The Role of Photolysis in the Atmospheric Fate of Perfluorinated Aldehydes: Gas Phase UV and IR Absorption Spectra

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Abstract

Long-chain perfluoroalkyl carboxylic acids (PFCAs) have been observed in remote locations and are presumed to be the atmospheric degradation products of precursor chemicals. Atmospheric oxidation of fluorotelomer alcohols (FTOHs), $C_xF_{2x+1}CH_2CH_2OH$, has been suggested as a possible source of PFCAs. It is well established that perfluorinated aldehydes (PFALs) are atmospheric oxidation products of FTOHs, but the subsequent fate of these aldehydes is unclear at this time.

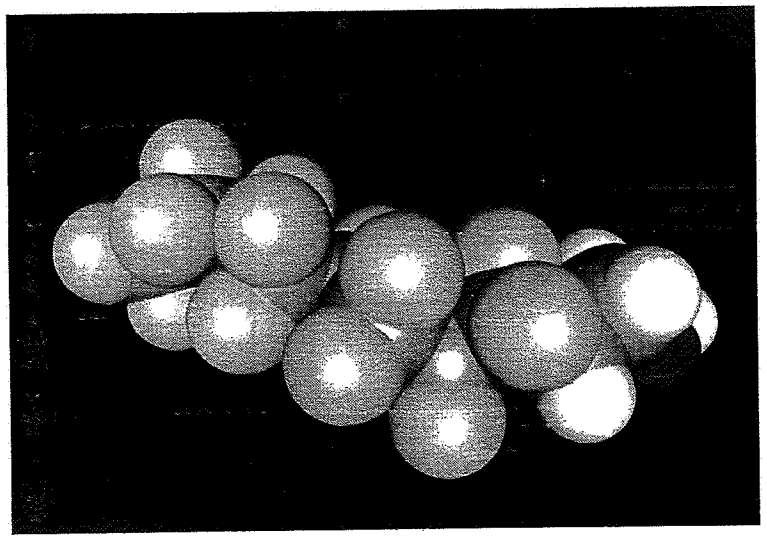
Since UV photolysis is likely to be an important removal process for PFALs, we have examined the UV and IR spectra of $C_xF_{2x+1}CHO$ (x=1-4) using computational and experimental techniques.

Introduction

Very recently, derivatives of perfluorooctanoic acid (PFOA, $C_7F_{15}COOH$) and of other perfluoroalkyl carboxylic acids ($C_xF_{2x+1}COOH$, where x = 6 - 12) have been observed in trace quantities in fish [2,3] and mammals [4] in remote locations.

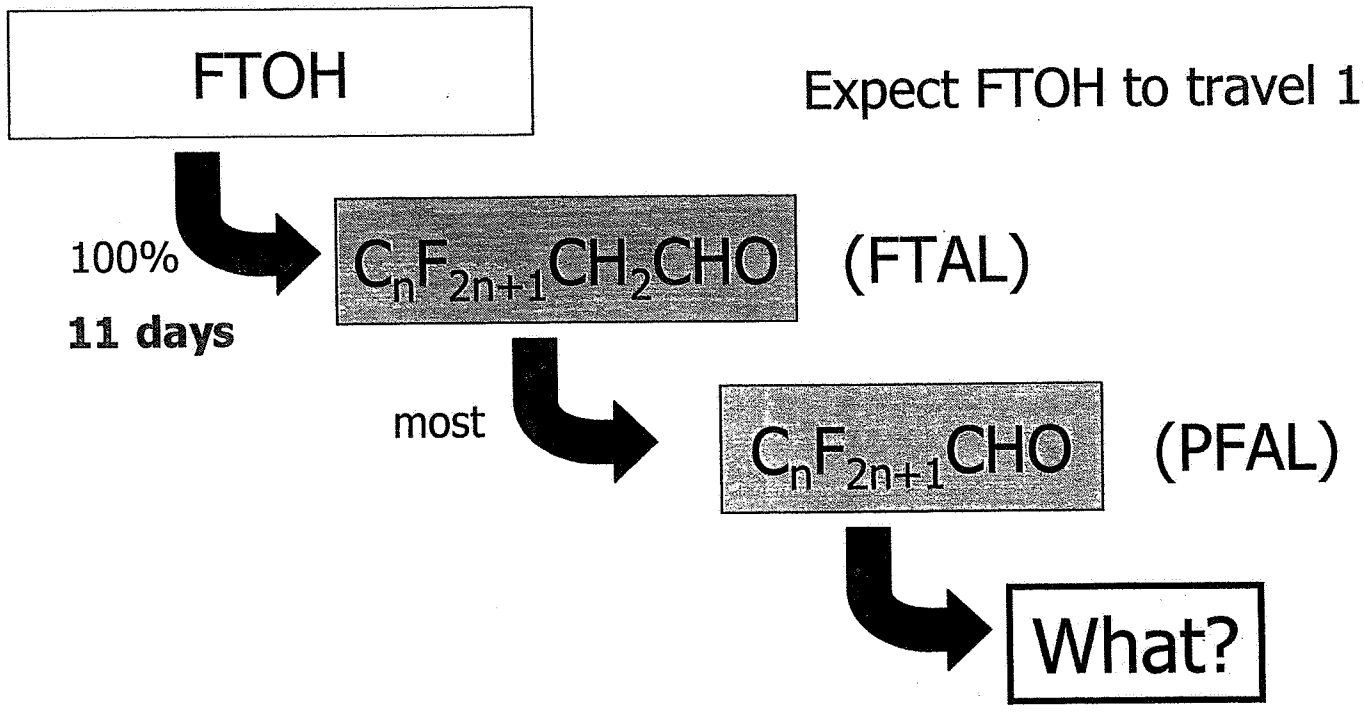
Fluorotelomer alcohols, (FTOHs, $C_xF_{2x+1}CH_2CH_2OH$) are chemical intermediates commonly used in the manufacture of fluorotelomer-based products and it has been suggested that atmospheric oxidation of FTOHs may be a source of PFCAs in the environment [5].

