

The enthalpy of the O–H bond homolytic dissociation: Basis-set extrapolated density functional theory and coupled cluster calculations

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Abstract

The O–H bond homolytic dissociation of water, hydrogen peroxide, methanol, phenol, and catechol is investigated by density functional theory (DFT) and ab initio coupled cluster calculations. DFT results are based on several recently proposed functionals, including B98, PBE, VSXC, and HCTH. The dependence of DFT results on the basis-set size is discussed using correlation-consistent polarized (cc-pVXZ) basis-sets ($X=2-5$). A scheme proposed by Truhlar is used to extrapolate CCSD energies. Basis-set extrapolated CCSD results for the O–H bond homolytic dissociation enthalpies of phenol and catechol are in excellent agreement with experimental information.

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1. Introduction

The generation of free radical species by homolytic bond dissociation is a subject of fundamental importance in chemistry and biochemistry. Free radical species are intermediates in several mechanisms such as green plant photosynthesis [1], biocatalysis [2] and protein redox reactions [3]. One particularly relevant aspect concerning the generation of free radical species is the energetics of the homolytic bond cleavage in phenolic compounds. Their role as antioxidant agents can be explained by the low enthalpies of the O–H bond homolytic cleavage. Therefore, numerous experimental (see [4,5] for reviews) and theoretical works [6–11] on this subject were reported. However, it is well known that for several molecules of interest the adequacy of theoretical methods for evaluating enthalpies of homolytic dis-

sociation remains open to discussion, making difficult a comparison with experimental information. On the other hand, significant discrepancies between experimental data exist [4,12].

The enthalpy associated with the O–H bond homolytic dissociation can be estimated through the gas phase reaction



Consequently, the prediction of $DH^{\circ}(\text{O–H})$ from (1) is dependent on the accuracy of the theoretical procedures for both closed and open-shell species. For large molecules, theoretical studies on the energetics of homolysis are usually based on density functional theory (DFT). However, the reliability of DFT for discussing homolytic bond cleavage has been questioned by several works [8,10,11].

In the present Letter, we report a theoretical investigation on the O–H homolytic bond dissociation for some compounds, including water (HO–H, $\text{R}=\text{OH}^{\bullet}$), hydrogen

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peroxide (HOO-H , $\text{R}=\text{HOO}^\bullet$), methanol ($\text{CH}_3\text{O-H}$, $\text{R}=\text{CH}_3\text{O}^\bullet$), phenol ($\text{C}_6\text{H}_5\text{O-H}$, $\text{R}=\text{C}_6\text{H}_5\text{O}^\bullet$), and catechol ($1,2\text{-C}_6\text{H}_4(\text{OH})_2$, $\text{R}=\text{C}_6\text{H}_4(\text{OH})\text{O}^\bullet$). We have two main objectives: first, to discuss the reliability of different DFT methods, including several recently proposed functionals, for predicting the energetics of homolytic dissociation; second, to compare DFT predictions with ab initio coupled cluster calculations. A special emphasis will be placed on the convergence of $DH^\circ(\text{O-H})$ with the basis-set size. In this sense, extrapolation of DFT and ab initio results to infinite basis-set will provide interesting elements to evaluate the accuracy of different theoretical procedures for predicting $DH^\circ(\text{O-H})$.

2. Computational details

The calculations were carried out with the hierarchical series of correlation-consistent polarized valence basis-sets, cc-pVXZ ($X = 2-5$), of Dunning and coworkers [13,14]. Several exchange-correlation functionals were applied to estimate the enthalpy of the O-H bond homolytic dissociation, including the B98 [15], PBE [16], VSXC [17], and HCTH [18] functionals. We are also reporting results based on the well known hybrid functionals B3LYP and B3P86, where the exchange correlation functional is the Becke's three parameter functional (B3) [19] combined, respectively, with the Lee, Yang, and Parr (LYP) [20] and the Perdew (P86) [21] correlation functionals. Geometry optimizations were performed at the DFT level with the cc-pVDZ and cc-pVTZ basis-sets. For $X = 4,5$ DFT single-point energy calculations were carried out with DFT/cc-pVTZ geometries.

