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Overtone-Induced Degradation of Perfluorinated Alcohols in the Atmosphere

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Perfluorinated alcohols (PFOHs) are thermally unstable and degrade via loss of HF, ultimately forming perfluorocarboxylic acids. Experiments and calculations of the high activation barrier for the decomposition of CF_3OH suggest that the reaction occurs exclusively heterogeneously, perhaps with the involvement of water. Here, we use density functional theory calculations to show that PFOHs may readily complex with water and are expected to be present as a few percent of the total PFOH concentration under ambient atmospheric conditions. The presence of water lowers the HF elimination barrier sufficiently that excitation to low-lying O−H vibrational overtone levels ($\upsilon_{OH} \geq 3$) may cause reaction. Photolysis rate constants for $CF_3OH{\cdot}H_2O$ and $CF_3CF_2OH{\cdot}H_2O$ were estimated to be 6.1×10^{-8} and 5.6×10^{-8} s^{-1}, respectively. PFOH−water complexes should undergo degradation much faster than the corresponding gas-phase unimolecular decomposition of PFOHs, which requires excitation into the $\upsilon_{OH} = 5$ or 6 vibrational level. Overtone-driven gas-phase reactions of PFOH−water complexes could be moderately competitive with heterogeneous reactions with water in dry locations. Overtone-induced degradation of PFOHs is likely a modest atmospheric source of PFCAs to the environment.

1. Introduction

Perfluorinated carboxylic acids (PFCAs) are ubiquitous in the environment, including in remote regions where local usage is not be expected to be a source.[1−3] Evidence suggests that atmospheric degradation of volatile precursors, such as fluorotelomer alcohols (FTOHs)[4,5] and fluorosulfonamides,[6,7] is a significant source of PFCA contamination to remote environments.[8−11] Thus, a greater understanding of the atmospheric mechanisms by which PFCAs are created is of importance.

Perfluorinated alcohols (PFOHs) are formed from oxidation of perfluorinated radicals, which are products of the atmospheric oxidation of hydrofluorocarbons[12] and FTOHs[5] as well as thermolysis of fluoropolymers.[13] PFOHs do not contain easily abstractable hydrogens and are not subject to hydroxyl or ozone attack. In addition, the lifetime due to photolysis of CF_3OH has been estimated at one million years for altitudes less than 40 km.[14] Given this lack of reactivity of PFOHs in the lower atmosphere, it is possible their persistence in this region may be limited by loss of HF via unimolecular decomposition:

$$F(CF_2)_xOH \rightarrow F(CF_2)_{x-1}C(O)F + HF \qquad (1)$$

For CF_3OH, this elimination channel is the most energetically favorable decomposition reaction:

$$CF_3OH \rightarrow COF_2 + HF \qquad (2)$$

with a calculated reaction barrier of 176 kJ mol^{-1} (42 kcal mol^{-1})[15] and a measured activation energy of 158 ± 33 kJ mol^{-1}.[16] This relatively high-energy barrier has previously been thought to preclude this reaction from occurring in the atmosphere at a significant rate. However, CF_3OH has been shown to degrade rapidly in smog chamber experiments to form COF_2 and this decomposition is enhanced in the presence of water:[17]

$$CF_3OH + H_2O \rightarrow COF_2 + HF + H_2O \qquad (3)$$

The presence of strong hydrogen bonds in water-containing clusters has been calculated to lower activation energies to reaction in a number of systems, including decarboxylation of dicarboxylic acids,[18] dehydration of H_2SO_4,[19] and HF elimination from CH_2FOH.[20] This barrier lowering is a consequence of the formation of cyclic transition state structures, which facilitate H-atom transfer processes. It is possible that the addition of water could stabilize the transition state of the decomposition of PFOHs as well, and decrease the barrier to reaction in the gas phase.

Schneider et al.[17] reported quantum chemical calculations that suggest water could act as a catalyst for HF elimination from CF_3OH, decreasing the activation barrier for the reaction to 67 kJ mol^{-1}. Although a significant binding energy of CF_3OH to water was calculated, the size of the barrier was still sufficient that the authors discounted the presence of a homogeneous reaction in the gas phase and concluded that heterogeneous reactions are the probable source of degradation for CF_3OH. Analogous reactions have been proposed to account for loss of HF from longer-chain PFOHs formed from the degradation of FTOHs,[5] though this mechanism has not been specifically examined by any experimental or modeling studies.