FTOHs: where in the environment?



- Will not be in water.
- Will not be in biota.
- Strongly sorbed to soil.
- Observed in air.

Atmospheric Fate of FTOHs



A. It depends on what else is around: NO_x and HO_x.

A′. It depends on where you are: urban/suburban or remote.

A. What else is around: NO_x.
A′. Where you are: urban/suburban.

$C_nF_{2n+1}CHO$

No perfluorinated acids formed

A. What else is around: HO_x.
A′. Where you are: remote regions.

$C_nF_{2n+1}CHO$

Some perfluorinated acids formed

Competition from photolysis?

- Do the fluoroaldehydes photolyze?
- If so, how does photolysis compete with chemical pathways?

$$C_nF_{2n+1}CHO + h\nu \longrightarrow \cdot C_nF_{2n+1} + \cdot CHO$$
$$\longrightarrow C_nF_{2n+1}H + CO$$

What is known:

The normal aldehydes $C_nH_{2n+1}CHO$ photodissociate readily (hours/days) by the corresponding pathways

Experimental Materials & Methods

- $C_xF_{2x+1}CHO$ (x=1-4) samples were synthesized at Ford Research and purified by vacuum distillation.
- UV spectra measured using a commercial dual beam UV spectrometer (Lambda 18, Perkin Elmer) operated at a spectral resolution of 1.0 nm.
- IR spectra were derived from 32 superposed interferograms measured using a Mattson Instruments, Sirius 100 FTIR spectrometer operated at a spectral resolution of 0.50 cm^{-1}, interfaced to a 140 liter, 2 m long evacuable Pyrex chamber.
- Spectra were recorded at 296 K in the presence of 700 Torr of air diluent.

Theoretical Methods

All calculations were performed using the Gaussian 03 [6] suite of programs using the B3LYP functional.

UV Spectra

Optimized geometries and frequencies were obtained using the DFT-derived DZVP basis set.

Vertical excitation energies and oscillator strengths were calculated with TD-DFT using the DZVP basis set augmented with Rydberg functions on all heavy atom centers.

Energies were rescaled using $E_{expt} = 1.144E_{calc} - 0.553$ eV

IR Spectra

Geometries, frequencies and intensities obtained using B3LYP/6-31G.

Frequencies were scaled by 0.961.

