Bonding in the ClOO(^{2}A″) and BrOO(^{2}A″) radical: Nonrelativistic single-reference *versus* relativistic multi-reference descriptions in density functional theory

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The ^{2}A″ state of ClOO and BrOO is investigated using single- and multi-reference DFT (density functional theory). Unrestricted DFT (UDFT) carried out with the BLYP functional exaggerates the ionic character of the X–OO bond (X = Cl, Br) and by this its bond dissociation energy, while UDFT with the B3LYP functional underestimates ionic character and bond dissociation energies. In previous investigations, this was overlooked and has led to a misleading interpretation of single determinant UDFT results for XOO(^{2}A″). The correct description of the two radicals can only be achieved by an appropriate configurational state mixing between the doublet ground state (leading to ionic character) and the first excited state, a quartet state leading to covalent character of the X–OO bond. REKS (spin-restricted ensemble-referenced Kohn–Sham) theory provides a multireference description and is capable of describing bonding in XOO correctly provided it is carried out with the hybrid functional B3LYP rather than BLYP, which is the result of the self-interaction error of pure exchange functionals and the inclusion of non-specific non-dynamic electron correlation effects suppressing the specific ones introduced by REKS. The relevance of results for the DFT description of related compounds (HOOO radical, MOO with M = Cu, Ag or Au) or multi-reference problems in general is discussed.

1. Introduction

Halogen oxides XO$_2$ are free radicals which show up in many chemical processes including the stratospheric depletion of ozone,[1–3] water disinfection,[4] pulp bleaching,[5] food conservation,[6] *etc.*[7] Thus, it is not surprising that many experimental[8–16] and theoretical studies[17–21] were dedicated to these compounds during the last decade.

In the gas phase, the asymmetric XOO species is the most stable form of halogen oxides. For a proper theoretical description of bonding in these open-shell species a correct treatment of correlation effects (both non-dynamic and dynamic) is extremely important. Thus, one needs to employ high-level *ab initio* methods with large basis sets, which makes the quantum chemical investigation of chemical reactions of these species especially demanding.

Density functional theory (DFT) methods[22] represent an inexpensive yet reliable alternative to the conventional wave-function methods. The performance of DFT methods for halogen oxides has been studied in the literature[23–28] and it has been claimed that these methods can achieve the same level of accuracy as the most sophisticated wave function-based methods of quantum chemistry.[21,23,26,27] Had this been true, DFT would have opened bright perspectives for the study of reactivity of halogen oxides towards various substrates. However, some worrying trends have been observed when applying the DFT methods to study halogen oxides.[21] For instance, the molecular geometry and the vibrational spectrum of XOO species for X = Cl, Br are best described with the use of pure density functionals[21] such as BLYP[29,30] whereas the thermochemistry is best described with the use of hybrid HF/DFT functionals[21] such

as B3LYP.[31] This performance of DFT contradicts a fundamental rule of quantum chemical investigations: The properties of a single molecule, a class of molecules or a variety of reaction systems must be described consistently with one and the same quantum chemical method to make consistent predictions with regard to unknown molecular quantities. The predictive power of such an approach will be lost if for each property and molecule a new method is chosen without quantum chemical reasoning just because a better agreement with some known experimental facts is sought.

It has been often claimed that the high spin contamination in the spin-unrestricted Kohn–Sham (UKS) formalism makes the results of calculations unreliable.[32] However, there is strong evidence for the alternative point of view that the value of $\langle \hat{S}^2 \rangle$ is not an indicator of performance in UKS because it is not strictly defined in DFT.[32–35] Indeed, with regard to the thermochemistry of halogen oxides, a relatively "clean" UKS description obtained with the use of pure density functionals is far inferior to a highly spin-contaminated UB3LYP description.[21] At the same time, for the molecular geometries the trend is precisely opposite, the least spin-contaminated method yields the best results.[21]

It is the purpose of the present paper to analyze the reasons for the failures of the usual UKS formalism applied to asymmetric dioxides of chlorine and bromine. The alternative description of bonding in these species is provided by multi-reference DFT approaches[36–39] such as the spin-restricted ensemble-referenced KS (REKS) method.[38,39] It will be shown that within the single-reference formalism such as UKS a reliable description of chemical bonding in these species is unlikely to be obtained, whereas the multi-reference DFT approach produces very good results when combined with a

hybrid density functional. A generalization of these findings will be discussed and its relevance for practical problems demonstrated.

2. Details of calculations

The energy, geometry, and vibrational frequency calculations reported in the present work were performed with the help of two density functionals: the B3LYP hybrid functional[31] which includes a fraction of exact exchange, and the BLYP functional[29,30] which is a pure density functional. For all calculations, the cc-pVTZ basis set of Dunning[40] was employed.

