

Article

Density Functional Theory Calculations for Interpretation of Infra-Red Spectra of Liquid Crystalline Chiral Compound

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Abstract: The experimental IR spectra of (S)-4'-(1-methylheptyloxycarbonyl) biphenyl-4-yl 4-[2-(2,2,3,3,4,4,4-heptafluorobutoxy) ethyl-1-oxy]-2-fluorobenzoate in the crystal phase are analyzed with the help of dispersion-corrected density functional theory (DFT+D3) calculations for isolated molecular monomer and dimer models, and a periodic model computed at the extended density functional tight-binding (xTB) level of theory. It is found that the frequency scaling coefficients obtained with the results of the molecular calculations are good matches for the crystal phase, being close to 1. The molecular and periodic models both confirm that varied intra- and intermolecular interactions are crucial in order to reproduce the broadened shape of the experimental band related to C=O stretching; the key factors are the conjugation of the ester groups with the aromatic rings and the varied intermolecular chemical environments, wherein the C=O group that bridges the biphenyl and F-substituted phenyl groups seems particularly sensitive. The C=O stretching vibrations are investigated as a function of temperature, covering the range of the crystal, smectic C_A^{*}, smectic C^{*} and isotropic liquid phases. The structure changes are followed based on the X-ray diffraction patterns collected in the same temperatures as the IR spectra. The experimental and computational results taken together indicate that the amount of weak C=O...H-C hydrogen bonds between the molecules in the smectic layers decreases with increasing temperature.

Keywords: smectic liquid crystal; FT-IR spectroscopy; DFT calculations; scaling coefficient; Fourier transform



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1. Introduction

Theoretical infra-red (IR) spectra simulated for isolated molecules by density functional theory (DFT) calculations are usually in agreement with the experimental spectra to the extent that enables the assignment of the observed absorption bands to intramolecular vibrations [1–6]. This is especially beneficial for liquid crystals, whose molecules consist of numerous atoms and consequently usually require a long computing time. On the other hand, the introduction of more molecules into calculations, by using dimers, trimers or periodic boundary conditions, provides the opportunity to include the effect of intermolecular interactions [5–7]. This paper presents the detailed analysis of the IR spectra of smectogenic (S)-4'-(1-methylheptyloxycarbonyl) biphenyl-4-yl 4-[2-(2,2,3,3,4,4,4-heptafluorobutoxy)ethyl-1-oxy]-2-fluorobenzoate [8–10], denoted as 3F2HPhF6 (Figure 1). On heating in the crystal phase, 3F2HPhF6 undergoes phase transitions in the sequence of Cr (325.7 K) SmC_A^{*} (364.5 K) SmC^{*} (372.3 K) Iso [10]. The Cr and Iso notations correspond to the crystal and isotropic liquid phases, while SmC_A^{*} and SmC^{*} denote the chiral tilted smectic phases: antiferroelectric smectic C_A^{*} and ferroelectric smectic C^{*}. The tilt angle in the SmC_A^{*} phase of 3F2HPhF6 and similar

compounds with a partially fluorinated terminal chain takes values close to 45° ; therefore, they are investigated as components of the orthoconic liquid crystalline mixtures to be applied in displays [8,11–14]. The experimental IR spectra of this compound had been previously reported only for the solution in CCl_4 and in the crystal phase in room temperature, and the full band assignment had not been performed [9,10]. Herein, the band assignment is based on the DFT+D3/BLYP-def2SVP calculations, performed for an isolated molecule in two different conformations, and, to include the intermolecular interactions, for head-to-head and head-to-tail dimers (Figure 1). The DFT molecular models are complemented with explicitly periodic models of an idealized tilted smectic phase at the extended density functional tight-binding (xTB) level of theory, primarily to obtain insight into how the intermolecular interactions of the crystal environment may broaden the C=O band shape. The temperature dependence of selected absorption bands is discussed. The interpretation of the IR spectra is supported by the X-ray diffraction (XRD) measurements, which enable the observation of the structural changes with temperature [15–18].

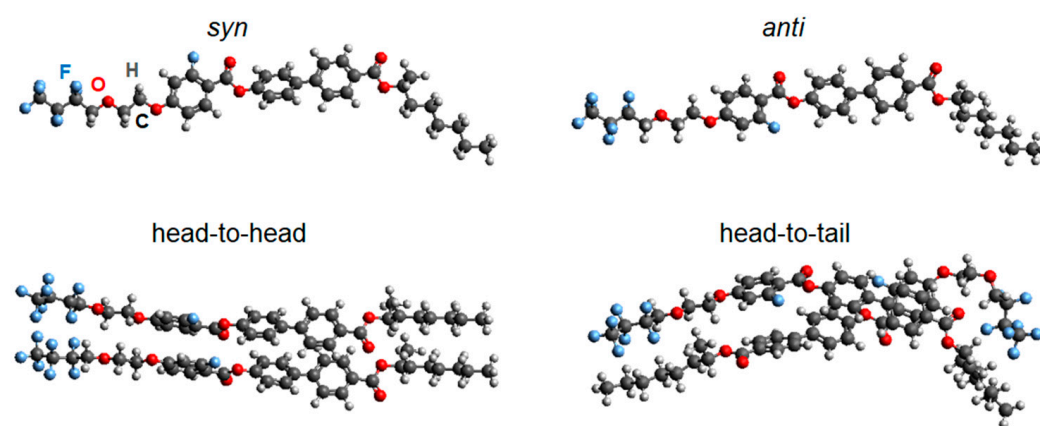


Figure 1. 3F2HPhF6 molecule in the *syn* and *anti* conformations, and two types of dimers consisting of molecules in the *anti* conformations, optimized with DFT+D3/BLYP-def2SVP. The symbols of atoms, given for the *syn* conformation, apply also for other models.