Although thermal degradation or gas-phase hydrolysis of PFOHs may be energetically unfavorable in the atmosphere, O−H stretching overtone excitations of PFOHs or PFOH−water complexes may be of sufficient energy to overcome the reported barriers to reaction. Reactions induced by overtone absorption have gained attention from atmospheric chemists in recent years, particularly those promoted by excitations of the O−H stretch.[21] These absorptions lie in the visible and near-infrared region of the spectrum, where actinic radiation fluxes are high. Although the transitions to overtone-excited levels are typically very weak,

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they are thus well matched to the most intense portions of the actinic spectrum. The excited vibrational levels accessed by overtone absorption are of sufficient energy to induce reactions with modest activation barriers in the ground electronic state. O−H overtone excitation was proposed[22] and demonstrated[23,24] to be critical in bringing the modeled and measured time dependence of stratospheric hydroxyl concentrations into accord. Overtone-driven dehydration of sulfuric acid[25] has recently been included in models to explain the upper stratospheric Junge layer of aerosols.[26]

The objectives of this study were to model the energetics of the unimolecular and water-catalyzed elimination of HF from CF_3OH and CF_3CF_2OH and to assess the importance of overtone-induced decomposition to atmospheric formation of PFCAs. The reaction path for HF elimination from PFOHs is expected to involve considerable motion of the alcoholic H-atom. This suggests that OH vibrational excitation may act to promote the reaction, if the energy thus deposited into the molecule is sufficient to overcome the activation barrier.

2. Methods

Calculations were performed using GAUSSIAN 03 programs and basis sets.[27] Geometries of all species were determined at MP2 level with the 6-311+g(d,p) basis set and using density functional theory (DFT) with the 6-311++g(3df,3pd) basis set and the B3LYP functionals. No significant differences were observed in the optimized geometries calculated using the MP2 versus DFT approaches. Only the results obtained using the higher basis set DFT calculations are presented here. Geometries of bound species were confirmed to be true minima by the absence of any imaginary frequencies within the calculated vibrational spectra. Similarly, geometries of transition states were confirmed by the presence of a sole imaginary frequency in each vibrational spectrum. The motion associated with this frequency was imaged using GaussView. Basis set superposition errors (BSSE) are anticipated to be of low significance for DFT calculations with such a large basis set.[28]

To determine the equilibrium constant for the formation of alcohol−water complexes, entropy and heat capacity values calculated by Gaussian were used to determine the Gibbs free energies of reaction at different temperatures. From these values, and assuming properties of an ideal gas, the equilibrium constants were determined. The Gaussian output was given for 298 K. Output energies and entropies were corrected for temperature by the following equations:

$$\Delta E(T_2) = \Delta E(T_1) + \Delta C_p \Delta T$$

$$S(T_2) = S(T_1) + C_p \ln T_2/T_1$$

Unless otherwise stated, all thermodynamic properties are given for a temperature of 273 K, appropriate for the lower troposphere.

Harmonic vibrational frequencies for the O−H stretch on the alcohol were calculated at the B3LYP/6-311++g(3df,3pd) level and scaled by a factor of 0.92 to match the measured frequencies of methanol (MeOH) and trifluoroethanol (TFEtOH).[29] These values were corrected for anharmonicity using the following equation:

$$E_n = \omega_e\left(n + \frac{1}{2}\right) - \omega_e\chi_e\left(n + \frac{1}{2}\right)^2$$

Values for the anharmonicity constant have been measured, and are similar, for water, nitric acid and water−nitric acid complexes.[30] A value of 80 cm^{-1} was chosen for the PFOHs. Similarly, the anharmonicity constant for the O−H stretch of the PFOH−water complexes was estimated at 95 cm^{-1} through comparison with water−nitric acid complexes and water dimers.[30]

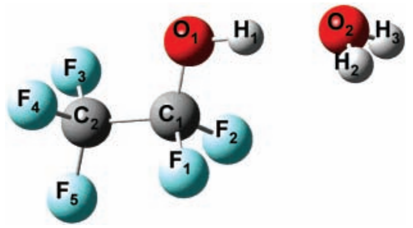

Figure 1. Optimized structure of $CF_3CF_2OH{\cdot}H_2O$. See Table S2 for bond lengths and angles.