Coupled cluster calculations with single and double excitations (CCSD) [22] were also carried out. Theoretical investigations for a series of radical species [23] indicated that B3LYP/cc-pVTZ optimized geometries and frequencies are in very good agreement with available experimental information. B3LYP/cc-pVTZ geometries were presently taken as reference structures for single-point energy CCSD calculations. Zero-point vibrational energies and thermal corrections at the same level were used for estimating CCSD enthalpies. Some authors [25] pointed out the importance of including triple excitations in coupled cluster calculations. However, we will assume that a CCSD/cc-pVXZ approach is an adequate compromise for our purposes, mainly if we take into consideration that the inclusion of triples is unaffordable for some of the compounds presently studied.

It is reasonable to assume that a reliable theoretical method for predicting $DH^\circ(\text{O-H})$ should lead to a better agreement with experiment as the basis-set is improved. An attractive possibility for investigating the adequacy of a given theoretical procedure is to extrapolate the energy to infinite basis-set. Extrapolation procedures for DFT are not of common practice and should be designed for each specific exchange-correlation combination. However, quite recently, different extrapolation schemes were applied to predict atomization energies based on DFT calculations carried out with correlation consistent basis-sets [24]. DFT results for $DH^\circ(\text{O-H})$ were presently extrapolated by assuming a power-law expression (see Section 3) for the Kohn-Sham total energies.

Several methods to extrapolate ab initio energies were proposed [25–31]. We have presently adopted the dual level, $(X-1, X) = (2,3)$ extrapolation scheme of Truhlar [29]. This scheme is based on ab initio calculations with

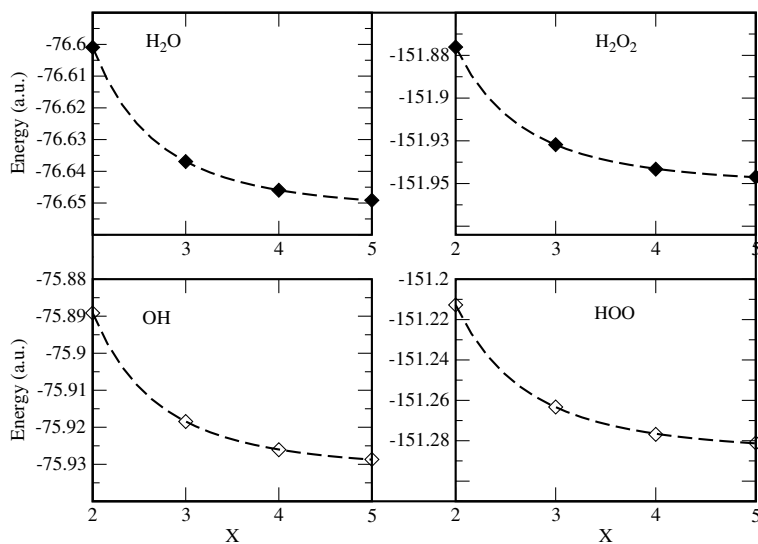


Fig. 1. Dependence of the total B3P86 Kohn-Sham energies (a.u.) on the cardinal number X for water, hydrogen peroxide, and the respective radical species. The curves were fitted using the power-law expression $E_X = E_\infty + A_3X^{-3} + A_5X^{-5}$.

the cc-pVDZ ($X=2$) and cc-pVTZ ($X=3$) basis-sets and on the use of separate power-law extrapolations for the Hartree–Fock and correlation energies. Extrapolated CCSD correlation energies predicted by the one-parameter rule proposed by Varandas [30] are also reported. The calculations were carried out with the GAUSSIAN-03 package of programs [32].

