Combustion Characterization of Fluorinated Polymers

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Abstract

The present paper presents some preliminary data from Fourier transform infrared spectroscopy of the thermal decomposition and combustion of highly fluorinated polymers. Two different compounds have been evaluated using resistive heating ignition to study the impact of different temperatures and combustion atmospheres. The tests indicate that the two compounds produce significantly different concentrations of hydrofluoric acid when combusted and that lower temperature or fuel-rich conditions may lead to an increase in this concentration.

Introduction

Being the most electronegative of the elements in the periodic table, fluorine is a strong oxidizing agent. The fact that it can outcompete oxygen for available reducing molecules and ions has made fluorine, in addition to its fellow halogens chlorine and bromine, key components in flame retardants and CFC-based fire suppressants. Through combining with hydrogen atoms released during the decomposition of the fuels, the production of combustion-promoting hydroxyl radicals is suppressed. Due to the negative impact on the ozone layer and greenhouse effect[1] of certain CFCs, a significant amount of research has been directed towards finding less harmful substances with similarly effective fire-fighting properties over the last decade[2]. One problem with many of the suggested replacement compounds is their increased tendency to release large amounts of toxic and corrosive hydrofluoric acid when used for quenching a fire[3]. The strong oxidizing tendency of fluorine also makes it a candidate for rendering toxic chemical substances less dangerous. Due to the difficulty involved in handling and delivering the highly corrosive fluorine gas itself, stable solid and liquid compounds that deliver large amounts of fluorine radicals when combusted, have been developed. The present paper presents preliminary findings about the combustion of two such compounds as investigated in a Fourier transform infrared (FT-IR) spectrometer.

Scope of Present Study

The purpose of the present study is to investigate the combustion characteristics of two fluorine-rich polymers. Ultimately, the ignition delay and vaporization rate in air under different conditions are to be investigated in a free-fall test cell. To assess the relevant temperature and time scales involved in this experiment and to determine which chemical reactions and products to expect, preliminary experiments were carried out using FT-IR spectroscopy. While this research project is still in an early stage and refinement of equipment and methods is an on-going process, some preliminary findings are presented in this paper.

Experimental Setup and Procedure

Samples

Two different fluorinated polymers were available for testing. GB1 is a light brown, wax-like substance with a degradation temperature of $T_{d10}=310^{o}C$ in air and a mean molecular weight of 3340 g/mol. GB2 is a dark brown viscous liquid with a degradation temperature of $T_{d10}=160^{o}C$ in air and a mean molecular weight of 920 g/mol. The chemical structures of the two compounds are given in Figure 1. The relative abundance of the different monomers is x=9%, y=75% and z=16% for GB1 and x=9%, y=72% and z= 19% for GB2.[4] Note that in addition to the slight difference in monomer distribution, GB1 the two polymers only differ in that

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GB1 has two fluorine atoms and GB2 hydrogen on the left carbon atom in the x monomer.

Test cell

The experimental setup used for the present experiments consisted of a cylindrical stainless steel test cell fitted with two CaF_2 windows and a heating wire as shown in Figure 2. The heating wire consisted of 0.25 mm diameter NiCr wire with a resistance at room temperature of 2.5 ohm, which was connected to a DC power supply providing up to 3 A current during the tests. A similar setup has been used previously for investigations of the combustion of high energy density compounds.[5]
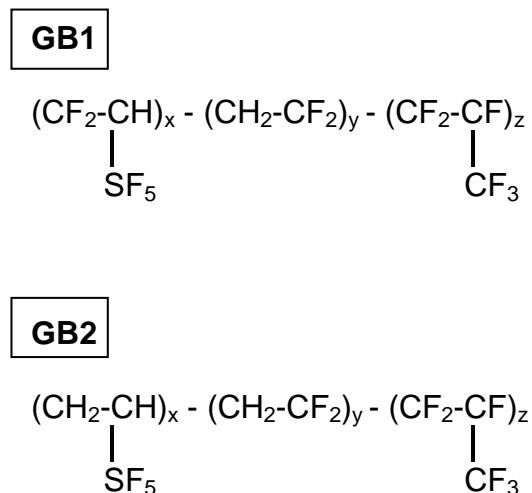
GB1

$$(CF_2\text{-}CH)_x - (CH_2\text{-}CF_2)_y - (CF_2\text{-}CF)_z$$
$$\quad | \qquad\qquad\qquad\qquad\qquad\qquad | $$
$$SF_5 \qquad\qquad\qquad\qquad\qquad\qquad CF_3$$

