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Infrared Intensity Studies in Fluorinated Macromolecules

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Summary: Functionalized perfluoropolyethers are investigated by infrared spectroscopy with the aim to give a quantitative estimate of the carboxylic acid groups species; since hydrogen bonded moieties have been observed, also the relative distribution of the associated species has been determined. The study is based both on measured and on theoretically predicted infrared intensities, as obtained by density functional theory (DFT) calculations on model systems.

Keywords: density functional theory simulations; hydrogen bonds; infrared spectroscopy; perfluoropolyethers

Introduction

Fluorinated polymers are high performance materials used in many technological fields. Functional groups are sometimes introduced in fluoropolymers in order to improve their adhesion on high energy surfaces or their compatibility with hydrogenated polymers. Perfluoropolyethers (PFPEs) are a peculiar family of fluid polymers, with outstanding properties such as high thermal and chemical stability and very low glass transition temperature (down to −120 °C), resulting in a wide working temperature range. These polymers are used in high-tech applications like high vacuum technology, special lubrication, aerospace and electronic industries, etc. Their synthesis and their chemical/physical properties have been described in previous papers.[1]

In the last decades PFPEs bearing functional groups were developed for specific applications such as coating or treatment of surfaces, film lubrication, and as additives and building blocks for the synthesis of new copolymers.[2] Moreover, functional groups (in particular carbonyl groups) are present in the intermediates of the PFPEs manufacture process. They also result from degradation of the PFPE chains in severe application conditions.

Vibrational spectroscopy is one of the most powerful analytical techniques used to identify and quantify functional groups in fluorinated polymers and especially in tetrafluoroethylene (TFE) based polymers.[3,4] Even if IR spectroscopy was frequently employed in case of PFPEs for the detection of carbonyl groups or carboxylic moieties[5,6] and references therein, the data regarding the absolute IR intensities of their characteristic bands and their evolution while changing the chemical environment are still to be investigated.

In this work we present experimental spectroscopic data obtained from samples of linear perfluoropolyether macromolecules containing different concentrations of –COOH end groups. These data are rationalized with the help of DFT simulations carried out on molecular models.

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On this basis a method is proposed for measuring the relative populations of free and associated macromolecules. The measure of absolute infrared intensities also provides a direct check of the reliability of the calculated intensity values.

Experimental Part

A polydispersed perfluoropolyether with backbone structure $-(CF_2O)_n(CF_2CF_2O)_m-$, average molecular weight of 8000 amu and having, on average, about 0.7 $-CF_2COOH$ end groups per chain was used as the source of carboxylic groups (corresponding to an absolute concentration of carboxylic end groups of 88.9 meq/Kg evaluated by acidimetric analysis and also checked by ^{19}F NMR spectroscopy).

This product was diluted with a commercial Fomblin® Z, which has the same backbone structure (and comparable molecular weight) but only perfluorinated chain ends (mainly $-CF_3$ groups). In this way several samples with $-CF_2COOH$ concentration in the range 0.05–10 meq/kg have been obtained. Some of the solutions (obtained by weighting) have been checked also by acidimetric analysis.

Spectra of the solutions and of neat Fomblin® Z have been recorded by FT-IR Nicolet Nexus instrument, with a spectral resolution of 2 cm^{-1}, coadding 256 scans for sample. A sealed cell for liquids with CaF_2 windows and optical path-length of 1 mm has been used.

Theoretical calculations have been carried out by means of Gaussian03 code[7] in the framework of Density Functional Theory (DFT). B3LYP functional[8] and the 6-311G** basis set have been used for all the calculations here reported. Moreover, in the investigation of hydrogen bonded dimers, we have also checked the influence of diffuse functions (6-311++G**) and basis set superposition error on the calculated IR spectra obtaining very small corrections with respect to the previous calculations. These results have not been introduced in the following discussion.