2. Materials and Methods

The mesogenic compound (*S*)-4'-(1-methylheptyloxycarbonyl) biphenyl-4-yl 4-[2-(2,2,3,3,4,4,4-heptafluorobutoxy) ethyl-1-oxy]-2-fluorobenzoate was synthesized according to the general method presented in [10,19].

The experimental IR spectra for the 3F2HPhF6/KBr tablet were measured upon heating at 273–393 K in the wavenumber range of $480\text{--}4000\text{ cm}^{-1}$ with a resolution of 2 cm^{-1} using the Bruker VERTEX 70v vacuum spectrometer (Bruker, Billerica, MA, USA) equipped with an Advanced Research System DE-202A cryostat and ARS-2HW water-cooled helium compressor (ARS, Macungie, PA, USA).

The simulated IR spectra were calculated with the DFT method in Gaussian09 [20] using the def2SVP basis set [21] and the BLYP exchange-correlation functional [22,23] with Grimme's semi-empirical dispersion corrections and Becke–Johnson damping [24,25]. The calculations were performed for an isolated molecule (a hockey-stick-shaped model, introduced in [7]) in two conformations differing in the position of the F atom (Figure 1). In the *syn* conformation, the F atom and a neighboring C=O group are on the same side of the benzene ring, while in the *anti* conformation they are on the opposite sides. Additionally, the IR spectra were calculated for two dimers consisting of molecules in the *anti* conformation, arranged in the head-to-head and head-to-tail manner. The molecular models were visualized in Avogadro [26]. The IR data were analyzed in OriginPro.

The periodic lattice was built by initially placing the molecules (in the more stable *anti* conformation) on a hexagonal lattice with 6 Å spacings between neighboring molecules

(the rigid core was initially aligned to be perpendicular to this hexagonal lattice), and then rotating the rigid core by 45° towards the plane of the lattice; the resulting models loosely represent idealized layers of a tilted smectic phase. Finally, a supercell, with cell vectors **a** and **b**, was constructed from the primitive hexagonal lattice vectors, **u** and **v**, via the following cell transformation: $\mathbf{a} = 1\mathbf{u} - 2\mathbf{v}$ and $\mathbf{b} = 3\mathbf{u} + 1\mathbf{v}$; this generated a simulation cell with seven molecules and ensured that no molecules were in direct contact with their own mirror images. It also created a model with intermolecular nearest-neighbor interactions that consisted exclusively of head-to-head relative orientations; such a setup most easily allowed us to create a close-packed distribution of 3F2HPhF6 molecules. The geometry optimizations and molecular dynamics simulations were run with the DFTB module of the Amsterdam Modelling Suite (AMS) [27], version 2023.1, and all simulations sampled only the gamma k-point and used the GFN1-xTB method [28]. After being equilibrated with NVE (constant particle number, volume and energy) and NVT (constant particle number, volume and temperature) simulations with the Berendsen thermostat, the final molecular dynamics simulations were performed at 250 K with the default Nose-Hoover thermostat that is implemented in the AMS program (the oscillatory period of the thermostat was set to 400 fs). To assess the dynamic contributions to the C=O vibrational band shape, the discrete Fourier transform was applied to the time evolution of each C=O distance in the molecular dynamics simulations, similar in spirit to what has been described before in the literature [29,30]. The production run lasted 6 ps, resulting in a frequency resolution of $\sim 8\text{ cm}^{-1}$ after the discrete Fourier transforms were applied.

The XRD patterns of the flat sample of 3F2HPhF6 were collected upon heating at 273–393 K in the angular 2θ range of $2\text{--}30^\circ$ using the Bragg–Brentano geometry. The measurements were performed with $\text{CuK}\alpha$ radiation ($\lambda = 1.5406\text{ \AA}$) with an X'Pert PRO (PANalytical, Malvern, UK) diffractometer with a TTK-450 (AntonPaar, Graz, Austria) temperature stage. The XRD results were analyzed in WinPLOTR 7.20 Oct2019 [31] and OriginPro 2020b.

3. Results and Discussion

3.1. Band Assignment

The simulated IR spectra, calculated with DFT+D3/BLYP-def2SVP, and the experimental IR spectrum of the 3F2HPhF6 compound in the crystal phase, measured at 253 K, are compared in Figure 2. The particular parts of the 3F2HPhF6 molecule are denoted by letters (a–j), as shown in Figure 3, and the detailed band assignments based on the simulated spectra are gathered in Tables 1–3. The notations of the vibrational motions in the tables are as follows: β —in-plane deformations of the aromatic ring, γ —out-of-plane deformations of the aromatic ring, δ —scissoring, ν —stretching, ρ —rocking, τ —twisting, ω —wagging. The absorption bands in the wavenumber range of $500\text{--}1000\text{ cm}^{-1}$ are assigned to the in-plane and out-of-plane deformations of the aromatic rings, scissoring vibrations in the terminal chains, wagging of the CF_2 and CH_2 groups, and twisting of the CH_2 groups. Most of the bands in the $1000\text{--}1400\text{ cm}^{-1}$ range originate from the in-plane deformations of the aromatic rings, wagging and twisting of the CH_2 groups and stretching of the C–C and C–O bonds in the terminal chains and in the spacer between the benzene ring and biphenyl. There are also bands assigned to the CH_2 rocking and C–F stretching. The $1400\text{--}1650\text{ cm}^{-1}$ range contains bands attributed to the in-plane deformations of the benzene rings and CH_2 wagging and scissoring. Three absorption bands between 1650 and 1750 cm^{-1} are related to the stretching of two double C=O bonds. The bands with the wavenumbers of $2800\text{--}3000\text{ cm}^{-1}$ originate from the C–H stretching vibrations in the terminal chains.

