Quantum Study of Peroxidic Bonds and Torsional Levels for ROOR′ Molecules (R, R′ = H, F, Cl, NO, CN)†

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We present here a systematic study by quantum mechanical methods of a series of molecules (HOOF, HOOCl, HOONO, HOOCN, FOOF, ClOOF, ClOOCl, and FOONO), corresponding to substitutions of one or both hydrogens in hydrogen peroxide. The emphasis is on the structural and energetic properties and on the features of the internal modes, in particular, the torsion around the O−O bond, which leads to the chirality changing isomerization. The cis and trans barriers appear to vary remarkably upon substitution by halogen groups. They are compared with experimental and theoretical information, when available, and analyzed by reference to a previous systematic analysis of the effects of alkyl substitutions. Torsional levels were calculated, and their distribution as a function of temperature was determined. This information is of interest for statistical approaches to equilibrium properties and to rates of processes where torsional anharmonicity is relevant, as required for recent atmospheric modeling studies and also for prototypical chiral separation experiments, in view of a possible dynamic mechanism for chirality exchange by molecular collisions. Dipole moments are also presented.

1. Introduction

Peroxides are interesting because of the peculiar nature of the O−O bond, which has profound relevance in wide areas of research, such as biological and combustion chemistry. We focus in this work on the effects of halogen substitution, and further motivation comes from the role of halogen peroxides in atmospheric chemistry (see ref 1 and references therein). Features of the torsional levels around the O−O bond will be presented: this is a very important case where anharmonicity has to be explicitly taken into account in statistical mechanics of equilibrium or rate processes (see refs 2 and 3 and references therein). Torsion also provides the simplest example of chirality changing processes (see ref 4 for a discussion of possible collisional mechanisms for such processes).

In recent decades, several investigations have been dedicated toward the understanding and control of the reactions involved in phenomena of strong environmental impact, such as, for example, acid rain and the decrease of the ozone shell.[5,6] In both processes, the participation of peroxides and of the corresponding radicals has been observed.[7] These systems are being investigated under different points of view, and several recent works have been concerned with the simplest of these molecules, H_2O_2.[8−22]

Hydrogen peroxide is well-known as the major oxidant of sulfur dioxide, producing sulfuric acid in clouds, and another group of peroxides is of great importance in the formation of acid rains,[7] the alkyl peroxides studied in ref 23. In a previous study,[22] a systematic and detailed analysis on the effect of the choice of both theory level and basis set has been carried out for hydrogen peroxide with respect to the determination of equilibrium geometry, dipole moment, and cis and trans barriers. Our results have shown that the use of a DFT method with B3LYP parametrization and a sufficiently large basis set produces results in agreement both with CCSD(T)/aug-cc-pVTZ computations and with experimental data. On the basis of these results, it has been possible to build a potential energy surface profile as a function of the dihedral angle for substitutions of hydrogens in H_2O_2 and in particular for the alkyl derivatives,[23] also of interest for applications in atmospheric science.[1]

The simplest examples in this series are methyl hydroperoxide (CH_3OOH) and ethyl hydroperoxide (C_2H_5OOH). For both compounds, the quantum mechanical studies involving them and other alkyl peroxides have been reported in ref 23. The effect of the substitution of one of the hydrogens in H_2O_2 by larger alkyl groups, such as, for example, *t*-butyl, or of double substitution were also reported in the same paper. For the monosubstituted alkyl peroxides, the torsional barriers (cis and trans) are lower than for hydrogen peroxide. Besides, for double substitution, the effect of the dimension of the groups is to make the cis barriers practically double that of monosubstitution and leads to an increase in the O−O bond lengths. Regarding the trans barriers, crucial for the torsional modes, a striking result was found that they are apparently small or negligible. For a previous discussion, see ref 24.

In this paper, we are interested in the study of these effects, with references to the substitution of the hydrogen of HOOH by halogens and in the comparison of these results with those obtained for alkyl groups. Substitution by NO and CN was also briefly considered to obtain further insight.