3. Results and discussion

The dependence of the total B3P86 Kohn–Sham energies on the basis-set size is illustrated in Fig. 1 for water, hydrogen peroxide and the respective radical species. They were fitted using the power-law expression [31]:

$$E_X = E_\infty + A_3X^{-3} + A_5X^{-5} \quad (2)$$

and the same expression was used for fitting $DH^\circ(\text{O–H})$, which involves the calculation of energy differences. As illustrated in Fig. 1, the same functional dependence on the cardinal number X leads to a correct fitting for both closed and open-shell species. DFT results for $DH^\circ(\text{O–H})$ are reported in Table 1, where they are compared with experimental results. A significant and regular dependence of $DH^\circ(\text{O–H})$ on the basis-set size is observed. For the dissociation of water, $DH^\circ(\text{O–H})$ increases by ~ 5 kcal/mol when we move from cc-pVDZ to cc-pVQZ. The difference between $DH^\circ(\text{O–H})$ calculated with $X=5$ and $X=4$ is quite small (≤ 0.5 kcal/mol), indicating the DFT/cc-pVQZ values are converged within ~ 1 kcal/mol. With the exception of B3P86 and HCTH

Table 1
DFT results for the enthalpy of the O–H bond homolytic dissociation $DH^\circ(\text{O–H})$ (in kcal/mol)

	cc-pVDZ	cc-pVTZ	cc-pVQZ	cc-pV5Z	Extrapolated
	$\text{H}_2\text{O} \rightarrow \text{OH}^\cdot + \text{H}^\cdot$		$DH^\circ_{\text{exp}}(\text{O–H}) = 118.8^{\text{a}}$		
B98	111.0	114.8	115.6	115.9	116.2
PBE	112.7	116.4	117.2	117.6	117.9
VSXC	111.9	115.6	116.5	116.7	117.0
HCTH	112.9	116.8	117.6	117.9	118.2
B3LYP	110.6	114.6	115.5	115.8	116.2
B3P86	114.8	118.5	119.3	119.6	119.9
	$\text{H}_2\text{O}_2 \rightarrow \text{HOO}^\cdot + \text{H}^\cdot$		$DH^\circ_{\text{exp}}(\text{O–H}) = 87.8 \pm 0.5^{\text{b}}$		
B98	77.9	81.5	82.0	82.2	82.3
PBE	75.8	79.8	80.4	80.7	80.8
VSXC	77.1	80.7	81.2	81.3	81.3
HCTH	75.0	79.2	79.8	79.9	80.1
B3LYP	78.0	82.0	82.5	82.8	82.9
B3P86	81.1	84.7	85.1	85.3	85.3
	$\text{CH}_3\text{OH} \rightarrow \text{CH}_3\text{O}^\cdot + \text{H}^\cdot$		$DH^\circ_{\text{exp}}(\text{O–H}) = 104.6 \pm 0.7^{\text{b}}$		
B98	96.2	99.00	99.5	99.6	99.8
PBE	95.3	98.0	98.5	98.6	98.7
VSXC	94.8	97.6	98.1	98.2	98.4
HCTH	95.3	98.3	98.7	98.8	98.9
B3LYP	96.1	99.0	99.6	99.8	99.9
B3P86	99.8	102.5	103.0	103.2	103.3
	$\text{PhOH} \rightarrow \text{PhO}^\cdot + \text{H}^\cdot$		$DH^\circ_{\text{exp}}(\text{O–H}) = 88.7^{\text{c}}; 90.1 \pm 3^{\text{d}}; 85.8 \pm 2^{\text{e}}$		
B98	81.2	83.6	84.0		84.2
PBE	80.8	83.0	83.3		83.4
VSXC	80.6	82.7	83.1		83.3
HCTH	80.0	82.3	82.4		82.4
B3LYP	81.5	83.7	84.1		84.3
B3P86	85.6	87.8	88.1		88.3
	$1,2\text{-C}_6\text{H}_4(\text{OH})_2 \rightarrow \text{C}_6\text{H}_4(\text{OH})\text{O}^\cdot + \text{H}^\cdot$		$DH^\circ_{\text{exp}}(\text{O–H}) = 82.5 \pm 1.2^{\text{f}}$		
B98	70.9	73.8	74.3		74.5
PBE	67.8	71.2	71.6		71.7
VSXC	69.7	72.5	72.7		72.7
HCTH	67.9	71.2	71.6		71.6
B3LYP	71.3	74.1	74.6		74.8
B3P86	74.7	77.6	77.9		78.0

