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Quantum chemistry studies of unbranched fluoropolymers

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ABSTRACT

The results of quantum chemistry calculations of energy and topology parameters, vibration and NMR spectra of model fluorocarbon and unbranched hydrocarbon molecules are presented in this work. The formation of radicals and branches in fluorocarbon molecules and mechanisms of hydrogen substitution by fluorine at fluorination of hydrocarbon paraffins and polymers are discussed based on obtained results.

1. Introduction

Although fluorocarbon compounds, in particular, fluoropolymers find an extensive application in many fields of science and industry [1,2], understanding of their structural features and interpretation of experimental data are not always unambiguous, in spite of active experimental studies performed using different methods [3–6], and more detailed theoretical insight is in many cases of crucial importance. The complexity of fluoropolymer studies consists in the fact that in this case theoretical calculations might not be performed with taking into consideration all the factors responsible for the material structure and properties. For example, the basic fluoropolymer – polytetrafluoroethylene (PTFE) – belongs to the class of high-molecular systems of a molecular weight up to one million, whereas accurate calculations are possible only for fragments whose size is limited by a few dozens of atoms. Nevertheless, a number of parameters characterizing the molecular structure of small macromolecules would be also valid for polymers built from the above fragments and, moreover, low-molecular forms (telomers, fluoro paraffins) themselves have been recently in high practical demand as coatings, nanofilms and composites [7,8]. In the latter case the problem of unambiguous and reliable interpretation of empirical data can be solved by performing quantum chemistry calculations of geometric parameters, conformation, IR-, Raman and NMR-spectra of small macromolecules comprising the polymer forming units [6,9–11]. In [11–13] we demonstrated that within the scopes of *ab initio* quantum chemistry methods the calculations of the electronic structure, geometric parameters and some physical–chemical characteristics of the conformers $C_{13}F_{26}$ could be performed with an acceptable accuracy. The obtained theoretical data can be useful in studying the mechanisms of radiolysis (formation of radicals, sites of chain disruption etc.) and fluoropolymers thermal decomposition. Such quantum chemistry calculations can be also an efficient tool to investigate the processes occurring during the low-molecular fluoropolymers synthesis, in particular, at direct fluorination of hydrocarbon polymers [14].

In the present work we describe the results of quantum chemistry calculations of energy and topology parameters, vibration and NMR spectra of model fluorocarbon and unbranched hydrocarbon molecules and discuss the formation of radicals and branches in fluorocarbon molecules and mechanisms of hydrogen substitution by fluorine at fluorination of hydrocarbon paraffins and polymers.

2. Calculation details

The results of quantum chemistry calculations are known to depend to a great extent on the used calculation method and atomic orbital basis set. In the present work we used two non-empirical methods (*ab initio*): the Hartree–Fock (HF) method and the density function theory (DFT). Within the scopes of the HF approximation, each system electron is subjected to the mean field created by all other electrons (the so-called self-consistent field). Then the state of the molecule electron becomes the function of its coordinates in a potential field created by other electrons and nuclear charges. The HF method provides reliable results in solving many problems relevant to different molecular systems. This

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Table 1
Calculated and experimental values of geometric parameters and vibration frequencies of molecules CH_4, CH_3F, CF_4.

Method	HF (6-31G)	DFT (B3LYP, 6-311+G(d))	Exp. [17]
CH_4			
R(C–H), Å	1.08	1.09	1.09
ν_{as}, cm^{-1}	3296	3135	3018
ν_{δ}, cm^{-1}	1516	1355	1306
CH_3F			
R(C–H), Å	1.08	1.09	1.09
R(C–F), Å	1.41	1.39	1.38
$\nu_{\alpha s(C-H)}$, cm^{-1}	3345	3123	3165
$\nu_{s(C-H)}$, cm^{-1}	3246	3037	3045
$\nu_{\delta(HCH)}$, cm^{-1}	1659	1506	1534
$\nu_{(C-F)}$, cm^{-1}	1096	1037	1076
CF_4			
R(C–F), Å	1.340	1.33	1.32
$\nu_{\alpha\sigma}$, cm^{-1}	1428	1254	1283
ν_{δ}, cm^{-1}	628	571	632

method is conventionally used at the first level of calculations – estimation of structure and vibration frequencies of stable molecules [15], since it has limitations imposed as a result of neglecting the correlation effects – taking into account the electron–electron interaction. The latter situations are related to accurate simulation of energy reactions or bond dissociation. There exist several approaches, which enable one to improve the calculations accuracy, and the best results here are provided by the DFT method [15] adding an extra step to each HF calculation stage. In case of an efficient selection of the basis set, the method allows performing the calculations of energy and stability of the system of interest, geometry of molecular systems, vibration frequencies, and chemical shifts (NMR) with an acceptable accuracy. In the course of performing the calculations within the scopes of both methods (just like of other methods, too), the necessary condition consists in preserving unified calculation conditions (specified accuracy, method used, basis set etc.).

The final criterion of the adequacy of the results obtained consists in their juxtaposition with experimental data. To select the calculation method and optimal basis, in the present paper we performed test calculations of the geometry and vibration frequencies of the molecules, for which respective experimental data are available, and included the data from our earlier works [11–13]. The calculations were performed within the scopes of the HF (using the basis 6-31G) and DFT (using the functional B3LYP and basis 6-311+G(d)) methods by means of the program GAUSSIAN-03 [16]. The results presented in Table 1 were obtained for full geometry optimization in the systems under study.