Additionally, in ref 23, some divergences between properties such as dihedral angles and dipole moments as obtained by experimental techniques and by theoretical methods have been discussed and clarified. Specifically, regarding the dipole moment of H_2O_2, the consideration of both energy and wavefunctions of torsional levels as well as of their temperature distributions leads to an excellent agreement between our calculated value, 1.58 D,[23] and the experimental value, 1.57 D.[8] The same type of calculations can be extended to other systems, and corresponding results are presented in this paper for FOOF,

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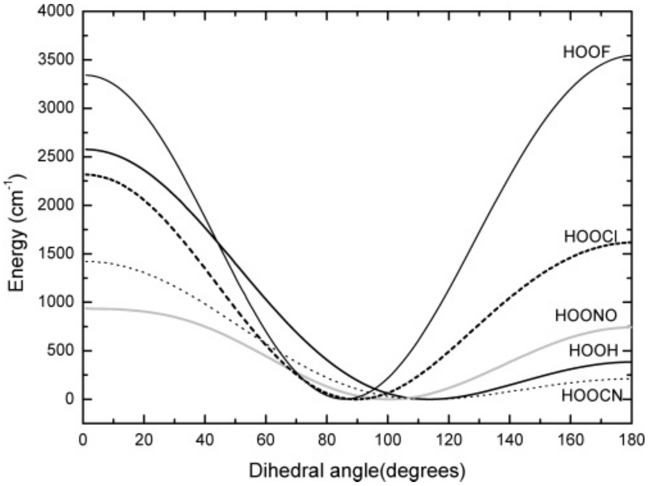

Figure 1. Profiles of the torsional potentials for the ROOR′ peroxides, where R = H and R′ = H, F, Cl, CN, and NO, as a function of dihedral angles (φ) for the optimized DFT calculations with B3LYP/6-311++G-(3df,3pd) parametrization and basis set. For HOOH, shown for comparison, see also ref 22.

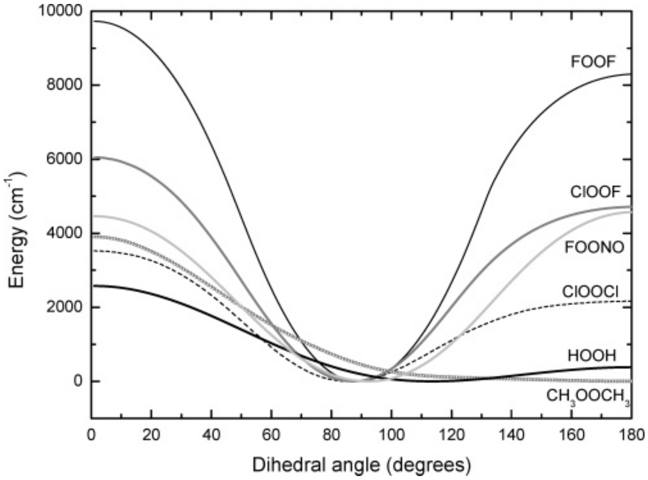

Figure 2. Profiles of the torsional potentials for the ROOR′ peroxides, where R and R′ = H, F, Cl, and CH$_3$, as a function of dihedral angles (φ) for the optimized DFT calculations with B3LYP/6-311++G(3df,-3pd) parametrization and basis set. For CH$_3$OOCH$_3$, shown for comparison with the case of double alkyl substitution, see also ref 23.

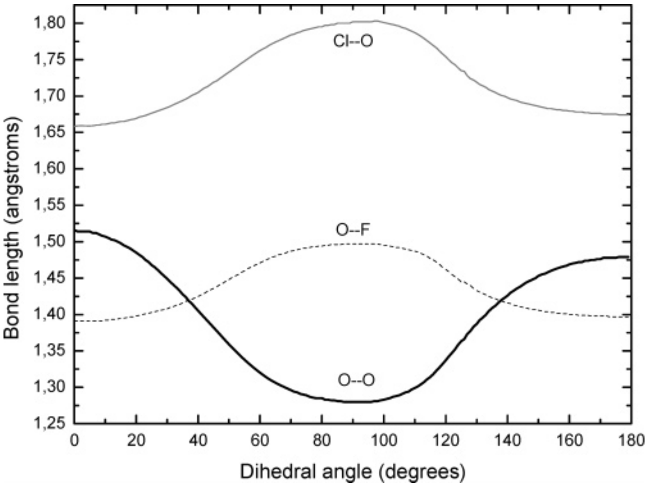

Figure 3. Bond lengths for ClOOF as a function of dihedral angles by the DFT method with B3LYP/6-311++G(3df,3pd) parametrization and basis set.

a system for which comparison with experimental data is possible.