^a Ref. [33].

^b Ref. [5].

^c Recommended experimental value. Ref. [4].

^d Ref. [34].

^e Ref. [12].

^f Ref. [35].

functionals, $DH^\circ(\text{O-H})$ is underestimated by DFT calculations. The B3P86/cc-pVTZ prediction (118.5 kcal/mol) is only 0.3 kcal/mol below the experimental value (118.8 kcal/mol) [33]. However, the extrapolated value (119.9 kcal/mol) is slightly above experiment. An excellent agreement between the extrapolated HCTH value for $DH^\circ(\text{O-H})$ (118.2 kcal/mol) and experiment is also observed. DFT results for hydrogen peroxide and catechol exhibit the largest deviation from experimental results. For catechol the only available experimental result (82.5 ± 1.2 kcal/mol) [35] is 4.5 kcal/mol above our better DFT prediction based on the B3P86 functional (78.0 kcal/mol). For the other compounds (water, methanol, and phenol), extrapolated B3P86 results are close to chemical accuracy (± 1 kcal/mol).

The tendency of DFT calculations to underestimate $DH^\circ(\text{O-H})$ can be also observed for all the other

calculations. Although this feature has been previously pointed out by some studies on the energetics of homolytic bond dissociation, our results show that this is not verified for the B3P86 functional, which for the present series of molecules leads to $DH^\circ(\text{O-H})$ in good agreement with experiment. It is also clear that at least a cc-pVQZ basis-set should be used for comparison between theoretical DFT results and experimental information. Therefore, the performance of DFT for evaluating the energetics of homolytic dissociation should take into consideration the rate of convergence of the calculations with the basis set.

CCSD energies are reported in Table 2, where extrapolated results are also shown. Table 3 reports total enthalpies, which were estimated by adding to the energies of Table 2, ZPVE and thermal corrections

Table 2
Ab initio (CCSD/cc-pVXZ//B3LYP/cc-pVTZ) energies for the reactants and products (in a.u.)