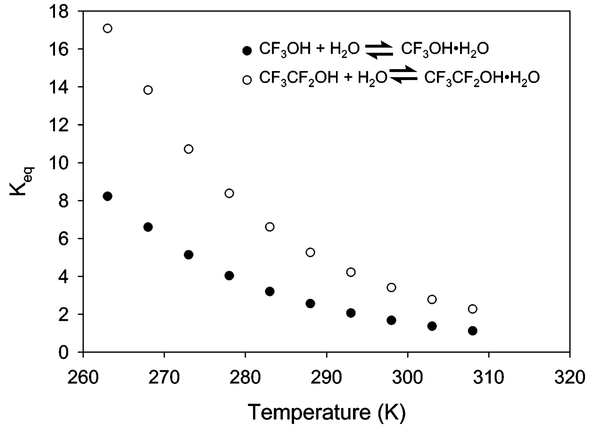

Figure 2. Calculated equilibrium constants for the reaction of CF_3OH and CF_3CF_2OH with water to form complexes. See Tables S1 and S2 for bond lengths and angles.

TABLE 1: Calculated Relative Energies of Species (kJ mol^{-1}) at 273 K

	relative energies
CF_3OH (+H_2O)	0
$[CF_3OH]^‡$	168.758
$CF_3OH{\cdot}H_2O$	−30.406
$[CF_3OH{\cdot}H_2O]^‡$	59.489
COF_2 + HF (+H_2O)	13.999
CF_3CF_2OH (+H_2O)	0
$[CF_3CF_2OH]^‡$	220.566
$CF_3CF_2OH{\cdot}H_2O$	−31.041
$[CF_3CF_2OH{\cdot}H_2O]^‡$	58.062
CF_3COF + HF (+H_2O)	15.363

3. Results and Discussion

3.1. Alcohol−Water Complexes. The calculated minimum energy structure of the $CF_3OH{\cdot}H_2O$ complex is in agreement with that determined by Schneider et al.[17] (bond lengths and angles are reported in Table S1). The structure of the $CF_3CF_2OH{\cdot}H_2O$ complex is shown in Figure 1 and described in Table S2. The binding energies determined in the current study are 30 kJ mol^{-1} for $CF_3OH{\cdot}H_2O$ and 31 kJ mol^{-1} for $CF_3CF_2OH{\cdot}H_2O$ (see Table 1). These are quite strong and comparable to that calculated for the nitric acid−water complex, of 31 kJ mol^{-1},[28] and are in good agreement with that calculated for $CF_3OH{\cdot}H_2O$ by Schneider et al.[17] Using calculated heat capacities, energies, and entropies, equilibrium constants were determined for the formation of both complex species at temperatures from 263 to 308 K and are displayed in Figure 2. Low, but potentially significant, levels of PFOH−water complexes are likely to be present in the atmosphere. The equilibrium constant is greater

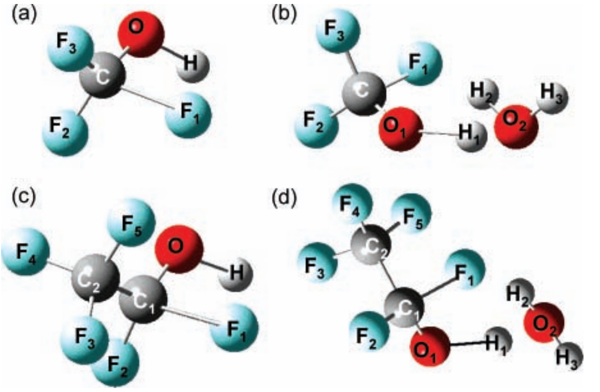

Figure 3. Optimized structures of the calculated transition states for reactions 4−7: (a) $[CF_3OH]^‡$; (b) $[CF_3OH{\cdot}H_2O]^‡$; (c) $[CF_3CF_2OH]^‡$; (d) $[CF_3CF_2OH{\cdot}H_2O]^‡$.