The work here is organized as follows: in section 2., we report the quantum mechanical methods of calculations and other methodological aspects, the issues being the choice of basis sets and theory levels that reproduce known information on features such as equilibrium geometry and cis and trans torsional barriers around the O−O bond. Section 3. reports an estimate of torsional levels and their distribution as a function of temperature of each system, in view of experimental and theoretical studies of the dynamics of chirality changing transitions induced by collision and of statistical analysis of torsional levels. Section 4. briefly discusses dipole moments, while section 5. contains conclusions and further remarks, while additional data are reported as Supporting Information.

2. Energetic and Geometrical Aspects

2.1. Quantum Chemical Calculations. The calculations of the structural aspects and electronic energy were carried out using the Gaussian 03 program package.[25] For the choice of appropriate basis set and level of theory, we have already studied[22] hydrogen peroxide as a prototypical molecule and performed several calculations using progressively larger basis sets employing both the Pople-type basis sets and the Dunning correlation consistent basis sets. The MP2, DFT, and CCSD-(T) levels of theory were compared, and the appropriate balance of quality and computational cost, between each level of theory and basis set, was used as criterion of the choice. This methodology has been used for other systems, such as the alkyl peroxides, which have been presented elsewhere.[23]

The systems investigated in this study are the derivatives of hydrogen peroxide (HOOH), where one or both hydrogen atoms in the molecule are substituted by one or two halogen atoms (HOOF, HOOCl, ClOOF, FOOF, and ClOOCl) or NO and CN. See ref 22, where we presented in detail the effects of the choice of the theory level and of the basis set employed for the determination of the structure and of the energetic properties of hydrogen peroxide. As already remarked, that study provided the starting point for the choice of the methodology utilized subsequently. A primary goal of this article consists of the study of the energy profile of the systems as a function of the variation of the dihedral angle φ around the O−O bond (Figures 1 and 2), calculated by optimizing other degrees of freedom at any φ value. In this study, a comparison is made among the different profiles obtained for HOOH and its derivatives, including the compounds having as substituents not only the halogen atoms but also alkyl groups (see ref 23). We calculated these profiles using DFT with B3LYP parametrization and the 6-311++G (3df, 3pd) previously chosen basis set, and in this way, we can obtain a consistent systematic investigation of the energetic properties as a function of the substituent groups in the peroxidic series, with comparable computational tools that yield a coherent picture of the substituent effects. Detailed analysis is also devoted to the behavior of bond lengths and bond angles when the dihedral angle spans the 0−180° range, as illustrated in Figure 3 for the bond lengths of the ClOOF molecule.

Once that the DFT method has provided the general dependence of energetic properties of the compounds as a function of the dihedral angle, we focused our attention on three points for each profile, which are specifically of crucial interest: the minima, which correspond to the equilibrium geometries, and the structures having dihedral angles at 0 and 180°, which correspond, respectively, to the cis and trans configurations, representing the barriers to stereomutation. For these three points for each system, detailed calculations were made using coupled

TABLE 1: Geometries, Dipole Moments, cis and trans Barriers, and Energies for ROOR′ Calculated by B3LYP/6-311++G(3df,3pd) Method