	HF	Δ CCSD	PUHF	Δ CCSD	HF
	$\text{H}_2\text{O} \rightarrow \text{OH}^\bullet + \text{H}^\bullet$				
	H_2O		OH^\bullet		H^\bullet
cc-pVDZ	-76.026571	-0.211486	-75.396309	-0.161283	-0.499278
cc-pVTZ	-76.056856	-0.267650	-75.422279	-0.210324	-0.499810
cc-pVQZ	-76.064507	-0.286231	-75.429027	-0.226389	-0.499946
cc-pV5Z	-76.066763	-0.292696	-75.430913	-0.232063	-0.499994
Extrapolated ^a	-76.067055	-0.301768	-75.431026	-0.240115	-0.499989
Extrapolated ^b		-0.293763		-0.230843	
	$\text{H}_2\text{O}_2 \rightarrow \text{HOO}^\bullet + \text{H}^\bullet$				
	H_2O_2		HOO^\bullet		
cc-pVDZ	-150.783940	-0.400655	-150.187335	-0.362594	
cc-pVTZ	-150.835796	-0.504292	-150.241191	-0.454371	
cc-pVQZ	-150.848083	-0.538982	-150.253413	-0.486893	
cc-pV5Z	-150.851409	-0.551433	-150.256695	-0.498661	
Extrapolated ^a	-150.853260	-0.567249	-150.259329	-0.510123	
Extrapolated ^b		-0.553492		-0.498700	
	$\text{CH}_3\text{OH} \rightarrow \text{CH}_3\text{O}^\bullet + \text{H}^\bullet$				
	CH_3OH		$\text{CH}_3\text{O}^\bullet$		
cc-pVDZ	-115.049126	-0.363281	-114.429523	-0.318568	
cc-pVTZ	-115.089152	-0.446817	-114.469645	-0.392342	
cc-pVQZ	-115.098655	-0.473542	-114.478553	-0.417092	
Extrapolated ^a	-115.102631	-0.497562	-114.483157	-0.437157	
Extrapolated ^b		-0.490409		-0.430619	
	$\text{PhOH} \rightarrow \text{PhO}^\bullet + \text{H}^\bullet$				
	PhOH		PhO^\bullet		
cc-pVDZ	-305.586185	-1.006660	-305.044213	-0.909209	
cc-pVTZ	-305.666508	-1.207555	-305.121412	-1.104292	
Extrapolated ^a	-305.693559	-1.329593	-305.147412	-1.222798	
Extrapolated ^b		-1.325366		-1.212027	
	$1,2\text{-C}_6\text{H}_4(\text{OH})_2 \rightarrow \text{C}_6\text{H}_4(\text{OH})\text{O}^\bullet + \text{H}^\bullet$				
	$1,2\text{-C}_6\text{H}_4(\text{OH})_2$		$\text{C}_6\text{H}_4(\text{OH})\text{O}^\bullet$		
cc-pVDZ	-380.452433	-1.186694	-379.904656	-1.108333	
cc-pVTZ	-380.557870	-1.438352	-381.256984	-1.354046	
Extrapolated ^a	-380.593379	-1.591225	-380.041305	-1.503308	
Extrapolated ^b		-1.578679		-1.486148	

^a Dual (2,3) extrapolation scheme of Truhlar [29].

^b Extrapolated correlation energy from the one parameter rule $E_\infty^{\text{cor}} = E_X^{\text{cor}} (1 - 2.4X^{-3})^{-1}$ [30], with $X = 3$.

Table 3

CCSD/cc-pVXZ//B3LYP/cc-pVTZ ($X = 2-5$) results for the enthalpy of the O–H bond homolytic dissociation ($DH^\circ(\text{O–H})$ in kcal/mol)

	cc-pVDZ	cc-pVTZ	cc-pVQZ	cc-pV5Z	Extrapolated		Exp.
					[1] ^a	[2] ^b	
H ₂ O → OH· + H·	106.8	113.7	115.7	116.4	117.2	117.9	118.8 ^c
H ₂ O ₂ → HOO· + H·	78.5	84.3	85.6	86.1	88.3	86.8	87.8 ± 0.5 ^d
CH ₃ OH → CH ₃ O· + H·	95.5	101.2	102.7		106.4	104.4	104.6 ± 0.7 ^d
PhOH → PhO· + H ^e	81.7	86.3			89.1	93.2	88.7 ^f ; 90.1 ± 3 ^g ; 85.8 ± 2 ^h
1,2-C ₆ H ₄ (OH) ₂ → C ₆ H ₄ (OH)O· + H ^e	73.3	78.7			81.5	84.4	82.5 ± 1.2 ⁱ

ZPVE and thermal corrections were estimated at the B3LYP/cc-pVTZ level.