TABLE 2: Calculated Energies and Zero-Point Corrections (Hartree) for All Species Investigated

	energy	zero-point correction
CF_3OH	−413.63567	0.02855
$[CF_3OH]^‡$	−413.56597	0.02308
COF_2	−313.13803	0.01396
HF	−100.48698	0.00932
$CF_3OH{\cdot}H_2O$	−490.11457	0.05274
$[CF_3OH{\cdot}H_2O]^‡$	−490.07739	0.04964
H_2O	−76.46451	0.02131
CF_3CF_2OH	−651.51032	0.04174
$[CF_3CF_2OH]^‡$	−651.42065	0.03503
CF_3COF	−551.01203	0.02602
$CF_3CF_2OH{\cdot}H_2O$	−727.98934	0.06481
$[CF_3CF_2OH{\cdot}H_2O]^‡$	−727.95267	0.06191

for the longer-chained alcohol, which is the result of a somewhat larger binding energy and a somewhat lower entropy cost to binding. In a tropical setting with a temperature of 303 K and a relative humidity of 80%, 4.4%, and 8.5% of the CF_3OH and CF_3CF_2OH, respectively, are predicted to be in the water-complexed form. In the spring or summer in the Arctic with a temperature of 273 K and a relative humidity of 50%, we estimate that 1.5% and 3.2% of the CF_3OH and CF_3CF_2OH, respectively, would be complexed.

3.2. Overall Features of the Reactions. The four reactions considered in this study were as follows:

$$CF_3OH \rightarrow COF_2 + HF \tag{4}$$

$$CF_3OH{\cdot}H_2O \rightarrow COF_2 + HF + H_2O \tag{5}$$

$$CF_3CF_2OH \rightarrow CF_3COF + HF \tag{6}$$

$$CF_3CF_2OH{\cdot}H_2O \rightarrow CF_3COF + HF + H_2O \tag{7}$$

The calculated energies for each species as well as the zero point corrections are shown in Table 2. As expected, the imaginary frequency at the transition state corresponds to alcoholic hydrogen motion between the oxygen atom and an adjacent fluorine (Figure S1). Optimized geometries of the transition states for each of the four reactions are depicted in Figure 3 and described in Tables S1 and S2. The transition state geometries for $[CF_3OH]^‡$ and $[CF_3OH{\cdot}H_2O]^‡$ are consistent with those determined by Schneider et al. (Table S1).[17] The PFOH− water complex transition states are composed of a cyclic double-hydrogen bond, in which water acts as both donor and acceptor. Energetics of the reactions involving water complexes are expected to be favored over the uncomplexed reactions due to the increased stability of the six-membered ring formed in the double-hydrogen-bonded structure relative to the four-membered ring transition state present in the unimolecular reaction. The calculated energetics for reactions 4 and 5 are shown in Figure 4, and those of reactions 6 and 7 are shown in Figure 5, with all values presented in Table 1.

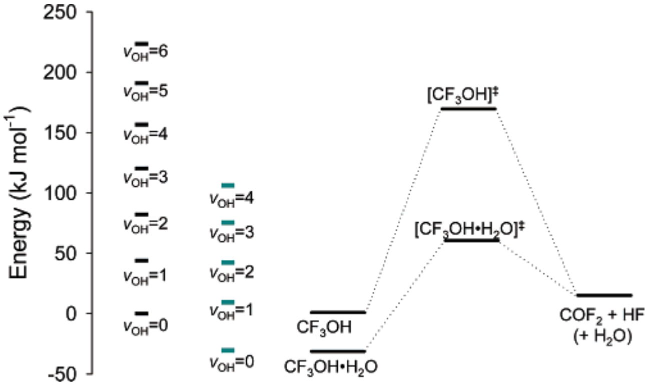

Figure 4. Energetics of reactions 4 and 5 with all energies relative to CF_3OH. Also shown are calculated overtone vibrations for CF_3OH (black) and $CF_3OH{\cdot}H_2O$ (red).