Results and Discussion

Experimental Observations

Optical density data and frequencies characteristic of the functional groups have been obtained subtracting from the IR spectra of the solutions the IR spectrum of neat Fomblin® Z. The characteristic vibration of the C=O stretching of perfluorinated carboxylic acids, near 1800 cm^{-1}, is about 100 cm^{-1} higher than in the case of hydrogenated homologues. Moreover, two main bands whose intensity ratio depends on the concentration of the functional groups (see Figure 1) can be easily observed in this spectral region. The component at higher wave-number (1820 cm^{-1}) is assigned to carboxylic acid group of "free" molecules (FM) while a second stronger band (1780 cm^{-1}) can be ascribed to CO groups involved in hydrogen bonds. Due to the high stabilization energy arising from the formation of a cyclic complex bonded through two Hydrogen Bonds (see a sketch of the structure in Figure 1, b (II)) we propose to assign this band to cyclic dimers (2HB). Other fluorinated carboxylic acids show a similar behavior in the infrared and a marked red-shift of the C=O stretching is observed upon formation of dimers.[9]

For increasing concentrations, the relative intensity of the 2HB band with respect to the FM band grows monotonically. This observation suggests that as soon as we increase the amount of the solute, the number of 2HB dimers increases, as it could be expected from simple arguments based on the likelihood that two –COOH groups approach within the interaction range.

A third component can be also identified in the CO stretching region as a shoulder on the higher frequency side of the strong (2HB) band. Its intensity seems to be only weakly dependent on the degree of concentration of the solution. Based on results from theoretical modeling (see below), this shoulder can be attributed to partially bonded dimers i.e. to dimers where only one hydrogen bond is linking the two molecules (see Figure 1, III). The occurrence of at least three components in the

