore, it is apparent that after this brief review that no one has investigated the importance of large one-particle basis sets for the FOOF molecule. Moreover, the theoretically most complete one reference based electron correlation method has not been tried. Namely, the coupled cluster approach has never been applied to the FOOF molecule.

Another molecular system which has proved difficult for theoreticians is the NO dimer. Several different isomers of $(NO)_2$ exist [18], with the most stable form adopting a *cis* structure with a long, weak N–Nσ-bond. In this study we consider only the *cis* ONNO isomer. Therefore, any reference to the NO dimer or $(NO)_2$ should be understood to refer to *cis*-ONNO. The NO dimer is interesting in that its binding energy is consistent with that of a van der Waals complex, but the ground electronic state of the dimer is a singlet. In other words, the free electrons of the two open-shell NO monomers are singlet coupled in $(NO)_2$.

Three different experimental structural determinations of *cis*-ONNO have been reported [19-21]. The first is an X-ray crystallographic study [19] which reports an N–N distance of 2.18 Å with a corresponding O–O distance of 2.62 Å. The N–O bond length is determined to be 1.12 Å. Thus, the NNO angle is found to be 101.3°. The second structural determination [20] is from the infrared (IR) spectrum of gaseous $(NO)_2$. Dinerman and Ewing were able to deduce the N–N distance and NNO angle (1.75 Å and 90°, respectively) by performing contour analyses of two IR bands. In their analysis, they assumed the N–O bond distance to be 1.15 Å, the value for the monomer. Of course, the large discrepancy between the gas phase and X-ray structures could be attributable to the different phases, especially since the weakly bound $(NO)_2$ is expected to exhibit several large amplitude motions. However, the third experimental structural determination [21] of $(NO)_2$ is also for the gas phase and it obtains an N–N distance of 2.33 ± 0.12 Å and an NNO angle of 95 ± 5°. The N–O bond distance was again assumed to be 1.15 Å. Thus, the NO dimer is very difficult to study experimentally as well as theoretically, and it appears that the true equilibrium structure of *cis*-ONNO is still open to debate.

However, the purpose of this study is to investigate the $(NO)_2$ equilibrium structure using different *ab initio* methods, and in so doing determine which *ab initio* methods are best suited. The best *ab initio* full geometry optimizations that have been published [22, 23] were performed at the SCF level of theory. Both of these studies obtain an N–N distance (1.768 Å [22], and 1.615 Å [23]) which is much shorter than the most recent experimental value. To the best of our knowledge, the structure of the NO dimer has never been determined at a correlated level of theory, despite the known importance of electron correlation [23].

Difluorodiazene is known to exist in *cis* and *trans* forms with the *cis* structure being 3.05 kcal/mole more stable than the *trans* isomer [24]. The vibrationally averaged structures of both isomers have been determined by electron diffraction experiments [25]. The structure of the *cis* isomer has also been determined from microwave spectroscopy [8]. The only noticeable discrepancy between the electron diffraction and microwave structures of *cis* FNNF is in the N–F bond distance where the microwave value is 0.026 Å less than the electron diffraction quantity. Because of the known uncertainties in electron diffraction structures, the microwave analysis is the generally accepted structure for *cis* FNNF. As noted previously, the first reported *ab initio* investigation [7] of the equilibrium structure of *cis* FNNF yielded N–N and N–F bond lengths of 1.373 Å and 1.277 Å, respectively. This qualitatively incorrect structure was determined at the

STO-3G minimum basis SCF level of theory. While larger one-particle basis set equilibrium geometries [26, 27] (at the SCF level of theory) produce qualitatively correct geometries, the absolute agreement with experiment is still not adequate. In this study we investigate *cis* and *trans* FNNF using large basis sets and electron correlation techniques. Our success in determining the equilibrium structures of *cis* and *trans* FNNF enabled vibrational spectra to be predicted as well as a search for the transition state to isomerization.

Our theoretical approach is described in the next section. The results of these investigations along with a discussion are presented in sect. 3. Section 4 contains our concluding remarks.

2. Theoretical approach

The purpose of this study is two-fold. Firstly, we wish to investigate the importance of using balanced, large one-particle basis sets which have not previously been reported. In a study of F_2, Jankowski et al. [28] demonstrated the need for multiple sets of polarization functions, including f and g functions. Therefore, we have employed four different one-particle basis sets. The first and smallest is the standard DZP basis which consists of Dunning's double zeta contraction [29] of Huzinaga's (9s5p) primitive set [30]. The polarization orbital exponents are $\alpha_d = 1.00, 0.85, 0.80$ for fluorine, oxygen and nitrogen, respectively. The second basis set investigated is termed triple zeta plus double polarization (TZ2P) and consists of Dunning's $[5s3p]$ contraction [31] of Huzinaga's $(10s6p)$ primitive set [30] with polarization function orbital exponents of $\alpha_d = 1.5, 0.35$ for F, O and N. We note that our double polarization set is constructed according to standard practice (i.e. $\alpha_d(1)/\alpha_d(2) \sim 3-4$) and has been recommended by van Duijneveldt [32].