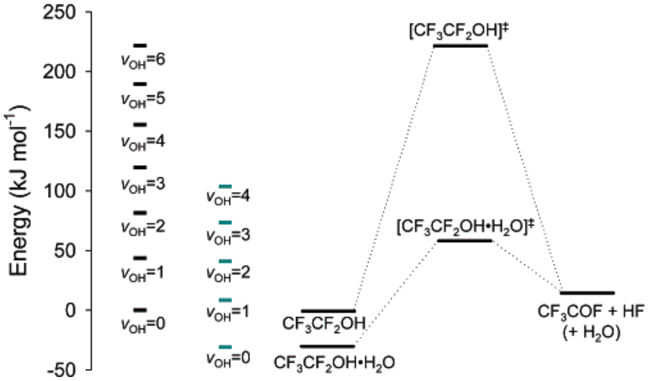

Figure 5. Energetics of reactions 6 and 7 with all energies relative to CF_3CF_2OH. Also shown are calculated overtone vibrations for CF_3CF_2OH (black) and $CF_3CF_2OH{\cdot}H_2O$ (red).

The unimolecular decomposition of CF_3OH (reaction 4) was determined to require 169 kJ mol^{-1} to achieve the transition state. This is in reasonable agreement with calculations by Schneider et al.,[17] who determined an energy of 175 kJ mol^{-1}, and with calculations by Fransisco,[15] who reported a barrier energy of 189 kJ mol^{-1}. The values also agree well with experimental measurements of the activation energy for decomposition of 158 ± 33 kJ mol^{-1} made by Huey et al.[16] The water-catalyzed reaction of CF_3OH (reaction 5) required less energy to reach the transition state, with a calculated barrier height of 90 kJ mol^{-1}. Schneider et al.[17] also calculated a lowering of the energy barrier for the water-catalyzed reaction, to 67 kJ mol^{-1}, which is slightly lower than the value determined herein. Similarly, unimolecular decomposition of CF_3CF_2OH (reaction 6) and the corresponding water-catalyzed reaction 7 are calculated to have transition state energies of 221 and 89 kJ mol^{-1}, respectively. The general lowering of the reaction barrier of the complexed species is consistent with observations that PFOHs degrade faster in smog chamber experiments in the presence of water[17] and confirm the important role of water in the decomposition of PFOHs.

3.3. Overtone-Induced Degradation. There have been no published measurements of the overtone absorption spectra or cross-sections for either CF_3OH or CF_3CF_2OH. Measurements have been made for methanol (MeOH), ethanol (EtOH), and trifluoroethanol (TFEtOH) up to the third vibrational overtone

TABLE 3: Comparison of Calculated Values (kJ mol^{-1} at 298 K) for Reactions 4 and 5 with Literature Values

	theoretical			experimental	
	this work	ref 14	ref 16	ref 15	ref 37
$[CF_3OH]^‡$	168.673	188.744	175.979	158 ± 33	
$CF_3OH{\cdot}H_2O$	−30.209		−41.348		
$[CF_3OH{\cdot}H_2O]^‡$	59.264		71.856		
$COF_2 + HF (+H_2O)$	14.146	32.643	15.568		12 ± 6

of the O−H stretch.[29] The observed vibrational frequencies are listed in Table 4. The band centers of the O−H stretching levels of all three alcohols are similar. In fact, those of EtOH and TFEtOH are within the estimated experimental error. The main differences among the alcohols lie in how the intensities vary with vibrational level. Lange et al.[29] demonstrated that electronegative substituents increased the absorption intensity of the OH stretching fundamental. However, alcohols with electronegative substituents also showed larger decreases in absorption strength with subsequent levels of excitation, with the result that there is little variability in intensity at the fourth OH stretch vibrational level. On average, band intensities decrease by approximately an order of magnitude for each excitation level. TFEtOH intensity decreases by a factor of 15 from $1\upsilon_{OH}$ to $2\upsilon_{OH}$ and a factor of 21 from $2\upsilon_{OH}$ to $3\upsilon_{OH}$. In contrast, EtOH intensity decreases by a factor of 7.5 from $1\upsilon_{OH}$ to $2\upsilon_{OH}$ and a factor of 16 from $2\upsilon_{OH}$ to $3\upsilon_{OH}$. Because TFEtOH has a higher fundamental intensity, the intensity of TFEtOH at $2\upsilon_{OH}$ is still higher than that of EtOH and at $3\upsilon_{OH}$, the intensities are approximately equal.