	geometry[a]								
	r(O−O)	r(R−O)	r(O−R′)	$R\hat{O}O$	$O\hat{O}R'$	φ(ROOR′)	dipole (D)	barrier (cm^{-1})	energy (Hartree)
HOOH[b]									
eq	1.446	0.966	0.966	100.9	100.9	112.4	1.776		−151.6131930
cis	1.457	0.966	0.966	105.2	105.2	0	3.105	2575.53	−151.6014580
trans	1.457	0.965	0.965	99.2	99.2	180	0	386.25	−151.6114331
HOOF									
eq	1.359	0.973	1.467	103.8	106.2	84.9	2.275		−250.7803721
cis	1.428	0.970	1.423	102.7	105.5	0	1.439	3338.65	−250.7651601
trans	1.441	0.971	1.400	98.7	101.7	180	2.177	3542.21	−250.7642326
HOOCl									
eq	1.410	0.970	1.730	102.4	110.1	88.8	1.729		−611.1825081
cis	1.454	0.969	1.692	104.3	110.9	0	1.908	2317.83	−611.1719473
trans	1.467	0.970	1.676	98.2	106.0	180	1.208	1617.77	−611.1751317
HOONO									
eq	1.417	0.968	1.479	102.1	106.9	99.6	1.770		−280.9436298
cis	1.426	0.974	1.432	102.8	108.2	0	1.690	935.40	−280.9393678
trans	1.436	0.967	1.446	99.0	104.9	180	1.845	744.13	−280.9402393
HOOCN									
eq	1.475	0.970	1.290	99.6	108.6	111.9	3.630		−243.8517734
cis	1.481	0.972	1.283	103.6	111.5	0	1.915	1420.90	−243.8452993
trans	1.483	0.970	1.284	97.9	107.9	180	4.188	213.50	−243.8508063
FOOF[b]									
eq	1.222	1.524	1.524	109.2	109.2	90	1.371		−349.9503046
cis	1.509	1.384	1.384	108.2	108.2	0	0.211	9728.50	−349.9059783
trans	1.474	1.394	1.394	99.5	99.5	180	0	8303.99	−349.9124734
ClOOCl[b]									
eq	1.362	1.748	1.748	111.5	111.5	84.8	0.53		−1070.7516783
cis	1.573	1.646	1.646	115.1	115.1	0	1.48	3523.66	−1070.7356233
trans	1.506	1.672	1.672	104.5	104.5	180	0	2166.81	−1070.7418056
ClOOF									
eq	1.281	1.802	1.497	112.9	108.0	86.1	1.148		−710.3496955
cis	1.516	1.660	1.391	114.1	109.7	0	0.886	6037.46	−710.3221868
trans	1.481	1.674	1.397	103.1	101.0	180	1.184	4718.40	−710.3281969
FOONO									
eq	1.308	1.494	1.662	106.9	107.0	88.6	2.561		−380.1089509
cis	1.365	1.471	1.672	109.7	129.1	0	2.194	5344.86	−380.0845979
trans	1.429	1.406	1.524	102.0	104.4	180	1.214	4461.57	−380.0886225

[a] Bond lengths in angstroms and angles in degrees. [b] For comparison, experimental data of HOOH, FOOF, and ClOOCl systems are available in refs 44, 39, and 41, respectively.

cluster theory, including simple and double excitations including triple excitations non-iteratively (CCSD(T)), with aug-cc-pVDZ basis set. Tables 1 and 2 show results of geometries and other features for equilibrium and cis and trans configurations from both methods.

2.2. Energy Profiles along the Torsional Angles. Tables 1 and 2 demonstrate the general consistency of results from the two levels of theory. As a general trend, main (although minor) differences are that the CCSD(T) method appears to give slightly larger bond lengths and dipole moments and smaller bond angles. The dihedral equilibrium angles, a very significant parameter for these systems, are in agreement, the largest difference being 1.5° for FOONO. The discussion in this section is based only on the CCSD(T) results (Table 2). However, the discussion of energy levels in the next section will be based on profiles as a function of the torsional angles obtained by DFT, for which it was practical to compute a very fine grid.

Monosubstitution:− Figure 1 shows energy profiles along the dihedral angles for substitution of one of the hydrogens in hydrogen peroxide by F, Cl, CN, and NO. Taking the case of HOOH as a reference for comparison, the trans barriers for CN, NO, Cl, and F substitution are progressively higher in this order, while for alkyl substituents, they are consistently lower[23] but increase with the group size. For all monosubstituted systems, except HOOF, the cis barriers are lower than HOOH. For halogen groups, the cis and trans barriers are of similar height, so that the energy profile looks reasonably symmetric, and dihedral equilibrium angles are close to 90° for HOOX (where X = F and Cl) and 100° for HOONO. For CN, we have an equilibrium dihedral angle of 109.1°, perhaps fortuitously close to the value of 112.5° for HOOH (Table 2). In general, the larger the dihedral angle at equilibrium, the lower the trans barriers.

Regarding the NO substitution on peroxidic bonds, for previous work, see refs 26−33. Our interest is in the behavior with respect to torsion around the O−O bond, and the designations as cis or trans refer to the HOON dihedral angle, while the OONO dihedral angle is 180° in all our structures (trans configurations). Ref 33 gives an extensive account of the cis configurations for the OONO dihedral angle. The chosen orientation of the NO group is the one expected to show minimal influence from the O atom on the peroxide bond under focus here. The same choice was made for CN substitution.