There are four differences between the DFT+D3/BLYP-def2SVP simulated spectra for the isolated molecule in the *syn* and *anti* conformations, which are the most significant:

(1) The proximity of the F atom and C=O group in the *syn* conformation leads to the strengthening and shifting of the band related to the in-plane deformations of the

aromatic rings and C–C and C–O stretching in the non-chiral chain to lower wavenumbers: 1008.8 cm^{-1} (*syn*) and 1013.5 cm^{-1} (*anti*).

(2) The location of the strongest absorption band is different for each conformation. For *syn*, it is the band at 1197.3 cm^{-1} , related to the in-plane deformations of the aromatic rings and C–C and C–O stretching in the spacer between the benzene and biphenyl part. For *anti*, the strongest band is at 1247.6 cm^{-1} and has the same origin as for *syn*, in addition of the C–C and C–O stretching of the bonds between the biphenyl part and the chiral center, as well as the CH₂ twisting in the chiral chain.

(3) The simulated spectrum of *syn* contains a strong band at 1365.6 cm^{-1} arising from the in-plane deformation of the fluorinated benzene ring and CH₂ wagging in the non-chiral chain, which is absent for *anti*.

(4) The bands related to the C=O stretching are strongly split for *syn* and located at 1719.1 cm^{-1} and 1756.5 cm^{-1} for C=O groups in the molecular core and close to the chiral center, respectively. Meanwhile, for *anti*, these bands are close to each other, at 1718.5 cm^{-1} and 1719.9 cm^{-1} , and each of them is related to the stretching of both C=O groups, anti-phase at a lower wavenumber and in-phase at a higher wavenumber.

To make an assignment for the experimental absorption bands purely from the results of the isolated molecule, it is necessary to consider the results for both the *syn* and *anti* conformations. This is especially visible for the C=O stretching bands: the experimental spectra contain three such bands, while the calculations for the isolated molecule presume only two bands in this region; this matter was discussed also in [9]. Meanwhile, the simulated spectra for the dimers enable the full assignment of the experimental IR spectrum. Namely, there are four C=O vibrations predicted for each dimer. For the head-to-head model, the positions of the bands are close to the ones obtained for the isolated molecule in the *syn* conformation. For the head-to-tail model, the splitting of the C=O stretching bands is also visible but their wavenumbers are shifted towards lower values than those of other models (Figure 2). Noteworthy, the splitting of the C=O stretching bands in the dimers is not caused by the proximity of the C=O group in the molecular core and the F atom substituted in the benzene ring, as it is for the *syn* model. In both dimers, the F atoms from one molecule are not in close contact with the C=O group from the neighboring molecule. The closest F–O contact, where O belongs to the C=O group, is 2.7 Å in the *syn* model and 4.2 Å in the *anti* model. In the head-to-head dimer, the closest F–O contact is also 4.2 Å , between atoms within the same molecule, and the closest F–O contact between atoms from different molecules is slightly larger, at 4.5 Å . For the head-to-tail dimer, the closest F–O contact is between atoms from different molecules and equals 3.8 Å . In this last case, the F atom is located in the terminal chain, not in the aromatic core. This indicates that the splitting of the C=O stretching bands does not have to be caused only by the proximity of the C=O group and F atom, as the interactions with other neighboring atoms may have a similar effect.

Figure 4 shows the plots of the experimental vs. calculated wavenumbers with the linear fits performed with an intercept fixed to zero to determine the scaling factor, equal to the slope of the fitted line [32], that can thus be used to assess the quality of a reproduction of the measured frequencies by the computations. The scaling factor $0.994(2)$ is close to 1 for results for the isolated molecule in both conformations, taken as one dataset. For the dimers, the scaling factor is $0.998(3)$ and $0.996(3)$ for the head-to-head and head-to-tail model, respectively. For all the linear fits, the coefficient of determination R^2 , defined according to [33], is also close to 1, which indicates good agreement with the assumed linear dependence. The linear fits performed in the ranges of $<1000\text{ cm}^{-1}$, $1000\text{--}2000\text{ cm}^{-1}$, and $>2000\text{ cm}^{-1}$ show that the calculated peak positions are mainly underestimated below 2000 cm^{-1} and overestimated above 2000 cm^{-1} (Table 4).

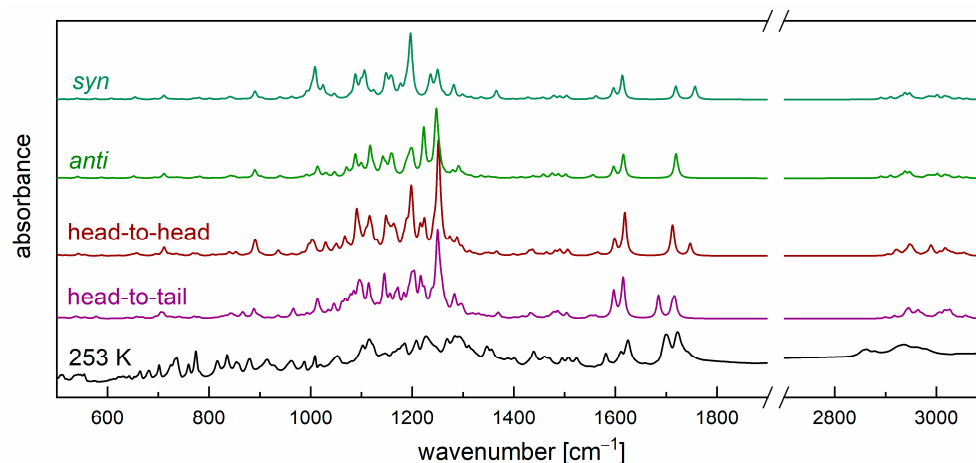


Figure 2. IR spectrum of 3F2HPhF6 measured in the crystal phase in 253 K, compared with simulated IR spectra for the isolated molecule in *syn* and *anti* conformations, and for two dimers.

