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Theoretical Characterization of Hydrogen Polyoxides: HOOH, HOOOH, HOOOOH, and HOOO

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We have investigated the polyoxides HOOH, HOOOH, HOOOOH, and HOOO employing the CCSD(T) methodology, and the correlation consistent basis sets. For all molecules, we have computed fundamental vibrational frequencies, structural parameters, rotational constants, and rotation-vibration corrections. For HOOOH, we have obtained a good agreement between our results and microwave and infrared spectra measurements, although for the symmetric OO stretch some important differences were found. Heats of formation were computed using atomization energies, and our recommendation is as follows: $\Delta H^{o}_{f,298}$(HOOOH) = −21.50 kcal/mol and $\Delta H^{o}_{f,298}$(HOOOOH) = −10.61 kcal/mol. In the case of HOOO, to estimate the heat of formation, we have constructed three isodesmic reactions to cancel high order correlation effects. The results obtained confirmed that the latter effects are very important for HOOO. The new $\Delta H^{o}_{f,298}$(HOOO) obtained is 5.5 kcal/mol. We have also calculated the zero-point energies of DO and DOOO to correct the experimental lower limit determined for the $\Delta H^{o}_{f,298}$(HOOO). The Δ(ΔZPE) decreases the binding energy of HOOO by 0.56 kcal/mol. Employing the latter value, the new experimental lower limit for $\Delta H^{o}_{f,298}$(HOOO) is 3.07 kcal/mol, just 2.4 kcal/mol lower than our determination. We expect that the fundamental vibrational frequencies and rotational constants determined for HOOOOH and DOOOOD contribute to its identification in the gas phase. The vibrational spectrum of HOOOOH shows some overlapping with that of HOOOH thus indicating that one may encounter some difficulties in its characterization. We discuss the consequences of the thermochemical properties determined in this work, and suggest that the amount of HOOO present in the atmosphere is smaller than that proposed recently in this journal (*J. Phys. Chem A* 2007, *111*, 4727).

1. Introduction

Closed-shell and radical polyoxides are species that have received much attention in the literature in the last ten years,[1–44] and of special concern are the studies related to the relevance of the roles they can play in atmospheric processes.[3,12,13,23] Several works have been devoted to investigate HOOO experimentally[1–9] and theoretically,[10–27] its cation $HOOO^{+}$,[28] the anion $HOOO^{-}$,[29–32] their reactions,[33–35] and higher polyoxides like HOOOH[36–42] and HOOOOH.[43,44] Indeed, Suma et al.[7] studied the microwave spectra of HOOO trans and recent investigations by Lester and co-workers[3–6] have suggested that HOOO should be included in atmospheric models because up to 66% of OH may be converted to HOOO in the tropopause.[3] In addition to this, it has been found that HOOO and HOOOH play an important role in the conversion of singlet O_2 plus water to HOOH,[34] in the ozonization of alcohols,[31] and of 1,3 dioxolanes.[32] While there have been important improvements, like the determination of the IR spectrum of HOOO[3–6] trans, and the IR[36] and microwave spectra of HOOOH,[42] some problems still remain because these molecules present a tremendous challenge for theorists[14,17] and experimentalists.[3–6,36,42] Among the problems that need to be solved to fully characterize these molecules, we can mention the following. First, significant differences exist between the experimental[2–6] and theoretical determinations[10–27] of the enthalpy of formation of HOOO. The theoretical values proposed span from −13 to 21 kcal/mol,[13] in marked disagreement with the recent experimental upper limit for the D_0(HO-OO) of 5.31 kcal/mol.[6] In addition, the latter value can be improved if the zero-point energy of the deuterated isomer DOOO is determined.[6] Second, $\Delta H^{o}_{f,298}$(HOOOH) is not known accurately, thus making it difficult to understand the mechanisms in which it participates.[31,32,34] To the best of our knowledge, there is no high level determination of this latter property,[13] like the one that can be achieved using coupled cluster theory in conjunction with very large correlation consistent basis sets, and with additional corrections for core−valence correlation effects, anharmonicites of the ZPEs, scalar relativistic and spin−orbit effects. Third, and final, to the best of our knowledge, HOOOOH has not been identified in the gas phase, although a method has been proposed to observe it.[42] The points raised above clearly point that extensive investigations of the closed-shell polyoxides HOOH, HOOOH and HOOOOH, and the radical HOOO are certainly in order. To that end, we used Dunning correlation consistent basis sets up to sextuple ζ, the CCSD(T) methodology, and in some cases DFT to compute, anharmonic force fields (most of them at the CCSD(T) level), fundamental vibrational frequencies, vibration–rotation constants, accurate zero-point energies corrected by anharmonic effects, and very accurate enthalpies of formation. Our new approach to the problem has reduced the differences between experiment and theory for the

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$\Delta H^{o}_{f,298}$(HOOO) to just 2.5 kcal/mol, and confirmed that high order correlation effects are extremely important for characterizing HOOO. In addition, we also computed the most accurate enthalpies of formation for HOOOH and HOOOOH reported to date. Finally, the fundamental vibrational frequencies and the rotational constants of HOOOOH are reported to guide in the experimental identification of this molecule. We expect that this work can stimulate new experimental investigations and help to understand the role that HOOO, HOOOH and HOOOOH play in the atmosphere.