The third basis set was utilized in the investigations of FOOF and $(NO)_2$ only. It is composed of Dunning's $[5s4p]$ contraction [31] of Huzinaga's $(10s6p)$ primitive set [30] with the addition of three sets of polarization functions to each atom. The polarization function orbital exponents are $\alpha_d = 2.25$, 0.75 and 0.25 and have been used by us previously [33]. This basis set is designated triple zeta plus triple polarization (TZ3P).

In the study by Jankowski et al. [28] on F_2, it was shown that including a set of f basis functions was certainly more important than adding a third set of d polarization functions. Therefore, the fourth and final basis set we have investigated consists of adding a set of f functions (orbital exponent, $\alpha_f = 0.80$) to the TZ2P basis set of each atom. This basis set will be designated TZ2P*f*. The choice of the f function orbital exponent requires some comment. The theoretically troublesome F, O and N compounds are usually characterized by having small binding energies (with respect to some dissociation products) and, hence exhibit rather long bonds. This is true even for F_2 where the bond strength [34] is 38.0 kcal/mole and the bond distance is 1.417 Å. Comparing these values to the C–C single bond of ethane (89.8 kcal/mole and 1.536 Å) it is apparent that the

F-F interaction is not very strong. Moreover, if the F-F and C-C bond distances are compared to twice the respective atomic radii (1.40 Å for C and 1.00 Å for F, as computed from Table 4.2 of [35]) then it is evident that the F-F bond distance is exceptionally long relative to the size of the fluorine atom. Therefore, we thought that it may be possible that somewhat more diffuse polarization functions would be important in the bonding of these systems since the molecular systems are spatially extended. We have already included a relatively diffuse set of *d* functions by incorporating multiple sets, however, using multiple sets of *f* functions is prohibitively expensive for these compounds.

Two studies [28, 36] have explicitly investigated the use of a set of *f* functions on fluorine compounds. In the first case [36] the "optimum" value was obtained by minimizing the energy of the F atom and in the second case [28] the optimum value was obtained by minimizing the energy of F_2 at a given bond distance. However it has been demonstrated many times in the past that the best polarization function(s) for a specific property are not necessarily the same set which minimize the total energy since the core electrons contribute substantially to the total energy but are not necessarily important in the valence region. As an example, consider the total energy, equilibrium structure and dipole moment of CH_2^-. Examining Tables 2 and 3 of [37] it becomes clear that, although the tighter set of triple or quadruple polarization functions yields a lower total energy, the dipole moment and probably the equilibrium structure are better described with the more diffuse set of polarization functions. Of course, the best approach would be to locate the equilibrium structures using several different *f* function orbital exponents. Unfortunately, the TZ2P*f* computations proved to be very expensive and we were not able to investigate other orbital exponents for the *f* function. Nevertheless, we include the TZ2P*f* results here because they do lead to some insight concerning the importance of including *f* functions in the one-particle basis. In all cases, the full set of cartesian *d* and *f* functions were included in the basis, yielding 144 contracted gaussian functions for the TZ2P*f* basis set. A test for linear dependencies in the basis set is standard in the methods used, and no such problems were encountered.

The importance of electron correlation for these compounds has been clearly demonstrated in past studies. Therefore, the lowest order of theory employed in this study is MP2 which is the simplest method capable of including the effects of dynamic electron correlation. The other electron correlation methods investigated are singles and doubles configuration interaction (CISD), the coupled pair functional [38] (CPF) approach and the singles and doubles coupled cluster (CCSD) theory. The CISD expansions for FOOF and the number of t_1 and t_2 amplitudes in the TZ2P CCSD wavefunctions for FOOF were limited by requiring the 1*s*-like molecular orbitals to remain doubly occupied ("frozen core") and deleting the corresponding unoccupied orbitals ("frozen virtual") from the procedures resulting in 292 140 configuration state functions (CSFs) for the TZ2P basis. In all other cases, all electrons and orbitals were allowed to be active which, for example, gave 244 588 CSFs for TZ2P $(NO)_2$.