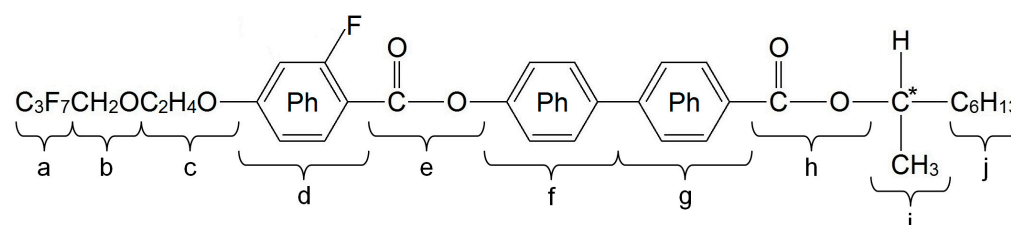


Figure 3. Notation of parts of the 3F2HPhF6 molecule used in assignment of IR absorption bands.

Table 1. Band assignments of the IR spectrum measured for 3F2HPhF6 in the crystal phase at 253 K (exp), based on DFT+D3/BLYP-def2SVP calculations for the isolated molecule in *anti* and *syn* conformations (calc). The wavenumbers are given in cm^{-1} . See the text for the notations of the vibrational motions.

exp	calc, <i>syn</i>	calc, <i>anti</i>	Description
511	497.3	496.2	$\delta\text{CCC}(\text{j})$
542	539.7	540.8	$\delta\text{CF}_2(\text{a}), \delta\text{COC}(\text{b,c}), \beta_{\text{asym}}\text{Ph}(\text{d})$
554	552.5	554.7	$\gamma\text{Ph}(\text{f,g})$
622	607.9		$\beta_{\text{asym}}\text{Ph}(\text{d,f,g})$
630		610.4	$\beta_{\text{asym}}\text{Ph}(\text{d,f,g})$
643	627.5	628.2	$\gamma\text{Ph}(\text{d})^{\text{syn}}, \beta_{\text{asym}}\text{Ph}(\text{d})^{\text{anti}}, \beta_{\text{asym}}\text{Ph}(\text{f,g})$
653	640.7	641.1	$\delta\text{CF}_2(\text{a}), \delta\text{COC}(\text{b,c}), \beta_{\text{asym}}\text{Ph}(\text{f,g})$
664		651.1	$\beta_{\text{asym}}\text{Ph}(\text{d,f,g})$
681	654.2		$\beta_{\text{asym}}\text{Ph}(\text{d,f,g})$
702	664.1	662.2	$\gamma\text{Ph}(\text{d})$
725	693.2	693.3	$\gamma\text{Ph}(\text{f,g})$
736	711.0	711.1	$\omega\text{CF}_2(\text{a}), \delta\text{CCO}(\text{a,b}), \beta_{\text{asym}}(\text{d})$
760	770.5	772.3	$\gamma\text{Ph}(\text{f,g})$
774	780.5	781.3	$\omega\text{CF}_2(\text{a}), \nu\text{CC}(\text{a,b}), \delta\text{CCO}(\text{a,b})$
816	800.5		$\gamma\text{Ph}(\text{d,f,g})$
835	839.5		$\tau\text{CH}_2(\text{c}), \gamma\text{Ph}(\text{d})$
854	841.5	841.6	$\gamma\text{Ph}(\text{f,g}), \tau\text{C}^*\text{HCH}_3(\text{i}), \tau\text{CH}_2(\text{j})$
880	846.1	849.5	$\gamma\text{Ph}(\text{f,g})^{\text{syn}}, \gamma\text{Ph}(\text{d})^{\text{anti}}$
914	890.3	890.1	$\omega\text{CF}_2(\text{a}), \nu_{\text{sym}}\text{CCO}(\text{a,b}), \omega\text{CH}_2(\text{b})$
926	903.5	902.9	$\nu_{\text{asym}}\text{OC}^*\text{C}(\text{h,i,j})$
962	939.5	939.6	$\tau\text{CH}_2(\text{b})$
987	992.0	991.6	$\beta_{\text{asym}}(\text{f,g})$

Table 1. Cont.