The investigation was carried out for the doublet $^2A''$ state of ClOO and BrOO both at the single-reference spin-unrestricted level of theory and with the help of the REKS method,[38,39] which represents a multi-reference DFT approach based on the ensemble representation for the density.[41] Purely theoretical[41a–d,g,h] and first principles computational[41e,f] arguments have been given in the literature in favour of the ensemble representation for the ground state density of systems characterized by strong non-dynamic correlation. The validity of the ensemble representation does not deny the validity of the original formulation of density functional theory, but amends it in those cases where (near) degeneracy effects lead to non-dynamic electron correlation. The use of the ensemble representation for the density leads to the appearance of fractional occupation numbers of Kohn–Sham orbitals, which can be viewed[41e] as analogs of the natural orbital occupation numbers in wavefunction theory. In REKS calculations, the 13a′ and 14a′ orbitals of ClOO and 19a′ and 20a′ orbitals of BrOO (see Fig. 1 below) were fractionally populated and the 4a″ orbital of ClOO and 7a″ orbital of BrOO were singly occupied.

The scalar-relativistic (SR) effects were taken into account with the help of NESC-EP (normalized elimination of the small component using an effective potential) method, which has been tested in calculations on molecular systems with heavy atoms and proved capable of providing a reliable description of the scalar-relativistic effects within the context of DFT.[42–44] The atomization and dissociation energies were corrected for the atomic first-order spin–orbit (SO) interaction energy taken from the compilation of Curtiss et al.[45,46] The corrections are -0.23 kcal mol^{-1} for O, -0.84 kcal mol^{-1} for Cl, and -3.63 kcal mol^{-1} for Br.

All calculations were carried out with the help of the Cologne2002 suite of quantum-chemical programs.[47]
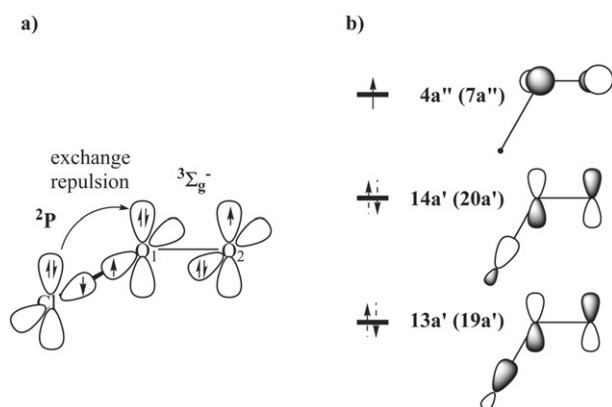

Fig. 1 Electronic configuration (a) and frontier molecular orbitals of ClOO (BrOO). (b) The electronic configuration is given as a result of the interaction between X(^{2}P) and O$_2$($^3\Sigma_g^-$). Only the 2p orbitals and their occupations are shown. The MOs of ClOO($^2A''$) are derived from the REKS orbitals and UKS natural orbitals. In parentheses the notation for BrOO($^2A''$) is given.

3. Results and discussion

The results of the DFT calculations of radicals ClOO and BrOO are presented in Tables 1 and 2, respectively, together with available experimental data[8–16] and the results of other quantum chemical calculations.[19–21]

3.1 Molecular geometry and atomization enthalpy of XOO

Although, experimental data for the molecular geometry of the XOO species for X = Cl, Br are missing, the results of high-level ab initio calculations can be used as a guide. It has to be noted that conventional wavefunction methods experience serious difficulties in describing the asymmetric halogen oxides, because both non-dynamic and dynamic correlation effects must be treated very accurately. Thus, the results of MR-(S)DCI calculations reported in ref. 19 are used as a reference for the geometry of ClOO. For BrOO, the most sophisticated ab initio calculations were performed at the QCISD(T) level employing a large basis set.[20]

Inspection of the data in Tables 1 and 2 reveals that the scalar-relativistic (SR) effects do not play an important role for the molecular geometries, leading only to a mild shortening of the X–O bond. As for the energies, there is a noticeable strengthening of the Br–O bond (by ca. 1 kcal mol^{-1}) due to scalar-relativistic effects. The first-order spin–orbit interaction is not expected to contribute much to the total energy of radical XOO, because the unpaired electron is located in the π^* orbital of the O$_2$ fragment. Much more important is the quenching of the atomic first-order spin–orbit interaction upon formation of the molecule, which reaches almost 4 kcal mol^{-1} for Br.[45,46] It is noteworthy, however, that the inclusion of both scalar-relativistic and spin–orbit corrections into the calculation is necessary for a reasonable description of the X–O binding energy in asymmetric halogen oxides in view of dissociation energies D_0 of just 4.8 (Cl–OO bond[11]) and 1.8 kcal mol^{-1} (Br–OO bond[20]).