Table 1. MP2 energies and equilibrium structures of FOOF (C_2 symmetry) using several large basis sets. See text for details of the basis sets. Energies in hartrees, bond lengths in Å and angles in degrees

	DZP	TZ2P	TZ3P	TZ2P*f*	Expt[a]
Energy	−349.108 698	−349.323 317	−349.428 975	−349.426 204	—
r_{O-O}	1.266	1.140	1.145	1.178	1.217
r_{O-F}	1.521	1.728	1.685	1.604	1.575
∠OOF	107.9°	112.3°	111.6°	110.0°	109.5°
τ	86.9°	89.3°	89.2°	88.2°	87.5°

[a] Taken from [9]

The MP2 optimum geometries and energetics were obtained with the Cambridge Analytic Derivatives Package [29] (CADPAC). The CISD investigations were performed with the shape driven graphical unitary group CI energy [40] and gradient [41] methods while all CCSD geometry optimizations were performed with the Berkeley suite of CCSD programs [42, 43] modified to run on a CRAY XMP. The grid of CCSD energies performed for FOOF and $(NO)_2$, and the single point energies for FNNF were performed with a recently developed vectorized closed shell CCSD method [44]. Our CPF gradient procedure was utilized in determining the CPF equilibrium structures [45].

3. Discussion of results

3.1. FOOF

The MP2 equilibrium structures using the four basis sets described above are presented in Table 1 with equilibrium structures for the CISD and CCSD methods given in Table 2. The first important point to note in examining Table 1 is that the MP2 equilibrium geometry of FOOF varies dramatically depending upon the choice of the one particle basis set. This is especially true for the O-F bond distance which increases by 0.207 Å when increasing the basis set from DZP to

Table 2. Total energies and equilibrium structures of FOOF from other correlated levels of theory. Energies in hartrees, bond lengths in Å and angles in degrees

	DZP		TZ2P		Expt[a]
	CISD	CCSD	CISD	CCSD[b]	
Energy	−348.958 659	−349.122 117	−349.124 078	—	—
r_{O-O}	1.316	1.307	1.301	1.278	1.217
r_{O-F}	1.412	1.474	1.407	1.482	1.575
∠OOF	106.2°	106.7°	106.5°	(109.5°)	109.5°
τ	85.6°	86.5°	85.7°	(87.5°)	87.5°

[a] [9]

[b] Least-squares fit of 9 points in Table 3. Angles fixed at experimental values

TZ2P. By comparison the O–F length for the TZ3P basis set (1.685 Å) is not that much changed from the TZ2P basis (1.728 Å), though by normal standards this decrease is still large. Moreover, the TZ2P*f* O–F bond distance is 0.124 Å shorter than the TZ2P value. Clearly the MP2 basis set limit O–F bond distance has not been reached and it is difficult to suggest how large the one-particle basis set must be. The TZ2P*f* results do suggest that *f* functions will be important for difluoroperoxide, at least for the MP2 level of theory.

The three other geometrical parameters listed in Table 1 do not exhibit such a large basis set effect, especially for the torsional angle which does not change by more than 1° once multiple sets of polarization functions are used. The OOF angle changes by only 2.3° between the TZ2P and TZ2P*f* structures, and both TZ2P*f* angles are close to the experimental values. The O–O bond distance increases by 0.126 Å between the DZP and TZ2P geometries, but varies by only 0.038 Å for the three largest basis sets.

Since the TZ2P*f* MP2 structure agrees reasonably well with the experimental r_0 structure ($\Delta R_{\mathrm{OO}} = 0.039$ Å, $\Delta R_{\mathrm{OF}} = 0.029$ Å, $\Delta\mathrm{OOF} = 0.05°$ and $\Delta\tau = 0.7°$), it is tempting to suggest that "the solution" to FOOF has been found. However, given the fantastic basis set effects that are present, such a conclusion would be erroneous. There is certainly no guarantee that QZ3P2*f* MP2 will give a better result than TZ2P*f*. Thus, the relatively good agreement must be considered fortuitous.

The first point to observe from Table 2 is that there are no CPF results. This is because the CPF approach caused FOOF to dissociate when using both the DZP and TZ2P basis sets (the O–F distance $\rightarrow \infty$). Secondly, it is obvious from examining the DZP and TZ2P CISD results that CISD theory does not exhibit the dramatic basis set effect found with MP2. Moreover, since the DZP and TZ2P CISD equilibrium structures vary so little, it appears that Ahlrichs and Taylor's [12] conclusion concerning the applicability of CISD theory to the FOOF molecule may be correct. Namely, that CISD may be incapable of properly describing the O–F bond in FOOF, regardless of the one-particle basis set.

Conversely, the DZP CCSD results seem quite encouraging when one compares them to the DZP MP2 equilibrium structure. One may conclude that the infinite order perturbation theory effect of singles and doubles (which are included in CCSD) causes the O–F bond distance to shorten and the O–O bond to lengthen when compared to second order perturbation theory (MP2). Thus, when the TZ2P MP2 O–F and O–O bonds become too long and too short, respectively, it may be that CCSD will correct them. It should be noted that implicit in this assertion is the hypothesis that the CISD method shows small basis set effects because of its lack of size extensivity. Therefore, it may be that CCSD will demonstrate a basis set effect analogous to MP2, though we certainly expect it to be smaller than that found with MP2.

