Theor Chem Acc (1997) 97:185–194

Theoretical
Chemistry Accounts

A challenge for density functional theory: the XONO and XNO_2 (X = F, Cl, and Br) molecules

Timothy J. Lee[1], **Charles W. Bauschlicher, Jr.**[1], **Dylan Jayatilaka**[2]

[1]MS230-3, NASA Ames Research Center, Moffett Field, CA 94035-1000, USA
[2]Department of Chemistry, The University of Western Australia, Nedlands 6907, Western Australia

Received: 12 February 1997 / Accepted: 25 March 1997

Abstract. The equilibrium geometries, harmonic frequencies, dipole moments, infrared intensities, and relative energies of the *cis*-XONO, *trans*-XONO, and XNO_2 (X=F, Cl, and Br) have been investigated using four functionals in common use in Kohn-Sham density functional theory (DFT) calculations. Two of the functionals include non-local or gradient correction terms, while the other two also incorporate some exact Hartree-Fock exchange and are labeled hybrid functionals. The quality of the results obtained from the functionals is determined by comparison to previously published high-level coupled-cluster calculations. The hybrid functionals perform better for prediction of the equilibrium geometries, where the two gradient corrected functionals yield qualitatively incorrect molecular structures for *cis*-FONO and *cis*-ClONO. None of the functionals perform well in predicting all six harmonic frequencies, showing that the correlation between equilibrium geometries and harmonic frequencies is not as strong for these DFT methods as it is for conventional wavefunction ab initio methods, such as coupled-cluster theory. Results from the various functionals generally come into better agreement with each other and also with the coupled-cluster results moving down the periodic table.

Key words: Density functional theory – Hybrid methods – Coupled-cluster theory – Cis-XONO (X=F, Cl and Br) molecules and isomers

1 Introduction

There has been an explosion of applications of density functional theory (DFT) to chemical phenomena over the last few years (e.g., see Refs. [1, 2] for several recent reviews). The progress made with regard to the accuracy and reliability of DFT methods during this time is largely responsible for this recent impact, although the relatively inexpensive nature of DFT calculations is also an important factor in their popularity. The enhanced accuracy is a result of two improvements. Firstly, standard DFT packages now use much better numerical grids and faster techniques for the numerical integration over these grids. Secondly, much better functionals, including non-local gradient corrections and hybrid schemes which incorporate some exact (Hartree-Fock) exchange have been developed and are now in standard use. However, even with all of these advances, there remain some noticeable problems. Perhaps the greatest difficulty when applying a single DFT functional to a particular species or class of species is that it is not possible to evaluate the reliability of the results without the aid of higher levels of theory [e.g., singles and doubles coupled-cluster theory including a perturbational estimate of the effects of connected triple excitations, denoted CCSD(T)], or the aid of accurate experimental values. That is, there is no series of functionals that will always converge systematically to the correct answer. As a result, there is an increasing number of molecules for which one or more of these new functionals is found not to perform very well. The *cis*- FONO molecule is an example of one such species. For example, it has been shown [3–6] that the equilibrium molecular geometry obtained with the local density approximation (LDA) is qualitatively incorrect, predicting the F—O bond distance to be too long by ≈0.25 Å and the central O—N bond distance to be too short by a similar amount, as compared to a CCSD(T) equilibrium structure obtained with a triple zeta, double polarized basis set that also includes a set of *f* functions on each atom (TZ2Pf). Additionally, the gradient-corrected BLYP functional predicts an equilibrium structure that differs even more from the CCSD(T)/TZ2Pf geometry.

One commonly used approach for estimating the reliability of a particular level of theory for a given species is to apply the same level of theory to similar molecules, but even this method fails to indicate that the LDA and BLYP DFT functionals will not perform well for *cis*-

---

Correspondence to: T. Lee

FONO, as both the LDA and BLYP DFT methods yield reasonable molecular geometries for *trans*-FONO [4–6]. Thus far, only the hybrid functional, B3LYP (see Ref. [7] and references therein), has been shown to yield reasonable molecular structures for both *trans*- and *cis*-FONO [6]. This functional includes some exact (i.e., Hartree- Fock) exchange, which is the primary difference between it and BLYP and thus is presumably the main reason for the difference in the BLYP and B3LYP *cis*-FONO equilibrium geometries. We should note, however, that even the B3LYP method yields a qualitatively incorrect geometry for some basis sets [8]; for example, the F—O bond length is 1.70 Å and the O—N bond length is 1.21 Å for the 6-31+G* basis set, compared to 1.4331 and 1.4454 Å for the CCSD(T)/TZ2Pf level of theory [6].

Interestingly, a recent investigation of fluorine-oxygen bonding [9] [using CCSD(T)/TZ2P results] showed an anomaly in the relationship between the F—O bond distance and the F—O quadratic force constant for the *cis*-FONO. That is, the F—O force constant was found to be smaller than expected based on the F—O bond distance relative to analogous data for several other molecules containing a fluorine-oxygen bond. It was concluded [9] that this effect was due to a combination of lone-pair repulsions between bonded atoms, and attractive dispersion interactions between the fluorine and terminal oxygen atoms. This may also explain why simple DFT functionals do not properly describe *cis*-FONO, since it is well known that they do not properly describe the interplay between electrostatic and dispersion interactions.