The performed calculations of the test molecules CH_4, CH_3F, CF_4, as well as other fluorocarbon molecules and oligomers C_nF_{2n+2}, C_nF_{2n} [11–13], demonstrated that the values of bond lengths C–F, C–C and C=C were described satisfactorily within the scopes of both methods (DFT (B3LYP), basis 6-311+G(d) and HF (basis 6-31G)). The values of C–F and C–H bond energies in the molecules CF_4 and CH_4 obtained using the DFT (B3LYP) method (114 and 102 kcal/mol, respectively) are in good agreement with the experimental values (116 and 104 kcal/mol, respectively) [18,19]. The HF method yields substantially understated values (70 and 49.6 kcal/mol, respectively). However, as was demonstrated in [11], if emphasis is made on the comparison of energy parameters, for example, tendencies of energy changes, differences of full energies in conformers or bond dissociation energies in different parts of a molecule, both methods provide the same change tendencies and similar results, which are good agreement with the experiment. Analysis of calculations of vibration frequencies presented in Table 1 and comparison of calculated and experimental data for a number of fluorocarbon molecules [11–13] demonstrated that in general the DFT (B3LYP) method described the frequency values with an error not higher than 2–3%, while within the scopes of the HF method the error attains in some cases 7%. Usually [15] the problem of errors during the vibration frequencies calculation is solved by introduction of scaling coefficients. After application of these coefficients, the frequency values obtained using both of the methods are very close, which has become a grounding of the possibility of using the HF method in such studies with significantly lower computer time expenditures [12,13].

The NMR spectra calculations are facilitated by the fact that experimental studies are concerned with using not absolute values of the nuclei magnetic shielding, but their differences, which is expressed in the chemical shift relatively to a standard compound, for example, tetramethylsilane (TMS), hexafluorobenzene (C_6F_6), fluorotricholoromethane ($CFCl_3$) etc. In this case, the requirements to the calculation method used are not so rigid, and even the HF method yields acceptable results [15] (Table 2).

3. Results and discussion

The first important question arising during application of model quantum chemistry calculations can be formulated as follows: how can one build a model to make it possible to correlate the data obtained using it to a real object? Simultaneously, one should select, as was shown above, a relevant calculation method and an atomic orbital basis. Since in this case PTFE serves as the above mentioned real object, whereas its molecular structure is represented by zigzag-like infinite chains built from the coiled fragments $(–CF_2–)_n$ and it is suggested to examine this polymer destruction or synthesis by fluorination, then the molecules $(–CF_2–)_n$ and $(–CH_2–)_n$ were selected for calculations. The calculations were performed within the scopes of two methods: DFT (B3LYP) and HF. Similar calculations for three different conformations of the molecule C_4F_{10} were performed in [11]. The conclusions from the calculations related to the most advantageous configuration and the values of differences in conformation energies were in good agreement for both theoretical methods and experimental data. The above methods describe in an identical way the tendencies of changes of geometric parameters and vibration

Table 2
Calculated and experimental values of shielding constants and chemical shifts of benzene and hexafluorobenzene molecules.

Shielding				Shift relatively to TMS	Exp.
Calculation method		TMS	C_6H_6		
HF(6-31G)	$NMR^{13}C$	208	76.5	131.5	130.9 [15]
DFT(6-311+G(d))	$NMR^{13}C$	184	50.5	133.5	130.9 [15]
		$CFCl_3$	C_6F_6	Shift relatively to $CFCl_3$	
HF(6-31G)	$NMR^{19}F$	222	377	155	162 [20]
DFT(6-311+G(d))	$NMR^{19}F$	173	337	168	162 [20]

frequencies not only due to conformational change, but also as a result of chain elongation.

3.1. Formation of radicals in fluorocarbon molecules

Unbranched fluorocarbon materials, including PTFE, belong to radiation-sensitive materials whose chain disrupts in the process of irradiation [21]. This process is basic in the radiation method of PTFE destruction and production of PTFE micropowders and modified forms [3]. The studies of the materials obtained by this method revealed the presence of short-chain oligomers, branched structures and radicals [22]. The process of the PTFE chain disruption has been repeatedly investigated experimentally [23]. The radical formation in a model short-chain molecule C_nF_{n+2} can be represented by the following mechanisms:

$$CF_3-(CF_2)_n-CF_3 = CF_3-(CF_2)_n-CF_2^{\bullet} + F \quad (1)$$

$$CF_3-(CF_2)_n-CF_3 = CF_3-(CF_2)_k-CF^{\bullet}-(CF_2)_m-CF_3 + F \quad (2)$$

The bonding energy of the fluorine atom in the chain was estimated from the difference between full energy of the model fragment C_nF_{2n+2} under examination and the sum of full energies of the F atom and C_nF_{2i+1}. The calculations of the molecules C_4F_{10} performed within the scopes of DFT (B3LYP, 6-311+G(d)) yielded the following results:

$$E(C_4F_{10}) \rightarrow E(C_4F_{9t}) + E(F), \quad \Delta E = 115.5\ \text{kcal/mol} \quad (3)$$

$$E(C_4F_{10}) \rightarrow E(C_4F_{9c}) + E(F), \quad \Delta E = 106.3\ \text{kcal/mol} \quad (4)$$

Thus, in accordance with the performed calculations, the bonding energies of the fluorine atom at the chain end (CF_3-group) and inside the chain (OT CF_2-group) are different. This very fact is in compliance with the values of the C–F bond length inside and at the end of the chain (R(C–F$_c$) – 1.32 Å, R(C–F$_t$) – 1.30 Å). One should mention that these values are preserved in the molecule C_7F_{16} as well, while the C–F bonding energy is close to its experimental value in polytetrafluoroethylene (114.7 kcal/mol) [24]. Although the calculation of the same molecule performed within the scopes of the HF method (6-31G),

$$E(C_4F_{10}) \rightarrow E(C_4F_{9t}) + E(F), \quad \Delta E = 62.7\ \text{kcal/mol} \quad (5)$$

$$E(C_4F_{10}) \rightarrow E(C_4F_{9c}) + E(F), \quad \Delta E = 53.3\ \text{kcal/mol} \quad (6)$$

yields different absolute values, it demonstrates the same tendency and gives rise to the same conclusion. Moreover, the difference of energies of the disruption of the C–F bonds of configurations 1 and 2 is virtually the same (~9 kcal/mol). The difference of energies of the configurations 1 and 2 is insignificant; however, if irradiation results in removal of fluorine atoms, the obtained results indicate to a preferable character of the fluorine atom removal inside the chain.