Unfortunately, the TZ2P basis was too large for a CCSD optimization with the current gradient implementation. However, it was possible to use our new vectorized CCSD energy method. Therefore, we performed a grid of CCSD energies using the TZ2P basis and fixing the OOF and torsional angles at their experimental values. This is a reasonable approximation since the angles vary little with level of theory and basis set augmentation. The CCSD energies are reported in Table 3.

As can be seen, the TZ2P CCSD equilibrium geometry of FOOF does not exhibit the large basis set effects that MP2 produced, which is as expected. The lowest total energy in the grid occurs at $R_{OF} = 1.475$ Å and $R_{OO} = 1.275$ Å, and a least-squares fit of a quadratic potential function using nine points around the minimum yields equilibrium bond lengths of 1.278 Å and 1.482 Å, for R_{OO} and R_{OF}, respectively. Thus, this TZ2P CCSD structure is an improvement over the DZP CCSD equilibrium geometry demonstrating that the CCSD level of theory does not exhibit the radical basis set effects which plague the MP2 method. However, it is difficult to make any definitive conclusions concerning the reliability of the CCSD method without actually obtaining the complete TZ2P, TZ3P and TZ2P*f* CCSD optimum structures.

In summary, we note that large basis sets will be required to obtain a reasonable description of the electronic structure of the FOOF molecule, especially multiple sets of polarization functions. It is also likely that a range of *f* functions will be necessary. These conclusions are based primarily on the MP2 results, though it seems likely that other size-extensive methods will exhibit similar behavior, albeit to a much smaller extent. We must also conclude that the MP2 level of theory, because of its wild basis set effects, is not an appropriate method to use on the FOOF molecule. Moreover, this study demonstrates that the CPF approach is not applicable to the FOOF molecule, since it causes the molecular system to dissociate. It is not clear whether any single reference based method will yield

Table 3. Grid of CCSD energies for FOOF using the TZ2P basis set. The bond angle and torsional angle were fixed at 109.5° and 87.5°, respectively. Energies are in hartrees and are reported as $-(E+349)$. See text for details

		O–O bond distance in Å							
		1.150	1.175	1.200	1.225	1.250	1.275	1.300	1.325
O–F	1.450	—	—	—	—	0.24927	0.25028	0.25049	0.25002
	1.475	—	—	0.24629	0.24891	0.25042	0.25101	0.25082	—
	1.500	—	—	0.24746	0.24960	0.25066	0.25083	0.25027	—
	1.525	—	0.24487	—	0.24950	0.25012	0.24989	—	—
	1.550	—	0.24497	0.24745	0.24869	0.24891	0.24830	—	—
	1.575	0.24086	0.24441	0.24646	0.24729	0.24712	—	—	—
	1.600	0.24013	0.24327	0.24492	0.24536	0.24483	—	—	—
	1.625	0.23886	0.24162	0.24290	0.24299	0.24211	—	—	—
	1.650	0.23710	0.23952	0.24047	0.24023	0.23903	—	—	—
	1.675	0.23492	0.23703	0.23768	0.23714	0.23565	—	—	—
	1.700	0.23237	0.23421	0.23458	0.23376	0.23201	—	—	—

Table 4. MP2 energies and equilibrium structures of *cis* $(NO)_2$ using several large basis sets. See text for details of the basis sets. Energies in hartrees, bond lengths in Å and angles in degrees

	DZP	TZ2P	TZ3P	TZ2P*f*	Expt[a]
Energy	−259.237 010	−259.393 528	−259.472 182	−259.477 664	—
r_{N-N}	2.251	2.223	2.213	2.186	1.75, 2.33
r_{N-O}	1.195	1.170	1.168	1.170	1.15[b]
∠NNO	90.5°	91.1°	91.4°	91.3°	90°, 95°

[a] The left column is taken from [20] and the right column is from [21]
[b] Assumed N-O bond distance

Table 5. Total energies and equilibrium structures of *cis* $(NO)_2$ from other correlated levels of theory. Energies in hartrees, bond lengths in Å and angles in degrees. See text for details

	DZP			TZ2P		Expt[a]
	CISD	CPF	CCSD	CISD	CPF	
Energy	−259.111 315	−259.250 674	−259.226 842	−259.245 514	−259.398 988	—
r_{N-N}	1.742	2.253	1.928	1.772	2.160	1.75, 2.33
r_{N-O}	1.164	1.178	1.176	1.140	1.154	1.15[b]
∠NNO	106.4°	97.0°	102.2°	105.6°	98.1°	90°, 95°

[a] The left column is taken from [20] and the right column is from [21]
[b] Assumed N-O bond distance

accurate theoretical predictions for FOOF, but the best possibilities would be CCSD with a large basis set or, more likely, some form of the CCSDT method (singles, doubles and triples coupled cluster theory). Of course, the CCSDT approach may be, and probably should be, considered a multi-reference technique (in the same sense that a full CI may be considered a multi-reference procedure).