exp	calc, <i>syn</i>	calc, <i>anti</i>	Description
1008	1008.8	1013.5	$\nu_{\text{sym}}\text{COC}(\text{b,c}), \nu_{\text{sym}}\text{CCO}(\text{c}), \beta_{\text{asym}}\text{Ph}(\text{d,g}), \beta_{\text{sym}}\text{Ph}(\text{f})^{\text{syn}}, \beta_{\text{asym}}\text{Ph}(\text{f})^{\text{anti}}$
1020	1024.3	1028.8	$\nu_{\text{sym}}\text{COC}(\text{b,c}), \nu_{\text{asym}}\text{CCO}(\text{c}), \beta_{\text{asym}}\text{Ph}(\text{d,f,g})$
1052	1046.8	1046.8	$\omega\text{C}^*\text{HCH}_3(\text{i}), \omega\text{CH}_2(\text{j})$
1103	1087.8	1087.8	$\beta_{\text{asym}}\text{Ph}(\text{g}), \nu_{\text{asym}}\text{COC}^*(\text{h,i}), \omega\text{CH}_2(\text{j})$
1116	1106.5	1117.1	$\beta_{\text{asym}}\text{Ph}(\text{d})$
1146	1123.4	1123.5	$\nu_{\text{asym}}\text{CF}_2(\text{a}), \rho\text{CH}_2(\text{c})$
1164		1141.7	$\beta_{\text{sym}}\text{Ph}(\text{f})$
1173	1147.4	1147.7	$\delta\text{CCC}(\text{a,b}), \nu_{\text{asym}}\text{COC}(\text{b,c}), \beta_{\text{sym}}\text{Ph}(\text{f})$
1185	1157.2	1157.1	$\beta_{\text{sym}}\text{Ph}(\text{g}), \rho\text{CH}_2(\text{j})$
1208	1176.4		$\nu_{\text{asym}}\text{COC}(\text{c,d}), \beta_{\text{asym}}\text{Ph}(\text{d})$
1228	1196.2	1196.1	$\nu_{\text{asym}}\text{CCC}(\text{a,b}), \tau\text{CH}_2(\text{b,c}), \beta_{\text{asym}}\text{Ph}(\text{d,f})^{\text{syn}}$
	1197.3	1200.2	$\beta_{\text{asym}}\text{Ph}(\text{d,f}), \nu_{\text{asym}}\text{CCO}(\text{d,e}), \nu_{\text{asym}}\text{COC}(\text{e,f})$
1269		1222.8	$\beta_{\text{asym}}\text{Ph}(\text{d,f}), \nu_{\text{asym}}\text{CCO}(\text{d,e}), \nu_{\text{asym}}\text{COC}(\text{e,f})$
1285		1247.6	$\beta_{\text{asym}}(\text{d,f,g}), \nu_{\text{asym}}\text{CCO}(\text{d,e}), \nu_{\text{asym}}\text{CCO}(\text{g,h}), \tau\text{CH}_2(\text{j})$
1292	1249.9		$\beta_{\text{asym}}(\text{g}), \nu_{\text{asym}}\text{CCO}(\text{g,h}), \tau\text{CH}_2(\text{j})$
1311	1281.5	1291.3	$\omega\text{CH}_2(\text{b,c}), \beta_{\text{asym}}\text{Ph}(\text{d,f,g})$
1347	1334.9	1335.2	$\omega\text{CH}_2(\text{j})$
1356		1349.6	$\omega\text{CH}_2(\text{b,c}), \beta_{\text{asym}}\text{Ph}(\text{d})$
1389	1365.6		$\omega\text{CH}_2(\text{b,c}), \beta_{\text{asym}}\text{Ph}(\text{d})$
1400	1398.0	1398.3	$\beta_{\text{asym}}\text{Ph}(\text{f,g})$
1439	1427.5		$\delta\text{CH}_2(\text{b}), \omega\text{CH}_2(\text{c}), \beta_{\text{asym}}\text{Ph}(\text{d})$
1461		1437.7	$\delta\text{CH}_2(\text{b,c}), \beta_{\text{asym}}\text{Ph}(\text{d})$
1468	1456.9	1458.3	$\delta\text{CH}_2(\text{b,c}), \beta_{\text{asym}}\text{Ph}(\text{d})$
1495	1478.9	1475.8	$\beta_{\text{asym}}\text{Ph}(\text{f,g})$
1507	1490.7	1487.6	$\delta\text{CH}_2(\text{c}), \beta_{\text{asym}}\text{Ph}(\text{d})$
1523	1504.4	1502.5	$\beta_{\text{asym}}\text{Ph}(\text{f,g})$
1581	1562.2	1555.9	$\beta_{\text{asym}}\text{Ph}(\text{d})$
1611	1596.4	1596.6	$\beta_{\text{sym}}\text{Ph}(\text{f,g})$
1625	1613.7	1615.6	$\beta_{\text{sym}}\text{Ph}(\text{d,f})$
1700	1719.1	1718.5	$\nu\text{C}=\text{O}(\text{h})^{\text{syn}}, \text{anti-phase } \nu\text{C}=\text{O}(\text{e,h})^{\text{anti}}$
1722		1719.9	$\text{in-phase } \nu\text{C}=\text{O}(\text{e,h})$
1737	1756.5		$\nu\text{C}=\text{O}(\text{e})$
2861	2937.6	2938.0	$\nu_{\text{sym}}\text{CH}_2(\text{c})$
	2938.0	2938.1	$\nu_{\text{sym}}\text{CH}_2(\text{j})$
	2945.2	2945.9	$\nu_{\text{sym}}\text{CH}_3(\text{j})$
2878	2948.1	2948.2	$\nu\text{C}^*\text{H}(\text{i}), \nu_{\text{sym}}\text{CH}_2(\text{j}), \nu_{\text{asym}}\text{CH}_2(\text{j})$
2936	3001.7	3001.9	$\nu_{\text{sym}}\text{CH}_2(\text{i}), \nu\text{C}^*\text{H}(\text{i}), \nu_{\text{asym}}\text{CH}_2(\text{j})$
2960	3016.8	3016.8	$\nu_{\text{asym}}\text{CH}_2(\text{j})$
2976	3024.7	3024.7	$\nu_{\text{asym}}\text{CH}_3(\text{j})$

Table 2. Band assignments of the IR spectrum measured for 3F2HPhF6 in the crystal phase at 253 K (exp), based on DFT+D3/BLYP-def2SVP calculations for the head-to-head dimer of molecules in the *anti* conformations (calc). The wavenumbers are given in cm^{-1} . See the text for the notations of the vibrational motions.

exp	calc	Description
511	505.8	$\gamma\text{Ph}(\text{f,g})$
542	541.8	$\beta_{\text{asym}}\text{Ph}(\text{d})$
554	554.7	$\beta_{\text{asym}}\text{Ph}(\text{d})$
622	588.0	$\beta_{\text{asym}}\text{Ph}(\text{d})$
630	609.5	$\gamma\text{Ph}(\text{d,f})$
643	621.0	$\gamma\text{Ph}(\text{d}), \beta_{\text{asym}}\text{Ph}(\text{f,g})$
653	640.0	$\beta_{\text{asym}}\text{Ph}(\text{f,g})$
664	649.5	$\gamma\text{Ph}(\text{d,f}), \beta_{\text{asym}}\text{Ph}(\text{g})$