2. Methods

Coupled cluster theory with single-, double-, and perturbative treatment of triple excitations, CCSD(T)[45–48] was employed to study the properties of the hydrogen polyoxides HOOH, HOOOH, HOOOOH and HOOO. The basis sets used were Dunning′s cc-pVnZ (n = T, Q, 5, 6).[49] Core−valence (CV) correlation effects were estimated as the difference between the full and frozen core CCSD(T) calculations employing the cc-pwCVTZ and cc-pwCVQZ basis sets.[50] The extrapolations to the complete basis set limit were carried out employing two procedures: (a) we performed a separate extrapolation of the correlation energy from the HF one; correlation energies were extrapolated employing the two-parameter expression $E = B + C/l^3$, suggested by Halkier et al.,[51] whereas HF energies were converged with the cc-pV6Z basis set; (b) the three-parameter exponential extrapolation of total energies suggested by Peterson et al.,[52] $E(n) = E_{\mathrm{CBS}} + B\exp[-(n-1)] + C\exp[-(n-1)^2]$. Scalar relativistic effects (SR) were estimated at the DKCCSD(T)/cc-pVQZ_DK level of theory,[53–55] where the cc-pVQZ_DK basis set is a recontraction of the cc-pVQZ basis set for relativistic calculations.[56] The spin−orbit splitting for atoms were taken from Moore's compilation,[57] and the molecular spin−orbit constant of FO and OH from the works of Tamassia et al.[58a] and Ruscic et al.,[79] respectively. The theoretical harmonic vibrational frequencies were determined at the CCSD(T)/cc-pVTZ level of theory, and fundamentals were calculated as implemented in ACESII.[59–61] Briefly, the full cubic force field together with the semidiagonal part of the quartic force field is calculated, and the fundamental vibrational frequencies are obtained employing second-order perturbation theory starting from the harmonic-oscillator rigid-rotor approximation. In addition to the CCSD(T) computations, we have also performed B3LYP[62,63] calculations employing the 6-311+G(3df,2p) basis set.[64] The reason for using different basis sets for the Coupled Cluster and DFT calculations is because it is well-known that DFT methods exhibit a weaker basis set dependence than the Coupled Cluster ones. For HOOH and HOOOH, the anharmonic force fields were evaluated to assess their accuracy when compared with the CCSD(T) results. As we will show in the following sections, this comparison allowed us to use the anharmonic corrections determined at the B3LYP/6-311+G(3df,2p) level for HOOOOH in conjunction with the harmonic CCSD(T) results. The CCSD(T) calculations were performed with ACESII (Mainz−Austin−Budapest version)[59,60] and the DFT ones with Gaussian 2003.[65]

The enthalpies of formation of HOOOH and HOOOOH were estimated employing the atomization reaction. Thus, the ultimate error relies on the methodology selected; in the present case, the most important source of error is the lack of complete quadruple excitations in the coupled cluster calculations.[63–73] However, since there is an error cancelation between the missing triples excitations in CCSD(T) and the quadruples ones, we expect this contribution to be small.[66–73] In a recent work,[14] we used the atomization reaction to estimate $\Delta H^{o}_{f,298}$(HOOO). However, despite the high level of the approach used, a large deviation from experiment still remained. As in the case of FOO,[70] we attributed this difference to higher order correlation effects. To avoid this problem, we used the following isodesmic reactions to estimate $\Delta H^{o}_{f,298}$(HOOO):

TABLE 1: Enthalpies of Formation Used as Reference (kcal/mol)

	experiment	theory
HOH	−57.83 ± 0.01[78]	−57.8 ± 0.2[66]
HOOH	−32.43 ± 0.02[78]	−32.00 ± 0.03[66]
		−32.46[a]
HO	8.91 ± 0.07[79]	8.91 ± 0.07[79]
HOO	2.94 ± 0.06[80]	2.96 ± 0.01[77]
		3.0 ± 0.2[66]
FO	26.58 ± 0.11[78]	26.6 ± 0.2[66]
FOO	5.49 ± 0.4[81]	5.8 ± 0.3[66]
	6.24 ± 0.5[82]	6.5 ± 1[70]

[a] This work.

$$\mathrm{HOO + HOOOH \rightarrow HOOO + HOOH} \qquad (1)$$

$$\mathrm{HO + HOOOH \rightarrow HOOO + HOH} \qquad (2)$$

$$\mathrm{HOO + FOO \rightarrow HOOO + FO} \qquad (3)$$

In general, we prefer to use the atomization reaction to estimate enthalpies of formation, however, HOOO is such a difficult case that forces us to use isodesmic reactions; in this approach, the high order effects tend to cancel as observed for HOO by Flowers et al.[77] Fortunately, for almost all of the molecules participating in reactions 1 and 2, there is an excellent agreement between experiment and theory for the heat of formation.[76–82] Indeed, the differences are below 0.1 kcal/mol; the enthalpies of formation used are listed in Table 1. There is only one molecule that presents problems, HOOOH. However, one of the purposes of the present work is also to accurately predict this quantity; taking into account the methodology selected, the determination is expected to be accurate enough to estimate $\Delta H^{o}_{f,298}$(HOOO) to within ±1 kcal/mol. To avoid the problem of the heat of formation of HOOOH, we constructed reaction 3, which has only one molecule which presents some uncertainty, FOO. In a previous work,[70] we suggested that high order correlation effects are very important for this molecule. Indeed, quite recently Feller et al.[66] found that high order correlation effects increase the total atomization energy of FOO by 3.22 kcal/mol, confirming our initial statement.[70] For this reason, we have selected FOO to estimate $\Delta H^{o}_{f,298}$(HOOO). The value suggested by Feller et al.[66] is $\Delta H^{o}_{f,298}$(FOO) = 5.8 ± 0.3 kcal/mol. This estimate is bracketed by the experimental results available 5.49 ± 0.4,[81] and 6.24 ± 0.5,[82] so it seems reasonable to adopt the theoretical recommendation.