3.2. *Cis-ONNO*

The MP2 equilibrium structures of *cis*-ONNO are presented in Table 4 with those obtained with the other electron correlation methods presented in Table 5. In striking contrast to the MP2 results for FOOF, the MP2 equilibrium structures of $(NO)_2$ show very little basis set dependence. The overall range in the three geometric parameters is only 0.065 Å, 0.025 Å and 0.9° for R_{NN}, R_{NO} and ∠NNO, respectively. Thus, first appearances suggest that reliable results for $(NO)_2$ may be obtained at the MP2 level of theory. It is interesting to note that the MP2 N-N distance (2.186 Å for TZ2P*f* MP2) is significantly longer than the SCF values reported previously [22, 23]. In addition, the MP2 results clearly favor the second gas phase structural determination [21] of *cis*-ONNO, with the TZ2P*f* MP2 structure ($R_{NN} = 2.186$ Å and $\angle = 91.3°$) nearly fitting within the experimental error bars (2.33 ± 12 Å and 95 ± 5°).

Table 6. Grid of CCSD energies for *cis* $(NO)_2$ using the TZ2P basis set. The N-O bond distance was kept constant at 1.15 Å. Energies in hartrees and reported as $-(E+259)$. See text for details

		N-N bond distance in Å			
		1.8	1.9	2.0	2.1
∠NNO	96°	0.35972	0.36913	0.37288	0.37296
	99°	0.36828	0.37350	0.37463	0.37314
	102°	0.37248	0.37502	0.37455	0.37216
	105°	0.37372	0.37463	0.37326	0.37046

However, turning to the $(NO)_2$ structures obtained with the other correlation methods it is clear that problems may exist with the MP2 results. Not surprisingly, the N-N distance is the geometrical parameter which demonstrates large deviations with respect to level of theory, though there is obviously a strong coupling between the N-N distance and the NNO angle. The CISD method predicts the shortest N-N distance (1.742 Å DZP; 1.772 Å TZ2P) with the CPF approach giving the largest N-N distance (2.253 Å DZP; 2.163 Å TZ2P). The CCSD method predicts an N-N distance of 1.928 Å (DZP) which is intermediate, though somewhat closer to CISD.

The DZP and TZ2P CISD and CPF results are consistent with the MP2 structures in that there is not a significant basis set effect. In order to verify that the CCSD method exhibits similar behavior we have performed a coarse grid of CCSD energies using the TZ2P basis and present these in Table 6. The N-O bond length has been fixed at 1.15 Å which seemed a good estimate based upon the structures in Tables 4 and 5. This is also the value assumed in the two gas phase structural determinations of $(NO)_2$. The lowest energy in Table 6 occurs at $R_{NN} = 1.9$ Å and ∠NNO = 102°, which is very close to the DZP CCSD equilibrium values of 1.928 Å and 102.2°, respectively. Thus, it would appear that the structure of $(NO)_2$ is not abnormally sensitive to the choice of the one-particle basis set.

In conclusion, the NO dimer, *cis*-ONNO, exhibits significantly different behavior with respect to level of theory than does difluoroperoxide. Using several basis sets with only one electron correlation method would probably result in a false sense of security. The results presented here do not allow a definitive choice between the two experimental structures. Furthermore, it is difficult to decide exactly which electron correlation method is the best to use. Generally, the best approach is to believe the results from the method which is theoretically most complete (CCSD in this study). However, for the few systems where we have used both CCSD and CPF, these two techniques generally yield quite similar theoretical predictions. Thus, given the very different N-N distances obtained with these two methods (1.928 Å CCSD and 2.253 Å CPF) it is not certain that either result is adequate. It is interesting to note that for both FOOF and $(NO)_2$, the CPF and CCSD methods gave substantially different descriptions. The results presented here indicate some of the pitfalls in studying nitrogen and oxygen compounds with single reference methods.