It has already been observed by Cooper et al.[21] that the results of the single-reference spin-unrestricted Kohn–Sham calculations employing the pure density functionals, such as BLYP, are quite different from the results of UKS calculations with hybrid functionals (e.g., B3LYP). At first glance, the UBLYP provides reasonable molecular geometries and inaccurate atomization enthalpies for ClOO and BrOO, whereas for the UB3LYP the situation is precisely opposite: the geometries are spurious, however the atomization enthalpies are now reasonable. Closer inspection of the data in Tables 1 and 2 reveals that the X–O bond dissociation energy is described not exceptionally accurately at the UB3LYP level. When corrected for the first-order SO interaction, D_0(Cl–O) (2.0 kcal mol^{-1}) deviates by more than 50% from the best experimentally based estimate of D_0 (4.8 kcal mol^{-1}, Table 1) and becomes even negative for BrOO (SO-corrected: -2.2 kcal mol^{-1}; SO-+ SR-corrected: -1.5 kcal mol^{-1}; exp.: 1.8 kcal mol^{-1}, Table 2). The seemingly good description of the atomization enthalpy with the UB3LYP method stems from an overestimation of the dissociation energy of O$_2$ by ca. 4 kcal mol^{-1} (UKS/B3LYP: 121.9 kcal mol^{-1}; exp.: 118.0 kcal mol^{-1}). The X–O stretching frequency ω_1 is underestimated by a factor of two and even three for BrOO. Thus, with the use of conventional pure or hybrid density functionals the single-reference spin-unrestricted KS formalism does not provide a reliable description of bonding in the asymmetric halogen oxides.

The use of multi-reference DFT methods, such as REKS, changes the situation. Whereas the results of REKS/BLYP calculations do not differ much from the UBLYP results, there is a drastic improvement for the hybrid B3LYP functional. The REKS/B3LYP results are in a good agreement both with the experimental thermochemical data and with the reference data on the molecular geometry of ClOO and BrOO. The

Table 1 Geometry, harmonic vibrational frequencies ω, orbital occupation numbers n, heats of atomization ΔH^0_{298} and dissociation energies $D_0^{\text{Cl–OO}}$ of the ClOO radical as obtained with various DFT methods

Parameter	Exptl.	REKS/B3LYP[a]	UKS/B3LYP[a]	REKS/BLYP[a]	UKS/BLYP[a]	Other theoretical results
Cl–O/Å		2.046(2.047)[b]	2.290(2.277)	2.051(2.049)	2.042(2.040)	2.139;[c] 1.716;[d] 2.032[e]
O–O/Å		1.203(1.203)	1.195(1.195)	1.229(1.229)	1.230(1.230)	1.201;[c] 1.263;[d] 1.227[e]
ClOO/degree		116.4(116.4)	116.6(116.7)	117.0(117.0)	116.8(116.8)	115.7;[c] 113.3;[d] 117.0[e]
ω_1/cm^{-1}	215;[f] 407[g]	298(297)	114(115)	320(318)	277(277)	194;[c] 499;[d] 276[e]
ω_2/cm^{-1}	432;[f] 373[g]	609(610)	311(317)	595(589)	487(488)	403;[c] 1112;[d] 490[e]
ω_3/cm^{-1}	1478;[f] 1441[g]	1544(1541)	1591(1586)	1399(1395)	1360(1356)	1538;[c] 1636;[d] 1376[e]
$n_{13a'}$[h]		1.905(1.904)	1.632(1.641)	1.979(1.979)	1.989(1.989)	
$n_{14a'}$[i]		0.095(0.096)	0.368(0.359)	0.021(0.021)	0.011(0.011)	
ΔH^0_{298}/ kcal mol^{-1}[j]		130.4(130.3)	126.8(126.6)	152.8(152.7)	149.7(149.7)	
ΔH^0_{298}, (SO)/ kcal mol^{-1}[k]	125.3[l]	129.1(129.0)	125.5(125.3)	151.5(151.4)	148.4(148.4)	107.6;[m] 110.4;[d] 146.2[e]
$D_0^{\text{Cl–OO}}$/ kcal mol^{-1}[n]		6.11(6.18)	2.80(2.85)	14.84(14.93)	12.92(13.02)	3.31[c,o]
$D_0^{\text{Cl–OO}}$(SO)/ kcal mol^{-1}[p]	4.76 ±[q]	5.27(5.34)	1.96(2.01)	14.00(14.09)	12.08(12.18)	