Further study of chlorine-oxygen and bromine-oxygen bonding [10] has shown that this same anomaly exists for the correlation between bond length and force constants in the chlorine and bromine analogs. Thus, the purpose of the present study is to investigate the equilibrium structures, dipole moments, harmonic frequencies, and infrared (IR) intensities of the *cis*- and *trans*-XONO (X=F, Cl, and Br) species as well as their XNO_2 isomers. Since all of the *cis*-XONO species appear to exhibit a through space interaction that is not present in the *trans* isomer, it is of interest to determine whether DFT methods will also have problems properly describing *cis*-ClONO and *cis*-BrONO as well. Four DFT functionals, in common use today, and two one-particle basis sets are investigated. Accurate CCSD(T) results are taken from Refs. [4, 6, 10–12] in order to assess the reliability of the various DFT results. We note that there is little reliable experimental data available for molecular geometries of the XONO compounds, with the only exception being the Cl—O bond distance in *cis*- ClONO. At least some experimental fundamental vibrational frequencies are available for all of the *cis*-XONO, as well as for *trans*-ClONO and *trans*-BrONO. In all of these cases, the CCSD(T)/TZ2P predictions are in very good agreement with the reliable experimental data. For the XNO_2 compounds, relatively more experimental information is available (one major exception being a molecular structure for $BrNO_2$), and in these cases the CCSD(T)/TZ2P predictions are also in very good agreement with experiment, except for the Br—N stretch of $BrNO_2$, where the experimental value has been conclusively shown to be in error by consideration of the trend in the X—N stretches. For detailed comparison of the CCSD(T)/TZ2P and experimental quantities, the interested reader is referred to Refs. [4, 6, 11, 12]. For purposes of the present study, it is important to recognize that the CCSD(T)/TZ2P data is in very good agreement with the available experimental information, and therefore that since the CCSD(T)/TZ2P data is complete, it provides a convenient and reliable benchmark set of results with which to compare the DFT results. Detailed description of the theoretical methods is presented in the next section, while the results and discussion are presented thereafter. Conclusions are presented in the final section.

2 Theoretical methods

Equilibrium structures, dipole moments, harmonic frequencies, and IR intensities were obtained using four different density functionals. The two simplest functionals contain local and non-local exchange and correlation terms, and only differ in the specific form used for the correlation functional. Both utilize the Slater local exchange together with Becke's [13] non-local (or gradient corrected) exchange term. One, denoted BLYP, is further comprised of the correlation functional from Lee et al. [14] (which includes both local and non-local terms), while the BP86 functional contains local [15] and non-local correlation terms from Perdew [16]. The other two approaches are so-called hybrid methods since they incorporate some degree of exact Hartree-Fock exchange. The Becke hybrid functional (B3PW91) [17] is of the following form:

$$E_{xc} = (1-A)*E_x^{\mathrm{Slater}} + A*E_x^{\mathrm{HF}} + B*E_x^{\mathrm{Becke}} + E_c^{\mathrm{LSD}} + C*E_c^{\mathrm{PW91}},$$

where E_x^{HF} is the Hartree-Fock exchange, E_x^{Slater} is the local exchange functional taken from Slater, E_x^{Becke} is the gradient correction for exchange taken from Becke [13], E_c^{LSD} is the local spin density (LSD) local correlation functional [18], and E_c^{PW91} is the 1991 gradient functional of Perdew and Wang [18]. The coefficients, A, B, and C, were determined using accurate experimental data [19] (56 atomization energies, 42 ionization potentials, and 8 proton affinities) and the ten first-row total atomic energies [20]. At the time of its introduction, the accuracy of this hybrid functional was dramatically better than for any of the existing functionals. The B3LYP hybrid functional, proposed by Stephens et al. [7], replaces $E_c^{\mathrm{LSD}} + C*E_c^{\mathrm{PW91}}$ by $C*E_c^{\mathrm{LYP}} + (1-C)E_c^{\mathrm{VWN}}$, where E_c^{LYP} is the correlation functional of Lee et al. [14], and E_c^{VWN} is the total correlation functional of Vosko et al. [21]. Note that the $(1-C)E_c^{\mathrm{VWN}}$ term is added because E_c^{LYP} contains both local and non-local terms.

Two basis sets were employed in the present investigations. The first consists of the 6-31G^* basis set for oxygen, fluorine, chlorine, and hydrogen together with the Binning and Curtiss [22] $9s6p2d$(d) basis set for bromine. The second basis set is denoted TZ2P (for triple zeta, double polarized) and is composed of Dunning's [23] $5s3p$ contraction for nitrogen, fluorine, and oxygen with polarization orbital exponents (two d functions for N, F, and O) taken from Dunning [24]. The Cl TZ2P basis set is composed of McLean and Chandler's [25] $[6s5p]$ contraction supplemented with two sets of polarization functions ($\alpha_d = 1.072, 0.357$). The Br TZ2P basis set is composed of a $6s5p2d$ contraction of a $17s13p6d$ primitive set as given by Schaefer et al. [26]. Orbital exponents of the two d polarization functions are $\alpha_d = 0.674$ and 0.225. All six components of the Cartesian d functions were included in the basis sets for consistency with previously published CCSD(T)/TZ2P results.

All calculations were performed with the Gaussian 94 program [27], and were performed either on the NASA Ames Computational Chemistry Branch's IBM RS/6000 590 computers or on DEC AlphaStations model 250 4/266 at the Department of Chemistry, University of Western Australia.

3 Results and discussion

3.1 Geometries and dipole moments

Equilibrium structures and dipole moments, obtained with the B3LYP, B3PW91, BP86, and BLYP functionals, for the *cis*-XONO, *trans*-XONO, and XNO_2 molecules are presented in Tables 1–3, respectively. For comparison, CCSD(T)/TZ2P geometries and dipole moments are also included [4, 10–12]. The results for *cis*-FONO are consistent with earlier studies [3–6]. That is, the BP86 and BLYP functionals yield a structure with a very long F—O bond distance (1.62–1.75 Å) and a short central O—N bond distance (1.21–1.27 Å), while both hybrid functionals, B3LYP and B3PW91, give equilibrium structures that are at least qualitatively similar to the CCSD(T)/TZ2P one. It should also be noted that the FON and ONO bond angles obtained with the BP86 and BLYP functionals exhibit large errors relative to the CCSD(T)/TZ2P values. For *cis*-FONO, the B3LYP/TZ2P equilibrium structure is in the best agreement with the CCSD(T)/TZ2P geometry, especially for the central O—N bond distance and the two bond angles. The best

Table 1. Summary of the *cis*-XONO geometries. Bond lengths are in Å, angles are in degrees, and the dipole moments are in Debye