3.3. FNNF

Equilibrium structures for *cis* FNNF, *trans* FNNF and the transition state to isomerization are reported in Table 7. All geometry optimizations for FNNF were carried out at the MP2 level of theory. The *cis* and *trans* structures have been reported previously [44] in a preliminary report of this work. Firstly, note that while the MP2 equilibrium structures for the minima change with improvements to the basis set, a large basis set dependence is not present. To wit, the variations in R_{NN}, R_{NF} and ∠NNF are only 0.026 Å, 0.012 Å and 0.6° for *cis* FNNF and 0.028 Å, 0.011 Å and 0.7° for *trans* FNNF, respectively. Furthermore, the TZ2P*f* *cis* FNNF structure agrees very well with the experimental microwave structure [8] with deviations of +0.010 Å, +0.002 Å and −0.1° for R_{NN}, R_{NF} and ∠NNF, respectively. The TZ2P*f* *trans* FNNF structure also agrees well with the experimental structure [25], exhibiting differences of $\Delta R_{\mathrm{NN}} = 0.003$ Å, $\Delta R_{\mathrm{NF}} =$

Table 7. MP2 equilibrium structures for *cis* and *trans* FNNF. Absolute energies are given in hartrees, bond lengths in Å and bond angles in degrees. The energy differences are given in kcal/mole

	DZP	TZ2P	TZ2P*f*	Expt[a]
Cis-FNNF				
E_{MP2}	−308.392691	−308.571828	−308.660199	—
$R_{\mathrm{N-N}}$	1.249	1.223	1.224	1.214
$R_{\mathrm{F-N}}$	1.394	1.398	1.386	1.384
∠NNF	113.9	114.5	114.4	114.5
Trans-FNNF				
E_{MP2}	−308.389145	−308.568832	−308.657096	—
$R_{\mathrm{N-N}}$	1.261	1.233	1.233	1.230
$R_{\mathrm{F-N}}$	1.393	1.395	1.384	1.396
∠NNF	103.9	104.5	104.6	105.5
Δ*E*(*Trans-Cis*)[b]	2.2	1.9	1.9	3.1
Transition state				
E_{MP2}	−308.278376	−308.468526	—	—
$R_{\mathrm{N_1-N_2}}$	1.177(1.176)[c]	1.150	—	—
$R_{\mathrm{F_1-N_1}}$	1.304(1.303)[c]	1.289	—	—
$R_{\mathrm{F_2-N_2}}$	1.742(1.743)[c]	1.777	—	—
$\angle \mathrm{N_1N_2F_2}$	109.0(108.9)[c]	107.5	—	—
$\angle \mathrm{F_1N_1N_2}$	165.4(170.0)[c]	170.1	—	—
τ	133.7(180.0)[c]	180.0	—	
Δ*E*(TS-*Cis*)[d]	71.7(71.71)[c]	64.8	—	32.2

[a] The *cis* microwave structure is from [8] and the electron diffraction structure of *trans* FNNF is from [25]

[b] The experimental Δ*E*(*Trans-Cis*) is from [24]

[c] The values in parentheses refer to the planar second order transition state lying at −308.278360 hartrees. N_1 is bonded to F_1 and N_2 is bonded to F_2

[d] The experimental Δ*E*(TS-*Cis*) is from [47]

0.012 Å and Δ∠NNF = 0.9°. Thus, based upon the small basis set effects and the comparisons with experiment, it appears that the electronic structure of FNNF is reliably described at the MP2 level of theory. In fact, consideration of the microwave [8] and electron diffraction [25] ($R_{NN} = 1.213$ Å, $R_{NF} = 1.410$ Å and ∠NNF = 114.5°) structures of *cis* FNNF where R_{NF} (electron diffraction) is 0.026 Å longer than R_{NF} (microwave), and the comparisons given above leads to the conclusion that the electron diffraction *trans* FNNF R_{NF} is probably a little too long.

The MP2 *trans-cis* energy differences listed in Table 7 are also in good agreement with the experimental value of +3.1 kcal/mole. *Trans-cis* energy differences determined with the other electron correlation methods are presented in Table 8. The differences among the various electron correlation methods is small which is another indication that *cis* and *trans* FNNF are well described by MP2. The one conclusion which might be supported by the results in Table 8 is that higher order correlation effects tend to favor the *trans* isomer, though the equilibrium structures must be determined at the higher levels of theory in order to make a definitive statement.

It would be convenient to know of a diagnostic which may be used to determine *a priori* whether a particular method is well suited for the chemical system of

Table 8. Total energies (hartrees), relative energies (kcal/mole), and number of configuration state functions (CSF) for the *cis* and *trans* isomers of FNNF. See text for the description of the basis sets. All energy evaluations were performed at the MP2 equilibrium geometries and are reported as $-(E+308)$

Basis	CISD	CPF	CCSD	CSF
DZP				
Cis-FNNF	0.302162	0.417060	0.404586	80 411
Trans-FNNF	0.300431	0.414014	0.402087	80 411
ΔE(Trans-Cis)[a]	1.1	1.9	1.6	—
Transition state (C_1)	0.168939	0.299162	0.278109	296 065
Transition state (C_s)	0.169558	0.296693	0.278433	160 435
ΔE(TS-*Cis*)[b]	83.6(83.2)[c]	74.0(75.5)[c]	79.4(79.2)[c]	—
TZ2P				
Cis-FNNF	0.454220	0.588916	0.575212	267 011
Trans-FNNF	0.454027	0.586544	0.573634	267 011
ΔE(*Trans-Cis*)[a]	0.1	1.5	1.0	—
Transition state (C_s)	0.331025	0.479828	0.439370	533 315
ΔE(TS-*Cis*)[b]	77.3	68.5	85.2	—
TZ2P*f*				
Cis-FNNF	0.530879	0.677614	0.662853	552 391
Trans-FNNF	0.530424	0.675000	0.661013	552 391
ΔE(*Trans-Cis*)[a]	0.3	1.6	1.2	—