Double substitution: regarding peroxides with double substitutions by halogens (Figure 2), both cis and trans barriers appear to increase consistently, the effect of F being larger than that of Cl, as just observed in the case of single substitution. The cis and trans barriers turn out to be of similar magnitudes in these cases. Equilibrium dihedral angles are only slightly less

TABLE 2: Geometries, Dipole Moments, cis and trans Barriers, and Energies for ROOR′ Calculated by the CCSD(T)/aug-cc-pVDZ Method

	geometry[a]								
	r(O−O)	r(R−O)	r(O−R′)	$R\hat{O}O$	$O\hat{O}R'$	φ(ROOR′)	dipole (D)	barrier (cm^{-1})	energy (Hartree)
HOOH									
eq	1.480	0.972	0.972	99.3	99.3	112.6	1.905		−151.2433406
cis	1.492	0.972	0.972	103.7	103.7	0	3.321	2608.30	−151.2314563
trans	1.495	0.971	0.971	97.9	97.9	180	0	404.14	−151.2414992
HOOF									
eq	1.387	0.978	1.501	102.1	105.0	84.8	2.430		−250.1969359
cis	1.465	0.976	1.458	100.5	103.8	0	1.514	3309.94	−250.1829766
trans	1.475	0.977	1.435	97.5	100.2	180	2.607	3063.71	−250.1815471
HOOCl									
eq	1.439	0.976	1.775	100.9	108.4	88.5	1.859		−610.2561892
cis	1.491	0.975	1.744	102.6	109.1	0	2.110	2297.77	−610.2457198
trans	1.499	0.975	1.728	97.3	103.9	180	1.319	1611.25	−610.2488478
HOONO									
eq	1.450	0.974	1.497	100.6	104.8	98.4	1.938		−280.2634350
cis	1.467	0.980	1.455	101.3	106.0	0	2.107	1227.26	−280.2578432
trans	1.476	0.974	1.467	97.8	102.5	180	1.731	882.73	−280.2634350
HOOCN									
eq	1.504	0.977	1.319	98.5	106.1	109.1	4.020		−243.2353352
cis	1.517	0.980	1.311	102.3	108.9	0	2.166	1544.79	−243.2282966
trans	1.515	0.976	1.313	97.02	105.1	180	4.692	309.00	−243.2339273
FOOF									
eq	1.209	1.628	1.628	109.2	109.2	88.7	1.774		−349.1568952
cis	1.562	1.416	1.416	106.8	106.8	0	0.570	9867.97	−349.1119334
trans	1.507	1.430	1.430	97.9	97.9	180	0	8332.38	−349.1189301
ClOOCl									
eq	1.384	1.794	1.794	109.6	109.6	84.2	0.905		−1069.2700103
trans	1.530	1.726	1.726	102.4	102.4	180	0	2289.67	−1069.2595778
ClOOF									
eq	1.277	1.877	1.567	111.9	107.3	86.3	1.772		−709.2111605
cis	1.562	1.711	1.424	112.4	108.8	0	1.029	6086.51	−709.1834283
trans	1.511	1.728	1.433	101.1	99.3	180	1.598	4618.38	−709.1901176
FOONO									
eq	1.335	1.533	1.668	105.7	104.4	87.1	2.887		−379.2168421

[a] Bond lengths in angstroms and angles in degrees.

than 90°, while for double substitution by alkyl groups, the trans barriers appeared to vanish,[23] and the equilibrium dihedral angle moved toward 180°: see the example of CH_3OOCH_3 in Figure 2 and ref 23.

2.3. Bond Lengths and Angles. The behavior of bond lengths with substitution and with configuration can be presumed by inspection of data in Tables 1 and 2. The constancy of the OH bond length (∼0.97 Å) for all systems is remarkable. Most interesting is the peroxidic bond length, which had been found to be practically invariant with alkyl substitutions in H_2O_2 (∼1.45−1.46 Å).[23] For CN substitution, it is larger, 1.50 Å. However, the O−O length shortens to 1.42, 1.41, and 1.36 Å for monosubstitution by NO, Cl, and F at the equilibrium configuration, for which still greater is the shrink for double substitution (1.36 Å for ClOOCl, 1.34 Å for FOONO, 1.28 Å for FOOCl, and 1.22 Å for FOOF: the latter value is similar to that in O_2). There appears to be a qualitative correlation between the energy profile and the lengths of the O−O bond and those of the OX bond, where X is Cl or F, as a function of the dihedral angle (Tables 1 and 2). Figure 3 for the case of ClOOF details an example of the shortening at equilibrium of the O−O bond, accompanied by lengthening of the O−F and O−Cl bonds.