To estimate the potential for overtone-driven chemistry, we used the overtone absorption frequencies calculated by using the Gaussian harmonic frequencies and estimated anharmonicity parameters, as described above. Values for the resulting O−H vibrational frequencies are shown in Table 4. To determine the level of absorption required to induce reaction, O−H stretch vibrational energies were compared to calculated reaction energies in Figures 4 and 5. Reactions 4 and 6 require >169 and >221 kJ mol^{-1}, respectively, to overcome the barrier to HF loss. For CF_3OH and CF_3CF_2OH, this entails excitation into $\upsilon_{OH} = 5$ and 6, respectively.

In contrast, reactions 5 and 7 require >90 and >89 kJ mol^{-1}, respectively, and could therefore be initiated through excitation into the $\upsilon_{OH} = 3$ energy level. Alternatively, excitation into the $\upsilon_{OH} = 2$ level with the addition of thermal energy[24] could also lead to reaction. The first-order photolysis rate constant, J, for the overtone-induced dissociation of PFOH−water complexes can be calculated as follows:

$$J = \int \varphi(\lambda)\, \sigma(\lambda)\, I(\lambda)\, d\lambda$$

where $I(\lambda)$ represents the wavelength-dependent flux of available light, $\sigma(\lambda)$ gives the quantitiative absorption spectrum of the overtone transition, the quantum yield is given by $\varphi(\lambda)$, and the integration is performed over each overtone absorption band. Actinic fluxes for solar radiation were obtained from published sources[31,32] or estimated using the equation for emission from a blackbody. Absorption cross-sections were estimated by taking the ratio of the measured cross-section of TFA to that of acetic acid at $\upsilon_{OH} = 3$,[33] then scaling measured cross-sections of MeOH and EtOH[29,34] to approximate the cross-sections of the CF_3OH, $CF_3OH{\cdot}H_2O$ and $CF_3CF_2OH{\cdot}H_2O$ species. There is insufficient information available about these high vibrational levels to allow accurate estimation of the rate. However, overtone-induced photolysis of trifluoroacetic acid (TFA) at $\upsilon_{OH} = 6$ has been calculated to occur with a rate constant between 2.5×10^{-10} and 3.7×10^{-9} s^{-1}, which corresponds to a lifetime between 8 and 127 years.[33]

The quantum yield for the overtone-induced reactions is not known. For direct bond cleavage-type reactions, such as the dissociation of nitric acid or pernitric acid into $NO_2 + OH$ or $NO_2 + HO_2$, respectively, the quantum yield is unity for excitation to vibrational levels above the barrier.[21] For levels close to the barrier, thermal excitation can aid the dissociation, leading to a temperature-dependent quantum yield.[24] The quantum yields for reactions involving molecular rearrangement have not been measured experimentally. Miller and Gerber[19] reported results of classical trajectory calculations on a semiempirical potential energy surface for the $H_2SO_4 \rightarrow H_2O + SO_3$ reaction. Five percent of the trajectories initiated at $\upsilon_{OH} = 6$ gave rise to direct dissociation in these calculations, though the water complex was found not to give reaction. Later calculations,[35] which included dissociation from $\upsilon_{OH} = 4$ and 5 as well, concluded that under conditions of low collisional deactivation, the quantum yield approaches unity. Another recent calculation[20] finds that reaction can compete with dissociation of the complex for $CH_2FOH{\cdot}H_2O \rightarrow HF + CH_2O + H_2O$. Here, a quantum yield for HF elimination was estimated to be 0.015 ± 0.01 using direct dynamics simulations. In the absence of other information, it seems reasonable to assume that the quantum yields for overtone-initiated HF elimination from $CF_3OH{\cdot}H_2O$ and $CF_3CF_2OH{\cdot}H_2O$ are in the range 0.01−0.10. Utilizing a quantum yield of 0.10 and other parameters discussed above, the photolysis rate constants for the complexed species in reactions 5 and 7 are determined to be 6.1×10^{-8} and 5.6×10^{-8} s^{-1}, corresponding to lifetimes of 191 and 207 days, respectively. Similarly, the photolysis rate constant for reaction 4 is 1.69×10^{-9} s^{-1}, which corresponds to a lifetime of approximately 19 years. The rate of reaction 6 cannot be estimated due to a lack of measured alcohol cross-sections for $\upsilon_{OH} = 6$. Overtone-induced photolysis lifetimes for reactions 4 and 6 are expected to be longer than those of reactions 5 and 7 as a result of the decrease in absorption cross-section with increasing vibrational levels. Even with an assumed quantum yield for reaction of 0.01 for reaction of the water-complexed species (and 0.1 for the uncomplexed compounds), the former are calculated to be more reactive than the latter. The approximate nature of these lifetimes must be stressed, due to the high degree of uncertainty regarding the quantum yields.

