Intramolecular hydrogen-bonding effects on O-H stretch overtone excitation for fluorinated hydroperoxides

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Abstract: Applying computational methods for predicting gas-phase O-H stretch overtone spectra to the series of fluorinated hydroperoxides CF_3OOH , CHF_2OOH , and CH_2FOOH reveals how intramolecular hydrogen bonding changes their overtone photochemistry, relative to their un-fluorinated analog CH_3OOH . Intramolecular hydrogen bonding between fluorine and the hydroxyl hydrogen atom decreases O-H stretch frequencies and raises the barrier for torsion about the O-O bond. Whereas O-O torsion accompanies O-H stretch overtone excitation for CH_3OOH , this is not the case for the fluorinated analogs that have intramolecular hydrogen bonding. The comparison highlights the molecular features that contribute to the feasibility of atmospheric overtone-induced O-O bond dissociation for CH_3OOH , but not for its fluorinated analogs.

Keywords: Hydroperoxide, hydrofluorocarbon, vibrational overtone

1. Introduction

Atmospheric oxidation of hydrocarbons in areas of low NO_x form organic hydroperoxides [1-3] that contribute to secondary aerosol formation [4-6] and sustain OH radical concentrations above forests and tropical rainforests [7-9]. Methyl hydroperoxide has been observed in rural and urban areas [10,11]. Photolysis breaks the weak O-O bond, generating OH radicals. While UV and near-UV wavelengths are mainly responsible for photolysis [12,13], visible and near-IR wavelengths can begin to have an impact at dawn and at dusk [14,15]. For hydroperoxides (ROOH), visible light excites OH stretch overtones, and imparts enough energy to cleave the O-O bond [16], as observed in the laboratory [16-18]. Here we apply methodology developed to predict ROOH overtone photochemistry [18-20] to the fluorinated relatives of methyl hydroperoxide (CH₂FOOH, CHF₂OOH, and CF₃OOH), to determine the effect of fluorination on their O-H overtone absorption spectra in the visible wavelength region and to address potential implications for atmospheric chemistry.

The series of fluorinated methyl hydroperoxides represent a larger class of secondary pollutants that form from anthropogenic emissions of hydrofluorocarbon (HFC) and other fluorinated organics. Fluorinated hydroperoxides have atmospheric lifetimes on the order of a day [21], and serve as temporary reservoirs for RO and OH radicals, via reaction with OH or photolysis. Several reviews illustrate the general mechanism of hydroperoxide formation in atmospheric HFC oxidation [21-23]. H-atom abstraction generates fluorinated alkyl radicals (R), which react with diatomic oxygen to generate peroxy (RO₂) radicals. Like their non-fluorinated RO₂ counterparts, the fluorinated peroxy radicals react with hydroperoxyl (HO₂) radicals in areas of low NO_x, to form fluorinated organic hydroperoxides. Unlike their non-fluorinated counterparts, however, fluorinated organic peroxides are not expected to occur as readily as their non-fluorinated counterparts, since fluorinated peroxy radicals have a competing pathway upon reaction with HO₂ that instead generates carbonyl products [21]. For example, rather than form CH₂FOOH, CH₂FO₂ + HO₂ favors the carbonyl product HC(O)F (84%) [24]. Similarly, Nielsen and co-workers [25] did not observe any hydroperoxides from the reaction CHF₂O₂ + HO₂. On the other hand, CF₃O₂ + HO₂ forms CF₃OOH [26,27], and since the main reaction of CF₃ radicals is with O₂ to form CF₃O₂ [28], CF₃OOH could result from any sources that generate CF₃. These include hydrogen abstraction from CF₃H (HFC-23), photo-degradation reactions [26] of HFC-134a, HFC-125, HFC-143a, HCFC-123, and HCFC-124, and decomposition of other fluorinated species, such as fluorinated anesthetics [22].

Calculations in this work illustrate how intramolecular hydrogen bonding between the hydroxyl hydrogen and fluorine atoms causes the fluorinated organic hydroperoxides to behave differently from their non-halogenated counterparts. While torsional motion about the O-O bond contributes to the possibility of OH formation from CH₃OOH at wavelengths as long as 750 nm [18], the intramolecular hydrogen bonding in the fluorinated hydroperoxides prohibits such long-wavelength photolysis pathways.