Method	r(X—O)	r(O—N)	r(N—O)	∠(XON)	∠(ONO)	μ
FONO 6-31G*						
B3LYP	1.4366	1.4120	1.1718	111.88	116.56	0.48
B3PW91	1.4345	1.3744	1.1732	112.80	117.60	0.45
BP86	1.6263	1.2559	1.1998	117.23	129.03	1.41
BLYP	1.6404	1.2650	1.2039	116.94	128.55	1.42
FONO TZ2P						
B3LYP	1.4426	1.4230	1.1559	112.86	117.41	0.77
B3PW91	1.4527	1.3558	1.1620	114.39	119.56	0.70
BP86	1.7309	1.2109	1.1864	117.82	135.98	2.68
BLYP	1.7547	1.2153	1.1903	117.61	135.89	2.75
CCSD(T)	1.4417	1.5019	1.1570	108.96	114.91	1.00
ClONO 6-31G*						
B3LYP	1.7779	1.3645	1.1783	117.03	118.55	0.15
B3PW91	1.7646	1.3498	1.1763	117.00	118.67	0.16
BP86	1.9572	1.2744	1.1994	117.27	125.68	0.98
BLYP	1.9903	1.2791	1.2038	117.73	126.11	1.05
ClONO TZ2P						
B3LYP	1.7442	1.4091	1.1607	116.58	117.53	0.30
B3PW91	1.7344	1.3824	1.1614	116.54	117.81	0.26
BP86	1.9484	1.2713	1.1895	117.39	125.88	0.84
BLYP	1.9906	1.2727	1.1934	118.11	126.70	0.92
CCSD(T)	1.7205	1.4894	1.1614	113.63	115.56	0.62
BrONO 6-31G*						
B3LYP	1.9572	1.3226	1.1852	116.93	119.80	0.48
B3PW91	1.9456	1.3094	1.1826	116.76	119.99	0.45
BP86	2.0538	1.2852	1.2023	116.36	123.47	0.24
BLYP	2.0747	1.2948	1.2065	116.95	123.48	0.20
BrONO TZ2P						
B3LYP	1.9369	1.3327	1.1723	117.80	119.84	0.55
B3PW91	1.9241	1.3182	1.1707	117.41	120.02	0.50
BP86	2.0677	1.2750	1.1920	117.34	124.77	0.35
BLYP	2.1015	1.2809	1.1956	118.08	125.19	0.34
CCSD(T)	1.8748	1.4322	1.1710	115.66	116.68	0.73

Table 2. Summary of the *trans*-XONO geometries. Bond lengths are in Å, angles are in degrees, and the dipole moments are in Debye

Method	r(X—O)	r(O—N)	r(N—O)	∠(XON)	∠(ONO)	μ
FONO 6-31G*						
B3LYP	1.4141	1.4934	1.1668	104.41	107.80	0.57
B3PW91	1.4027	1.4678	1.1668	104.70	107.80	0.40
BP86	1.4251	1.5512	1.1772	105.28	107.56	0.59
BLYP	1.4382	1.5911	1.1761	104.94	107.81	0.81
FONO TZ2P						
B3LYP	1.4151	1.5279	1.1471	104.74	108.00	1.07
B3PW91	1.4016	1.4936	1.1495	104.95	108.01	0.80
BP86	1.4287	1.5821	1.1587	105.72	107.67	1.11
BLYP	1.4448	1.6300	1.1562	105.64	107.92	1.42
CCSD(T)	1.4367	1.5322	1.1582	103.06	107.71	1.15
ClONO 6-31G*						
B3LYP	1.7148	1.5027	1.1649	109.79	107.57	0.61
B3PW91	1.7008	1.4803	1.1632	109.86	107.66	0.60
BP86	1.7222	1.5563	1.1747	110.23	107.22	0.54
BLYP	1.7405	1.5879	1.1754	110.32	107.25	0.62
ClONO TZ2P						
B3LYP	1.7021	1.5346	1.1457	109.75	108.15	0.70
B3PW91	1.6871	1.5100	1.1463	109.70	108.18	0.60
BP86	1.7060	1.5968	1.1561	110.29	107.90	0.74
BLYP	1.7242	1.6372	1.1554	110.59	107.94	0.89
CCSD(T)	1.7128	1.5417	1.1560	107.48	108.05	0.76
BrONO 6-31G*						
B3LYP	1.8616	1.4808	1.1681	110.18	107.79	0.96
B3PW91	1.8499	1.4624	1.1668	110.13	107.81	0.99
BP86	1.8699	1.5379	1.1776	110.19	107.39	0.74
BLYP	1.8876	1.5666	1.1785	110.39	107.41	0.73
BrONO TZ2P						
B3LYP	1.8453	1.5120	1.1495	110.36	108.29	0.84
B3PW91	1.8322	1.4853	1.1504	110.11	108.37	0.83
BP86	1.8524	1.5707	1.1599	110.59	107.97	0.72
BLYP	1.8668	1.6150	1.1582	111.07	108.06	0.81
CCSD(T)	1.8488	1.5285	1.1584	108.42	108.13	0.81

fully optimized theoretical structure for *cis*-FONO, obtained at the CCSD(T)/TZ2Pf level of theory [6], is $r_{\mathrm{FO}} = 1.4331$ Å, $r_{\mathrm{ON}} = 1.4454$ Å, $r_{\mathrm{NO}} = 1.1619$ Å, ∠FON = 110.4, and ∠ONO = 115.8. Moreover, with the other four parameters fixed at these values, the r_{ON} quantity was optimized [8] using the aug-cc-pVQZ basis set, without the diffuse f and g functions. A value of 1.438 Å was obtained, supporting the accuracy of the CCSD(T)/TZ2Pf structure. Hence the noticeable deviation between the B3LYP/TZ2P and CCSD(T)/TZ2P r_{ON} values is mainly due to one-particle basis set deficiencies for the CCSD(T) approach [the previous CCSD(T) studies have shown that the central O—N bond distance is the geometrical parameter most sensitive to one-particle basis set improvements].

The B3LYP/TZ2P and B3PW91/TZ2P dipole moments are also in qualitative agreement with the CCSD(T)/TZ2P value, but, as for the equilibrium structure, there is certainly not quantitative agreement. Dipole moments obtained with the BP86 and BLYP functionals are much too large, especially with the TZ2P basis set.