If we assume that the energy barrier calculated for reaction 5 by Schneider et al.[17] is correct (67 kJ mol^{-1}), excitation into $\upsilon_{OH} = 2$ would be sufficient to induce reaction. Again, the photolysis rate can be estimated for this reaction. The actinic flux was estimated assuming Planck intensity, and a quantum yield of 0.1 was used. Estimated absorption cross-sections were estimated using measured MeOH cross-sections at $\upsilon_{OH} = 2$, which were scaled with the ratio of TFA to acetic acid cross-sections at $\upsilon_{OH} = 3$, given that cross-sections have not been measured at lower vibrational levels for TFA. A photolysis rate of 3.65×10^{-7} s^{-1} was calculated, corresponding to a lifetime of approximately 32 days.

4. Atmospheric Implications

The calculations performed in this study demonstrate that overtone-induced dissociation could be an important fate for PFOHs when they are complexed with water molecules. Atmospheric lifetimes for $CF_3OH{\cdot}H_2O$ and $CF_3CF_2OH{\cdot}H_2O$ with respect to this process may be as short as a few months. We stress here that these estimates depend upon a significant quantum yield for the elimination, on the order of 1−10%.

TABLE 4: Band Centers of PFOHS and PFOH−Water Complexes

		band centres (cm^{-1})					band centres (nm)						
		$1\upsilon_{OH}$	$2\upsilon_{OH}$	$3\upsilon_{OH}$	$4\upsilon_{OH}$	$5\upsilon_{OH}$	$6\upsilon_{OH}$	$1\upsilon_{OH}$	$2\upsilon_{OH}$	$3\upsilon_{OH}$	$4\upsilon_{OH}$	$5\upsilon_{OH}$	$6\upsilon_{OH}$
measd[a]	CH_3OH	3681(8)	7199(15)	10541(16)	13706(28)			2717	1389	949	730		
	CH_3CH_2OH	3665(8)	7168(15)	10489(24)	13643(56)			2729	1395	953	732		
	CF_3CH_2OH	3657(8)	7148(15)	10466(16)	13620(28)			2734	1399	955	934		
calcd	CF_3OH	3669	6858	10047	13075	15944	18653	2726	1458	995	765	627	536
	CF_3CF_2OH	3646	6811	9977	12983	15828	18514	2743	1468	1002	770	632	540
	$CF_3OH{\cdot}H_2O$	3325	6080	8835	11401			3007	1645	1132	877		
	$CF_3CF_2OH{\cdot}H_2O$	3289	6007	8726	11254			3041	1665	1146	889		

[a] Adapted from Table 1 in Lange et al.[29] Experimental uncertainties are expressed in parentheses and reflect uncertainty in the smallest significant digit(s) of the number presented.

Because there is no experimental measurement of this quantity, this remains a significant uncertainty in the result presented here. However, quantum dynamics calculations do indicate an HF elimination yield of ~1% for a water-complexed species, lending some credibility to our assumptions.