3. Benchmark Results

Prior to the characterization of HOOO, HOOOH and HOOOOH, we decided to perform a benchmark of the methodology selected. While it is well know that the CCSD(T) methodology, in conjunction with the correlation consistent basis set can give very accurate structural and thermochemical parameters,[66–77,83–88] we consider that is important to perform a fine-tuning of the methodology because there is a large number of combinations of extrapolations and basis set that can employed. The molecule selected to make the test is HOOH. We have used hydrogen peroxide because it is the smallest closed-shell molecule in which there is an OO bond. The

TABLE 2: Structural and Spectroscopic Parameters Determined for HOOH. (Å, °, cm^{-1}, km/mol, MHz)

		r_{O-H}	r_{O-O}	OOH	HOOH			
CCSD(T)	cc-pVTZ	0.9640	1.4579	99.54	113.95			
CCSD(T)	cc-pVQZ	0.9627	1.4525	99.92	112.38			
CCSD(T)	cc-pV5Z	0.9629	1.4511	100.05	112.61			
B3LYP	6-311+G(3df,2p)	0.9659	1.4464	100.89	111.97			
	expt[89]	0.9670	1.4556	102.32	119.1			
	fundamentals	$v_{torsion}$	$v_{OOstretch}$	$v_{OOHasymbend}$	$v_{OOHsymbend}$	v_{OHsym}	v_{OHasym}	ZPE
CCSD(T)	cc-pVTZ[a]	320(169)	879(1)	1281(105)	1390(0.2)	3624(47)	3616(12)	16.38
B3LYP	6-311+G(3df,2p)	352	926	1283	1401	3587	3590	16.43
	expt	370.6[90]	877.9[90]	1264.6[90]	1393.5	3618.8[90]	3617.8[90]	16.44[90]
		254.6[90]	865.9[90]			3610.7[90]	3609.8[90]	
	harmonics	$\omega_{torsion}$	$\omega_{OOstretch}$	$\omega_{OOHasymbend}$	$\omega_{OOHsymbend}$	ω_{OHsym}	ω_{OHasym}	ZPE
CCSD(T)	cc-pVTZ	372	912	1324	1436	3808	3809	16.67
B3LYP	6-311+G(3df,2p)	396	952	1337	1444	3780	3779	16.71
	$\omega - v$	$\omega - v$	$\omega - v$	$\omega - v$	$\omega - v$	$\omega - v$	$\omega - v$	
CCSD(T)	cc-pVTZ	52	33	43	46	184	193	
B3LYP	6-311+G(3df,2p)	44	26	54	43	193	189	
	rotational constants	A_e	B_e	C_e	A_o	B_o	C_o	
CCSD(T)	cc-pVTZ	302143	26301	25434	299443	25984	25025	
B3LYP	6-311+G(3df,2p)	304349	26545	25743	301521	26308	25385	
	vibration−rotation corrections	$A_e - A_o$	$B_e - B_o$	$C_e - C_o$				
CCSD(T)	cc-pVTZ	2700	317	409				
B3LYP	6-311+G(3df,2p)	2828	237	358				

[a] Values in parentheses denote the infrared intensities in km/mol.

structural and spectroscopic parameters of HOOH are summarized in Table 2. In the case of the fundamental vibrational frequencies, there is a very nice agreement between the CCSD(T)/cc-pVTZ values and the experimental results and only two modes present problems: the torsion mode, and the OOH asymmetric bending mode. For the rest of the vibrations, the differences between experiment and theory are below 6 cm^{-1}. The performance of the B3LYP density functional is also good, although it is not as good as that of CCSD(T). For the purposes of the present work, the most important conclusion is that the anharmonic corrections to vibrational frequencies determined at the CCSD(T)/cc-pVTZ and B3LYP/6-311+G(3df,2p) levels of theory are good in agreement. In Table 2, we also present the rotational constants. While there are some discrepancies between absolute values determined by the coupled cluster and the DFT approaches, the vibration−rotation corrections are in good agreement, thus we can use the corrections determined for HOOOOH at the DFT level in conjunction with the CCSD(T) equilibrium values. Finally, we report the structural parameters for HOOH. The determination of the structural parameters of HOOH has been somewhat problematic.[89,93]At the CCSD(T)/cc-pV5Z level of theory, the bond distances are shorter than the experimental values. Therefore, if extrapolations to the CBS limit are performed and core corrections are included the agreement will be even worse, and it will be difficult that complete quadruple excitations will solve the differences between experiment and theory. In short, the comparison between experiment and theory for the structural parameters is not useful because the experimental structure needs revision as suggested by Bak et al.[93]

TABLE 3: Enthalpies of Formation of HOOH, HOOOH, and HOOOOH (kcal/mol)