Table 2. Cont.

exp	calc	Description
681	657.0	$\beta_{\text{asym}}\text{Ph(d,f,g)}$
	660.4	$\gamma\text{Ph(d)}$
702	668.5	$\gamma\text{Ph(d)}$
	693.6	$\gamma\text{Ph(f,g)}$
725	695.4	$\gamma\text{Ph(f,g)}$
	709.8	$\omega\text{CF}_2(\text{a}), \delta\text{CCO}(\text{a,b})$
736	711.4	$\omega\text{CF}_2(\text{a}), \delta\text{CCO}(\text{a,b})$
760	767.9	$\gamma\text{Ph(f,g)}$
	776.5	$\omega\text{CF}_2(\text{a}), \nu\text{CC}(\text{a,b}), \delta\text{CCO}(\text{a,b})$
774	777.0	$\omega\text{CF}_2(\text{a}), \nu\text{CC}(\text{a,b}), \delta\text{CCO}(\text{a,b})$
816	819.2	$\tau\text{CH}_2(\text{c}), \gamma\text{Ph(d)}$
835	839.2	$\tau\text{CH}_2(\text{c}), \gamma\text{Ph(d)}$
854	852.9	$\gamma\text{Ph(f,g)}$
880	854.2	$\gamma\text{Ph(f,g)}$
	887.6	$\omega\text{CF}_2(\text{a}), \nu_{\text{sym}}\text{CCO}(\text{a,b}), \omega\text{CH}_2(\text{b})$
914	891.0	$\omega\text{CF}_2(\text{a}), \nu_{\text{sym}}\text{CCO}(\text{a,b}), \omega\text{CH}_2(\text{b})$
	892.5	$\nu_{\text{asym}}\text{OC}^*\text{C}(\text{h,i,j})$
926	903.5	$\nu_{\text{asym}}\text{OC}^*\text{C}(\text{h,i,j})$
962	935.8	$\tau\text{CH}_2(\text{b})$
987	995.5	$\beta_{\text{asym}}(\text{f,g})$
1008	1002.5	$\nu_{\text{sym}}\text{COC}(\text{b,c}), \nu_{\text{sym}}\text{CCO}(\text{c}), \beta_{\text{asym}}\text{Ph(d,f)}$
	1007.7	$\nu_{\text{sym}}\text{COC}(\text{b,c}), \nu_{\text{sym}}\text{CCO}(\text{c}), \beta_{\text{asym}}\text{Ph(d)}$
1020	1029.1	$\nu_{\text{sym}}\text{COC}(\text{b,c}), \nu_{\text{asym}}\text{CCO}(\text{c}), \beta_{\text{asym}}\text{Ph(d,f,g)}$
1052	1050.6	$\omega\text{C}^*\text{HCH}_3(\text{i}), \omega\text{CH}_2(\text{j})$
1103	1090.3	$\beta_{\text{asym}}\text{Ph(g)}, \nu_{\text{asym}}\text{COC}^*(\text{h,i})$
1116	1115.7	$\beta_{\text{asym}}\text{Ph(d)}$
1146	1120.7	$\nu_{\text{asym}}\text{CF}_2(\text{a}), \nu_{\text{asym}}\text{COC}(\text{b,c}), \rho\text{CH}_2(\text{c})$
1164	1147.8	$\delta\text{CCC}(\text{a,b}), \nu_{\text{asym}}\text{COC}(\text{b,c}), \beta_{\text{sym}}\text{Ph(f)}$
1173	1154.4	$\nu_{\text{asym}}\text{COC}(\text{c,d}), \beta_{\text{asym}}\text{Ph(d)}, \beta_{\text{sym}}\text{Ph(f)}$
	1163.7	$\beta_{\text{sym}}\text{Ph(g)}$
1185	1168.4	$\nu_{\text{asym}}\text{CCO}(\text{c}), \nu_{\text{asym}}\text{COC}(\text{c,d}), \beta_{\text{asym}}\text{Ph(d)}, \beta_{\text{sym}}\text{Ph(f,g)}$
1208	1188.0	$\nu_{\text{asym}}\text{CF}_2(\text{a}), \tau\text{CH}_2(\text{c})$
	1197.6	$\nu_{\text{asym}}\text{CCC}(\text{a,b}), \tau\text{CH}_2(\text{b,c})$
1228	1198.7	$\tau\text{CH}_2(\text{c}), \beta_{\text{asym}}\text{Ph(d,f)}, \nu_{\text{asym}}\text{COC}(\text{e,f})$
	1215.7	$\beta_{\text{asym}}\text{Ph(d,f)}, \nu_{\text{asym}}\text{CCO}(\text{d,e})$
1269	1224.1	$\beta_{\text{asym}}\text{Ph(d,f)}, \nu_{\text{asym}}\text{CCO}(\text{d,e})$
	1241.8	$\nu_{\text{asym}}\text{CF}_3(\text{a}), \nu_{\text{sym}}\text{CF}_2(\text{a}), \nu\text{CC}(\text{a}), \tau\text{CH}_2(\text{b,c})$
1285	1243.7	$\beta_{\text{asym}}\text{Ph(d,f,g)}, \nu_{\text{asym}}\text{CCO}(\text{g,h}), \tau\text{C}^*\text{HCH}_3(\text{i})$
1292	1251.5	$\tau\text{CH}_2(\text{b,c}), \beta_{\text{asym}}(\text{d,f,g}), \nu_{\text{asym}}\text{CCO}(\text{d,e}), \nu_{\text{asym}}\text{CCO}(\text{g,h}), \tau\text{C}^*\text{HCH}_3(\text{i})$
1311	1288.2	$\omega\text{CH}_2(\text{b,c}), \beta_{\text{asym}}\text{Ph(d)}$
1347	1344.2	$\beta_{\text{asym}}\text{Ph(f,g)}, \omega\text{CH}_2(\text{i}), \omega\text{C}^*\text{HCH}_3(\text{j})$
1356	1350.7	$\omega\text{CH}_2(\text{b,c}), \beta_{\text{asym}}\text{Ph(d)}$
1389	1365.6	$\omega\text{CH}_2(\text{b,c}), \beta_{\text{asym}}\text{Ph(d)}$
1400	1398.1	$\beta_{\text{asym}}\text{Ph(f,g)}$
1439	1430.6	$\delta\text{CH}_2(\text{b}), \omega\text{CH}_2(\text{c}), \beta_{\text{asym}}\text{Ph(d)}$
1461	1437.0	$\delta\text{CH}_2(\text{b,c}), \beta_{\text{asym}}\text{Ph(d)}$
1468	1464.4	$\delta\text{CH}_2(\text{b,c}), \beta_{\text{asym}}\text{Ph(d)}$
1495	1481.3	$\beta_{\text{asym}}\text{Ph(f,g)}$
1507	1491.1	$\delta\text{CH}_2(\text{c}), \beta_{\text{asym}}\text{Ph(d)}$
	1505.5	$\beta_{\text{asym}}\text{Ph(f,g)}$
1523	1506.8	$\beta_{\text{asym}}\text{Ph(f,g)}$
1581	1565.7	$\beta_{\text{asym}}\text{Ph(d)}$
1611	1598.6	$\beta_{\text{sym}}\text{Ph(f,g)}$
1625	1618.6	$\beta_{\text{asym}}\text{Ph(d)}$
1700	1712.0	$\nu\text{C}=\text{O}(\text{h})$
1722	1713.5	anti-phase $\nu\text{C}=\text{O}(\text{e,h})$
	1714.6	in-phase $\nu\text{C}=\text{O}(\text{e,h})$
1737	1747.3	$\nu\text{C}=\text{O}(\text{e})$