2. Computational

Gaussian09 [29] calculations are at the B3LYP/aug-cc-pVTZ level. For each optimized conformer, energies and dipole moments are obtained for O-H bond stretches / compressions ± 0.3 Å from the potential minimum, in 0.05 Å steps. The energies for each O-H bond stretch/compression yield frequencies (ω) and anharmonicities (ωx) via a non-linear least squares fits of the Morse parameters as in previous work [20]. While our method has achieved calculated overtone frequencies in agreement with experiment for ethyl hydroperoxide [20], it has also been known to generate anharmonicities that are high compared to experimental values [30]. Transition energies $\tilde{\nu}_{e \leftarrow g}$ are those for a Morse oscillator with the parameters ω and ωx from the ground (g , here $v'' = 0$) to excited vibrational state (e , here $v' = 3-6$). Cross sections (σ) come from the standard expression [31], here given in units of $\text{cm}^2 \text{ molecule}^{-1}$,

$$\sigma = \frac{f e^2}{4 m_e c^2 \epsilon_0} \quad (1)$$

where f is the unitless oscillator strength [31] for a transition

$$f_{e \leftarrow g} = 4.70165 \times 10^7 [\text{cm D}^{-2}] \tilde{\nu}_{e \leftarrow g} |\mu_{e \leftarrow g}|^2 \quad (2)$$

and $|\mu_{e \leftarrow g}|^2$ is the sum of squares of transition moments for the x-, y-, and z-components of the dipole moment. Each transition moment for the a th ($a = x, y, z$) axis is evaluated as

$$\mu_{a, e \leftarrow g} = \sum_{i=1}^6 \int_{-\infty}^{\infty} \psi_e(q) \left| q^i \frac{1}{i!} \left(\frac{\partial^i \mu_a}{\partial q} \right)_{q=0} \right| \psi_g(q) dq \quad (3)$$

using Morse wavefunctions ψ as a function of O-H bond displacement from the potential minimum (q) and derivatives from seven-term polynomial fits to the a th component of the dipole moment.

Since torsional motion about the O-O bond can accompany O-H stretch overtone excitation in hydroperoxides [17-20], we evaluate torsional potentials. Potentials are based on Gaussian09 calculations at torsional angles (C-O-O-H dihedral) from $\chi = 0^\circ$ to 360° , in 10° increments. At each torsional angle χ , we obtain energies, frequencies, and dipole components, for the optimized geometry (holding the torsional angle fixed) at six compressed, and six extended O-H bond lengths in 0.05 Å steps. The torsional potentials take into account electronic and zero-point energies, scaled by a factor of 0.9674, for all vibrations except the C-O-O-H torsion and O-H stretch. The O-H stretch contribution at each vibrational level comes from Morse energies incorporating the O-H frequencies and anharmonicities determined at each torsional angle. Potentials are fit to a Fourier series consisting of 11 cosine and 3 sine terms. The sine terms are necessary for describing conformer potentials that are not symmetric about $\chi=180^\circ$, where the hydroxyl H is trans to the carbon atom.

To examine the effect of torsion on O-H stretch overtone excitation, we determine transition energies and intensities for exciting O-H stretch overtones and O-O torsional motion for a subset of conformers. We apply existing tools [20] that are suitable for addressing the conformers that have symmetric torsional potentials. Torsional energies and wave functions at each vibrational level come from solving the Schrödinger equation using a 20-term basis set of sines and cosines. We determine the kinetic energy operator identically to previous work [20], with parameters that depend on geometries (average O-H bond length and equilibrium C-O-O-H torsional angle) in the ground and vibrationally excited states as described for HOOH [32]. Numerical methods are used to evaluate the integrals necessary for transition intensities, as shown for the $\hat{\mu}$ th dipole (μ) derivative of the a th component,

$$\left\langle v' n' \left| \frac{1}{i!} q^i \left(\frac{d^i \mu_a}{dq^i} \right)_{q=0} \right| v'' n'' \right\rangle \quad (4)$$

where n designates torsional quantum number. Components in each integral that are independent of the torsional wave functions are evaluated at 10° increments, from $\chi = 0^\circ$ to 360° , and fit to a Fourier series in χ with 10 cosine terms, so that the integration in χ is for the product of three Fourier series. For spectral simulations, we consider the transitions involving the first eight torsional levels within each vibrational level, weight the resulting intensities by the Boltzmann population of the initial state at 298 K, and convolute the weighted intensities with 40 cm^{-1} wide Gaussian functions to approximate the rotational envelope.