	HOOH	HOOOH	HOOOOH
$TAE_e(5,Q)$	268.77	318.82	368.6
$TAE_e(6,5)$	268.55	318.58	
core (cc-pwCVQZ)	0.54	0.60	0.80
scalar relativistic	−0.37	−0.43	−0.49
spin−orbit	−0.446	−0.669	−0.892
ZPE (anharmonic)[a]	−16.44	−18.74	−20.83
$TAE_0(5,Q)$	252.05	299.58	347.19
$TAE_0(6,5)$	251.83	299.34	
$\Delta H^{o}_{f,0}(5,Q)$	−30.83	−19.38	−8.01
$\Delta H^{o}_{f,0}(6,5)$	−30.61	−19.14	
$\Delta H^{o}_{f,298}(5,Q)$	−32.28	−21.50	−10.61
$\Delta H^{o}_{f,298}(6,5)$	−32.06	−21.26	
expt[75]	−32.43 ±0.02		

[a] Obtained from an anharmonic force field computed at the CCSD(T)/cc-pVTZ level for HOOH and HOOOH; for HOOOOH it was determined at the B3LYP/6-311+G(3df,2p) level. The harmonic ZPEs are 16.67, 19.07, and 21.18 kcal/mol for HOOH, HOOOH, and HOOOOH, respectively.

The heat of formation $\Delta H^{o}_{f,298}$(HOOH), and the corrections used to compute it are presented in Table 3. Three estimates were performed: two of them employ the two-parameter[51] exponential extrapolation scheme, and the third one uses the three-parameter exponential scheme of Peterson et al.[52] The values obtained by the (6,5,Q), (5,Q) and (6,5) extrapolations are 31.50, 32.28 and 32.06 kcal/mol, respectively; they can be compared with the experimental value of 32.43 kcal/mol. Thus, the best agreement between experiment and theory is achieved if the (5,Q) extrapolation is used. As usual, the three-parameter exponential scheme underestimates the total atomization energies.[66] It is important to note that this does not mean that the two parameter exponential scheme is closer to the true CBS limit, although it provides a better agreement between experiment and theory. The performance of the (5,Q) extrapolation is better than that of the (6,5) one because we have not estimated diagonal Born−Oppenheimer corrections and higher order correlation effects. Indeed, for HOOH both quantities increase the total atomization energy by 0.40 kcal/mol.[66] Thus, if they

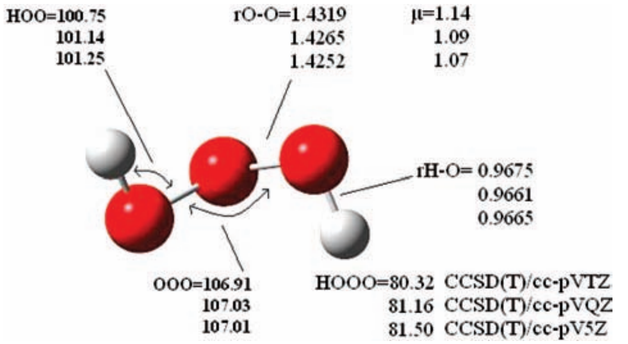

Figure 1. Structural parameters (Å, deg), and dipole moment (Debye) determined for HOOOH at the CCSD(T) level of theory. Top is cc-pVTZ; middle, cc-pVQZ; and bottom, cc-pV5Z.

are included, the best agreement between experiment and theory will be obtained with the (6,5) extrapolation. Since we are not including these corrections for HOOOH and HOOOOH, we are going to adopt the results obtained with the (5,Q) extrapolation to cancel part of the higher order correlation effects. Thus, the error of the procedure is 0.15 kcal/mol for HOOH.

4. Results and Discussion

HOOOH. The structural parameters determined for HOOOH are presented in Figure 1 and the spectroscopic constants are listed in Table 4. The vibrational spectrum of HOOOH has been determined by Engdahl and Nelander.[36] The comparison between experiment and theory cannot be made in quantitative terms because HOOOH was observed in an argon matrix and thus, a shift in the frequencies from the gas phase is expected. Overall, there is a good agreement between experiment and CCSD(T) results, in most cases the differences are below 10 cm^{-1}. The most problematic modes are the OH stretching modes, the symmetric OO stretch, and the antisymmetric torsional rotation. For the HO modes, an error between 30 and 40 cm^{-1} can be expected, and it is reasonable considering the strong anharmonic characteristics of these vibrations; also we cannot forget the matrix effect. However, the symmetric OO stretch presents an abnormal error of 58 cm^{-1}. This is also manifested in the B3LYP results for which the latter mode presents the largest discrepancy $\approx$100 cm^{-1}. We have considered the possibility that this mode corresponds to the cis isomer of HOOOH. It is important to note that the cis isomer of HOOOH is only slightly less stable than the trans one, 2.6 kcal/mol at the CCSD(T)/cc-pVTZ level of theory. However, the symmetric OO stretch of the cis isomer has a nearly identical position as the trans isomer. Indeed, the harmonic symmetric OO vibration is located at 908 cm^{-1} for the cis isomer and at 906 cm^{-1} for the trans. Thus, we attribute the differences observed for the symmetric OO stretch to a problem in the methodology selected by us.

The rotational spectrum of HOOOH has been determined experimentally by Suma et al.;[42] the results are also presented in Table 4. The agreement between the CCSD(T)/cc-pV5Z results and experiment is good, the differences are about 0.1% for the three rotational constants. However, at the B3LYP/6-311+G(3df,2p) level there are some problems for A_0, the error is 2 orders of magnitude larger than that observed for the other two rotational constants. This affects the vibration−rotation corrections, making the correction for the A constant almost twice the value suggested by the CCSD(T)/cc-pVTZ calculations. This situation is completely different from that observed for HOOH, and may compromise the use of the vibration−rotation corrections determined at the B3LYP/6-311+G(3df,2p) level for HOOOOH.