These elimination rate constants are only of significance if the complex is present in appreciable amounts in the atmosphere. As discussed above, depending on atmospheric conditions PFOH−water complexes should be present as a few percent of the total PFOH concentration. Making the assumption that overtone absorption cross-sections decrease by approximately an order of magnitude for each successive level implies that PFOH−water complexes, which can react through absorption at $\upsilon_{OH} = 3$, would react 2 or 3 orders of magnitude faster than PFOHs alone, which require absorption into $\upsilon_{OH} = 5$ or 6. The calculated fraction of PFOH−water complex (see above) of a few percent would make the reaction of this species approximately 1 order of magnitude faster in the atmosphere relative to that of PFOH, assuming similar quantum yields for the complexed and uncomplexed species. Takahashi et al.[20] determined that the formation of water complexes with CH_2FOH gives rise to higher reactivity when the complex contained an increasing number of water molecules. It is reasonable to assume that the same trend would hold for PFOHs, making multi-water−PFOH complexes even more reactive than the single water complexes studied here. Further studies would be required to assess the full importance of these larger complexes. Regardless of the complex size, degradation of PFOH−water complexes should be the dominant homogeneous fate for PFOHs in the lower atmosphere.

A previous study examining the fate of CF_3OH and $CF_3OH{\cdot}H_2O$ reported that the homogeneous gas-phase reaction of CF_3OH and water would likely occur with a lifetime on the order of 2 years.[17] This study did not take into account the possibility of additional energy input into the system through overtone absorption. A reaction with the calculated energy barrier of 67 kJ mol^{-1} (calculated as 89 kJ mol^{-1} in the current study) would not react with an appreciable rate in the atmosphere. As a result, those authors concluded that heterogeneous processes are likely to be of much greater significance to the fate of this compound. Heterogeneous reaction rates have been studied for CF_3OH by Lovejoy et al.[36] The authors observed that heterogeneous loss on cloud particles was an effective loss process for CF_3OH in the troposphere, with a lifetime of approximately 20 s after contact with an average-sized cloud droplet. As a result, the total lifetime of CF_3OH in the lower atmosphere depends on the time before contact with a cloud, which is estimated to be 2 days. In the stratosphere, heterogeneous loss will also be important but will depend on transport to regions where aerosols are present.[36] If this is the case, the lifetime with respect to overtone-induced degradation of PFOH−water complexes into $\upsilon_{OH} = 3$ is approximately 2 orders of magnitude slower than heterogeneous degradation of CF_3OH, but this difference will be strongly dependent on meteorological conditions. For instance, in regions that receive a moderate to large amount of precipitation, heterogeneous reaction will be the primary route of degradation of PFOHs. However, in very dry regions, such as the Arctic, there is the potential for overtone-induced degradation to be a modestly competitive loss mechanism. It is also possible that PFOHs could adsorb onto ice in the form of cirrus clouds or on the surface of the Earth and then be subject to heterogeneous photochemistry, though more studies would be necessary to verify this as a degradation mechanism.

One branch of the atmospheric oxidation of FTOHs into PFCAs proceeds through PFOH intermediates. PFOHs are only formed under low-NO_x conditions, due to reaction of perfluorinated radicals with alkyl peroxy radicals. This occurs primarily in remote regions, such as the Arctic. The PFOHs are transformed into acid fluorides and finally into PFCAs. The mechanism has not been specifically studied but was presumed to occur via heterogeneous reaction with water.[5,11] Results from the current work suggest that overtone-induced degradation of PFOH−water complexes is potentially a modestly competing mechanism for degradation of PFOHs in the transformation into PFCAs.

The fate of CF_3OH is of fundamental interest, but of greater environmental interest is the fate of longer-chained PFOHs. These compounds form acid fluorides through reactions described earlier and ultimately degrade into PFCAs. It is possible that results of this study can be extrapolated to PFOHs with longer perfluorinated chains. Increasing the chain length in water complexes from CF_3OH to CF_3CF_2OH resulted in a slightly lower transition state energy being observed. In addition, the binding energy to form the water complex was somewhat larger for CF_3CF_2OH, leading to a larger proportion in the complexed form. If these trends were to continue with increasing chain length, it would be expected that longer-chain PFOHs should be more likely to form water complexes. These would then be more likely to degrade into acid fluorides and, thus, PFCAs in the atmosphere. As a result, the overtone-induced degradation of longer-chained PFOHs may play a more important role in their atmospheric fate.

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Supporting Information Available: Optimized geometries and vector diagrams. This material is available free of charge via the Internet at http://pubs.acs.org.

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