[a] Calculations employ cc-pVTZ basis set with cartesian primitive functions. [b] Results of quasi-relativistic calculations in parentheses. [c] MR-(S)DCI values from ref. 19. [d] MP2 values from ref. 21. [e] UG98LYP values from ref. 21. [f] Fundamental frequencies from ref. 12. [g] Fundamental frequencies from ref. 8. [h] Fractional occupation number of 13a′ orbital. [i] Fractional occupation number of 14a′ orbital. [j] Atomization enthalpy without spin–orbit contribution. [k] Atomization enthalpy with spin–orbit contribution. [l] Value obtained in ref. 21 from experimental heats of formation. [m] CCSD(T) value obtained in ref. 21 by using the geometry from ref. 19. [n] Cl–OO bond dissociation energy without spin–orbit contribution. [o] Value reported in ref. 19 corrected for ZPVE. [p] Cl–OO bond dissociation energy with spin–orbit contribution. [q] From ref. 11.

REKS/B3LYP dissociation energies of the X–O bonds corrected for the scalar-relativistic and spin–orbit effects deviate from the experimental values by less than 1 kcal mol^{-1}. A certain overestimation of the total atomization enthalpy of ClOO (exp: 125.3; REKS/B3LYP: 129.1 kcal mol^{-1}, Table 1) and BrOO (exp: 120.0; REKS/B3LYP: 124.0 kcal mol^{-1}, Table 2) can be traced back to an overestimation of the dissociation energy of O$_2$ by *ca.* 4 kcal mol^{-1} typical of the B3LYP exchange-correlation functional (ROKS/B3LYP: 122.3 kcal mol^{-1}; exp.: 118.0 kcal mol^{-1}). Thus, a reliable description of bonding in the asymmetric halogen oxides is achieved at the multi-reference DFT level with the use of a hybrid exchange-correlation functional.

3.2 Bonding in XOO: Qualitative description

The electronic structure of halogen oxides XOO is outlined in Fig. 1. In the doublet $^2A''$ state, a weak covalent bond exists between halogen atom and atom O1 due to interaction of a single electron in the p-orbital of halogen X and an electron in the antibonding π orbital of the fragment O$_2$. Due to strong exchange repulsion between the electron lone pairs of the halogen and the electrons in bonding π and σ orbitals of the O$_2$ moiety (not shown in Fig. 1 for brevity), the X–O bond is strongly elongated (X = Cl: 2.05 Å, Table 1; X = Br: 2.22 Å, Table 2) relative to the sum of the atomic covalent radii (Cl–O: 0.99 + 0.72 = 1.71; Br–O: 1.14 + 0.72 = 1.86 Å[48]). The

unpaired electron in the XOO radical resides in the antibonding π-type orbital of O$_2$ perpendicular to the molecular plane.

The quartet $^4A''$ state of XOO is unbound due to repulsion of electrons with parallel spin in the halogen's p and the oxygen's π* orbitals. The unbound character of the quartet state has already been documented in previous work on asymmetric halogen oxides.[21] Because the quartet state mixes into the doublet $^2A''$ state at the spin-unrestricted level of theory, its unbound character plays an important role for understanding the failure of spin-unrestricted DFT calculations to describe properly the structure and thermochemistry of XOO radicals.

3.3 Bonding in XOO: Analysis of spin-unrestricted description

The analysis presented in this section is valid for the spin-unrestricted Hartree–Fock (UHF) method and is not strict for the UKS method. However, in view of similarity between the two methods, the general trends obtained for UHF should be applicable to UKS. In the following the discussion is limited to the three electrons contained in the three frontier orbitals of XOO shown in Fig. 1. The normalized spin-unrestricted wavefunction for the doublet $^2A''$ state of XOO can be written as in eqn. (1),

$$\Psi^{\text{UHF}} = |\phi_a \bar{\phi}_b \phi_c\rangle \qquad (1)$$

where $\bar{\phi}$ indicates that the orbital is occupied with a beta-spin electron. The spin–orbital ϕ_c in eqn. (1) is the singly-occupied

Table 2 Geometry, harmonic vibrational frequencies ω, orbital occupation numbers n, heats of atomization ΔH^0_{298} and dissociation energies D^{Br-OO}_0 of the BrOO radical as obtained with various DFT methods