As expressed above, the determination of the structural parameters of HOOH is not an easy task, and because of the presence of the OOO moiety, that of HOOOH is expected to be more difficult. Considering the good agreement obtained between the rotational constants determined at the CCSD(T)/cc-pV5Z level of theory and the experimental results, we suggest the structural parameters determined at the latter level of theory. We do not attempt to include core-correlation effects because they shorten bond distances, and thus worsen the agreement between experiment and theory.[90–92] To include core-correlation effects, we need to include CCSDTQ corrections to bond distances. In general, CCSDTQ increases bond distances with respect to CCSD(T) compensating the contraction caused by core−valence correlation.[92]

In Table 3, we present the estimated enthalpy of formation of HOOOH, along with the corrections used. It is important to remark the importance of the anharmonic corrections to the ZPE, they decrease it by 0.33 kcal/mol. The values determined are −21.50 and −21.26 kcal/mol for the (5,Q) and (6,5) extrapolations. The difference between the values predicted by both extrapolations is 0.24 kcal/mol and, as observed for HOOH the (5,Q), one gives a more negative enthalpy of formation. For HOOOH, we suggest $\Delta H^{\circ}_{f,298}$(HOOOH) = −21.50 ± 0.5 kcal/mol; we have adopted the more negative value to compensate the higher order correlation effects. This value is almost 0.5 kcal/mol lower than that previously suggested one of by us.[13]

HOOO. In a previous work,[14] we have shown that the problem of spin contamination is very important for HOOO and that the use of an improper HF highly contaminated reference can lead to wrong conclusions, also the T1 diagnostic were found to be huge, namely T1 = 0.04. Thus, we are not going to discuss them here, we refer the reader to references[13] and,[14] and references therein. In the latter work,[14] we determined $\Delta H^{\circ}_{f,298}$(HOOO) = 7.53 kcal/mol employing the atomization reaction. This value is in marked disagreement with the recent determination suggested by Lester and co-workers.[3–6] Employing infrared action spectroscopy, they obtained an upper limit for the HO−OH dissociation energy (D_0) < 5.31 kcal/mol, which, employing $\Delta H^{\circ}_{f,298}$(HO), and thermodynamic corrections becomes $\Delta H^{\circ}_{f,298}$(HOOO) > 2.51 kcal/mol. In Table 5, we present $\Delta H^{\circ}_{f,298}$(HOOO) values determined employing the isodesmic reactions. The values suggested by reactions 1 and 2 are 7.62 and 7.58 kcal/mol. The latter results are very similar to that obtained by the atomization procedure. However, using reaction 3, we get $\Delta H^{\circ}_{f,298}$(HOOO) = 5.46 kcal/mol, about 2 kcal/mol lower than those obtained employing reactions 1 and 2. The only one explanation that we can find for such discrepancy is that the higher order correlation effects are very large for HOOO and thus, they are canceled in reaction 3 but not for the reactions 1 and 2. There are three pieces of evidence that support that conclusion. First, the T1 diagnostics of FOO and HOOO are very similar, 0.04, and are unusually huge.[14,70,71] Second, the higher order correlation correction determined for FOO is very large, 3.22[66] kcal/mol, and third, the higher order correlation corrections reported for HO, HOO, HOH, HOOOH, and HOOOH are not that large. Indeed they have been determined by Feller et al.[66] as 0.05, 0.53, −0.02, and 0.28 kcal/mol, for HO, HOO, HOH, and HOOOH, respectively; for HOOOH we have not calculated them but since the T1 is 0.014, we expect a small contribution. Therefore, none of the molecules present in reactions 1 and 2 can cancel the abnormally huge higher order correlation correction expected for HOOO. For the remaining

TABLE 4: Spectroscopic Parameters of HOOOH. (Å, deg, cm^{-1}, km/mol)

	CCSD(T) cc-pVTZ	B3LYP 6-311+G(3df,2p)	expt,[b]	CCSD(T) cc-pVTZ	B3LYP 6-311+G(3df,2p)	CCSD(T) cc-pVTZ	B3LYP 6-311+G(3df,2p)
	fundamentals[c]	fundamentals		harmonics	harmonics	anharmonic contribution	anharmonic contribution
STR[d]	350(113)	351	346.4	357	377	7	16
ASTR[e]	403(106)	394	387.0	415	434	12	40
OOO bend	508(30)	516	509.1	529	535	21	19
asymm OO stretch	784(56)	795	776.3	815	804	31	9
symm OO stretch	879(5)	925	821.0	906	946	27	21
OOH bend symm	1355(33)	1363	1347.4	1394	1398	39	35
OOH bend asym	1365(49)	1377	1359.1	1401	1405	36	28
antisymm OH stretch	3562(59)	3522	3529.6	3757	3728	195	206
symm OH stretch	3567(4)	3527	3529.6	3762	3732	195	205

	CCSD(T) cc-pV5Z	B3LYP 6-311+G(3df,2p)	expt[42]
A_e	51519	52406	
B_e	10815	10736	
C_e	9492	9461	
A_o	51205	51628	51149
B_o	10704	10689	10688
C_o	9371	9364	9355
$A_e - A_o$	314[a]	778	
$B_e - B_o$	111[a]	47	
$C_e - C_o$	121[a]	97	