^a Dual (2,3) extrapolation scheme of Truhlar [29].^b Extrapolated correlation energy from the one parameter rule $E_\infty^{\text{cor}} = E_X^{\text{cor}} (1-2.4X^{-3})^{-1}$ [30], with $X = 3$.^c Ref. [33].^d Ref. [5].^e Recent theoretical results based on the CBS-QMPW1 approach (Ref. [11]) are: 86.9 kcal/mol (phenol) and 78.9 kcal/mol (catechol).^f Recommended experimental value. Ref. [4].^g Ref. [34].^h Ref. [12].ⁱ Ref. [35].

calculated at the B3LYP/cc-pVTZ level. The results of Table 2 illustrate the slow convergence of the energies with the basis-set. For water and hydrogen peroxide, calculations were carried out up to $X = 5$. For water, extrapolated energies based on the (2,3) scheme of Truhlar are, as it should be expected, below our better energy estimates (cc-pV5Z). However, some discrepancies are observed when the one-parameter rule [30] with $X = 3$ is used, particularly for radical species.

In keeping with DFT calculations, CCSD results for $DH^\circ(\text{O–H})$ also exhibit a clear basis-set size dependence. For water, CCSD/cc-pVDZ are ~ 10 kcal/mol below the results at CCSD/cc-pV5Z results. CCSD results with $X = 4$ are typically more than 1 kcal/mol below extrapolated results, illustrating the importance of extrapolation schemes for comparison of ab initio results with experiment. A recent study pointed out significant deviations from experiment of CCSD(T)/6-311+G(d,p) bond dissociation enthalpies [10]. However, the present work shows that comparison with experiment should be carried out, preferentially, with basis-set extrapolated theoretical results. This is illustrated in Table 3, where an excellent agreement between extrapolated CCSD results and experiment is observed for all the compounds. Specifically, the present result for phenol (89.1 kcal/mol) is in excellent agreement with the recommended experimental value (88.7 kcal/mol) [4], and with a prediction by Turi and Ervin (90.1 ± 3 kcal/mol) [34]. However, it is ~ 3 kcal/mol above a more recent experimental data (85.8 ± 2 kcal/mol) [12], which according to the present extrapolated DFT and ab initio results seems to underestimate $DH^\circ(\text{O–H})$ of phenol. An excellent agreement between CCSD (2,3) extrapolated value (81.5 kcal/mol) and experiment (82.5 ± 1.2 kcal/mol) [35] is also observed for catechol. Finally, we note that the basis-set extrapolated CCSD results for $DH^\circ(\text{O–H})$ of phenol

and catechol are in much better agreement with experiment than recent predictions based on the CBS-QMPW1 approach [11] (see Table 3). This agreement supports the experimental value [35] and strongly indicates that extrapolated DFT results underestimate $DH^\circ(\text{O–H})$ for catechol.

4. Conclusions

Density functional theory and CCSD calculations were carried out to investigate the energetics of homolytic dissociation for some compounds of reference. The performance of several recently proposed functionals was assessed and a special emphasis was placed on the convergence of $DH^\circ(\text{O–H})$ with the basis-set size. A first conclusion concerns the reliability of DFT calculations. Extrapolated results support the view that DFT calculations underestimate O–H bond homolytic dissociation energies. We are providing further evidence that some approximations for the exchange-correlation energy, as for example, B3P86 and HCTH, may accurately predict the energetics of homolysis for some of the present series of compounds, provided that the calculations are performed with, at least, a cc-pVQZ basis-set. Extrapolated results for $DH^\circ(\text{O–H})$ based on B3P86 calculations are near to chemical accuracy for most of the compounds presently studied. B3P86 extrapolated results for hydrogen peroxide and catechol significantly underestimate the experimental results. Although energetic properties based on DFT converge quicker with the basis-set than CCSD calculations, extrapolation schemes are of interest for comparison with experimental results.

Not surprisingly, a slow convergence of $DH^\circ(\text{O–H})$ with the basis-set size is also observed for CCSD

calculations. However, by using a simple dual (2,3) scheme proposed by Truhlar, extrapolated CCSD results are also near chemical accuracy for the present series of compounds. The present results illustrate the importance of carrying out extrapolation to infinite basis-set and indicate that for larger systems the Truhlar (2,3) extrapolation scheme is a practical and reliable solution for ab initio studies on the energetics of homolytic dissociation.

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