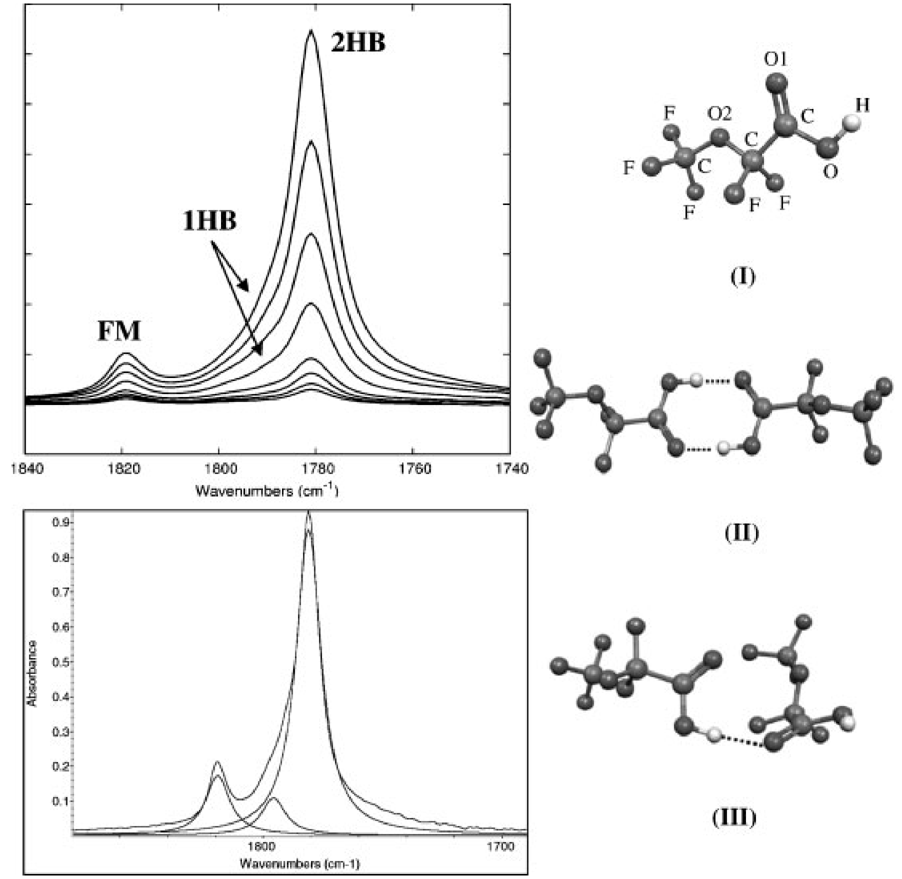

Figure 1.
Left: (upper) Experimental IR Spectra at increasing concentrations (after subtraction of the spectrum of the solvent) (lower): example of a curve fitting. Right: structures of the model molecule (I) and of the two hydrogen bonded dimers considered in this work (II) and (III).

CO stretching region is supported by a curve fitting (see Figure 1) which reproduces very well the experimental shape of IR spectra. Notice that the curve fitting procedure (frequency range 1900–1700 cm^{-1}, Lorentzian band-shapes, Lab Calc® software, Galactic Industries) has been necessary in order to measure both the optical densities and integrated areas of the three components observed.

The presence of free and associated species in the samples under study is also confirmed by the observation of characteristic features in the OH stretching region.

Theoretical Modeling

First principles calculations have been carried out with the following aims:

- to confirm the band assignments proposed on the basis of the experimental findings.
- to obtain a reliable prediction of the relative CO stretching transition dipole strength of free and associated molecules (both 2HB and 1HB).

This second point opens the way for building a model (based on measured IR intensities) that allows to estimate the fraction of hydrogen bonded molecules as a function of the total concentration of perfluorinated carboxylic acid in the solution.

The first step requires the choice of a (possibly small) molecular model. In the sketch (I) of Figure 1 a short chain is illustrated (CF_3–O–CF_2–COOH), that is supposed to mimic one functionalized end of the macromolecule under study (perfluoropolyether functionalized with carboxylic acid end group). The chemical groups that are supposed to be mainly affected by HB association are indeed present in our molecular model. Before analyzing the effect of intermolecular hydrogen bonding on the frequency and intensity of the C=O stretching band it is necessary to check whether conformational effects could introduce frequency shifts and/or intensity changes on the IR spectrum of the "free" molecule. Even if the sterical hindrance of fluorine atoms lowers the number of possible stable conformations (e.g. with respect to the case of hydrogenated species), we have recently demonstrated in the case of partially halogenated ethers that only an accurate consideration of the whole molecular structures corresponding to the different potential energy minima in the conformational space allows for a careful interpretation of the IR spectra.[10] For this reasons, effects ascribed to the presence of different conformers cannot be *a priori* overlooked. The conformational analysis presented here is developed as follows:

- determination of the potential energy surface (PES) as a function of the torsional angle (θ) defined by the sequence of atoms O1-C-C-O2 (see Figure 1.I).
- calculation and comparison of the IR spectra for the structures corresponding to the minima of PES.

As it can be seen from Figure 2.a, the more extended conformation ($\theta = 10°$) is only a relative minimum of the curve while two other (almost energetically equivalent minima) are found for $\theta = 115°$ and $\theta = -115°$. It should be noted that the energy barrier between these minima is quite small (about 0.7 kcal/mol), thus implying the occurrence of the three conformations already for relatively low temperatures. In Figure 2.b the calculated IR spectra of the three conformers are shown in the region of the C=O stretching band.

The effect of the molecular conformation on both frequency and intensity is found to be small; it is indeed completely negligible with respect to the effect expected in the case of intermolecular hydrogen bonding. This effect can be discussed with the help of DFT calculations that have been carried out for the three