It is well known that convergence of DFT calculated properties due to improvements in the one-particle basis set is much more rapid than for conventional ab initio methods, especially with respect to high angular momentum functions. This is due to the fact that DFT methods are not describing the wavefunction of the molecule (and hence do not need to describe the electron–electron correlation cusp), but rather they are describing the electron density, which is a more smoothly varying function over all space. Nonetheless, differences between the 6-31G* and TZ2P basis sets for the structure and dipole moment of *cis*-FONO are reasonably large and are certainly larger than is typically found for DFT methods. Interestingly, this effect is much more pronounced for the BP86 and BLYP functionals (e.g., the F—O bond distance changes by > 0.1 Å), perhaps suggesting that examination of one-particle basis set convergence may be one approach for detecting cases where the DFT results may be unreliable.

Examination of the structures and dipole moments for *cis*-ClONO shows that the hybrid functionals yield qualitatively correct results relative to the CCSD(T)/TZ2P values, but again there is definitely not quantitative agreement with the CCSD(T)/TZ2P level of theory. More importantly, the BP86 and BLYP functionals yield geometries for *cis*-ClONO that are qualitatively incor-

Table 3. Summary of the XNO_2 geometries. Bond lengths are in Å, angles are in degrees, and the dipole moments are in Debye

Method	r(X—N)	r(N—O)	∠(ONO)	μ
FNO_2 6-31G*				
B3LYP	1.4574	1.1889	134.98	0.13
B3PW91	1.4438	1.1848	134.83	0.08
BP86	1.4967	1.1998	135.43	0.34
BLYP	1.5185	1.2041	135.60	0.44
FNO_2 TZ2P				
B3LYP	1.4857	1.1753	136.24	0.60
B3PW91	1.4662	1.1729	135.91	0.49
BP86	1.5313	1.1868	136.88	0.89
BLYP	1.5584	1.1898	137.19	1.04
CCSD(T)	1.4733	1.1849	135.72	0.49
$ClNO_2$ 6-31G*				
B3LYP	1.9120	1.1946	132.71	0.04
B3PW91	1.8879	1.1906	132.64	0.03
BP86	1.9594	1.2048	133.61	0.53
BLYP	1.9945	1.2093	133.72	0.64
$ClNO_2$ TZ2P				
B3LYP	1.9047	1.1859	132.77	0.16
B3PW91	1.8817	1.1825	132.74	0.18
BP86	1.9494	1.1969	133.60	0.32
BLYP	1.9827	1.2011	133.63	0.37
CCSD(T)	1.8771	1.1978	132.03	0.45
$BrNO_2$ 6-31G*				
B3LYP	2.0705	1.1971	132.06	0.39
B3PW91	2.0508	1.1924	132.18	0.37
BP86	2.1058	1.2081	132.77	0.07
BLYP	2.1330	1.2136	132.63	0.07
$BrNO_2$ TZ2P				
B3LYP	2.0648	1.1888	132.01	0.50
B3PW91	2.0441	1.1847	132.12	0.45
BP86	2.1043	1.2000	132.78	0.01
BLYP	2.1338	1.2051	132.61	0.03
CCSD(T)	2.0396	1.2005	131.41	0.75

rect. In this case, the major discrepancies are for the Cl—O and central O—N bond distances, and the ONO bond angle. The error for the ClON bond angle is not small either, but here the variation among the various functionals is much smaller than the overall difference to the CCSD(T)/TZ2P value, which is not the case for *cis*-FONO (see the B3LYP/TZ2P results for *cis*-FONO). Another difference between the results for *cis*-FONO and *cis*-ClONO is the fact that the error in the BP86/TZ2P and BLYP/TZ2P X—O and central O—N bond distances is ≈0.25–0.30 Å for X=F, but is ≈ 0.20–0.25 Å for X=Cl. Similarly, errors in the two bond angles are smaller for *cis*-ClONO relative to *cis*-FONO. It is thus apparent that the BP86 and BLYP functionals do not have as much difficulty describing *cis*-ClONO as they do *cis*-FONO.

Similar to the situation for *cis*-FONO, the B3LYP and B3PW91 dipole moments are smaller than the CCSD(T) value whereas the BP86 and BLYP values are too large. One difference, however, is that the magnitude of the underestimate for the hybrid functionals is similar to the magnitude of the overestimate for the other two functionals, again suggesting that the BP86 and BLYP functionals do not have as much difficulty in describing *cis*-ClONO as they do *cis*-FONO.

Examination of the various equilibrium structures for *cis*-BrONO shows that the BP86 and BLYP methods yield a Br—O bond distance that is too long and a central O—N bond distance that is too short, similar to the situation for *cis*-FONO and *cis*-ClONO. However, the difference between geometries obtained with the (B3LYP/B3PW91) and (BP86/BLYP) functionals is even smaller for *cis*-BrONO than it was for *cis*-ClONO. Indeed, for BP86 and BLYP Br—O bond distances are only about 0.13–0.18 Å longer than the B3LYP and B3PW91 values. A similar trend is observed for the other geometerical parameters also. While the BP86 and BLYP geometries are not as accurate as the B3LYP and B3PW91 structures [relative to the CCSD(T)/TZ2P geometry], they are not "qualitatively" incorrect, which is a departure from the situation for *cis*-FONO and *cis*-ClONO. Thus, the differences between the functionals with and without exact exchange become smaller on going from X=F, to X=Cl, to X=Br for *cis*-XONO. This trend is also observed for the dipole moment, where for *cis*-BrONO all of the DFT values are now smaller than the CCSD(T)/TZ2P quantity.

For *cis*-FONO, it was noted above that the BP86 and BLYP geometries were more sensitive to one-particle basis set improvements than were the B3LYP and B3PW91 functionals. For *cis*-ClONO and *cis*-BrONO, however, the geometrical changes due to improvement of the basis set from 6-31G* to TZ2P are much smaller for all of the functionals, and the BP86 and BLYP functionals do not appear to be any more sensitive than are the hybrid functionals. Since the BP86 and BLYP functionals do not describe *cis*-FONO as well as they describe *cis*-ClONO and *cis*-BrONO, it is perhaps the case that significant basis set effects are not exhibited unless the molecule under study is very poorly described by the particular functional, thus limiting the usefulness of this technique for estimating the reliability of results obtained from the particular functional.