Parameter	Exptl.	REKS/B3LYP[a]	UKS/B3LYP[a]	REKS/BLYP[a]	UKS/BLYP[a]	Other theoretical results
Br–O/Å		2.218(2.204)[b]	2.527(2.479)	2.188(2.176)	2.178(2.163)	2.290;[c] 2.319;[d] 2.171[e]
O–O/Å		1.206(1.207)	1.198(1.199)	1.235(1.235)	1.236(1.237)	1.217;[c] 1.164;[d] 1.233[e]
BrOO/degree	117.8(117.8)	118.4(118.4)	118.2(118.3)	118.0(118.1)	117.2;[c] 119.5;[d] 118.2[e]	
ω_1/cm^{-1}	(160)[f]	198(191)	85(95)	246(242)	217(216)	261;[c] 162;[d] 217[e]
ω_2/cm^{-1}	(250)[f]	541(533)	253(254)	566(559)	446(448)	450;[c] 427;[d] 449[e]
ω_3/cm^{-1}	(1487)[f]	1541(1531)	1595(1594)	1381(1375)	1337(1331)	1486;[c] 1903;[d] 1358[e]
$n_{19a'}$[g]		1.861(1.865)	1.525(1.553)	1.974(1.974)	1.983(1.985)	
$n_{20a'}$[h]		0.139(0.135)	0.475(0.447)	0.026(0.026)	0.017(0.015)	
ΔH^0_{298}/ kcal mol^{-1}[i]		128.1(128.8)	125.4(125.9)	149.8(150.7)	147.1(147.9)	
ΔH^0_{298}(SO)/ kcal mol^{-1}[j]	120.0[k]	124.0(124.7)	121.3(121.8)	145.7(146.6)	143.0(143.8)	111.9;[c] 195.9;[d] 143.3[e]
D^{Br-OO}_0/ kcal mol^{-1}[l]		3.75(4.66)	1.38(2.13)	11.90(12.90)	10.29(11.29)	−1.4;[c] 4.0[m]
D^{Br-OO}_0(SO)/ kcal mol^{-1}[n]	1.8[o]	0.11(1.03)	−2.25(−1.50)	8.27(9.27)	6.66(7.66)	

[a] Calculations employ cc-pVTZ basis set with cartesian primitive functions. [b] Results of quasi-relativistic calculations in parentheses. [c] QCISD(T) values from ref. 21. [d] MP2 values from ref. 21. [e] UG98LYP values from ref. 21. [f] Fundamental frequencies estimated in ref. 13 by extrapolating the frequencies of FOO and ClOO. [g] Fractional occupation number of 19a' orbital. [h] Fractional occupation number of 20a' orbital. [i] Atomization enthalpy without spin–orbit contribution. [j] Atomization enthalpy with spin–orbit contribution. [k] Value obtained in ref. 21 from experimental heats of formation. [l] Br–OO bond dissociation energy without spin–orbit contribution. [m] G2//QCI value reported in ref. 20. [n] Br–OO bond dissociation energy with spin–orbit contribution. [o] Value obtained in ref. 20 from experimental heats of formation.

orbital of a'' symmetry, whereas the spin–orbitals ϕ_a and ϕ_b can be represented as in eqn. (2)

$$|\phi_a\rangle = \left(\frac{n_r}{2}\right)^{1/2}|\psi_r\rangle + \left(\frac{n_s}{2}\right)^{1/2}|\psi_s\rangle \quad (2a)$$

$$|\phi_b\rangle = \left(\frac{n_r}{2}\right)^{1/2}|\psi_r\rangle - \left(\frac{n_s}{2}\right)^{1/2}|\psi_s\rangle \quad (2b)$$

in terms of the UHF natural orbitals ψ_r and ψ_s, which in turn can be identified with the frontier orbitals of a' symmetry shown in Fig. 1. With this representation of the spin–orbitals, the UHF wavefunction (1) can be rewritten as in eqn. (3),

$$\Psi^{UHF} = \frac{n_r}{2}|\psi_r\bar\psi_r\phi_c\rangle - \frac{n_s}{2}|\psi_s\bar\psi_s\phi_c\rangle$$
$$- \left(\frac{n_r n_s}{2}\right)^{1/2}\frac{1}{\sqrt{2}}\left(|\psi_r\bar\psi_s\phi_c\rangle - |\psi_s\bar\psi_r\phi_c\rangle\right) \quad (3)$$

which shows that the UHF wavefunction (1) is not a pure doublet state, but includes a fraction of a quartet state wavefunction (in the second line) provided that the spin–orbitals ϕ_a and ϕ_b are not identical. The identification of the coefficients in eqns. (2) and (3) as the occupation numbers of the natural orbitals ψ_r and ψ_s stems from the representation of the density for wavefunction eqn. (1) (see eqn. 4).