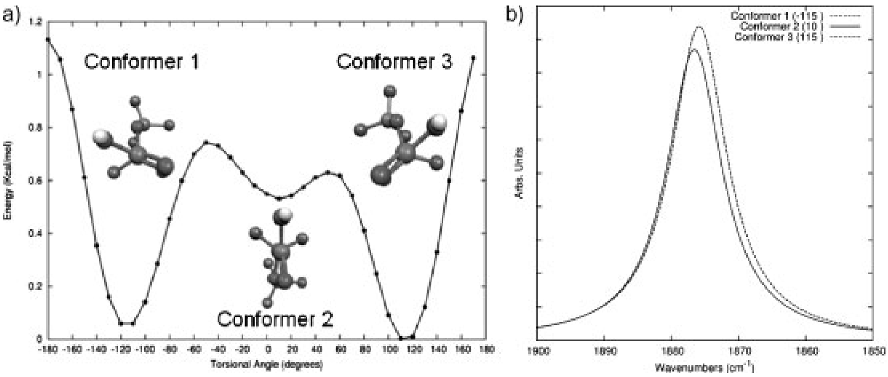

Figure 2.
(a) Torsional potential energy from DFT simulations. (b) Predicted infrared spectra (CO stretching region) for the three equilibrium structures of the molecule.

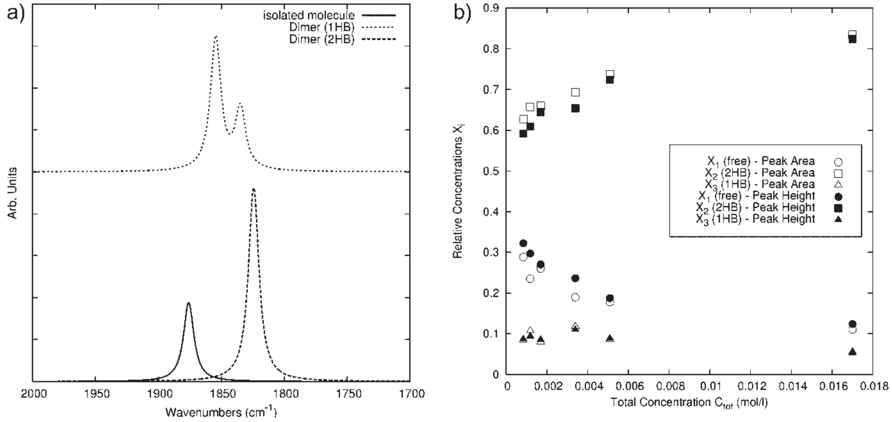

Figure 3.

(a) Predicted infrared spectra (CO stretching region for the isolated model molecule and two dimers (1HB and 2HB, see text). (b) Relative concentration of free and associated CO bonds as a function of the total concentration of functional groups (see text).

model systems represented in Figure 1, were the starting conformation of the model molecule corresponds to the conformer number 2 in Figure 2.a. IR spectra of the free molecule, the 2HB dimer and the 1HB dimer have been calculated and they are compared in Figure 3.

As expected, the frequency trend from DFT is consistent with experimental findings and confirms the assignment proposed above: a downshift in frequency is found for the 2HB dimer with respect to FM while the 1HB dimer shows intermediate frequencies, between FM and 2HB. As for the intensities, it should be noted that the total intensities of the dimers have to be divided by two in order to make a comparison with the CO stretching intensity of the free molecule (i.e. one should refer to the intensity of *one* associated CO bond). The so-normalized CO stretching intensities obtained from DFT calculations are:

$$a_{FM} = 273\ \mathrm{km/mol};$$

$$a_{2HB} = 363\ \mathrm{km/mol};$$

$$a_{1HB} = 361\ \mathrm{km/mol}.$$

These results show that the occurrence of intermolecular hydrogen bonds causes a slight increase of the intensity of the C=O stretching band.

Finally, we note that even if a stable geometry is found for 1HB dimers, a slight displacement from this equilibrium geometry, followed by a structure re-optimization often relaxes into the most stable 2HB dimer. Accordingly, it seems that the occurrence of 1HB dimers should be explained as a consequence of the interactions with the several solvent molecules present in the real system, that sometimes can hinder the relaxation into the more stable 2HB dimers. To this respect it must be also considered that the real molecules are much longer (and than less mobile) than the model molecule chosen in this work.