Results: UV Spectra

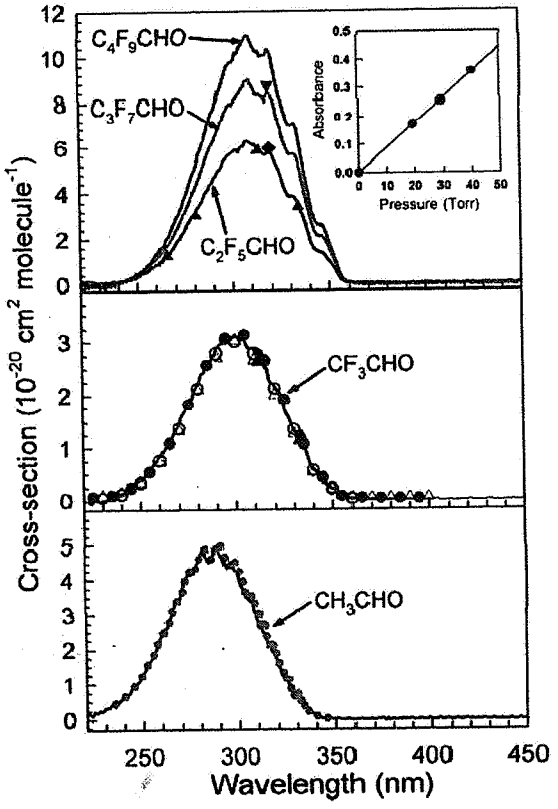


Figure 1

Experiment:

UV absorption increases with chain length.

Absorption peak shifted to higher λ vs. normal aldehydes.

Solar flux 1000X higher at peak of C_4F_9CHO vs. CH_3CHO.

Theory:

Excellent agreement for spectral peak locations.

TD-DFT shows how these peaks shift as the perfluorinated chain lengthens.

TD-DFT cannot explain the relative peak intensity: no treatment of vibronic coupling.

Results: IR Spectra

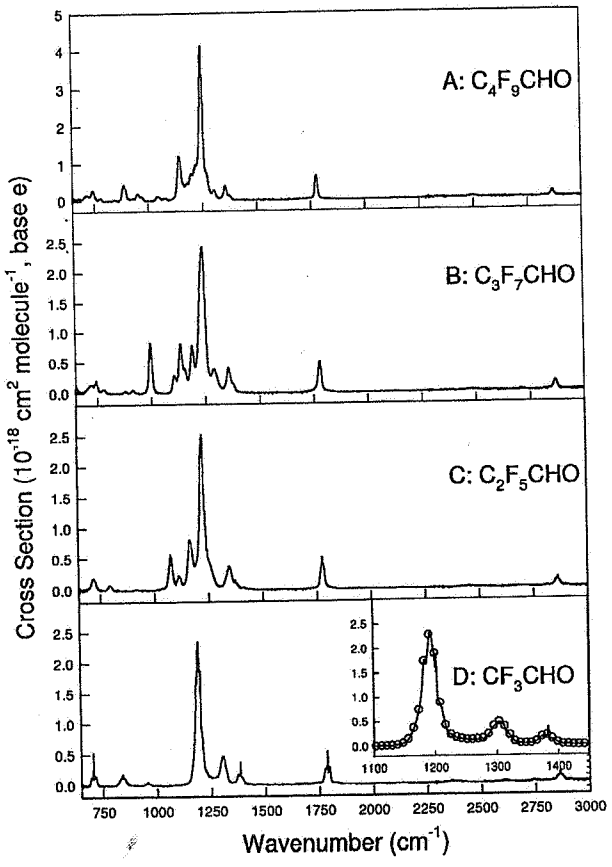


Figure 2

Theory & Experiment agree well:

- Taking all four molecules together, for those transitions for which both experimental and theoretical data exist
  - root mean square error is 24 cm^{-1}
  - maximum absolute error is 54 cm^{-1}.
- The relative computed IR intensities also agree quite well with experiment.

Discussion

The PFALs $C_xF_{2x+1}CHO$ (x=1 - 4), absorb strongly in the critical UV region above 290 nm.

- absorption is concentrated in a broad single band.
- for the higher aldehydes, the peak absorption is at 309 nm.
- anticipate that the higher homologues (x>4), will absorb at a very similar wavelength.
- absorption maximum increases monotonically and rapidly with increasing length of the perfluorinated tail. Peak absorption of C_4F_9CHO is about 3.5 times greater than that of CF_3CHO.
- The higher perfluoroalkyl aldehydes absorb more strongly than the corresponding non-halogenated counterparts.

Conclusion

PFALs will absorb solar UV much more readily than their non-halogenated analogues.

Discussion

However, in the absence of quantum yield data it is unclear whether the rate of *photolysis* of long chain perfluoroaldehydes is greater than, comparable to, or less than that of the corresponding normal aldehydes.

Studies of the photolysis quantum yields for $C_xF_{2x+1}CHO$ ($x > 1$) under atmospheric conditions are needed to quantify the degree to which photolysis competes with, and perhaps eliminates, formation of perfluorocarboxylic acids by chemical pathways.

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