[a] Vibration−rotation corrections determined at the CCSD(T)/cc-pVTZ level of theory [b] Determined in Ar matrix. [c] Values in brackets are the infrared intensities in km/mol. [d] STR - Symmetric torsional rotation [e] ASTR - Antisymmetric torsional rotation

TABLE 5: Enthalpy of Formation of HOOO Employing Isodesmic Reactions (kcal/mol)

	$\Delta H^{o}_{r,298}$[a]	$\Delta H^{o}_{f,298}$
OOH + HOOOH → HOOO + HOOH	−6.22	7.62
HO + HOOOH → HOOO + HOH	−37.52[b]	7.58
HOO + FOO → HOOO + FO	23.29[c]	5.46

[a] In all cases the core valence and scalar relativistic effects are canceled when the enthalpy of reaction is computed, the effect is smaller than 0.06 kcal/mol in all cases. [b] Includes a spin−orbit correction for HO of 0.11 kcal/mol [c] Includes a spin−orbit correction for FO of 0.28 kcal/mol

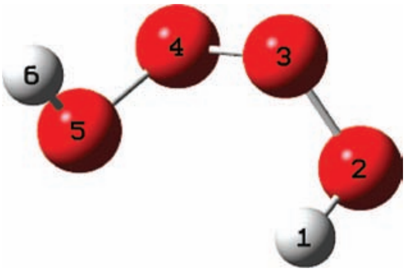

Figure 2. Optimized structure of HOOOOH.

corrections we have observed that core-correlation and scalar relativistic effects affect the enthalpy changes of reactions 1−3 by less than 0.06 kcal/mol, confirming the error cancelation suggested above. Also, the results are converged with respect to the extension of the basis set. For reactions 1 and 2, the enthalpy changes at the CCSD(T)/cc-pVQZ and CCSD(T)/cc-pV5Z levels are the same. In the case of reaction 3, the result is almost convergent.

Taking into consideration the evidence presented in the previous paragraph, we suggest $\Delta H^{o}_{f,298}$(HOOO) = 5.5 ± 1 kcal/mol. This value is in agreement with the one determined by Fabian et al.[15] 5.1 kcal/mol, obtained at the MR-ACPF-CBS level of theory. The latter values can be compared with the recent lower limit determined by Derro et al.,[6] $\Delta H^{o}_{f,298}$(HOOO) > 2.51 kcal/mol. The difference with our estimation is still very important, 3 kcal/mol, although it is important to highlight that Derro et al.[6] explained that a larger $\Delta H^{o}_{f,298}$(HOOO) is expected because the ZPE of HOOO and HO are expected to be much larger than those of DOOO and DO. Indeed, we have estimated the ZPE of DOOO and HOOO at the B3LYP/6-311+G(3df,2p) level of theory: they are 8.99 and 10.99 kcal/mol, respectively. These values, in conjunction with the ZPEs determined for OH and OD, which at the same level of theory are 5.32 and 3.88 kcal/mol, respectively, give a Δ(ΔZPE) of 0.56 kcal/mol for the reactions: HOOO → OH + OO and DOOO → DO + OO. Therefore, as previously suggested by Derro et al.,[6] the consideration of the Δ(ΔZPE) decreases the binding energy of HOOO. The corrected experimental lower limit for $\Delta H^{o}_{f,298}$(HOOO) is thus, 2.51 + 0.56 kcal/mol, namely 3.07 kcal/mol. It is important to emphasize that the prediction of accurate ZPE for HOOO and DOOO is very difficult.[3–6,14,17] However, since we are interested in their difference and not in their absolute values, we expect that the error of the methodology cancels when we estimate Δ(ΔZPE). The corrected experimental value is much closer to our prediction; now the differences are reduced to just 2.5 kcal/mol, a tremendous improvement since our first work, where the differences between experiment and theory were close to 10 kcal/mol.

HOOOOH. The last polyoxide considered in this work is H_2O_4. The most stable structure that we have found is the C_1 chain presented in Figure 2, in agreement with the previous results obtained by Fermann et al.[43] The structural parameters determined for HOOOOH are presented in Table 6. It is very interesting to note that HOOH has the largest OO bond distances in the sequence, HOOH, HOOOH and HOOOOH. At the CCSD(T)/cc-pVQZ level, the OO bond distance in HOOH is 1.4525 Å, 0.026 Å longer than that in HOOOH; furthermore, it is longer than the OO bonds in HOOOOH. Indeed, HOOOOH has three different OO bonds, the values are 1.4267, 1.4013 and 1.4360 Å. Thus, HOOOOH presents shorter bonds than HOOH and for one the OO bonds, the distance is shorter than

TABLE 6: Structural Parameters (Å, deg) Determined for HOOOOH

HOOOOH	CCSD(T)/PVTZ	CCSD(T)/PVQZ	Δcore	Δrel	B3LYP/6-311+g(3df,2p)
*r*H−O1	0.9688	0.9674	−0.0006	0.0000	0.9698
*r*O1−O2	1.4316	1.4267	−0.002	0.0006	1.4241
*r*O2−O3	1.4084	1.4013	−0.0027	0.0002	1.3963
*r*O3−O4	1.4412	1.4360	−0.0021	0.0006	1.4326
*r*O4−H2	0.9676	0.9663	−0.0006	0.0000	0.9693
∠H−O1−O2	100.3	100.7	0.0	0.0	101.8
∠O1−O2−O3	107.3	107.4	0.0	0.0	108.3
∠O2−O3−O4	106.4	106.6	0.0	0.0	107.7
∠O3−O4−H2	100.5	100.9	0.0	0.0	101.8
*τ*H−O1−O2-O3	−81.5	−82.3	0.0	0.1	−86.0
*τ*O1−O2−O3−O4	79.9	80.2	0.0	−0.1	83.0
*τ*O2−O3−O4−H2	84.4	84.9	0.0	0.1	85.2