3. Results and Discussion

3.1. Optimized conformers and barriers for torsion about the O-O bond. Optimized geometries have been determined in previous computational works [17,33,34], and findings here are similar. Following our work that distinguished contributions from different conformers in experimental overtone spectra [20], we consider anti and gauche conformers with respect to the X-C-O-O dihedral ($X = \text{F or H}$). For CH_2FOOH , the lower-energy conformer has the F atom gauche to the hydroxyl O (F-C-O-O dihedral 76°), and the higher-energy conformer places the F atom anti (F-C-O-O dihedral 176°). While the anti conformer has less steric repulsion, it is 2260 cm^{-1} higher in energy (2056 cm^{-1} in free energy at 298 K), consistent with a stabilizing effect through hydrogen bonding for the gauche conformer where the F atom is closer to the hydroxyl H (Figure 1). Two conformers for CHF_2OOH are similar enough in energy for both to be thermally populated at tropospheric temperatures. The symmetric conformer with both fluorine atoms closer to the hydroxyl group (F-C-O-O dihedrals $-58^\circ, 62^\circ$) and the H anti is 168 cm^{-1} lower in energy (170 cm^{-1} in free energy at 298 K) than the asymmetric gauche conformer (F-C-O-O dihedrals $-75^\circ, 169^\circ$), which allows only one such interaction (Figure 1).

Calculated torsional potentials for internal rotation about the O-O bond are shown in Figure 2. The potential for CH₃OOH is similar to previous work [16-18], with a maximum where the carbon is anti to the hydroxyl hydrogen ($\chi = 180^\circ$). By the same methods used in our torsional potentials for ethyl hydroperoxide [20], ours are symmetric about $\chi = 180^\circ$ only for the conformers that are symmetric through the C-O-O plane (Figure 2). The lack of symmetry upon internal rotation about the O-O bond for conformers that have different substituents (F or H) on either side of the O-O-C plane comes from the assumption that high barriers to internal rotation about the C-O bond (> 4 kcal/mol [33]) effectively prevent the fluoromethyl group from rotating, so that the hydroxyl H experiences different chemical environments on either side of $\chi = 180^\circ$. While computational work on fluorinated hydroperoxides in the literature [33] do not show this asymmetry, our barrier heights for O-O torsion appear similar to those reported [33] (Figure 2). The barrier heights are consistent with higher calculated O-O torsion frequencies (290, 238 and 262 cm⁻¹ for CH₂FOOH, CHF₂OOH and CF₃OOH respectively) than for CH₃OOH (164 cm⁻¹) [34]. Higher barrier heights for fluorinated hydroperoxides (~1.7 kcal/mol) compared to CH₃OOH (0.4 kcal/mol) are consistent with stabilization from hydrogen-bonding that effectively lowers the potential minima and increases the energy required to reach the potential maximum. Like CH₃OOH, the higher-energy anti conformer of CH₂FOOH has a lower torsional barrier (0.8 kcal/mol) and also no opportunity for hydrogen-bonding. The stabilization that lowers the potential minima is consistent with previous work that shows fluoromethyl hydroperoxides to be thermodynamically stable, compared to other halogenated hydroperoxides [34].