The situation is quite different for the *trans*-isomers (Table 2). Here all of the functionals yield qualitatively correct geometries, even for *trans*-FONO. The central O—N bond distance is the most sensitive geometerical parameter for all three *trans* isomers. The variation among the different functionals is only ≈0.14 Å for *cis*-FONO and this decreases to ≈0.13 Å for both *cis*-ClONO and *cis*-BrONO. It is noteworthy that in every case, the BP86 and BLYP functionals yield central O—N bond distances that are noticeably too long, but nevertheless, the BP86 and BLYP structures would still have to be classified as qualitatively correct. As for the *cis* isomers, the two hybrid functionals generally yield the better equilibrium geometries. Also similar to the *cis* isomers, differences in the predicted geometries among the various functionals generally decrease in the order *trans*-FONO > *trans*-ClONO > *trans*-BrONO.

The various functionals all yield dipole moments that are in reasonable agreement with each other and with the CCSD(T)/TZ2P value for *trans*-ClONO and *trans*-BrONO. The variation is larger for *trans*-FONO, but this variation is still considerably smaller than that observed for *cis*-FONO. Similar to the trend for the geometries, the variation among the functionals of the *trans*-XONO dipole moment decreases in the order X=F > X=Cl > X=Br.

Examination of the results in Table 3 shows that the X—N bond distance exhibits the largest sensitivity with respect to the functional. Even so, the variation of this parameter (TZ2P basis set) among the density functional methods is only ≈0.09–0.10 Å for all three XNO_2 molecules, which is less than the variation of the central O—N bond distance for the *trans*-XONO species, and thus all of the density functional methods give XNO_2 geometries that are qualitatively correct. The BP86 and BLYP functionals yield the longest X—N bond distances and those that are in the worst agreement with the CCSD(T)/TZ2P values. The B3LYP and B3PW91 hybrid functionals therefore yield XNO_2 structures that are in the best agreement with the CCSD(T)/TZ2P geometries, similar to the situation for both the *cis*- and *trans*-XONO molecules. The variation among the XNO_2 DFT geometrical structures generally decreases in the order X=F > X=Cl > X=Br, also similar to the trend observed for the XONO species.

The trend for the XNO_2 dipole moment values is, however, different to that observed for the XONO molecules. There is a reasonably large variation among the different DFT methods for all three XNO_2 molecules, with this variation being largest (TZ2P basis) for FNO_2 and $BrNO_2$. For FNO_2 and $BrNO_2$, the hybrid functionals give the better agreement with the CCSD(T)/TZ2P value, but for $ClNO_2$ the BP86 and BLYP functionals give the better agreement. Furthermore, the absolute agreement between the CCSD(T)/TZ2P quantity and the best DFT value is worst for $BrNO_2$, contrary to all of the other trends previously noted.

3.2 Harmonic frequencies and IR intensities

Harmonic vibrational frequencies and IR intensities, obtained with the various DFT functionals, are presented in Tables 4–6, for the *cis*-XONO, *trans*-XONO, and XNO_2 isomers, respectively. Again, CCSD(T)/TZ2P values [4, 10–12] are included for comparison. Examination of the harmonic frequencies for *cis*-FONO shows some similarities with observations reported for the

Table 4. Summary of the *cis*-XONO harmonic frequencies and intensities, in cm^{-1} and km/mol

Method	$\omega_1(a')$	I	$\omega_2(a')$	I	$\omega_3(a')$	I	$\omega_4(a')$	I	$\omega_5(a')$	I	$\omega_6(a'')$	I
FONO 6-31G*												
B3LYP	1793	179	956	15	829	62	440	89	268	1	417	0.2
B3PW91	1799	178	958	18	842	74	491	70	265	2	446	0.2
BP86	1682	185	1086	27	758	4	481	149	184	10	533	0.3
BLYP	1636	179	1044	24	745	5	463	137	185	9	518	0.3
FONO TZ2P												
B3LYP	1775	227	934	16	812	82	333	91	217	17	417	0.2
B3PW91	1762	219	940	16	817	107	376	60	181	17	466	0.2
BP86	1725	232	1183	78	715	22	465	172	176	10	548	0.6
BLYP	1674	230	1156	74	705	25	453	152	174	8	533	0.6
CCSD(T)	1743	215	929	5	771	47	405	158	271	0.4	349	0.3
ClONO 6-31G*												
B3LYP	1752	261	872	3	705	69	436	38	228	2	425	1
B3PW91	1776	263	886	5	744	69	459	40	231	2	439	1
BP86	1657	234	1021	70	768	59	315	98	155	17	483	1
BLYP	1616	232	994	68	753	62	315	90	155	13	472	1
ClONO TZ2P												
B3LYP	1741	290	868	0.5	647	63	365	80	229	1	398	1
B3PW91	1755	281	883	0.6	678	75	413	59	233	1	416	1
BP86	1612	279	978	55.8	758	63	295	97	146	25	484	1
BLYP	1571	284	960	57.7	742	70	301	93	148	16	474	2
CCSD(T)	1715	252	850	16.9	638	21	416	167	249	0.1	341	1
BrONO 6-31G*												
B3LYP	1714	278	876	22	784	62	391	30	191	1	437	2
B3PW91	1742	281	907	36	818	54	396	35	192	1	450	2
BP86	1632	236	985	76	778	71	321	58	158	3	464	2
BLYP	1591	236	939	64	764	72	320	53	155	3	452	2
BrONO TZ2P												
B3LYP	1681	327	864	14	701	80	360	26	181	1	428	2
B3PW91	1708	321	881	19	754	76	375	29	184	1	441	2
BP86	1593	295	968	74	764	94	296	63	142	5	465	2
BLYP	1552	302	934	68	748	98	274	57	138	6	454	2
CCSD(T)	1664	254	845	8	558	69	429	96	210	0.1	357	1

Table 5. Summary of the *trans*-XONO harmonic frequencies and intensities, in cm^{-1} and km/mol