GB2

$$(CH_2\text{-}CH)_x - (CH_2\text{-}CF_2)_y - (CF_2\text{-}CF)_z$$
$$\quad | \qquad\qquad\qquad\qquad\qquad\qquad | $$
$$SF_5 \qquad\qquad\qquad\qquad\qquad\qquad CF_3$$

Figure 1. Molecular structure of the two tested polymers, the wax-like solid GB1 and the viscous liquid GB2.
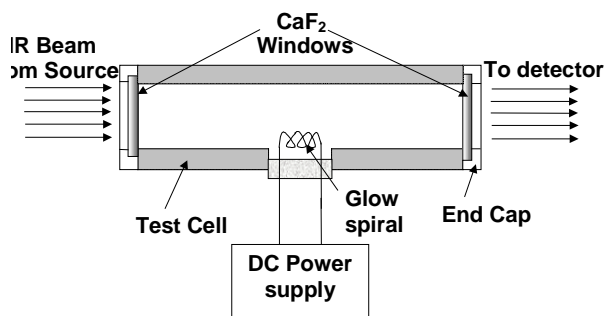

Figure 2. Cross section of test cell

The inner and outer diameter of the test cell were 22 and 46 mm, respectively, and its inner length 95 mm. The heating wire was inserted trough a 7×32 mm cutout in the bottom of the cell which was covered by a stainless steel plate with a rubber seal during the tests. The cutout also allowed the introduction of a 0.13 mm diameter type K thermocouple which was positioned with the tip as close as possible to the negative end of the glow spiral. The cell was fitted with two 6 mm OD ports on the opposite side of the wire access. During the experiments, one of these ports was connected to a 700kPa Omega PX-303 pressure transducer. For the inert gas tests, one of the ports was connected to the Grade 4.8 nitrogen supply used for the spectrometer while the other was left open to vent to the atmosphere. After the purging had been completed, the two ports were closed with ball valves. The two 3 mm thick CaF_2 windows allowed IR light pass along the centerline of the cell, approximately 5 mm above the top of the heating wire. The windows have a transmittance of 97% up to 7 μm (1430 cm^{-1}) and then it drops to 35% at 10 μm (1000 cm^{-1}) and reaches zero at 11 μm (910 cm^{-1}). The signals from heating wire thermocouple, amplified using an Omega Omni Amp III, the pressure transducer and the voltage supplied to the wire were connected to a NI AT-MIO-16E-2 data acquisition board read at 1 kHz sampling frequency using a LabView VI.

FT-IR spectrometer

The test cell was inserted into the sample compartment of a Nicolet Magna-IR 560 FT-IR spectrometer. To reduce the absorption from CO_2 and H_2O vapor in ambient air, the spectrometer was purged using dried Grade 4.8 nitrogen. The spectrometer was fitted with a KBr beamsplitter, an IR light source and a liquid nitrogen-cooled MCT/B sensor, which allowed the spectral region 900-4200 cm^{-1} to be scanned. Using a resolution of 2 cm^{-1}, a single spectral scan could be acquired every 9 seconds. For more information about FT-IR, see the textbook by Smith[6]. For further examples of the application of FT-IR spectroscopy to combustion involving halogens, the reader is referred to the reports by Black et al[3] and Speitel[7], both of which are available online.

Experimental procedure

A couple of milligram of the compound to be tested was spread across the surface of the glow spiral. In the case of the wax-like polymer GB1, the sample was dissolved in ~0.1 ml acetone before being applied. The glow spiral was then inserted into the test cell and the cell was sealed before being inserted into the spectrometer beam path. Several background scans were acquired before the tests with the test cell mounted in the spectrometer but without the power switched on. This allowed the decreasing CO_2 and H_2O absorption of the surrounding air to be monitored as the spectrometer was purged. Once the impurity level was deemed sufficiently low, the data acquisition was

started and one spectral scan was acquired on the FT-IR. Immediately after this scan, the power to the heating wire was switched on and another scan acquired. While the applied voltage was left on at a constant level, 10−15 additional scans were acquired, initially with ~10s spacing and later on with up to 1 min spacing. Once the scans, which were monitored in real time on the computer connected to the FT-IR, were deemed stable, the power to the heating wire was switched off and several additional spectral scans were acquired. The test was concluded by switching off the data acquisition and performing post-processing of the collected data files using a Matlab script.