On the basis of the estimation of bonding energies in the PTFE chain, in particular, the fact that the C–C bonding energy is substantially weaker than that of C–F (C–C=69.4 kcal/mol, C–F = 114.7 kcal/mol [24]), it was suggested in this work that irradiation of PTFE [25] disrupts preferentially weaker C–C bonds, while the C–F bonds remain intact. The latter is not in agreement with the revealed fact [22] of the branches formation in the PTFE chain during irradiation. Here a bulk of experimental data shows that irradiation results in formation of chain branching and cross-linking and, after increasing the irradiation dose, chain disruption.

According to [22], the branches formation in PTFE is assumed to occur according to the reaction:

$$\sim CF_2-CF^{\bullet}-CF_2 \sim \; + \; -CF_3 \rightarrow \; \sim CF_2-CF-CF_2 \sim CF_3$$

The hypothesis that branching takes place due to formation of side trifluoromethyl groups was repeatedly put forward [4,22,23,26] on the basis of studies of IR spectra of PTFE samples subjected to radiation, thermal and mechanical treatment. The calculations of energy parameters of the process of the CF_3-group addition to C_4F_9 radicals performed by the DFT (B3LYP, 6-311+G(d)) method:

$$E(C_4F_9)_c + E(-CF_3) \rightarrow E(C_5F_{12})_d, \quad \Delta E = 73\ \text{kcal/mol} \quad (7)$$

$$E(C_4F_9)_t + E(-CF_3) \rightarrow E(C_5F_{12}), \quad \Delta E = 78\ \text{kcal/mol} \quad (8)$$

(c – intra-chain radical, t – terminal radical) demonstrated that addition of the CF_3-group to a radical formed, for example, as a result of irradiation yielded the system stabilization. Here the system stabilization occurs independently of whether the trifluoromethyl group is added inside the chain or at the terminal position. The stabilization energy estimated from the difference between the sum of the fragments energies and the energy of the system formed during their integration are close for both cases. That is why if one suggests that irradiation results in removal of fluorine atoms with consecutive formation of radicals, then addition of the trifluoromethyl group will take place in the site of the radical formation.

The calculations performed within the scopes of the HF(6-31G) method produce the same conclusions:

$$E(C_4F_{9c}) + E(-CF_3) \rightarrow E(C_5F_{12})_d, \quad \Delta E = 57\ \text{kcal/mol}, \quad (9)$$

$$E(C_4F_{9t}) + E(-CF_3) \rightarrow E(C_5F_{12}), \quad \Delta E = 65\ \text{kcal/mol}. \quad (10)$$

Emerging of the trifluoromethyl group near the radical formed after affecting the fluorocarbon molecule is quite understandable. This group can form during the C–C bond disruption at the chain end, which results in formation of the terminal radical and trifluoromethyl group.

As seen from Fig. 1 representing the calculated IR-spectra of the C_5F_{12} molecules with conformations of a regular chain and that with a side CF_3-group, emerging of the branch (CF_3-group) is clearly identified by emerging of a band at 986 cm^{-1} in the IR spectrum (correction coefficient 1.01 during calculations within the scopes of DFT (B3LYP, 6-311+G(d)) and its absence in the spectra of unbranched conformers. This band is characteristic for stretching vibrations of a side trifluoromethyl group and, as seen from Fig. 1, is clearly distinguishable. Fig. 2 shows the IR-spectra of a longer molecule $C_{13}F_{28}$. The calculations were performed within the scopes of the HF (6-31-G) method using the correction coefficient 0.9. In general, one can see here the same result: emerging of a side trifluoromethyl group in the chain is accompanied by emerging of a band in the same range of the IR spectrum.

Analysis of experimental data demonstrates that in the IR-spectrum of the standard PTFE, which is known [27] to be built from C_nF_{2n+2} chains, the bands in the range 980–995 cm^{-1} are indeed absent. On the contrary, in the IR spectra of PTFE irradiated samples [22] or ultradispersed modifications obtained by polymer pyrolysis [23,26] the above range is characterized by the presence of rather weak, albeit in most cases identifiable, band at 986 cm^{-1}. This band is usually attributed to the –CF_3 groups' vibrations. The performed calculations enable one to correct the location of the –CF_3 group, namely in the side chain. The latter correction, however small could it be, is rather important, since it allows identification of the presence of branches (defects) in the materials under study. This conclusion is corroborated by increase of the band intensity at 986 cm^{-1} after pulse mechanical impact or pressure imposing on ultradispersed PTFE sample [23] (Fig. 3).