Method	$\omega_1(a')$	I	$\omega_2(a')$	I	$\omega_3(a')$	I	$\omega_4(a')$	I	$\omega_5(a')$	I	$\omega_6(a'')$	I
FONO 6-31G*												
B3LYP	1835	193	1045	70	829	114	448	92	328	2	225	0.4
B3PW91	1848	182	1066	74	847	119	473	90	339	2	234	0.4
BP86	1765	205	997	90	787	58	382	58	274	1	224	0.1
BLYP	1757	224	972	83	769	56	366	54	260	1	212	0.1
FONO TZ2P												
B3LYP	1833	253	1023	80	813	123	411	123	308	3	217	0.3
B3PW91	1839	227	1051	83	833	127	435	122	323	3	228	0.3
BP86	1762	264	969	104	776	68	367	75	258	1	215	0.1
BLYP	1756	294	936	96	754	64	352	67	242	1	203	0.1
CCSD(T)	1747	213	955	58	783	117	413	112	303	2	216	0.5
ClONO 6-31G*												
B3LYP	1843	278	894	147	675	131	433	70	270	0.13	185	0.001
B3PW91	1859	267	915	152	697	142	453	66	277	0.12	191	0.001
BP86	1771	289	857	122	628	49	379	49	237	0.01	186	0.044
BLYP	1754	305	831	116	607	42	362	47	228	0.01	180	0.050
ClONO TZ2P												
B3LYP	1834	362	879	124	660	157	404	113	259	0.8	178	0.007
B3PW91	1847	338	902	124	681	173	422	112	267	0.6	184	0.002
BP86	1769	396	838	111	630	69	360	67	223	0.1	176	0.085
BLYP	1755	431	806	105	607	55	344	59	212	0.2	170	0.119
CCSD(T)	1754	297	855	102	662	182	407	98	262	0.2	170	0.009
BrONO 6-31G*												
B3LYP	1820	279	882	187	621	188	409	30	234	0.005	175	0.002
B3PW91	1839	270	900	199	643	192	423	24	238	0.010	180	0.001
BP86	1754	293	841	139	550	79	360	37	206	0.147	176	0.052
BLYP	1735	311	817	131	531	71	345	37	199	0.132	171	0.062
BrONO TZ2P												
B3LYP	1813	364	863	154	595	234	388	72	223	0.33	169	0.009
B3PW91	1825	334	885	165	619	248	408	61	230	0.13	174	0.002
BP86	1747	394	822	132	553	104	345	58	193	0.04	171	0.084
BLYP	1738	444	790	119	534	87	326	53	182	0.12	163	0.130
CCSD(T)	1740	308	835	134	601	254	385	61	226	0.19	158	0.016

geometries, but interestingly there are also some dissimilarities, in spite of the fact that there is usually a strong correlation between harmonic frequencies and equilibrium structures. Harmonic frequencies from the two hybrid methods are in general agreement, although even here the difference for ω_4 and ω_6 is larger than $40\,\text{cm}^{-1}$ (TZ2P basis set). Similarly, values from the BP86 and BLYP functionals are in general agreement, except for ω_1 where the difference is $51\,\text{cm}^{-1}$. Also consistent with the geometries, there are some large differences between harmonic frequencies obtained from the hybrid functionals and the BP86 and BLYP functionals, especially for $\omega_2, \omega_3, \omega_4$, and ω_6. The dissimilarity (relative to the equilibrium structures) arises when comparing to the CCSD(T) harmonic frequencies. Here the hybrid functionals usually yield harmonic frequencies that are in better agreement with the CCSD(T)/TZ2P value, but not in every case. For example, the BP86 and BLYP ω_4 values are in much better agreement with the CCSD(T)/TZ2P quantity relative to the frequency obtained from the B3LYP hybrid functional. It is also interesting that of the two hybrid functionals, neither is consistently better at giving a result that is closest to the CCSD(T)/TZ2P quantity. For example, for ω_4 and ω_6 the B3PW91 functional predicts the better harmonic frequency, while for ω_5 the B3LYP functional yields the better value. For ω_1, ω_2, and ω_3 the difference between B3LYP and B3PW91 is small and they are both in reasonable agreement with the CCSD(T) value. It is also worthy of note that the reliability of the CCSD(T)/TZ2P harmonic frequencies is supported by CCSD(T)/TZ2Pf values [6] (1747, 933, 787, 441, 277, and $381\,\text{cm}^{-1}$ for ω_1 through ω_6, respectively), where the largest deviation is only $36\,\text{cm}^{-1}$ for ω_4.

For the harmonic frequencies of *cis*-ClONO and *cis*-BrONO, the hybrid functionals agree reasonably well while the BP86 and BLYP functionals agree reasonably well with each other, consistent with the results for *cis*-FONO. One interesting observation is that the hybrid/(BP86, BLYP) difference is actually larger for *cis*-ClONO and *cis*-BrONO than found for *cis*-FONO. Unlike the situation for *cis*-FONO, harmonic frequencies for *cis*-ClONO and *cis*-BrONO determined with one of the two hybrid functionals are in every case closer to the CCSD(T)/TZ2P value than are those determined with the BP86 or BLYP functionals. However, this is not to say that harmonic frequencies determined with the hybrid functionals are always in good agreement with the

Table 6. Summary of the XNO_2 harmonic frequencies and intensities, in cm^{-1} and km/mol

Method	$\omega_1(a_1)$	I	$\omega_2(a_1)$	I	$\omega_3(a_1)$	I	$\omega_4(b_2)$	I	$\omega_5(b_1)$	I	$\omega_6(b_1)$	I
FNO_2 6-31G*												
B3LYP	1390	188	867	215	606	28	754	15	1879	428	566	4
B3PW91	1418	192	880	224	621	27	770	15	1922	444	580	4
BP86	1346	176	830	183	566	30	715	10	1833	347	530	4
BLYP	1318	172	815	172	547	31	696	10	1788	332	513	3
FNO_2 TZ2P												
B3LYP	1359	194	840	239	578	78	765	13	1843	528	562	4
B3PW91	1384	196	853	246	598	74	781	13	1882	535	577	4
BP86	1316	185	806	206	540	70	721	9	1804	430	521	4
BLYP	1290	181	795	194	519	69	702	9	1761	416	502	3
CCSD(T)	1317	189	838	213	576	67	742	10	1789	437	561	3
$ClNO_2$ 6-31G*												
B3LYP	1370	380	798	248	366	59	659	8	1818	347	406	0.7
B3PW91	1394	385	809	255	381	62	675	8	1860	358	418	0.7
BP86	1324	335	765	214	342	52	625	5	1783	274	383	0.7
BLYP	1297	327	755	205	328	46	606	5	1736	263	368	0.6
$ClNO_2$ TZ2P												
B3LYP	1339	379	810	250	370	61	673	6	1748	420	409	0.3
B3PW91	1363	380	819	255	386	63	688	6	1792	424	418	0.4
BP86	1292	339	774	219	347	55	638	4	1714	338	385	0.5
BLYP	1266	333	766	210	333	49	620	4	1665	329	373	0.4
CCSD(T)	1290	334	805	215	371	55	658	5	1688	371	409	0.4
$BrNO_2$ 6-31G*												
B3LYP	1374	447	804	244	306	22	620	5	1795	314	348	0.2
B3PW91	1398	456	812	255	312	25	635	5	1842	324	356	0.2
BP86	1324	391	773	209	295	20	593	3	1754	246	333	0.2
BLYP	1297	380	763	197	285	18	576	3	1701	237	323	0.1
$BrNO_2$ TZ2P												
B3LYP	1339	461	811	262	296	27	635	4	1723	391	354	0.1
B3PW91	1363	462	817	269	303	29	649	4	1771	394	361	0.1
BP86	1292	407	777	228	285	24	604	2	1689	312	336	0.1
BLYP	1263	399	768	217	272	22	588	3	1633	305	328	0.1
CCSD(T)	1288	396	799	228	281	30	613	3	1663	340	349	0.1