Data Analysis

While the voltages obtained from the thermocouple amplifier and the heating spiral supply were kept unmodified, a linear calibration converting the pressure transducer voltage to pressure was applied in the LabView VI. Through comparing the voltages from the thermocouple and from the heating spiral, it was determined that the heating spiral could be approximated by a first-order system with a time constant of 3 s, as shown in Figure 3. In separate response tests, the 0.13 mm diameter thermocouple was found to have a time constant of 0.5 s. Through comparing the thermocouple reading using an Omega HH-603 reader with the voltage out from the amplifier read by the computer, a rough linear calibration of the thermocouple output was obtained.
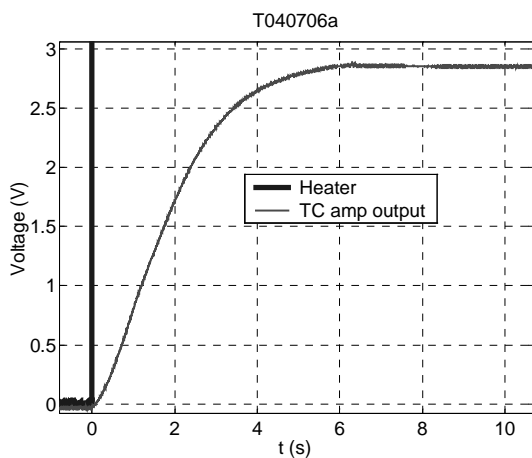

Figure 3. Measured heater and thermocouple amplifier voltage as the power to the heating spiral is switched on.

The background-corrected FT-IR spectra are processed in Matlab in several steps. First, a baseline curve in the form of a piecewise linear curve is fitted through a number of points where no spectral features are found

to enable spectra with shifted baselines to be compared. Next, spectral regions containing spectral features of several major species are identified and the absorbance in each of these regions is integrated to provide a measure of the concentrations of these species. The Aldrich Vapor Phase library was used as a reference for the peak identification.[8] Through repeating this process for each spectrum acquired during a test, qualitative concentration versus time curves for each of the identified species were obtained. The spectral regions used are given in Table 1.

Table 1. Spectral regions integrated over for determining concentrations of major species.

Species	Spectral region
	cm^{-1}
CO	2050-2220
CO_2	2310-2380
H_2O	1610-1750
H_2O	3600-3670
H-C	2750-3100
HF	3910-4210

Results

Using the techniques described in the preceding section, the FT-IR and voltage data files were evaluated to determine the composition of the gas in the test cell as a function of time under different conditions. All runs were started from ambient temperature and pressure and used the same power setting of the glow spiral. In addition to testing the two different polymer samples, the impact of atmospheric oxygen was tested through running a test of GB1 after purging the test cell with pure nitrogen. The steady-state temperature indicated by the thermocouple inside the cell was generally low and varied widely between different tests. This was believed to be due to differences in how close to the heating wire the thermocouple ended up in each test. There was also significant heat loss through radiation and through conduction in the thermocouple connecting wires[9] leading to an underestimation of the actual wire temperature by several hundred degrees. Ultimately, the temperature under all conditions should be practically identical. Based heat dissipation calculations and the yellow glow of the spiral, its temperature was estimated to be 1450K at 22 W. At the 4.8 W used for one GB1 test, the surface temperature was estimated at 850K. Given the fast response of the thermocouple compared to that of the heat spiral, it may be assumed that the difference between the ambient and indicated temperatures of the heating spiral and the thermocouple in each test were proportional with a proportionality constant varying from test to test. While its absolute

reading proved unreliable, the thermocouple 0.5 s response time was short enough to accurately capture the ~3 s rise of the heat spiral temperature. This suggested that initial heating rates of 400 K/s were achieved.