3.2. Effects of fluorination on O-H stretch frequencies and intensities. Calculated frequencies and anharmonicities are listed in Table 1. Fluorination has been shown to cause a red shift on the order of 10 cm⁻¹ in fundamental O-H stretch frequencies in alcohols in the gas-phase [35,36]. Experimentally, trifluoroethanol (3657 cm⁻¹ [35]) shows an 8 cm⁻¹ red shift from ethanol (3665 cm⁻¹ [35]). The calculated frequency for the O-H stretch in trifluoromethanol (3669 cm⁻¹ [37]) is 12 cm⁻¹ lower than the experimental fundamental (3681 cm⁻¹ [35]). For hydroperoxides, Wallington and co-workers [24] used the red shift for the fluorinated species CH₂FOOH, 3596 cm⁻¹ versus 3601 cm⁻¹ for CH₃OOH, to distinguish the two hydroperoxides experimentally by infrared spectroscopy. Gaussian09 shows a red shift of similar magnitude for anti-CH₂FOOH, 3752 cm⁻¹ versus 3757 cm⁻¹ for CH₃OOH. For our conformers with intramolecular attraction between the hydroxyl H and a fluorine atom, Gaussian09 predicts larger red shifts in the O-H stretch fundamental, ~ 20-30 cm⁻¹. Hydrogen bonding is expected to increase the red shift; for example, calculations show that adding a water molecule to form a hydrogen-bonded CF₃OH-H₂O complex red-shifts the O-H stretch fundamental in CF₃OH by another 344 cm⁻¹ [37]. Experimental O-H fundamental frequencies show a 470 cm⁻¹ red shift for trifluoroethanol upon complexation with amines, larger than the red shift (300 cm⁻¹) for ethanol and methanol [36]. Compared to other molecules with intramolecular hydrogen bonding, the O-H stretch red shifts observed here are at the low end of those

reported in the literature, which range from ~ 20 to over 100 cm^{-1} [38-43]. Red shifts for fluorinated [37] and hydrogen-bonded [30,37,38,40-43] species become even more pronounced at higher overtones.

In an experimental survey of O-H containing compounds, Phillips and coworkers [35] found that increasing electronegativity on adjacent substituents correlated to increasing absorption intensity for the fundamental, but a more rapid decrease in absorption cross section, relative to the fundamental, with increasing overtones. Our calculations for fluorinated hydroperoxides (equations 1-3) mirror both findings (Table 2). Table 2 shows a general trend in infrared intensities for the fundamental as determined in Gaussian09; intensities tend to increase with increasing numbers of fluorines on the methyl group. There is also a drop in relative cross section, compared to the fundamental's, as the number of fluorines on the hydroperoxide increases (Table 2). Hydrogen bonding is known to increase the relative drop in overtone intensity even further.. Sinha and co-workers [40,41] have documented more dramatic drops in overtone intensity relative to the fundamental and attributed them to intramolecular hydrogen bonding in peroxyformic and peroxyacetic acids.

3.3. Effects of fluorination on the role of torsional excitation in O-H stretch overtone spectra.

Features in experimental O-H stretch overtone spectra for hydroperoxides have been attributed to excitation involving torsion about the O-O bond. Experimental overtone spectra for hydroperoxides with lower calculated torsional barriers have more prominent absorption features associated with torsional excitation, including low-frequency hot bands [44]. With a torsional barrier of (275 cm^{-1}) , for example, tert-butyl hydroperoxide has simpler experimental OH-stretch overtone spectra than CH_3OOH or $\text{CH}_3\text{CH}_2\text{OOH}$ [44]. Simulated overtone spectra for a subset of fluorinated hydroperoxides (Figure 3) predict similar effects. While simulated overtone spectra for conformers with lower torsional barriers (CH_3OOH and the higher-energy anti conformer of CH_2FOOH) have prominent features related to torsional excitation, those for conformers with higher torsional barriers (CF_3OOH and the anti conformer of CF_2HOOH) do not.

Conclusions

Fluoromethyl hydroperoxides adopt conformations stabilized by intramolecular hydrogen bonding between the hydroxyl H and F. Comparison with a high-energy conformer that lacks hydrogen bonding, the anti conformer of CH_2FOOH , illustrates effects that are due to fluorination from those that involve hydrogen bonding. In the absence of hydrogen bonding, a single F increases the barrier for torsion about the O-O bond relative to CH_3OOH . The stabilization from hydrogen bonding, however, increases the barrier even further. The hydrogen bonding also leads to O-H stretching frequency and intensity trends similar to those observed in other compounds with hydrogen bonding. While the addition of fluorines is expected to red-shift O-H stretch frequencies [35,36], the hydrogen bonding increases the red-shifts.

While the addition of fluorines is expected to increase the intensity ratio of fundamentals to overtones [35], the hydrogen bonding effect further increases the ratio.