As far as bond angles are concerned, in the case of alkyl substitution,[23] the effect on the $O\hat{O}H$ angle of hydrogen peroxide has been found to be negligible, and for halogens, CN and NO substitution (Tables 1 and 2) is also small, fluctuations being of the order of ±3°. For monosubstitution, the $O\hat{O}R$ angles increase with respect to the $O\hat{O}H$ in hydrogen peroxide by 5−6° in most cases, similar to what is observed in the alkyl cases. This increase is somewhat smaller for substitution by F of one of the hydrogens.

The $O\hat{O}N$ angles show values around 104.5° both in HOONO and in FOONO. Regarding the angle $O\hat{O}F$, that in the FOONO case is practically the same as in HOOF and increases by 2 and 3° in the equilibrium configurations obtained for substitution of H by Cl and F, respectively. Likewise, the $O\hat{O}Cl$ angle increases slightly (1 or 2°) by insertion of a second electronegative atom.

With reference to structural features for HOOCl, our results are in agreement with previous work (see ref 34 and particularly ref 35). This is similar to F_2O_2, for which merits of various basis sets and methods have been extensively studied[36−38] (see also ref 39 for experimental information). For ClOOCl, the literature is also ample, and Quack and Willeke[40] report a state-of-the-art computational study with detailed reference to both previous theory and experimental data. With respect to geometries of equilibrium and cis and trans configurations, our results agree with theirs. They also discuss torsional dynamics, with particular reference to parity violation in tunneling switching stereomutation. Our results for cis and trans barrier heights confirm deficiencies of previous analysis of available experimental data[41] (see also ref 42). New spectra and their analysis

TABLE 3: Zero-Point Energies (cm^{-1})

molecule	accurate fitting	truncated fitting[a]
HOOF[b]	275.27	271.68
HOOCl[b]	206.87	199.48
HOONO[c]	142.99	130.80
	143.01	130.83
HOOCN[c]	94.84	93.24
	100.65	98.98
FOOF[b]	128.90	164.73
ClOOF[b]	103.33	124.05
ClOOCl[b]	94.84	84.75
FOONO[b]	70.37	105.59

[a] See ref 44. [b] For these systems, $n = 0$ levels (degenerate for $\tau = 1$, 2, 3, and 4) are given. [c] For these systems, $n = 0$ levels are given, upper values for degenerate $\tau = 1$ and 2 symmetries and lower values for degenerate $\tau = 3$ and 4 symmetries.

are needed (see ref 43 in addition to refs 1−7, where also further discussion of the relevance of these molecules in atmospheric science is reported).

3. Torsional Dynamics

The floppy nature of these molecules poses the interesting problem of the dynamics around the very anharmonic mode associated with torsion around the O−O bond.

In a previous paper[22] on H_2O_2, the observation that the torsional dynamics in H_2O_2 is best described in local orthogonal coordinates was crucial, which amounts to interpreting the OH groups as rigid rotors executing a torsion motion around a (Jacobi) vector joining their centers of mass. The corresponding dihedral angle is thus the variable, while the other five degrees of freedom are frozen at the equilibrium configuration. Formulas relating geometrical and local vector parameters are given in ref 22. In both cases, one has to consider the Hamiltonian as involving three vectors, which for the local vector parametrization, in view of their orthogonality, leads to very simple expressions, rigorously eliminating couplings. As discussed in ref 23, this approach is not easily extendable for the case of substituents. Accordingly, energy levels were estimated using the torsional potential profile as a function of the dihedral angle. The Supporting Information lists calculated data for these profiles, for a 10° spacing; a finer grid is available on request. The simplified procedure adopted before,[23] namely, an expansion of the torsional potential as

$$V(\varphi) = \sum_k C_k \cos k\varphi \tag{1}$$

truncated to only four terms according to a recipe given in ref 44, which used as input cis and trans barrier heights, and the equilibrium dihedral angle is now compared to a more accurate expansion where moments C_k were obtained by a Newton−Raphson fitting including at least six terms. See the Supporting Information for a list of expansion coefficients. As before,[23] basis sets in terms of sine and cosine functions were used, giving rise to secular equations, where the matrix elements are analytical integrals over trigonometric functions. Table 3 compares zero-point energies from the two approaches, exhibiting the level of accuracy that can be obtained by truncation to only four terms, when only equilibrium and cis and trans information is available.