GB1 in air

Spectra obtained at three different times during a single test of GB1 combustion in air are shown in Figure 4-6. In the first spectrum, obtained just after the heater was turned on, the peaks produced by decomposition and partial oxidation of the fuel, e. g. the characteristic, widely spaced peaks near 4000 cm^{-1} from HF, COF2 near 1900 are clearly visible. The broad feature covering the range 1100-1400 cm^{-1}, which dominates the spectrum in Figure 4, is believed to be a result of overlapping peaks primarily from COF_2, SO_2 and CH_4. The hydrocarbons are also responsible for the small, broad peak around 3000 cm^{-1}.

In addition to the rapidly growing peaks corresponding to CO_2 and CO, found near 2350 cm^{-1} and 2100 cm^{-1}, respectively, the broad features due to H_2O, which increase gradually over time, can be found in the 1400−1900 cm^{-1} and 3600-3900 cm^{-1} ranges. That this is a fluorinated compound can be seen by the widely spaced peaks due to HF near 4000 cm^{-1} and the broad feature near 1900 cm^{-1} due to COF_2. The broad feature covering the range 1100-1400 cm^{-1}, which dominates the spectrum in Figure 4, is believed to be a result of overlapping peaks primarily from COF_2, SO_2 and CH_4. The source of the peak in the 1700-1780 cm^{-1} range remains uncertain – one candidate is acetone or a combustion intermediate containing a carbonyl group. A closer look at this spectral region reveals two sharp peaks at 1728 and 1741 cm^{-1}. Acetone also has broad peaks centered at 1218 and 1365 cm^{-1}, potentially contributing the broad feature found in this region.
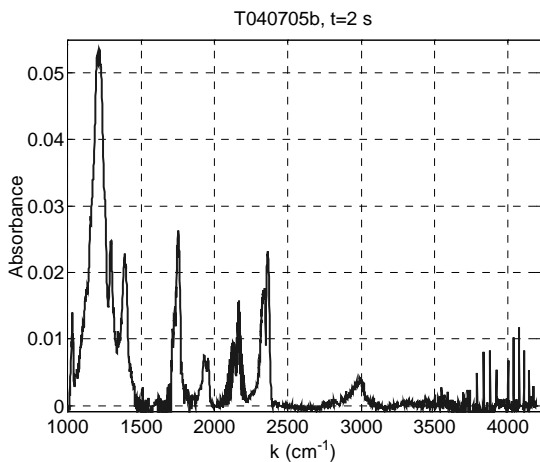

Figure 4. Spectrum obtained 2 s after the heater was turned on with a GB1 sample in air.

As time progresses, oxidization of the polymer carbon skeleton producing increasingly strong peaks due to CO_2 and CO, found near 2350 cm^{-1} and 2100 cm^{-1}, respectively. Furthermore, a gradual increase in the concentration of water vapor produces absorption in the 1400−1900 cm^{-1} and 3600-3900 cm^{-1} ranges.
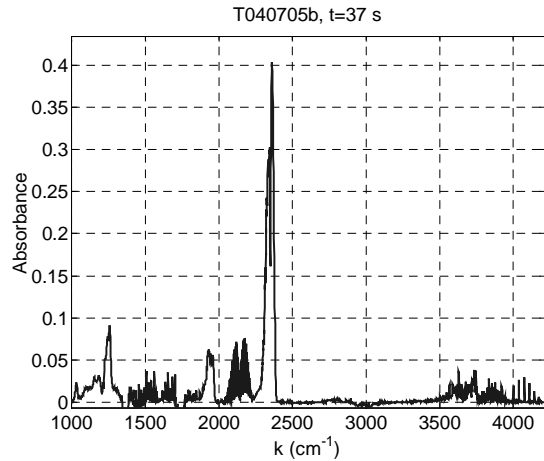

Figure 5. Spectrum obtained 37 s after the heater was turned on with a GB1 sample in air.
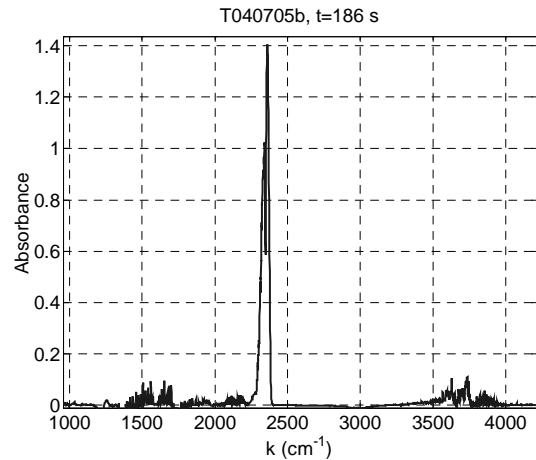

Figure 6. Spectrum obtained 186 s after the heater was turned on with a GB1 sample in air.