A motivation for this computational work has been to explore the possibility that fluorinated organic hydroperoxides might share the photochemistry of their non-halogenated counterparts. Hydroperoxides CH_3OOH and $\text{CH}_3\text{CH}_2\text{OOH}$ are susceptible to photochemistry at visible wavelengths, through overtone excitation. Excitation to $5\nu\text{OH}$ and above results in O-O dissociation, and thermally populated states of CH_3OOH can dissociate with four quanta of O-H stretch at wavelengths as long as 750 nm, through accompanying torsion transitions [18]. For the fluorinated analogs, such low-energy photolysis is unlikely for three reasons. First, the fluorinated molecules lack accessible torsionally excited states. Figure 3 shows that the higher torsional barriers for fluoromethyl hydroperoxides make torsional transitions lose prominence for the fluoromethyl hydroperoxides with intramolecular hydrogen bonding. Second, significant red shifts mean less energy in these molecules compared to CH_3OOH and $\text{CH}_3\text{CH}_2\text{OOH}$ upon excitation to the same O-H stretch overtone. Third, fluorinated peroxides are predicted to require more energy for breaking the O-O bond. Reints and co-workers [45] interpolate an O-O bond dissociation energy of 49 kcal/mol for CF_3OOH , in contrast to 44.1 kcal/mol tert-butyl hydroperoxide $(\text{CH}_3)_3\text{COOH}$. Computed dissociation energies for $(\text{CH}_3)_3\text{COOH}$ are similar to those for other non-fluorinated hydroperoxides [46]. Based on experimental O-O bond dissociation energies for CH_3OOH [16] and $\text{CH}_3\text{CH}_2\text{OOH}$ [19] (42 kcal/mol), we therefore expect the CF_3OOH bond dissociation energy to be no lower than 47 kcal/mol. While $5\nu\text{OH}$ is well above the threshold for O-O bond dissociation in the case of CH_3OOH , our calculations here place $5\nu\text{OH}$ under the threshold for breaking O-O bonds in CF_3OOH . In summary, fluorinated organic hydroperoxides are poor candidates for photochemistry at dawn and dusk, and unlikely to contribute atmospheric OH radical formation through visible-light chemistry.

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Table 1. Calculated O-H stretch frequencies and anharmonicities.

	CH ₃ OOH	CH ₂ FOOH anti	CH ₂ FOOH gauche	CHF ₂ OOH symmetric	CHF ₂ OOH asymmetric	CF ₃ OOH
Frequency (cm ⁻¹)	3811.4	3807.6	3794.7	3789.7	3787.0	3784.5
Anharmonicity (cm ⁻¹)	102.7	102.6	102.2	102.0	102.2	102.0

Table 2. O-H stretch fundamental intensity and intensity ratios between the fundamental (1v_{OH}) and overtones (Xv_{OH} where X = 3-6).

		Intensity ratios			
	1v _{OH} intensity (cm ² /molecule) ^a	1v _{OH} /3v _{OH} (x 10)	1v _{OH} /4v _{OH} (x 10 ²)	1v _{OH} /5v _{OH} (x 10 ³)	1v _{OH} /6v _{OH} (x 10 ⁴)
CH ₃ OOH	6.5 x 10 ⁻¹⁹	1.3	1.8	1.7	1.3
CH ₂ FOOH anti	8.0 x 10 ⁻¹⁹	1.7	2.3	2.2	1.6
CH ₂ FOOH gauche	7.7 x 10 ⁻¹⁹	1.8	2.4	2.4	1.8
CHF ₂ OOH symmetric	8.7 x 10 ⁻¹⁹	2.0	2.6	2.5	1.8
CHF ₂ OOH asymmetric	8.2 x 10 ⁻¹⁹	1.8	2.4	2.3	1.6
CF ₃ OOH	9.2 x 10 ⁻¹⁹	2.1	2.7	2.6	1.8

^aFrom Gaussian09.

Figure 1. Optimized conformer geometries.

Figure 2. Potentials for torsion about the O-O bond.

I, the symmetric conformer of CHF₂OOH and CF₃OOH (right), from three (top row) to six (bottom row) quanta.