Aside from IR absorption spectra, the NMR method is an appropriate one in view of identification of emerging of side

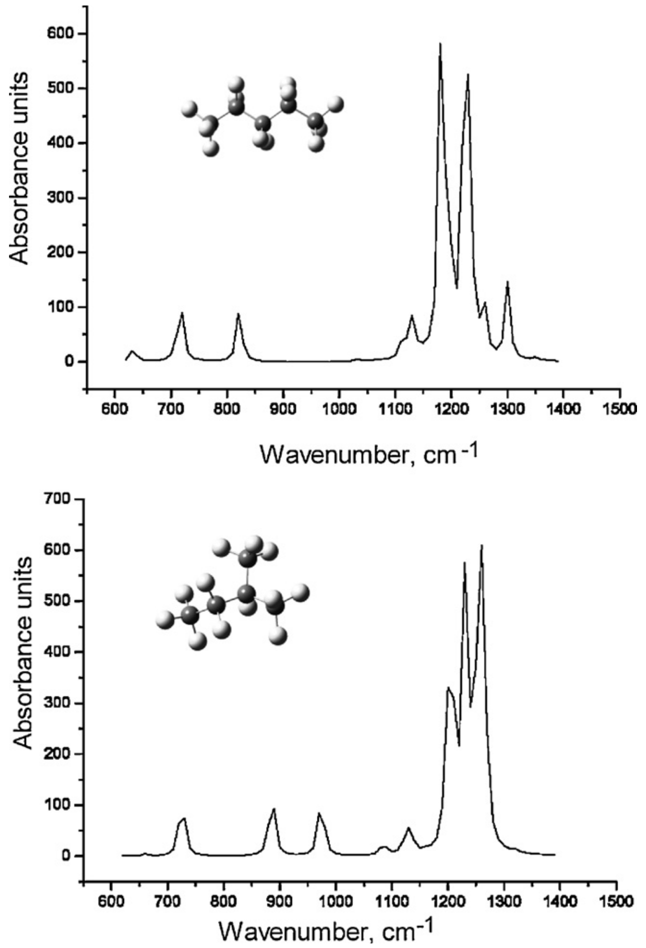


Fig. 1. Calculated IR-spectra of C_5F_{12} molecules with conformations of a regular chain and a chain with a side CF_3-group (DFT, B3LYP, 6-311+G(d)).

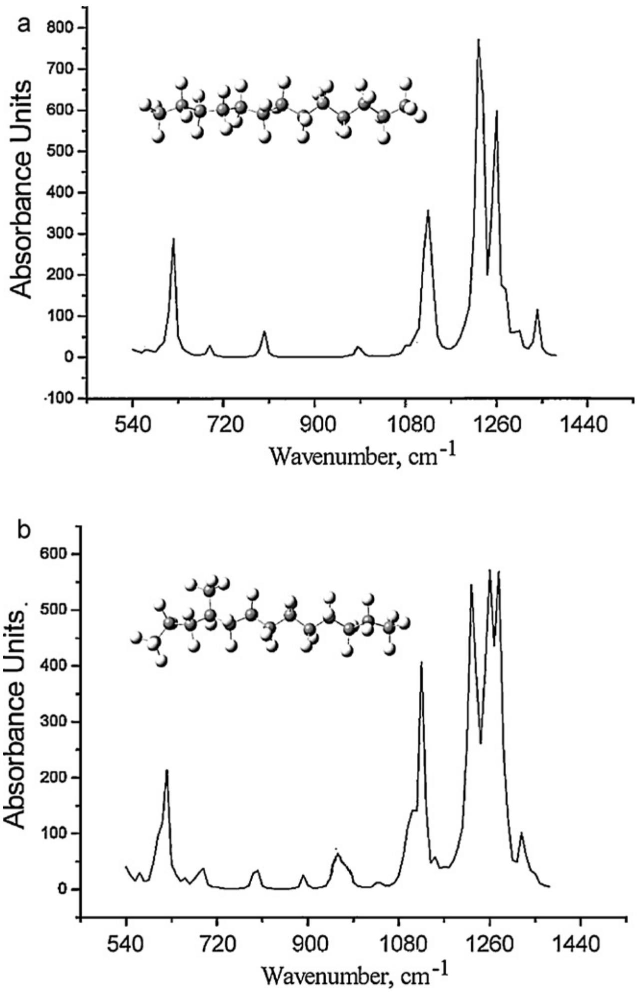


Fig. 2. Calculated IR-spectra of the molecule $C_{13}F_{28}$ (HF (6-31-G)).

groups. In the present work we obtained, by means of the calculation methods, the values of signals in ^{19}F NMR spectra of the unbranched molecule $C_{13}F_{28}$ and model molecules with different numbers of side branches due to formation of CF_3 groups. The calculations were performed within the scopes of the method HF (6-31-G), the chemical shift values were calculated relatively to the reference compound C_6F_6. One should mention that the values of chemical shifts of the unbranched molecule $C_{13}F_{28}$ are in good agreement with the experimental chemical shift values for ^{19}F NMR of polytetrafluoroethylene [28], its low-molecular form FORUM^{TM}, as well as the low-molecular fraction isolated from the FORUM^{TM} material (Fig. 4) which, as was shown in [29], consists mainly of short chains C_nF_{2n+2} ($n = 7–10$). According to the calculation data, the characteristic feature of emerging of side trifluoromethyl groups in an unbranched fluorocarbon molecule consists in the presence of the signals at 90–96 ppm and near −14 ppm (relatively to C_6F_6), corresponding to fluorine atoms in side CF_3 and C–F groups, respectively, in the ^{19}F NMR spectra. The experimental mass ^{19}F NMR spectrum of the low molecular fraction isolated from Forum material at 70 °C is shown in Fig. 4. The interpretation of the signals observed was done on the basis of the carried out calculations. The made interpretation fits with the assumptions made on the basis of infrared spectroscopic study.