After carrying out the spectral integrations as specified in Table 1, the variation in the concentration of several major species over time can be plotted as in Figure 7. These curves show that the combustion rate rapidly overtakes the rate of vaporization, making the amount of hydrocarbons detected decrease after peaking just after the heater was turned on. CO and HF peaks significantly later, 30-50 s after the heater was turned on, and then decrease only slowly. CO_2 and H_2O keep growing throughout the measured time period, approaching steady state values at 200 s when the heater is turned off again. Early on, the first water peak

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is over-estimated due to the appearance of a peak in the integrated spectral region due to another compound, potentially containing a carbonyl group.
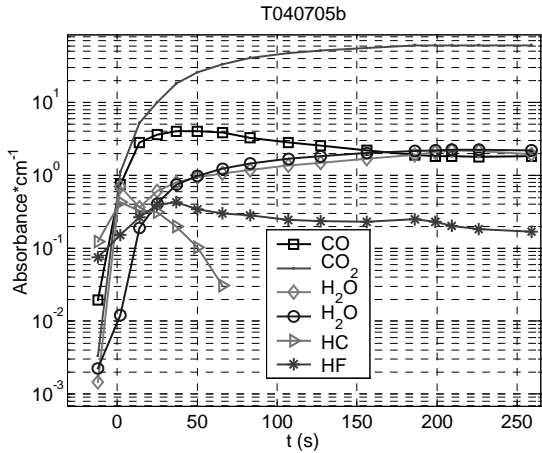

Figure 7. Species concentrations versus time when GB1 is combusted in air.

GB1 in nitrogen

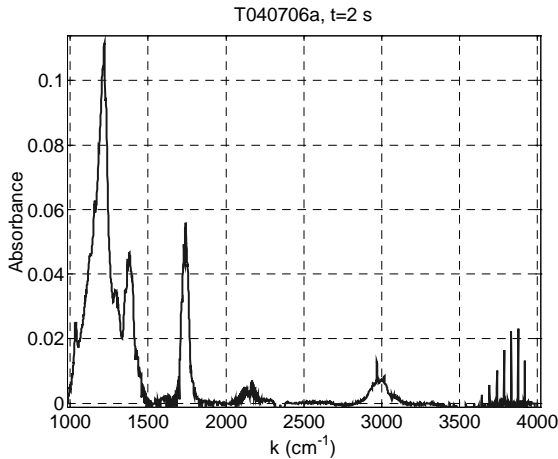When GB1 is heated up in an inert atmosphere, a significantly different set of spectra are obtained as shown in Figure 8.

Figure 8. Spectrum obtained when GB1 is heated up in nitrogen 2 s after the heat was turned on.

When comparing Figure 8 to Figure 4 – please note the different scales - it is immediately noted that the peaks due to COF_2, H_2O and CO_2 are missing in the nitrogen atmosphere, as expected. Instead, the feature near 3000 cm^{-1} produced by hydrocarbons as the polymer is vaporized and partially decomposed is more prominent. Also note the growing CO feature, indicating that some oxygen contamination must be present, probably signifying a leak in the test cell. When the integrated absorptions are plotted as functions of time, the results shown in Figure 9 are obtained.
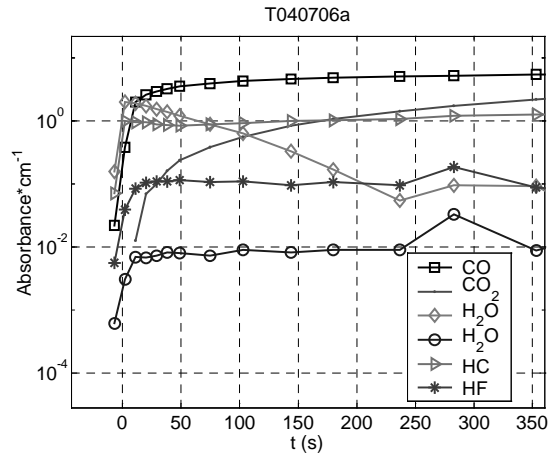

Figure 9. Spectrally integrated absorbance of products formed when GB1 is heated up in a nitrogen atmosphere.