$$\rho^{UHF}(r) = |\phi_a(\boldsymbol{r})|^2 + |\phi_b(\boldsymbol{r})|^2 + |\phi_c(\boldsymbol{r})|^2$$
$$= n_r|\psi_r(\boldsymbol{r})|^2 + n_s|\psi_s(\boldsymbol{r})|^2 + |\phi_c(\boldsymbol{r})|^2 \quad (4)$$

The total energy of the state described by wavefunction (1) is presented in eqn. (5) in terms of the natural orbital occupation numbers (NOONs) and the energies of single determinants constructed from the natural orbitals of UHF.

$$E^{UHF} = E(a\bar bc) = \frac{n_r}{2}E(r\bar rc) + \frac{n_s}{2}E(s\bar sc)$$
$$+ n_r n_s\left(E(rsc) - \frac{1}{4}E(r\bar sc) - \frac{1}{4}E(s\bar rc)\right.$$
$$\left. - \frac{1}{4}E(r\bar rc) - \frac{1}{4}E(s\bar sc)\right) \quad (5)$$

Note, that the coupling terms, which appear when calculating the expectation value of the Hamiltonian with wavefunction (3), are expressed in eqn. (5) as energy differences. Minimization of the total energy eqn. (5) with respect to the NOONs yields eqn. (6),

$$n_r = 1 + \frac{\Delta_1}{\Delta_2 + \Delta_3} \quad (6a)$$

$$n_s = 2 - n_r \quad (6b)$$

where the quantities Δ_k $(k = 1, 2, 3)$ are given in eqn. (7),

$$\Delta_1 = \frac{1}{2}\left(E(r\bar rc) - E(s\bar sc)\right) \quad (7a)$$

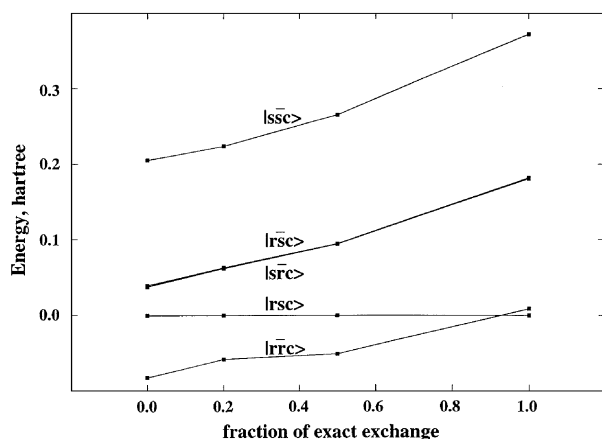$$\Delta_2 = E(rsc) - \frac{1}{2}E(r\bar sc) - \frac{1}{2}E(s\bar rc) \quad (7b)$$

Fig. 2 Decomposition of the energy of the doublet $^2A''$ state of a model electronic system made up by 3 electrons in 3 orbitals (ψ_r, ψ_s, and ϕ_c, see eqn. (1) in the text): low-spin doublet determinants $|\psi_r\bar{\psi}_r\phi_c\rangle$, $|\psi_r\bar{\psi}_s\phi_c\rangle$, $|\psi_s\bar{\psi}_r\phi_c\rangle$, and $|\psi_s\bar{\psi}_s\phi_c\rangle$ (see eqn. 5). Energies are given in hartree (E_h) relative to that of the quartet state $|\psi_r\psi_s\phi_c\rangle$ (zero line) in dependence of the amount of exact exchange: 0 for BLYP; 20% for B3LYP; 50% for BH&HLYP; 100% for HF.

$$\Delta_3 = E(rsc) - \frac{1}{2}E(r\bar{r}c) - \frac{1}{2}E(s\bar{s}c) \qquad (7c)$$

From eqn. (6) it is evident that if $\Delta_1/(\Delta_2 + \Delta_3) < 1$, then the UHF wavefunction (1) will be spin-polarized (*i.e.*, $\phi_a \not\equiv \phi_b$) and fractional occupation numbers of the natural orbitals emerge. In such a case, the spin-unrestricted wavefunction for a low-spin state contains a contribution from the high-spin state as evidenced by eqn. 3.