On the basis of the results obtained so far, a simple model has been built to estimate the evolution of the relative concentration X_i of the different CO species (FM, $i=1$; 2HB, $i=2$; 1HB, $i=3$) as a function of the total concentration C_{tot} of functional groups in a given sample. The following definitions have been applied:

$$C_{tot} = C_1 + C_2 + C_3;$$

$$X_1 + X_2 + X_3 = C_1/C_{tot} + C_2/C_{tot} + C_3/C_{tot} \equiv 1$$

The model makes use of the measured CO stretching intensity ratios Y_i, ($Y_i = I_i/I_{tot}$, $I_{tot} = I_1 + I_2 + I_3$, were I_i is the experimentally determined intensity of the band or component assigned to the i-th species). Relative intensities $R_2 = a_2/a_1$ and $R_3 = a_3/a_1$ of the associated CO oscillators with respect to the free one are introduced in the model taking the results from DFT calculations.

Following the definitions above and considering that $I_i \propto C_i\ a_i$, one obtains a system of three equations in the unknown X_1, X_2, X_3, namely:

$$\frac{I_1}{I_{tot}} = \frac{X_1}{X_1 + X_2R_2 + X_3R_3}$$

$$\frac{I_2}{I_{tot}} = \frac{X_2R_2}{X_1 + X_2R_2 + X_3R_3}$$

$$\frac{I_3}{I_{tot}} = \frac{X_3R_3}{X_1 + X_2R_2 + X_3R_3}$$

This system can be put in the form of an homogeneous linear system of three (linearly dependent) equations. Introducing in the system the theoretical values of the intensity ratio R_i (which are fixed by DFT predictions) and of the experimental ratios Y_i (which are deduced from the spectra of Figure 1.a) the system can be solved for every value of the total concentration. In this way, the evolution of the concentrations of each species can be investigated as a function of the total concentration of the functional groups in the sample.

In Figure 3.b the results of the model are shown both for Y_i values obtained as ratios of experimental peak height (optical densities) and as ratios of integrated band areas. As expected, the relative concentration of the 2HB cyclic dimers increases with total concentration while that of FM decreases; a slowly varying trend is obtained for 1HB dimers.

Moreover, the above obtained concentrations were used to evaluate the equilibrium constant K for the association of carboxylic functional groups, defined as follows:

$$K = ([\mathrm{Complex}])/[\mathrm{FM}]^2$$

Where Complex is defined as [Complex] = ([1HB] + [2HB])/2, since in the complex two functional groups are present. Using the data reported in Figure 3.b, we obtained a value for K of the order of 2000 L/mol, in agreement with literature for vapor phase association of neat trifluoroacetic acid (5000 L/mol)[9] and very different from trifluoroacetic acid in supercritical carbon dioxide (SC–CO_2) (50 L/mol).[9] We explain this behavior considering the low polarity of Fomblin® Z dilutant which is not expected to interact significantly with the functional groups, so stabilizing the complexes.

As a final check, absolute IR intensities have been obtained from the experimental spectra making use of the relative concentrations determined with the model. The values obtained after averaging over the whole set of experimental data at different total concentration are:

281 km/mol (FM); 371 km/mol (1HB);
373 km/mol (2HB).

These values are in very good agreement with DFT results, thus justifying the soundness of this approach.

Conclusions

In this study we presented experimental spectroscopic data on linear perfluoropolyether macromolecules bearing –COOH chain ends at different concentrations. First principles DFT calculations have been carried out on molecular models in order to evaluate the absolute CO stretching IR intensity for free and associated molecules. On this basis, a description of the system in terms of relative populations (associated/non associated molecules) is obtained from experimental IR intensity data. The knowledge of the relative concentration of free and bonded species allows to obtain an experimental determination of the absolute intensity of the CO stretching bands for the different species which favorably compares with the theoretically predicted values. Moreover, a third structure where the two interacting molecules are linked by just one hydrogen bond is observed and investigated.

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