The curves show that while CO reaches its steady-state level after 200s, CO_2 keeps rising from a very low level throughout the test, again signifying that there is a leak in the test section. The discrepancy between the two spectral regions integrated for water content suggest that the first region overlaps with some other species that shows high concentrations early in the heating process.

GB2 in air

A set of five spectra obtained during the early phase of combustion of the liquid polymer sample GB2 in air is shown in Figure 10. As a comparison with the GB1 data in Figure 4 shows, the qualitative spectra are similar. The height of the peaks corresponding to CO_2, H_2O, HF and COF_2 are an order of magnitude larger for GB2 than for GB1, but this may be explained by small differences in the timing of the two scans since the overall vapor concentrations rise rapidly during the heat-up. The relative prominence of CO and the peaks near 1750 cm^{-1} and 1200 cm^{-1} is greater in the GB1 run. The relatively weak 1700 cm^{-1} peak in GB2 strengthens the suspicion that it is due to acetone used for dissolving GB1. The development of the gas mixture in the test cell over time is shown in Figure 11. Again, the similarities to the development in the GB1 test are striking with an early sharp peak corresponding to decomposing hydrocarbons, followed by peaks in HF and CO. These compounds do however reach their maximum concentrations significantly earlier, at 10 s rather than 30-50s after ignition, than in the GB1 run. H_2O and CO_2 show a slow approach to steady state, again with the exception of the first water peak which is affected by the presence of the compound generating a broad peak in the 1700−1780 cm^{-1} range. Comparing Figure 11 to Figure 7, it can also be noted that the HF

production by GB2 seems several times higher than that of GB1, while the production of COF_2 appears comparable.
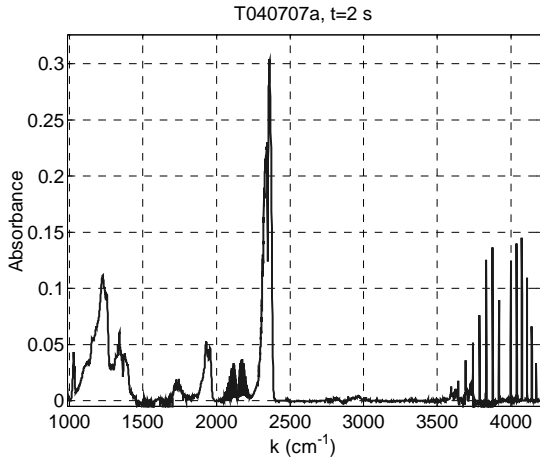

Figure 10. IR absorption spectrum of GB2 combustion in air 2 s after the heater power was turned on.
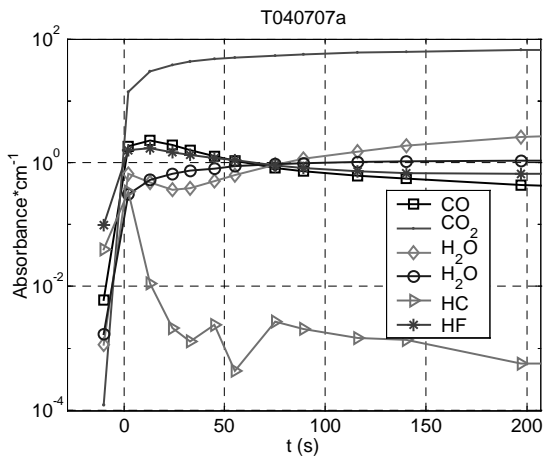

Figure 11. Integrated absorption produced by different species plotted against time for GB2 combustion in air.