3.2. Fluorination of hydrocarbon polymer

Another way of producing low-molecular fluoropolymers is concerned with fluorination of hydrocarbon materials, such as paraffin and low-molecular polyethylene. The quantum chemistry calculations can serve as an efficient tool to study the processes of formation of these polymers and make a substantial contribution to interpretation of experimental data obtained by means of the methods of vibration spectroscopy, NMR and XPS, which are usually applied to control the process of the polymers pretreatment and investigate the produced materials structures. The calculation data are also important for understanding of technological processes of hydrocarbon molecules fluorination. Let us examine the process of hydrocarbon material fluorination on the example of the model molecule $C_{10}H_{22}$ with consecutive substitution of hydrogen atoms by those of fluorine.

Fluorination (proton substitution by fluorine) can proceed in two ways: hydrogen atom substitution at the chain end (Fig. 5(1)) or inside the chain (Fig. 5(2)). According to the calculation data for the reaction $C_{10}H_{22} \rightarrow CH_{21} + H$, the bond energy of the proton in the end group is equal to 89.6 kcal/mol, whereas the respective value for the intra-chain proton is equal to 86.5 kcal/mol. Therefore, the preferable substitution must proceed on the intra-chain protons, and the configuration with the fluorine atom inside the chain will be preferable in energy terms for the fragment $C_{10}FH_{21}$.

This is indeed the case: full energy of the $C_{10}FH_{21}$ molecule configuration is equal to: −490.179 a.u. (atomic units) at intra-chain substitution and −490.170 a.u. at end substitution.

According to the calculation data, emerging of just one fluorine atom in the $C_{10}H_{22}$ molecule chain results in changes in the vibration spectra. The changes in the range of deformation

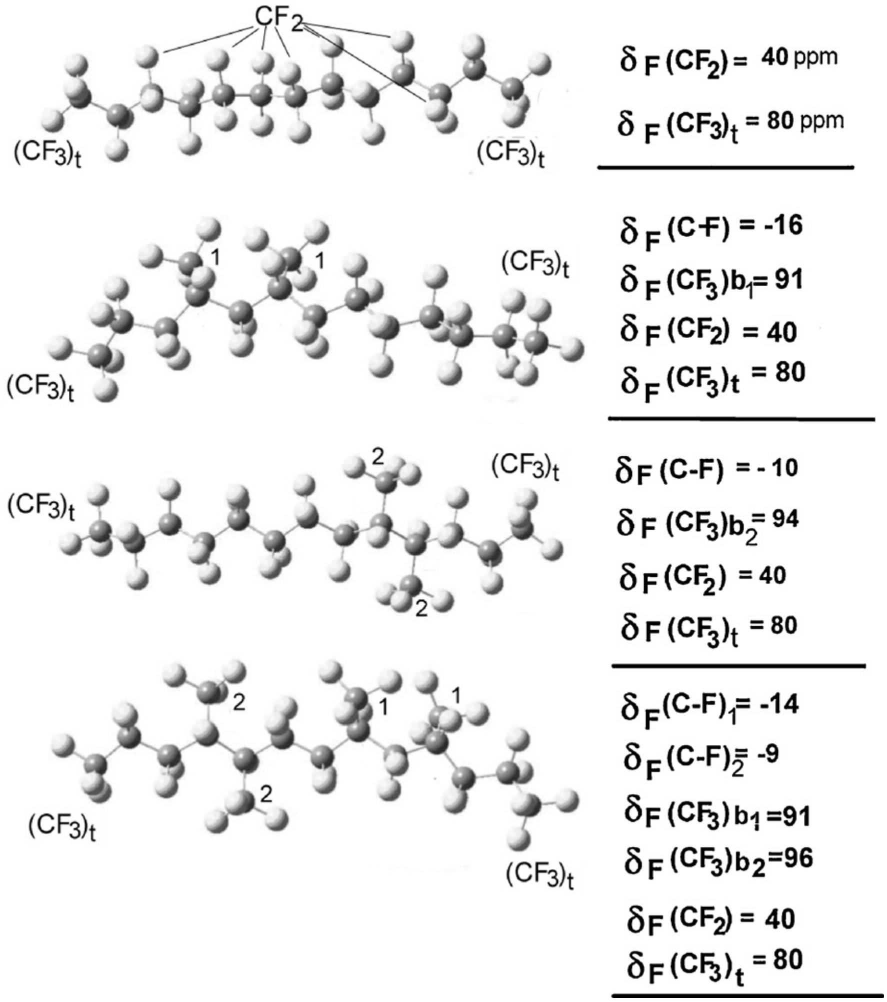


Fig. 3. Models with different locations of CF_3 groups and ^{19}F NMR chemical shift values (ppm) calculated for them: 1 – $(CF_3)b1$, 2 – $(CF_3)b2$.

vibration of the molecule $C_{10}H_{22}$ (1000–1500 cm^{-1}) are expected, since the stretching vibrations C–F are located in this very range (~1200 cm^{-1}).

However, since emerging of fluorine atom in a chain not only shifts the electronic density to the fluorine atom in the fragment H–C–F, but also, results re-distribution of electron density over the whole chain, as seen from Fig. 6 spectrum becomes more complex.

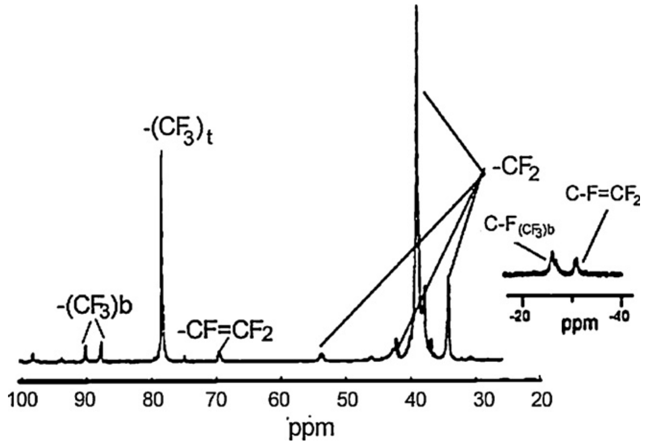


Fig. 4. Experimental ^{19}F NMR spectrum (at room temperature) of the FORUM^{TM} fraction separated at 70 °C [29] interpreted on the basis of quantum chemistry calculation results.