The single-determinant wavefunction $|\psi_r\psi_s\phi_c\rangle$, which describes the high-spin quartet state, is purely covalent within the three electron–three orbital model. All low-spin configurations adopt some ionic contribution, because two electrons with antiparallel spin can reside on the same atomic orbital. The higher the ionicity, the more stable the configuration is. Enhanced ionicity shifts the energies of low-spin configurations towards the high-spin configuration (see Fig. 2), thus making Δ_2 and Δ_3 in eqn. (7) smaller. This leads to fractional occupation numbers n_r and n_s close to (or identical with) integer values 2 and 0 which define the most ionic state (the covalent state is defined by $n_r = n_s = 1$). Based on this consideration the conclusion can be made that the more polar the bond is, the less pronounced is spin-polarization.

A peculiar feature of all modern exchange-correlation density functionals is the lack of perfect cancellation of the electron self-interaction by the approximate exchange-correlation functional. The self-interaction error (SIE)[49–52] leads to stabilization (with respect to purely covalent configurations) of the configurations adopting the ionic character. Consequently, it can be expected that the spin-unrestricted Kohn–Sham (KS) calculations employing the pure density functionals (these functionals yield larger SIE[49–52]) will converge to a solution with the occupation numbers of the UKS natural orbitals only marginally different from the integral values.

Mixing in a fraction of the exact exchange, like in hybrid HF/DFT exchange-correlation functionals, reduces the SIE and destabilizes the configurations with ionic contributions. Thus, the fractional occupation numbers of the UKS natural orbitals will deviate from the integral values much more strongly than in the case of pure density functionals. The larger the fraction of the exact exchange, the larger the deviation is.

This reasoning is confirmed by a diagram shown in Fig. 2. Using the natural orbitals from a UKS calculation of ClOO (the molecular geometry optimized at UBLYP is used), the KS energies of the single determinants, which appear in eqn.

(3), (5) and (6), were calculated. Fig. 2 displays these energies with respect to the energy of the high-spin (quartet) determinant $|\psi_r\psi_s\phi_c\rangle$. The UKS calculations employed the functionals BLYP, B3LYP, BH&HLYP, and HF0 whereas the latter combines exact Hartree–Fock (HF) exchange with the normal Coulomb interaction without any correlation functional (thus leading to a UHF calculation). The diagram of Fig. 2 reveals that the smaller the exact exchange contribution (that is the larger the SIE) is, the more stable the low-spin determinants are. The energy differences Δ_2 and Δ_3 in eqn. (6) became smaller and, synchronously with this development, the NOONs approach integral values (2 and 0).

Using the data from Fig. 2, the fractional occupation number of the natural orbital 13a' of ClOO estimated with eqn. (6) is 2.000 (UBLYP), 1.968 (UB3LYP), 1.784 (UBH&HLYP) and 1.489 (UHF) in close agreement with its value in the actual UKS calculations: 1.989 (UBLYP), 1.875 (UB3LYP), 1.641 (UBH&HLYP) and 1.463 (UHF). Albeit there exists some difference between the estimated and the actual NOON values due to the effect of other orbitals not considered in eqn. (6), the trend in the NOON values is reproduced correctly. It is interesting to note, that the polarity of the Cl–O bond follows the same trend: it is largest with UBLYP and decreases as the fraction of the exact exchange increases. For instance, the spin-unrestricted calculations yield for the Mulliken charge on Cl -0.091 (UBLYP), -0.083 (UB3LYP), -0.059 (UBH&HLYP), and -0.030 (UHF), thereby confirming the anticorrelation between bond polarity and the preference for the spin-polarized solution in UHF.

In the spin-unrestricted formalism, the larger the deviation of NOONs from integer values 2 and 0, the larger the fraction of the high-spin state that mixes in. Because the quartet $^4A''$ state of XOO (X = Cl, Br) is unbound, this artificial mixing leads to unrealistically long (and weak) X–O bond. If one avoids an admixture of the quartet state by the use of pure density functionals, a more realistic molecular geometry and more accurate vibrational frequencies will be obtained. However, the same feature that prevents the mixing of the quartet into the doublet state (large SIE and a preference for the ionic configurations) makes the pure density functionals prone to overbinding. As a consequence, the X–O binding energy obtained with the pure density functionals is *ca.* 3 to 4 times as large as the experimental value. Thus, a reliable description of bonding in the asymmetric halogen oxides can not be achieved at the single-reference spin-unrestricted level of theory as confirmed by the results of UKS calculations undertaken in the present work.

4. Conclusions

The problems discussed in this work are relevant for the correct application of DFT when describing electronic systems (atoms and molecules) with low lying excited state(s) and resulting non-dynamic electron correlation.