Table 2. Cont.

exp	calc	Description
2861	2919.9	$\nu_{\text{sym}}\text{CH}_2(\text{b,c})$
	2924.1	$\nu_{\text{sym}}\text{CH}_2(\text{b,c})$
	2946.7	$\nu_{\text{sym}}\text{CH}_2(\text{j})$
2878	2950.6	$\nu_{\text{asym}}\text{CH}_2(\text{j}), \nu_{\text{sym}}\text{CH}_3(\text{j})$
	2952.3	$\nu_{\text{asym}}\text{CH}_2(\text{b,c})$
2936	2988.7	$\nu_{\text{asym}}\text{CH}_2(\text{j})$
2960	3006.7	$\nu_{\text{asym}}\text{CH}_2(\text{b,c})$
2976	3017.1	$\nu_{\text{asym}}\text{CH}_2(\text{j})$

Table 3. Band assignments of the IR spectrum measured for 3F2HPhF6 in the crystal phase at 253 K (exp), based on DFT+D3/BLYP-def2SVP calculations for the head-to-tail dimer of molecules in the *anti* conformations (calc). The wavenumbers are given in cm^{-1} . See the text for the notations of the vibrational motions.

exp	calc	Description
511	505.6	$\gamma\text{Ph}(\text{d,f,g})$
542	535.6	$\delta\text{CF}_2(\text{a}), \delta\text{COC}(\text{b,c}), \beta_{\text{asym}}\text{Ph}(\text{d})$
	539.4	$\beta_{\text{asym}}\text{Ph}(\text{d}), \gamma\text{Ph}(\text{f,g})$
554	556.0	$\beta_{\text{asym}}\text{Ph}(\text{d}), \gamma\text{Ph}(\text{f,g})$
622	577.6	$\delta\text{COC}(\text{c,d}), \beta_{\text{asym}}\text{Ph}(\text{d})$
630	610.6	$\gamma\text{Ph}(\text{d,f})$
643	620.1	$\gamma\text{Ph}(\text{d}), \beta_{\text{asym}}\text{Ph}(\text{f,g})$
653	638.2	$\gamma\text{Ph}(\text{d}), \beta_{\text{asym}}\text{Ph}(\text{f,g})$
664	656.8	$\gamma\text{Ph}(\text{d}), \beta_{\text{asym}}\text{Ph}(\text{f,g})$
681	663.4	$\gamma\text{Ph}(\text{d})$
702	668.9	$\gamma\text{Ph}(\text{d})$
725	693.9	$\gamma\text{Ph}(\text{f,g})$
	695.0	$\gamma\text{Ph}(\text{f,g})$
736	704.5	$\omega\text{CF}_2(\text{a}), \delta\text{CCO}(\text{a,b})$
	709.8	$\omega\text{CF}_2(\text{a}), \delta\text{CCO}(\text{a,b})$
760	770.0	$\gamma\text{Ph}(\text{f,g})$
	770.6	$\gamma\text{Ph}(\text{f,g})$
774	779.8	$\omega\text{CF}_2(\text{a}), \delta\text{CCO}(\text{a,b})$
816	823.9	$\gamma\text{Ph}(\text{f,g}), \nu_{\text{sym}}\text{OC}^*\text{C}(\text{h,i,j}), \tau\text{CH}_2(\text{j})$
835	840.5	$\gamma\text{Ph}(\text{d,f,g})$
854	845.9	$\gamma\text{Ph}(\text{f,g})$
880	866.1	$\omega\text{CF}_2(\text{a}), \nu_{\text{sym}}\text{CCO}(\text{a,b}), \tau\text{CH}_2(\text{b,c})$
914	888.2	$\omega\text{CF}_2(\text{a}), \nu_{\text{sym}}\text{CCO}(\text{a,b}), \omega\text{CH}_2(\text{b})$
	894.9	$\nu_{\text{asym}}\text{OC}^*\text{C}(\text{h,i,j})$
926	899.9	$\nu_{\text{asym}}\text{OC}^*\text{C}(\text{h,i,j})$
962	936.1	$\nu_{\text{asym}}\text{CF}_2(\text{a}), \rho\text{CH}_2(\text{b})$
987	992.3	$\beta_{\text{asym}}(\text{f,g})$
1008	1012.8	$\nu_{\text{sym}}\text{CCO}(\text{c}), \beta_{\text{asym}}\text{Ph}(\text{d})$
1020	1014.4	$\nu_{\text{sym}}\text{COC}(\text{b,c}), \beta_{\text{asym}}\text{Ph}(\text{d,f,g})$