There emerge new bands corresponding to vibrations contributed by valent C–F vibrations and deformation vibrations of CH_2 groups adjacent to this specific carbon atom, as well as the bands attributed to out-of-plane vibrations of CH_2 groups adjacent to the carbon atom bonded to the fluorine atom. The net result here consists in experimentally observed IR spectrum complication.

At further fluorination – increase of the number of protons substituted by fluorine in the chain – the number of substitution variants also increases. A fluorine atom can substitute the second proton in the end group and belong to one or different carbon atoms in a chain. The calculations of different configurations of the model molecule $C_{10}F_2H_{20}$ demonstrated that the configuration with intra-chain substitution, in which both fluorine atoms belong to the same carbon atom, would be the most preferable in energy terms (Table 3). The reason here is concerned with the peculiarities of distribution of electronic density in a chain resulting in differences (albeit negligible ~2 kcal/mol) in proton bond energies in the groups H–C–F and H–C–H. According to the calculation data, the proton bond energy in the group H–C–F in $C_{10}FH_{21}$ molecule is equal to 84.6 kcal/mole, whereas in the group H–C–H it is equal to 86.5 kcal/mole. Besides, such a configuration is characterized by the lowest distortion of the carbon chain network (Table 3).

As expected, the vibration spectra differ in the cases of different configurations. It appears natural to assume (and this fact correlates to the calculation data) that only in the IR spectrum of the configuration preferable in energy terms one must observe the band characterizing the vibrations of the group CF_2, according

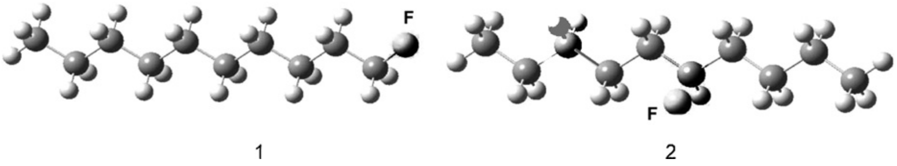


Fig. 5. Calculated models of the molecule $C_{10}FH_{21}$.

to the calculation data, at 1163 cm^{-1}. For all other configurations this part of the spectrum does not have any bands. Re-distribution of the electron density along the chain and emerging of structurally non-equivalent groups CH_2 in it (related to emerging of groups bound and unbound to fluorinated groups) result in changes of the spectrum in the range of valent vibrations C–H as well. In particular, the band characterizing asymmetric vibrations C–H in CH_2 groups of the molecule $C_{10}H_{22}$ split in the spectrum of the $CH_{21}F$ molecule and, besides, there emerge the bands corresponding to vibrations of CH_2 groups located in different parts of the chain. Naturally, the intensity of bands characterizing valent vibrations C–H decreases in the course of increase of the polymer fluorination degree.

The changes of the IR spectrum in the range of valent vibrations with increase of the fluorination degree are clearly demonstrated by Fig. 7. The up-to-date instruments of high resolution and sensitivity allow experimental detection of the changes in IR spectra at fluorination of carbon polymer by means of calculation methods.

Since the main reason of the changes of molecular parameters at proton substitution by fluorine consists in re-distribution of the electronic density in a chain, it seems reasonable to assume that the chemical shifts of NMR spectral bands would be sensitive to the fluorination process. The performed calculations demonstrated that the ^{19}F NMR spectrum of the $CH_{21}F$ molecule contained a signal at 47 ppm (relatively to C_6F_6), whereas in the ^{13}C NMR spectrum there emerged a new band at 53 ppm corresponding to the carbon atom bound to fluorine atom. If the substitution occurs at the chain end (in the CH_3 group), there occur the shifts of the ^{19}F and ^{13}C NMR signals to 67 and 65 ppm, respectively. From the calculation data, the ^1H NMR spectrum of the molecule $C_{10}H_{22}$ is characterized by the group of adjacent bands (32.3–32.6 ppm), while in the ^1H NMR spectrum of the molecule $C_{10}H_{21}F$ the band degeneracy is eliminated and there emerges the signal at 29.2 ppm (proton in the group CHF).

It is easy to identify the most stable configuration of the molecule $C_{10}F_2H_{20}$ from NMR spectra: this configuration is characterized by the presence of signals with the lowest shielding