Note that in view of the symmetry of the torsional potential by reflection on the two (cis and trans) planar configurations ($\varphi = 0$ and π), the problem block diagonalizes in four symmetry classes, denoted by the quantum label $\tau = 1$, 2, 3, and 4. Levels within each symmetry classes are denoted by the quantum number $n = 0, 1, 2, ...$ The energy separation between levels with same n and different τ is associated to tunneling through cis and trans barriers. Specifically, splitting between $\tau = 1$ and 2 and between 3 and 4 is for tunneling through the cis barriers, which are practically degenerate for lower levels. The trans tunneling is responsible for the separation between levels with $\tau = 1$ and 3 or with 2 and 4.

TABLE 4: Population of Torsional Levels at 300 K

		n								
molecule	τ	0	1	2	3	4	5	6	7	8
HOOF	1−4	92.52	6.83	0.58	0.06	0.01	0.00	0.00	0.00	0.00
HOOCl	1−4	84.55	12.60	2.20	0.47	0.13	0.04	0.00	0.00	0.00
HOONO	1	17.35	4.81	1.70	0.81	0.41	0.22	0.08	0.02	0.00
	2	17.35	4.81	1.70	0.80	0.35	0.14	0.04	0.01	0.00
	3	17.34	4.78	1.57	0.61	0.31	0.14	0.04	0.01	0.00
	4	17.34	4.78	1.57	0.58	0.22	0.08	0.02	0.00	0.00
HOOCN	1, 2	29.60	15.21	6.68	2.15	0.61	0.17	0.05	0.02	0.01
	3, 4	29.20	13.21	5.28	1.65	0.47	0.14	0.04	0.00	0.00
FOOF	1−4	81.63	14.99	2.76	0.51	0.09	0.02	0.00	0.00	0.00
ClOOF	1−4	75.32	18.40	4.63	1.20	0.32	0.09	0.03	0.01	0.00
ClOOCl	1−4	62.01	23.00	8.83	3.52	1.46	0.63	0.28	0.13	0.06
FOONO	1−4	64.52	22.69	8.10	2.94	1.09	0.41	0.16	0.06	0.02

In ref 23, we showed, for the case of HOOH, a comparison between the obtained levels with both approaches and those observed experimentally. For FOOF, the corresponding sequences of obtained levels for the four symmetries are represented graphically in Figure 2 of the Supporting Information. The corresponding wavefunctions were also obtained; some numerical information is indicated in the captions, while more complete data are made available as Supporting Information, also for the other systems.

Once the energy $E_{n\tau}$ of levels has been obtained, another interesting property of these molecules can be easily calculated, namely, their relative population ($N_{n\tau}/N$) as a function of temperature T, using the Boltzmann distribution formula

$$\frac{N_{n\tau}}{N} = \frac{\exp[-E_{n\tau}/k_B T]}{\sum_{n\tau} \exp[-E_{n\tau}/k_B T]} \tag{2}$$

where k_B is Boltzmann's constant. Results are exhibited in Table 4 for the distributions at room temperature for all systems. An extensive recent study of a set of approaches to the level distributions, also for isotopic substitutions in H_2O_2, is to be consulted for the general issue of the statistical thermodynamics of bond torsional modes.[2]

4. Dipole Moments

As we have seen in a previous paper on H_2O_2,[22] there have been in the past controversies regarding the important feature of the equilibrium dihedral angle, and correspondingly, uncertainties were also reported in a property such as the dipole moment, for which there are conflicting experimental values in the literature, obtained with different methodologies. To explain the large discrepancy that has been observed between experimental and calculated dipole moments, we have considered the correlation between the dipole moment and the dihedral angle. Such a relationship explains the discrepancies. In fact, in the calculations, the molecule is considered to be frozen in the vacuum, while in the measurements, it is in the gaseous state in an ensemble of torsional levels, and the corresponding distribution of dihedral angles must be taken into account (for a detailed discussion, see ref 22). This would lead to averaged distributions more probably toward the trans rather than the cis