TABLE 7: Spectroscopic Parameters of HOOOOH (cm^{-1}, km/mol, MHz)

	CCSD(T) cc-pVTZ	B3LYP 6-311+G(3df,2p)	CCSD(T) cc-pVTZ	B3LYP6-311+G(3df,2p)	B3LYP 6-311+G(3df,2p)
	fundamentals[a,b]	fundamentals	harmonics	harmonics	$\omega - \upsilon$
OH stretch 2	3563(41)	3537	3763	3737	200
OH stretch 1	3542(29)	3525	3747	3730	205
HOO bend 1	1368(50)	1364	1415	1411	47
HOO bend 2	1338(46)	1343	1385	1390	47
υ^d	882(4)	922	905	945	23
υ^d	833(41)	847	862	876	29
υ^d	672(15)	629	704	661	32
υ^d	601(15)	607	620	626	19
υ^d	470(52)	479	499	508	29
HO_3 torsion 2	374(131)	383	396	392	9
HO_3 torsion 1	279(37)	296	354	371	75
O_4 torsion	166(4)	172	170	176	4

	CCSD(T) cc-pVQZ[c]	B3LYP 6-311+G(3df,2p)
A_e	20048	20859
B_e	5879	5693
C_e	5097	5005
A_o	20056[c]	20867
B_o	5803[c]	5617
C_o	5032[c]	4940
$A_e - A_o$		−8
$B_e - B_o$		76
$C_e - C_o$		65

[a] Anharmonic corrections determined at the B3LYP/6-311+G(3df,2p) level of theory. [b] Values in brackets are the infrared intensities in km/mol. [c] Vibration−rotation corrections determined at the B3LYP/6-311+G(3df,2p) level of theory. [d] These modes are OOO bending and OO stretching ones, but due to the difficulty in the assignment we preferred to not distinguish them.

that of HOOOH. This is quite interesting, considering that HOOOOH is less bound than HOOH and HOOOH, from a thermodynamic standpoint. This evidence confirms the previous finding of McKay and Wright[37] that observed the same behavior: HOOH has the longest OO bond among the close shell polyoxides. The rotational constants determined at the CCSD(T)/cc-pVQZ and B3LYP/6-311+G(3df,2p) levels are included also in Table 7. The coupled cluster and DFT equilibrium rotational constants are in very good agreement. Indeed, they show the lowest deviation among the three closed-shell polyoxides considered. Thus, we can safely use the vibration−rotation corrections determined at the DFT level to correct the equilibrium rotational constants determined at the CCSD(T)/cc-pVQZ level. The A_0, B_0 and C_0 values suggested are: 20056, 5803 and 5032 MHz, respectively. We expect that these values can help to identify HOOOOH in the gas phase. Table 7 presents the harmonic vibrational frequencies determined at the CCSD(T)/cc-pVTZ and B3LYP/6-311+G(3df,2p) levels of theory. Due to the size of the molecule, we report fundamentals determined at the DFT level only. The most intense corresponds to one of the HOO torsional modes located at 374 cm^{-1}. This is in agreement with the results obtained for HOOH and HOOOH, for which the HOO torsional modes are the most intense ones. Finally, in Table 8 we report the fundamental vibrational frequencies and rotational constants determined for the deuterated isomer and DOOOOD to help in the assignment of the vibrational modes. The shifts of the OD modes to lower frequencies are very important, however, the modes that involve only oxygen atoms, namely those in the interval 470 to 922 cm^{-1}, and change very little upon deuteration, as we can verify in Table 8. One of the OOO modes, the one located at 833 cm^{-1} is close to the antisymmetric OO stretch in HOOOH, which is predicted to be observed at 784 cm^{-1}. Since both modes have nearly the same intensity, it is expected that the experimental identification of HOOOOH will be difficult if HOOOH is present.

The enthalpy of formation of HOOOOH, the total atomization energies, and the corrections employed to estimate $\Delta H^{o}_{f,298}$(HOOOOH) are presented in Table 3. The proposed value is $\Delta H^{o}_{f,298}$(HOOOOH) = −10.61 kcal/mol. There is a difference of about 10 kcal/mol per oxygen atom added to HOOH. Indeed, the $\Delta H^{o}_{f,298}$(HOOH) is 9.44 kcal/mol more negative than that of HOOOH, and the $\Delta H^{o}_{f,298}$(HOOOH) is 12.23 smaller that that of HOOOOH.