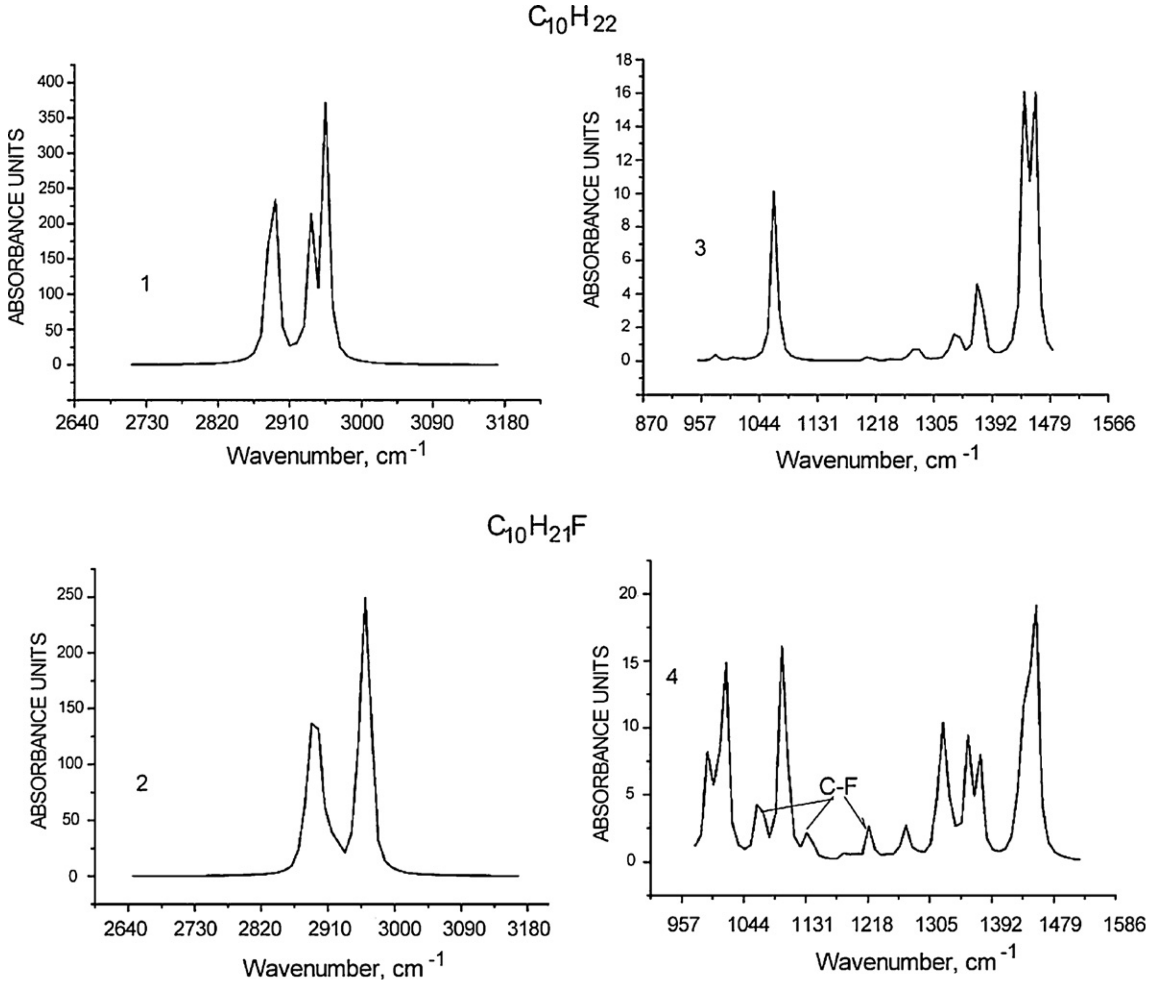
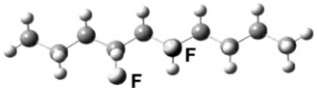
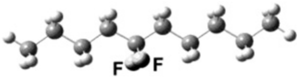
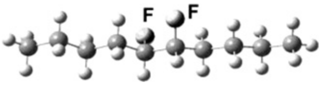
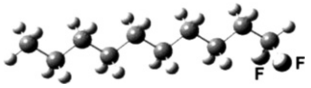


Fig. 6. Calculated IR absorption spectra of molecules $C_{10}H_{22}$ (1 and 2) and $C_{10}H_{21}F$ (3 and 4).

Table 3
Values of full energy (*E*, a.u.), shielding constants (ppm) and dihedral angles (°) of the molecule $C_{10}F_2H_{20}$.

Molecule	$-E$	^{19}F NMR	^{13}C NMR	^1H NMR	Dihedral angle	Configuration
$C_{10}F_2H_{20}$	589.013	427.563	120.83	28.63	−178.4	
						
		427.716	170–195	32		
$C_{10}F_2H_{20}$	589.005	411.438	119.84	29.0	174.2	
						
		423.344	120.44			
			170–195	32		
$C_{10}F_2H_{20}$	589.019	346.805	85.89	31.38	−179.9	
						
		346.821	170–195	32		
$C_{10}F_2H_{20}$	589.009	433.94	118	29.5	179.6	
						
			177–193	32		
$C_{10}F_2H_{20}$	589.006	435.23	117	29.5	166.2	
						
			178–193	32		
$C_{10}F_2H_{20}$	589.006	354.76	94.73	28	179.9	
						
			176–193	32		

constant values related to the signal of the fluorine atom and bound to it carbon atom (Table 3). The obtained values are similar to those for the fluorocarbon chain built from CF_2 fragments. In particular, as was shown by the calculations of the $C_{13}F_{28}$ molecule, the shielding constants of fluorine atoms are located within the range 340–344 ppm, whereas the carbon atom constants are equal to 98 ppm. Further fluorination will be accompanied by increase of the number of signals in both ^{19}F and ^{13}C NMR spectra. The latter is concerned with the fact that shielding in the groups CF_2 and CHF is substantially different (Table 3, Fig. 8).

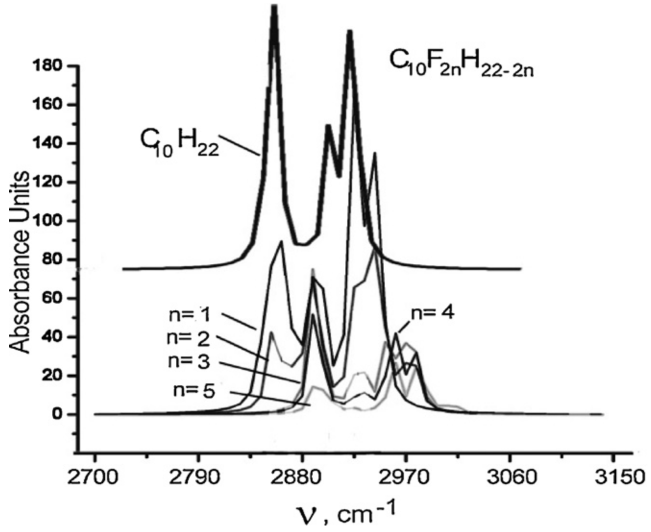


Fig. 7. Calculated IR absorption spectra of the molecule $C_nF_{2n}H_{22-2n}$.