[a] Experimental value from [24] is 3.05 kcal/mole

[b] Experimental value from [47] is 32.3 kcal/mole

[c] Values in parentheses refer to the energy difference for the second order planar transition state, C_s symmetry

interest. The reference coefficient, C_0, is often used as such a diagnostic, though it is becoming evident that this simple test is not always reliable since the molecular orbitals are biased towards the reference. However, we have noticed another simple test which seems to be more reliable. Namely, the euclidean norm of the CCSD t_1 vector gives an indication of the degree of orbital relaxation taking place in the CCSD procedure [46]. We have noticed that for "problem molecules" such as FOOF the norm of the t_1 vector is large (e.g. TZ2P FOOF $\sim$ 0.168), whereas for normal, well-behaved chemical systems this quantity is significantly smaller (e.g. TZ2P $H_2O \sim 0.027$). The norm of t_1 for *cis* and *trans* FNNF (0.091 and 0.081 for TZ2P) is consistent with our observations that *cis* and *trans* FNNF are reasonably well-behaved.

The success with *cis* and *trans* FNNF lead us to consider the isomerization transition state (TS). The TS equilibrium structure and energetics are also given in Tables 7 and 8. The DZP MP2 TS is non-planar and has no symmetry, though the planar structure (C_s symmetry) is only 0.01 kcal/mole higher in energy, and has a second imaginary frequency of only 58 cm^{-1}. Thus, the potential energy surface along the torsional mode is very flat and even for the DZP non-planar structure the N–N distance is consistent with that of at least a double bond. It is not too surprising, then, to find that the TZ2P MP2 TS is planar. Aside from the torsional angle τ, the TS geometrical parameters do not change dramatically as the basis set size is increased from DZP to TZ2P. However, the TS N–F bond distances do exhibit a larger basis set effect than did the *cis* or *trans* quantities.

A second indication that problems may exist with the TS is the fact that the theoretical barrier height to isomerization is much larger than the experimentally determined value [47]. Moreover, the barrier heights determined by the different electron correlation methods span a large range indicating that the precise structure of the TS is probably very dependent upon the level of theory utilized. Finally, we note that the norm of the CCSD t_1 vector for the TS (TZ2P) is 0.118, suggesting that the FNNF TS will not be well represented at the MP2 level of theory. Interestingly, the TZ2P MP2 C_0 for *cis*, *trans* and TS FNNF (0.91, 0.91, 0.90, respectively) provides further evidence that the value of C_0 is not a good measure of the non-dynamical electron correlation requirements. Therefore, we believe that the TS would have to be optimized at the CCSD level of theory to obtain a more reliable barrier to isomerization.

The success with *cis* and *trans* FNNF also lead us to predict their vibrational spectra and these results are presented in Table 9. To the best of our knowledge, only one of the fundamentals of *cis* FNNF has been deduced [8]. As can be seen from Table 9 the *cis* FNNF TZ2P MP2 harmonic frequency ω_3 is in very good agreement with the ν_4 value of Kuczkowski and Wilson [8]. Based upon the accuracy of the *cis* and *trans* structures and the results of previous studies [48–50] we expect the TZ2P MP2 harmonic frequencies to be quite accurate with the N–N and N–F stretching modes probably somewhat too low. Additionally, it is encouraging to note that the imaginary mode for the TZ2P MP2 TS takes the TS towards the more stable *cis* isomer.

Table 9. Harmonic frequencies (cm^{-1}) for the isomers of FNNF determined at the MP2 level of theory

Isomer/basis	$\omega_1(a_g)$	$\omega_2(a_g)$	$\omega_3(a_g)$	$\omega_4(a_u)$	$\omega_5(b_u)$	$\omega_6(b_u)$
trans-FNNF						
DZP	1457	1047	608	360	1028	419
TZ2P	1471	1005	601	361	984	421
	$\omega_1(a_1)$	$\omega_2(a_1)$	$\omega_3(a_1)$	$\omega_4(a_2)$	$\omega_5(b_2)$	$\omega_6(b_2)$
cis-FNNF						
DZP	1482	936	337	550	1001	755
TZ2P	1494	880	340	555	957	723
Expt[a]			300 ± 35			
	$\omega_1(a')$	$\omega_2(a')$	$\omega_3(a')$	$\omega_4(a')$	$\omega_5(a')$	$\omega_6(a'')$
Transition state[b]						
DZP	2209	1003	542	289	830*i*	80
TZ2P	2201	996	538	276	759*i*	96