CCSD(T)/TZ2P values, because this is not the case. This difference is most notable for ω_6 (57–75 cm^{-1}) of *cis*-ClONO and for ω_3 (143–196 cm^{-1}), ω_4 (54–69 cm^{-1}), and ω_6 (71–84 cm^{-1}) of *cis*-BrONO. In summary, it is fair to say that the hybrid functionals predict harmonic frequencies for the *cis*-XONO compounds that are qualitatively correct, but there are substantial quantitative errors.

Inspection of the IR intensities for the *cis*-XONO species shows that in some cases, the agreement between the various DFT methods and the CCSD(T) approach can be considered qualitative, but in others the agreement cannot even be classified as qualitative (e.g., I_2 and I_5 for all three *cis*-XONO molecules). These observations are not too surprising given the previous discussion concerning dipole moments.

For *trans*-FONO (see Table 5), the ω_1, ω_2, and ω_3 values obtained with the BP86 and BLYP functionals (TZ2P basis set) are actually closer to the CCSD(T)/TZ2P quantities than those given by the hybrid functionals. For ω_4 and ω_5, the hybrid functionals yield harmonic frequencies that are closer to the CCSD(T) values, whereas all four DFT functionals are in reasonable agreement with CCSD(T) for ω_6. The pattern is slightly different for *trans*-ClONO and *trans*-BrONO, but it is evident that neither the hybrid functionals nor the BP86/BLYP functionals are consistently in better agreement with CCSD(T) for all of the harmonic frequencies. In fact, for the two hybrid functionals ω_1, the N=O stretch is consistently too high relative to the CCSD(T) value. This is similar to the situation observed for the *cis*-XONO compounds, and suggests that the correlation between equilibrium geometries and harmonic frequencies is not as strong for DFT methods as is commonly found for wavefunction ab initio methods.

Generally, there is qualitative agreement between the various DFT methods and CCSD(T) for the IR intensities for the *trans* isomers, where qualitative agreement indicates that modes with the larger intensity are medium to large for all methods and modes with small intensities are small to very small for all methods. Qualitative agreement, in this case, does not mean that the relative ordering of the intensities is the same for every method, because this is not the case.

Examination of Table 6 shows that none of the DFT methods is consistently closer to CCSD(T) in describing the harmonic frequencies of the XNO_2 compounds, similar to the situation for both the *cis*- and *trans*-XONO compounds. In this case, the hybrid methods seem to have great difficulty in describing the antisymmetric N—O stretch, ω_5, as they systematically predict a frequency that is too large. Interestingly, this exact same tendency has previously been noted for the MP2 level of theory [4]. For IR intensities, however, the agreement between the various DFT methods and CCSD(T) is reasonably good, and can be classified as semi-quantitative. In this case, the relative ordering of the IR intensities is almost always the same among the different methods, with the only exception involving vibrational modes with similar IR intensity (ω_1 and ω_5 for $ClNO_2$/ TZ2P).

To summarize this section, in spite of the fact that the hybrid methods, B3LYP and B3PW91, consistently gave better geometries for the *cis*-XONO, *trans*-XONO, and XNO_2 compounds, by comparison to the CCSD(T) structure, they did not necessarily yield better harmonic frequencies for every vibrational mode. This is true even for *cis*-FONO, where the BLYP and BP86 equilibrium structures are qualitatively incorrect. However, it should be noted that for some vibrational modes the BP86 and BLYP functionals yield harmonic frequencies that are in error by more than $200\,\mathrm{cm}^{-1}$. It is therefore apparent that the correlation between equilibrium structure and harmonic frequencies is not as strong for the DFT methods investigated here as it is for conventional wavefunction ab initio methods, such as CCSD(T).

3.3 Relative energies

Table 7 contains the energy that *cis*-XONO is below the *trans*-XONO isomer for the various DFT functionals, while Table 8 presents the energy that the XNO_2 isomer is below the *cis*-XONO compound. For comparison, CCSD(T)/TZ2P and CCSD(T)/atomic natural orbital [28] (ANO) energy differences [4, 10–12] are included (see Refs. [4, 10–12] for specifies about the ANO basis sets). The large ANO basis sets include up through *g*-type basis functions. None of the DFT methods give relative energies that are in quantitative agreement with CCSD(T), and usually they overestimate the energy difference. For the (*trans–cis*) energy difference, the hybrid functionals yield a value that is in better agreement with CCSD(T) rather than the BP86/BLYP functionals. Of the two hybrid functionals, B3LYP is always in better agreement with the CCSD(T) value [this is the same whether comparing to the CCSD(T)/TZ2P or CCSD(T)/ANO values]. The situation is opposite for the (*cis*-XONO—XNO_2) energy difference in that the BP86 and BLYP functionals generally give a value that is in better agreement with the CCSD(T) quantity relative to that obtained from the two hybrid functionals. However, neither the BP86 nor BLYP (*cis*-XONO—XNO_2) energy differences are in quantitative agreement with the CCSD(T)/TZ2P or CCSD(T)/ANO values.