If one has to use multi-reference DFT as in the case of the XOO radicals, the choice of the functional is essential to avoid a double counting of correlation effects. The approximate pure exchange functionals include *via* a relatively large SIE non-dynamic electron correlation effects as has been shown by Cremer and co-workers.[49–52] This largely suppresses a configurational mixing initiated by the multi-reference approach. So the extra work carried out in a method such as REKS is reduced in its effectiveness by using a pure density functional. The SIE is however decreased when using a hybrid functional.[49–52] Hence, the unspecified non-dynamic correlation effects no longer suppress configurational mixing so that the advantages of the multi-reference approach can be better used to get a reasonable description including configurational mixing.

In the case of the XOO doublet radicals, a low-lying quartet state (about 20 kcal mol^{-1} above the doublet state) can mix in and change the predominantly ionic character of the X–O bond (ionic state: occupation numbers $n_r = 2$; $n_s = 0$) into a more covalent character (covalent quartet state: occupation numbers $n_r = 1$; $n_s = 1$). The admixture of the quartet state is essential for the correct description of the X–OO bond. Single determinant UDFT with pure density functionals suppresses the covalent character of the bond, exaggerates its ionic character, and by this overestimates its bond strength. Single determinant UDFT with a hybrid functional that mixes in a large amount of exact exchange exaggerates the covalent character of the X–OO bond and by this underestimates the bond dissociation energy.

In Table 1, experimental (fundamental) frequencies of ClOO are listed. The measurement of the frequencies is fairly difficult and is associated with large experimental uncertainties. Errors as large as 70 cm^{-1} are not unusual. For BrOO (Table 2), it was not possible to measure the vibrational spectra and therefore estimates of the three fundamental frequencies were obtained[13] by extrapolating the frequencies measured for FOO and ClOO to those of BrOO, which of course leaves room for large uncertainties.

Theory can provide much more reliable frequencies where of course some justification has to be given, as to which set of frequencies is most reliable. As pointed out above, the BLYP functional is not reliable, because it leads with REKS or UKS to a double counting of correlation effects (see also ref. 35). REKS and UKS provide typically different fractional occupation numbers in the way that for REKS the n-values of HOMO and LUMO are closer to 2 and 0 contrary to the case of UKS where they are closer to 1.5 and 0.5 (Tables 1 and 2). This is a direct consequence of using a restricted description on the one side and an unrestricted highly contaminated one on the other side.

The fractional occupation numbers n determine the degree of XO bonding (compare with Fig. 1) and by this also the vibrational frequencies of the XO stretching mode (ω_1) and the XOO bending mode (ω_2), which both increase with stiffer bonding. Considering the fact that relativistically corrected REKS/B3LYP provides the most reliable dissociation enthalpies D_0, the harmonic vibrational frequencies given in Tables 1 and 2 can definitely be considered as more reliable than the measured ones[12] or the experimentally based estimates given in the literature.[13] After scaling of the harmonic frequencies (the scaling factor is determined from the OO stretching frequency: 0.971), we suggest for BrOO a new set of frequencies $\omega_1 = 185$, $\omega_2 = 518$, $\omega_3 = 1487$ cm^{-1} (see Table 2) to replace the estimates presently available in the literature.[13]

The correct description of the XOO doublet radicals can only be obtained by using REKS with the B3LYP functional (to suppress nonspecific description of non-dynamic electron correlation), and by including quasi-relativistic and spin–orbital corrections. Previous claims[18,21] that single determinant DFT with the hybrid functional B3LYP can describe these systems are misleading and ignore the poor performance of this approach with regard to X–OO bond properties.

Similar considerations and conclusions drawn here for the DFT description of the ground state properties of ClOO and BrOO are also relevant for the description of the FOO doublet radical,[21] the hydrogentrioxide radical, HOOO,[53,54] or related system of the general type XYY$^\bullet$ with the group X containing a hetero atom (X = F, Cl, Br, I; HO, HS, HSe; H$_2$N, H$_2$P, etc.) and YY representing OO, SS, SeSe, etc. It has been shown that the problem of the description of the X–YY bond is even more problematic in the case of the corresponding anions as, e.g. the HOOO$^-$ anion.[55,56] Finally we note that the oxidation of some metals such as Cu, Ag, and Au by molecular oxygen leads to doublet radicals MOO$^\bullet$, which have a similar electro-

nic structure to ClOO$^\bullet$ and BrOO$^\bullet$ and, therefore also require a multi-reference DFT description.

In all these cases a REKS description will be much more economic than expensive multi-reference descriptions based on wave function theory. This argument will become particularly convincing if, e.g., the reaction of XOO$^\bullet$ (or XYY$^\bullet$) with a large molecular system (ClOO$^\bullet$ with lignin[17]) has to be investigated.

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