[a] [8]

[b] The DZP transition state contains no elements of symmetry whereas the TZ2P transition state conforms to C_s symmetry

In summary of our FNNF studies, we note that *cis* and trans difluorodiazene are reasonably well represented at the MP2 level of theory but that the TS to isomerization is not. At the TZ2P*f* MP2 level of theory, the equilibrium structures of *cis* and *trans* FNNF agree very well with the experimental structures. The norm of the CCSD t_1 vector seems to give a good indication of the reliability of the results obtained with single reference electron correlation methods.

4. Concluding remarks

The results of this study indicate that all compounds containing fluorine, oxygen and nitrogen only, will not require similar theoretical treatments in order to obtain a specific level of accuracy. Thus, for the time being each system must be carefully and individually examined.

We have suggested a new diagnostic test whereby the reliability of single reference electron correlation methods may be determined *a priori*, which is the norm of the CCSD t_1 vector. It is well established [46, 51, 52] that the e^{T_1} present in the CCSD wavefunction accounts for orbital relaxation or non-dynamical electron correlation effects. Thus, the norm of the t_1 vector being large indicates that non-dynamical electron correlation is important. However, a large $|t_1|$ does not mean that one should attempt using "optimized" molecular orbitals for the CCSD procedure. Studies using localized orbitals [51, 52] and Brueckner-like orbitals [46] (i.e. $|t_1| \sim 0$) for the CCSD method have established that the e^{T_1} component of the CCSD wavefunction essentially accounts for non-dynamical electron correlation. A large $|t_1|$ (for canonical RHF SCF molecular orbitals) does indicate that there are other important configurations in the n-particle space that should probably be used as references in a singles and doubles dynamical electron correlation procedure. Therefore, a large $|t_1|$ suggests that the additional dynamic electron correlation which would be recovered in a multi-reference CCSD (MR-CCSD) method (and not included in a single reference CCSD procedure) will be important.

Comparison of the TZ2P CCSD $|t_1|$ for the chemical systems included in this study [0.168 FOOF; 0.099 $(NO)_2$; 0.091 *cis* FNNF; 0.081 *trans* FNNF; 0.118 TS FNNF] with the analogous value for H_2O (0.027) along with consideration of the quality of the single reference results, indicates that reasonably well-behaved systems will have smaller $|t_1|$ values. We expect that this criterion for well-behaved systems will be refined as more molecules (both well-behaved and difficult systems) are studied with the CCSD method. The important point is that the norm of the t_1 vector seems to be a much more sensitive diagnostic for determining the reliability of a single reference based dynamical electron correlation technique than is the coefficient (C_0) of the reference in the correlated wavefunction.

Finally, because of the importance of f functions for both FOOF and FNNF, and similar results in the past for F_2 [28] and other fluorine containing compounds, we believe that a range of f functions is probably necessary in order to obtain highly accurate theoretical predictions for chemical systems which contain fluorine, at least when using segmented contracted gaussian basis sets. Given the rather large basis sets which must be used in order to obtain highly accurate theoretical predictions for these systems, it would seem worthwhile to investigate the use of ANO basis sets [53] in an attempt to reduce the resulting n-particle basis.

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Note added in proof. In order to compare the $|t_1|$ diagnostic between chemical systems with different numbers of electrons, the diagnostic must be normalized by the number of electrons. This conclusion becomes obvious if one considers the CCSD wavefunction for two Be atoms at infinite separation (correlating only the valence). Clearly, a desirable characteristic of our diagnostic is that for this situation it be equivalent to that of a single Be atom. This property will only hold if the $[\mathrm{Be} \ldots \mathrm{Be}] t_1$ norm is divided by $2^{1/2}$. Thus, in order to compare the diagnostic for different chemical systems with different numbers of electrons, it must be normalized by the number of electrons included in the correlation procedure. However, in viewing $|t_1|$ as a measure of orbital relaxation, it would also seem necessary to count only the valence electrons since the core electrons should contribute very little to t_1. Reevaluating the diagnostic as $[(\Sigma(t_u^\beta)^2)/(\text{no. of valence electrons})]^{1/2}$ for the systems included in this study we obtain 0.0211, 0.0329, 0.0186, 0.0165, 0.0241 and 0.0095 for $(NO)_2$, FOOF, cis FNNF, *trans* FNNF, TS FNNF and H_2O, respectively. These values are entirely consistent with our discussion and conclusions in the last two sections and provide even stronger evidence that the MP2 level of theory is not adequate for TS FNNF.