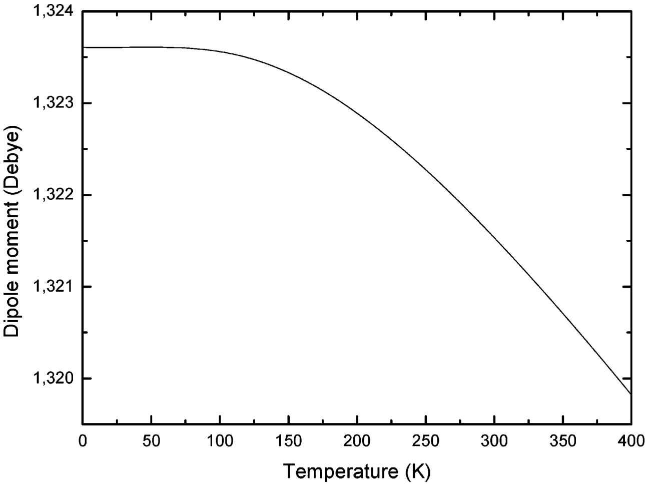

Figure 4. Dipole moment of FOOF as a function of temperature (K).

configuration, so that dynamically one may observe an effective larger dihedral angle and thus a dipole moment, lower than that corresponding to the calculated equilibrium structure. Using the fact that, as discussed previously[22,23] and in section 3., we can compute the wavefunctions for the torsional states populated as a function of temperature, it is possible to compute also the effective dipole moment by averaging the calculated dipole moment dependence from the torsional angle over the square of the wavefunction and over the torsional level distribution. In the case of H_2O_2, this led to reconciling theoretical and experimental results

Tables 1 and 2 list dipole moments calculated with specific geometric configurations. As stressed in ref 37 for FOOF, for which experimental comparison is possible, such a comparison is a sensitive antenna for the quality of theoretical descriptions of this molecule. The results on torsional levels, and the temperature dependence of their distribution for FOOF, served for the calculation of the effective dipole moment as a function of temperature following the same steps outlined previously for H_2O_2[22] (Figure 4). Such a dependence is weak in this case and does not improve the agreement with experiment: in fact, our DFT value for the room-temperature dipole moments, accounting for the relative population of the torsional levels, is 1.32 D, to be compared with the accepted experimental value of 1.44 D.[47] Note, however, that probably the most accurate CCSD(T) values are consistently higher (Table 2). Similar results for the other cases are available, but for them, there appear to be no experimental data for comparison.

5. Conclusion

A previous article[23] was concerned with the extension of the study presented in ref 22 on quantum chemical exploration of the potential energy surface of hydrogen peroxide to the case of alkyl substitutions. Torsional barriers around the O−O bond have been shown to vary enormously by substitution of alkyl groups, and this paper is a report of the systematic investigation of the effects of substitution by halogen atoms and CN and NO groups. Results are compared with limited experimental and computational information, special attention having been devoted to the energy and dipole moment profile upon variation of the dihedral angle. The steric hindrance of the substituent group has been seen to be a determining factor for energetic and geometric effects.[23] In the case of halogens, the observed systematics should be discussed by paying future attention to more specific features such as electronegativity differences between atoms or groups involved in the bonds. Further work is also being reported elsewhere on the torsional modes of the S−S bond by substituent groups of the hydrogens in H_2S_2, also of relevance for stereomutation issues.[48]

Regarding intermolecular interactions, of specific importance for collisional chirality exchange,[4] a study has been completed on the H_2O_2 rare gas systems,[49] for which information should also come from molecular beam experiments in our laboratory. This will extend to these systems the joint experimental and theoretical approach already tackled for interactions of H_2O[50] and H_2S[51] with the rare gases.

Attention has also been dedicated in this work to a study of energy levels in the very anharmonic torsional potentials, obtaining their distributions as a function of temperature. This has been shown to be of relevance for the comparison of calculated and experimental quantities such as dipole moments but can be straightforwardly extended to prospective estimates of torsional partition functions.[52]

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Supporting Information Available: Calculation procedures and details of results for the study of the torsional mode around the O−O bonds of the title compounds. Tables of DFT data, torsional profiles, and torsional energy levels. This material is available free of charge via the Internet at http://pubs.acs.org.

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