If during incomplete fluorination only CF_2 groups are formed in the chain, which is, as was shown above, the most probable situation, the ^{19}F NMR spectrum is also characterized by the group of adjacent signals in the range 339–349 ppm. Significant differences between incomplete and complete chain fluorination are observed in the ^{13}C NMR spectrum, since the carbon atoms are associated with the signals as follows: CH_2 groups – in the range 170–200 ppm (Fig. 8); CHF groups – at 117 ppm (Table 3); CF_2 groups – at 80 ppm. There are no signals at 170–200 and 117 ppm in the ^{13}C NMR spectra of the chains C_nF_{2n+2} (Fig. 9).

During complete fluorination, in the ^{19}F NMR spectra (in the range 339–341 ppm) one can observe an intensive signal corresponding to fluorine signals in CF_2 groups. However, as was demonstrated above, in the case of complete fluorination of a short-chain oligomer (Fig. 3) one might reveal the signals from the fluorine atoms of the end CF_3 groups (294–299 ppm, according to the calculation data). The latter is in agreement with the experimental data for the low-molecular fraction of polytetrafluoroethylene, for which such signals were indeed found [4,28,29]. Finally, it is quite expected that at incomplete chain fluorination the ^1H NMR spectra would contain proton signals (near 32 ppm), whereas, according to the calculation data, the higher is the fluorination degree, the narrower is the signal.

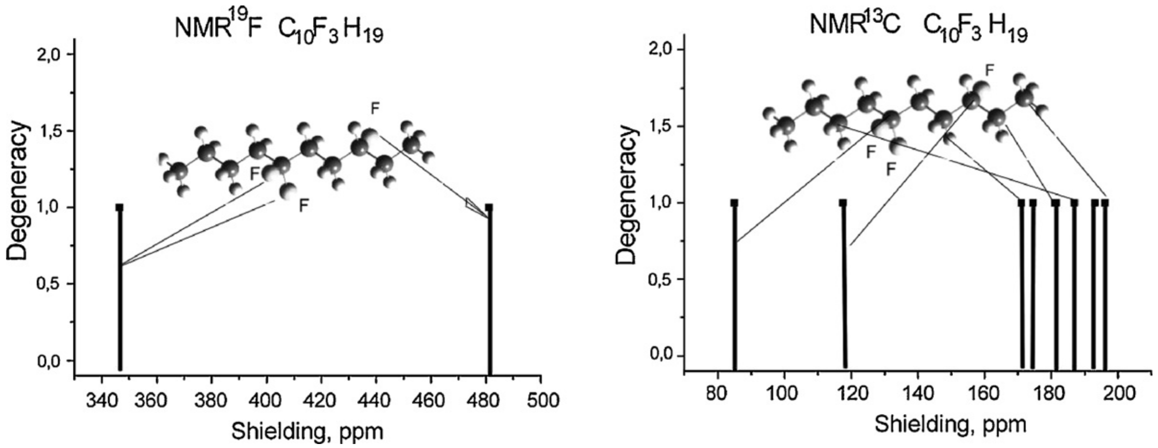


Fig. 8. ^{19}F and ^{13}C NMR spectra of the molecule $C_{10}F_3H_{19}$.

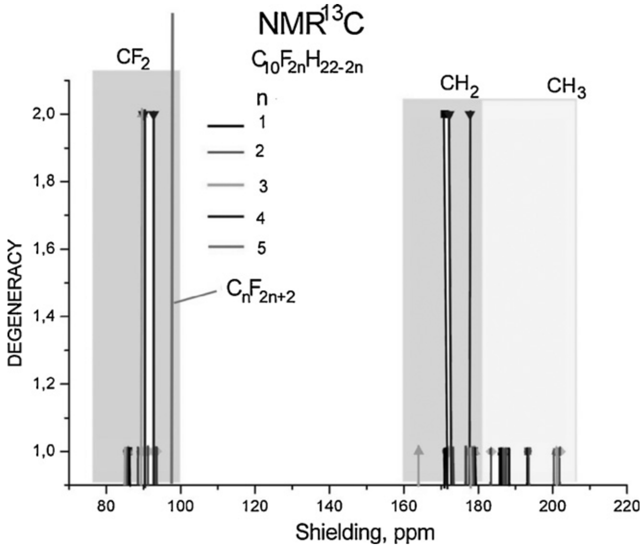


Fig. 9. Calculated ^{13}C spectra of the molecules $C_{10}F_{2n}H_{22-2n}$.

4. Conclusions

Two non-empirical quantum-chemical methods (*ab initio*): HF and DFT were used to calculate energy and topological parameters, IR- and NMR-spectra of the C_nF_{2n-2} and $C_{10}F_nH_{22-n}$ model molecules. The formation of radicals and branching in fluorocarbon molecules and fluorination of the hydrocarbon polymers are discussed on the basis of obtained results. The characteristics features of IR and NMR spectra, which can identify the emergence of CF_3 branches in C_nF_{2n-2} chains, have been revealed. The preferred configurations of fluorine-substituted paraffins were found. It has shown capabilities to control the serial and partial fluorinations of hydrocarbon polymers by the changes in the IR and NMR spectra.

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