4 Conclusions

The equilibrium structures, harmonic vibrational frequencies, dipole moments, IR intensities, and relative energies of the *cis*-XONO, *trans*-XONO, and XNO_2 (X=F, Cl, and Br) molecules have been studied using four DFT functionals that are in common use. These include the two gradient-corrected or non-local functionals, BP86 and BLYP, and two so-called hybrid functionals, B3LYP and B3PW91, which additionally mix in some exact Hartree-Fock exchange. The quality of the computed results was judged by comparison to analogous CCSD(T)/TZ2P or CCSD(T)/ANO values. The two hybrid functionals generally perform better than the BP86 and BLYP functionals, especially for the *cis*-XONO equilibrium geometries. However, for harmonic frequencies and the (*cis*-XONO—XNO_2) energy difference, there are many instances where either the BP86 or BLYP method yields the best prediction. This is particularly surprising for the harmonic frequencies, as it implies that the correlation between equilibrium struc-

Table 7. Energy that *cis*-XONO is below *trans*-XONO, kcal/mol[a]

Molecule	6-31G*				TZ2P					ANO
	B3LYP	B3PW91	BP86	BLYP	B3LYP	B3PW91	BP86	BLYP	CCSD(T)	CCSD(T)
FONO	3.56	3.91	6.67	5.44	3.20	3.60	10.49	9.54	2.41	2.63
ClONO	5.43	5.85	7.86	7.16	3.87	4.35	5.52	4.62	2.86	3.27
BrONO	7.33	7.90	9.78	8.72	5.40	6.02	7.88	6.77	3.34	3.92

[a] Zero-point energies not included

Table 8. Energy that XNO_2 is below *cis*-XONO, kcal/mol[a]

Molecule	6-31G*				TZ2P					ANO
	B3LYP	B3PW91	BP86	BLYP	B3LYP	B3PW91	BP86	BLYP	CCSD(T)	CCSD(T)
FNO_2	38.93	42.22	37.23	34.38	41.22	44.17	35.44	32.55	36.90	39.91
$ClNO_2$	13.53	15.77	14.07	11.99	15.65	17.88	16.38	14.35	11.95	12.11
$BrNO_2$	8.38	10.40	8.90	7.15	11.00	12.97	11.21	9.46	7.76	7.50

[a] Zero-point energies not included

ture and harmonic frequencies is not as strong for current DFT methods as it is for conventional wavefunction ab initio methods. Moving down the periodic table, the results from the various functionals were usually in better agreement. That is, the variation of some property among the different functionals was generally smaller for X=Br relative to X=Cl, and also for X=Cl relative to X=F. In fact, only for *cis*-FONO and *cis*- ClONO did the BP86 and BLYP functionals give equilibrium structures that would be classified as qualitatively incorrect. None of the functionals studied here can be considered to yield quantitative agreement with CCSD(T) for these molecules, and so the *cis*-XONO, *trans*-XONO, and XNO_2 species should provide convenient benchmarks for the development of new functionals.

Acknowledgements. D.J. acknowledges funding from the QEII research fellowship scheme, Australian Research Council.

References

1. Chong DP (ed) (1995) Recent advances in density functional methods, part I. World Scientific, London
2. Chong DP (ed) (1997) Recent advances in density functional methods, part II. World Scientific, London
3. Dixon DA, Christe KO (1992) J Phys Chem 96:1018
4. Lee TJ, Rice JE (1992) J Chem Phys 97:4223
5. Amos RD, Murray CW, Handy NC (1993) Chem Phys Lett 202:489
6. Lee TJ, Bauschlicher CW, Dateo CE, Rice JE (1994) Chem Phys Lett 228:583
7. Stephens PJ, Devlin FJ, Chablowski CF, Frisch MJ (1994) J Phys Chem 98:11623
8. Bauschlicher CW, Ricca A, Partridge H, Langhoff SR (1997) In: Chong DP (ed) Recent advances in density functional methods, part II. World Scientific, London, pp 165
9. Lee TJ, Rice JE, Dateo CE (1996) Mol Phys 89:1359
10. Lee TJ to be published
11. Lee TJ (1994) J Phys Chem 98:111
12. Lee TJ (1996) J Phys Chem 100:19847
13. Becke AD (1988) Phys Rev A 38:3098
14. Lee C, Yang W, Parr RG (1988) Phys Rev B 37:785
15. Perdew JP, Zunger A (1981) Phys Rev B 23:5048
16. Perdew JP (1986) Phys Rev B 33:8822; (1986) Phys Rev B 34:7406(E)
17. Becke AD (1993) J Chem Phys 98:5648
18. Perdew JP, Wang Y (1992) Phys Rev B 45:13244
19. Curtiss LA, Raghavachari K, Trucks GW, Pople JA (1991) J Chem Phys 94:7221 and references therein
20. Gill PMW, Johnson BG, Pople JA, Frisch MJ (1992) Int J Quantum Chem Symp 26:319
21. Vosko SH, Wilk L, Nusair M (1980) Can J Phys 58:1200
22. Binning RC, Curtiss LA (1990) J Comp Chem 11:1206
23. Dunning TH (1971) J Chem Phys 55:716
24. Dunning TH (1989) J Chem Phys 90:1007
25. McLean AD, Chandler G (1980) J Chem Phys 72:5639
26. Schaefer A, Huber C, Ahlrichs R (1994) J Chem Phys 100:5829
27. Frisch MJ, Trucks GW, Schlegel HB, Gill PMW, Johnson BG, Robb MA, Cheeseman JR, Keith T, Petersson GA, Montgomery JA, Raghavachari K, Al-Laham MA, Zakrzewski VG, Ortiz JV, Foresman JB, Cioslowski J, Stefanov BB, Nanayakkara A, Challacombe M, Peng CY, Ayala PY, Chen W, Wong MW, Andres JL, Replogle ES, Gomperts R, Martin RL, Fox DJ, Binkley JS, DeFrees DJ, Baker J, Stewart JJP, Head-Gordon M, Gonzalez C, Pople JA (1995) GAUSSIAN94 Revision D.1. Gaussian, Inc., Pittsburgh
28. Almlöf JE, Taylor PR (1987) J Chem Phys 86:4070