GB1 in air at lower temperature

One test was carried out at reduced heater voltage – 4.0V providing a current of 1.2A and a power of 4.8W. An early absorption spectrum obtained in this case is shown in Figure 12. This spectrum is dramatically different from that obtained in the higher-temperature run shown in Figure 4. A comparison reveals that the CO, CO_2 and water vapor concentrations are an order of magnitude smaller, while the remaining peaks are approximately as prominent as in the higher-temperature run, indicating a significantly lower burn rate than in the test illustrated in Figure 4.
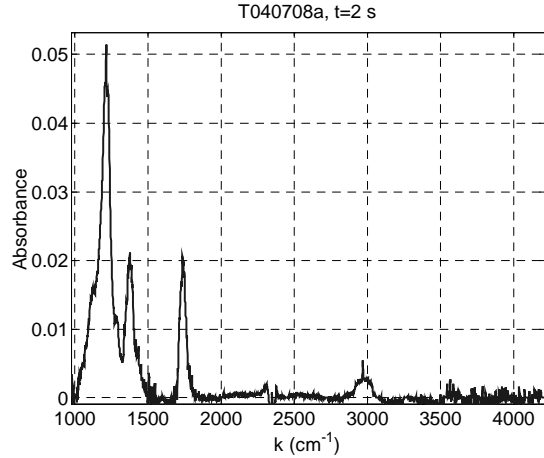

Figure 12. Absorption spectrum obtained for combustion of GB1 in air at reduced temperature acquired 2 s after the power was turned on.

The time series plot for this run presented in Figure 13 illustrates this more clearly. Rather than showing a sharp peak just after the heater is turned on, the hydrocarbons level off on a nearly constant, high level, indicating incomplete combustion. Furthermore, CO does not show the smooth peaks some time into the test found at higher temperature, but more closely resemble the monotonically increasing CO_2 concentration. Unlike the N_2 atmosphere test, CO_2 here dominates over CO throughout the test. While the impure first water-related band shows a constant level attained just after the heating was applied, the more reliable second band shows a slow increase in water concentration throughout the test. The HF concentration peaks much later, near 200 s rather than near 30 s, and at a higher level than in the high-temperature GB1 test.
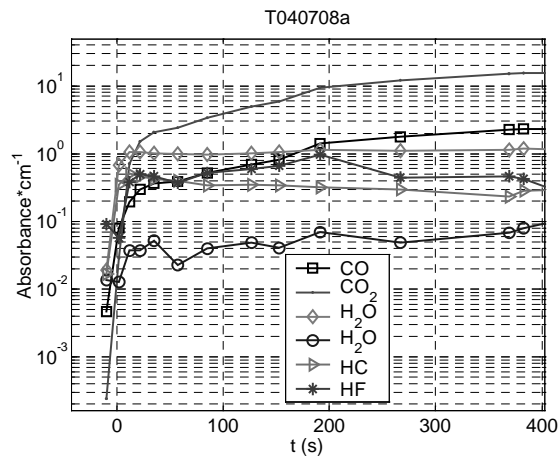

Figure 13. Spectrally integrated absorptions as functions of time for GB1 combustion at lower temperature.

Conclusions

Preliminary results of a study of the combustion characteristics of two fluorinated polymers have been reported. The following conclusions can be drawn on the data acquired so far:

- The dissociation of the hydrocarbon skeleton and the groups attached to it is accomplished in a few seconds, leaving hydrocarbon levels below the detection threshold after 50 s.
- CO and HF follow similar trends, peaking 30-50 s after the heat is applied for GB1 and ~10 s after the heat is applied for GB2. Thereafter the concentrations slowly decrease by a factor 2 over ~100 s.
- The ultimate products H_2O and CO_2 don't reach steady-state concentrations until ~200 s after the heating started.
- GB2 releases several times the concentration of HF produced by GB1. Given the higher fluorine content of GB1, and the similar concentrations of COF_2 found in both tests, this suggests that other fluorine compounds are likely to be present at significant concentrations.
- Even under fuel-rich conditions simulated through application of nitrogen purge to the test cell, HF is formed in large concentrations by GB1 when the heater is turned on.
- At lower temperature GB1 combustion, 850 rather than 1450K, the reactions proceed slower with HF peaking at 200 s rather than at 30 s. The combustion is incomplete, leaving a significant, constant level of hydrocarbons in the test cell.

Planned Future Work

- The setup will be refined to provide accurate temperature measurements on the glow spiral as well as in the gas phase.
- Using correlations between measured spectra and library spectra for all relevant species, quantitative concentration measurements will be carried out.
- Mass spectrometry of the ultimate combustion products to determine the concentrations of other fluorine compounds will be tested.
- Free-fall droplet/particle burn tests in combustion test cell to determine ignition delay and burn rate under more realistic conditions are to be completed.

Acknowledgements

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