Thermochemical and Atmospheric Implications. The value proposed for HOOOOH indicates that it is stable against

TABLE 8: Spectroscopic Parameters of DOOOOD and HOOOOH at the B3LYP/6-311+G(3df,2p) level. (cm^{-1}, MHz)

	HOOOOH	HOOOOH	DOOOOD	DOOOOD
	fund.	harm.	fund.	harm.
OH stretch 2	3537	3737	2616	2722
OH stretch 1	3525	3730	2608	2718
HOO bend 1	1364	1411	1024	1051
HOO bend 2	1343	1390	1004	1032
v^a	922	945	921	943
v^a	847	876	845	874
v^a	629	661	644	661
v^a	607	626	602	616
v^a	479	508	468	482
HO_3 torsion 2	383	392	291	297
HO_3 torsion 1	296	371	238	279
O_4 torsion	172	176	162	165

	HOOOOH	DOOOOD
A_e	20859	19060
B_e	5693	5349
C_e	5005	4700
A_o	20867	19092
B_o	5617	5276
C_o	4940	4639
$A_e - A_o$	−8	−32
$B_e - B_o$	76	73
$C_e - C_o$	65	61

[a] These modes are OOO bending and OO stretching ones; it can be confirmed that they do not present large shifts with respect to the deuterated ones, but due to the difficulty in the assignment we preferred to not distinguish them.

decomposition into 2 HOO molecules by 16.5 kcal/mol, in fact, it is much more stable than HOOO against decomposition into HO and OO. Thus, the predicted stability of HOOOOH indicates that in can be a sink for HOO molecules. At low temperatures, HOOOOH will be slightly less stable, but even at 0 K it is more stable than two isolated HOO molecules by 13−14 kcal/mol.

In the case of HOOOH, the molecule is stable against decomposition into OOH and OH by 33 kcal/mol, thus HOOOH is another molecule that is likely to be present in the atmosphere. It is important to note that HOOH is stable against decomposition into two OH groups by almost 50 kcal/mol. Thus, the addition of an oxygen atom to HOOH does not cause an important change in stability.

Finally, we have HOOO, which is the most important molecule in atmospheric chemistry among the polyoxides investigated in this work. The values determined by us indicate that at 298 K it is more stable than OO + OH by 3.4 kcal/mol, although we must consider that the temperatures in the atmosphere will be lower. For example, at 0 K the stability decreases to 2.2 kcal/mol. This will change the amount of HOOO present in the atmosphere because its abundance is strongly dependent on the binding energy,[3] although it is important to note that Aloisio and Francisco[27] suggested that HOOO can be stabilized by water in the atmosphere by formation of a complex, which is 6.5 kcal/mol lower in energy than isolated HOOO and H_2O.

5. Conclusions

This is the first systematic investigation of a polyoxide series of molecules, HOOH, HOOOH, HOOOOH, and HOOO, at a high level of approach, namely the CCSD(T) methodology, and very large correlation consistent basis sets. For **HOOH**, the structural parameters obtained present significant deviations from experiment, and thus, in agreement with previous works, we suggest that a revision of the experimental structure is urgently needed.[93] In the case of **HOOOH,** the rotational constants determined are in reasonable agreement with experiment. For the vibrational spectra, the theoretical results are very close to the experimental values, although the comparison could be performed only in semiquantitative terms because the experimental spectra was determined in Ar matrix, and thus, a shift from the gas phase is expected. The OH stretching modes, the symmetric OO stretch, and the antisymmetric torsional rotation resulted to be the most problematic. For the OH stretch, and the torsional mode the differences can be explained by the matrix effect; however, for the symmetric OO stretch this is not the case. The differences were attributed to a problem of methodology. Finally, we propose a value of −21.50 ± 0.5 kcal/mol for $\Delta H^{o}_{f,298}$(HOOOH). For the species **HOOOOH**, our suggestion for $\Delta H^{o}_{f,298}$(HOOOOH) is −10.61 ± 0.5 kcal/mol. We have also determined the fundamental vibrational frequencies of HOOOOH and DOOOOD, which are expected to be an invaluable guide to experimentalists in making its IR assignment. The vibrational spectrum of HOOOOH indicated that some overlapping bands with those of HOOOH can make its characterization more difficult. Also, we recommend the following rotational constants, $A_0 = 20056$ MHz, $B_0 = 5803$ MHz and $C_0 = 5032$ MHz. For the structural parameters, our best results recommended are those obtained at the CCSD(T)/cc-pVQZ level of theory. Finally, for **HOOO,** we first point out that in the last years the discrepancies between experiment and theory for $\Delta H^{o}_{f,298}$(HOOO) have been significantly reduced. In our previous work, we explained that the first experimental value determined by Speranza,[2] −1 ± 5 kcal/mol had some problems in the interpretation of the results, and a revision was recommended. This proposal has been confirmed by the new experimental lower limit suggested by Derro et al.,[6] $\Delta H^{o}_{f,298}$(HOOO) > 2.51 kcal/mol. Employing the ZPE of the deuterated isomers, we have corrected the experimental limit setting $\Delta H^{o}_{f,298}$(HOOO) > 3.07 kcal/mol. Among the theoretical determinations, our first recommendation was $\Delta H^{o}_{f,298}$(HOOO) = 7.1 ± 2 kcal/mol. Quite recently, we have realized about the importance of higher order excitations in XOO radicals, X = OH, F, Cl, Br.[14,70,71] For that reason, we have employed isodesmic reactions and the CCSD(T) methodology and confirmed our hypothesis. Our new revised value is 5.5 ± 1 kcal/mol. We would like to note that higher order correlation effects are tremendously important for HOOO that, even for some of the isodesmic reactions employed, we have observed that they do not cancel. Therefore, the differences between experiment and theory have been reduced to just 2.5 kcal/mol, a tremendous improvement if we consider that in 2002 they were close to 10 kcal/mol.[13] We expect that further theoretical and experimental investigations will reduce this discrepancy to less than 1 kcal/mol, although it is important to highlight the important role that theory has played to improve the older experimental accepted value.[2]

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