1052	1045.2	$\omega\text{C}^*\text{HCH}_3(\text{i}), \omega\text{CH}_2(\text{j})$
1103	1092.8	$\beta_{\text{asym}}\text{Ph}(\text{d})$
	1096.4	$\beta_{\text{asym}}\text{Ph}(\text{d})$
1116	1114.1	$\beta_{\text{asym}}\text{Ph}(\text{d})$
1146	1122.1	$\nu_{\text{asym}}\text{CF}_2(\text{a}), \rho\text{CH}_2(\text{c})$
1164	1145.0	$\nu_{\text{asym}}\text{CF}_3(\text{a}), \nu_{\text{sym}}\text{CF}_2(\text{a}), \rho\text{CH}_2(\text{b,c}), \beta_{\text{asym}}\text{Ph}(\text{d}), \beta_{\text{sym}}\text{Ph}(\text{f})$
1173	1156.7	$\beta_{\text{sym}}\text{Ph}(\text{f}), \rho\text{CH}_2(\text{j})$
1185	1166.0	$\beta_{\text{sym}}\text{Ph}(\text{g})$
	1171.4	$\nu_{\text{asym}}\text{CF}_3(\text{a}), \nu_{\text{sym}}\text{CF}_2(\text{a}), \nu_{\text{asym}}\text{CCC}(\text{a,b}), \beta_{\text{asym}}\text{Ph}(\text{d})$
1208	1183.2	$\nu_{\text{asym}}\text{CF}_3(\text{a}), \delta\text{CCC}(\text{a}), \tau\text{CH}_2(\text{b,c})$
1228	1192.8	$\nu_{\text{asym}}\text{CF}_3(\text{a}), \nu_{\text{sym}}\text{CF}_2(\text{a}), \nu_{\text{asym}}\text{CCC}(\text{a,b}), \tau\text{CH}_2(\text{b,c})$
	1197.7	$\nu_{\text{asym}}\text{CF}_2(\text{a}), \tau\text{CH}_2(\text{b})$

Table 3. Cont.

exp	calc	Description
1269	1216.5	$\tau\text{CH}_2(\text{c})$, $\beta_{\text{asym}}\text{Ph}(\text{d})$, $\nu_{\text{asym}}\text{CCO}(\text{d,e})$, $\nu_{\text{asym}}\text{COC}(\text{e,f})$
	1224.0	$\beta_{\text{asym}}\text{Ph}(\text{d,f})$, $\nu_{\text{asym}}\text{CCO}(\text{d,e})$
1285	1246.6	$\beta_{\text{asym}}(\text{d,f})$, $\nu_{\text{asym}}\text{CCO}(\text{d,e})$, $\nu_{\text{asym}}\text{CCO}(\text{g,h})$, $\tau\text{C}^*\text{HCH}_3(\text{i})$, $\tau\text{CH}_2(\text{j})$
1292	1250.0	$\beta_{\text{asym}}(\text{d,f})$, $\nu_{\text{asym}}\text{CCO}(\text{d,e})$, $\nu_{\text{asym}}\text{CCO}(\text{g,h})$, $\tau\text{C}^*\text{HCH}_3(\text{i})$, $\tau\text{CH}_2(\text{j})$
1311	1283.3	$\tau\text{CH}_2(\text{b,c,j})$, $\beta_{\text{asym}}\text{Ph}(\text{d,f,g})$
1347	1339.0	$\nu_{\text{asym}}\text{CCO}(\text{g,h})$, $\omega\text{CH}_2(\text{i})$, $\omega\text{C}^*\text{HCH}_3(\text{j})$
1356	1351.0	$\omega\text{CH}_2(\text{c})$, $\tau\text{CH}_2(\text{c})$, $\beta_{\text{asym}}\text{Ph}(\text{d})$
1389	1369.8	$\beta_{\text{asym}}\text{Ph}(\text{d})$
1400	1404.4	$\beta_{\text{asym}}\text{Ph}(\text{f,g})$
1439	1432.2	$\beta_{\text{asym}}\text{Ph}(\text{d})$, $\delta\text{CH}_2(\text{i,j})$
1461	1438.1	$\beta_{\text{asym}}\text{Ph}(\text{d})$, $\delta\text{CH}_2(\text{i,j})$
1468	1464.4	$\delta\text{CH}_2(\text{b,c})$, $\beta_{\text{asym}}\text{Ph}(\text{d})$
1495	1479.0	$\beta_{\text{asym}}\text{Ph}(\text{f,g})$
1507	1486.3	$\delta\text{CH}_2(\text{c})$, $\beta_{\text{asym}}\text{Ph}(\text{d,f,g})$
1523	1503.8	$\beta_{\text{asym}}\text{Ph}(\text{f,g})$
1581	1560.8	$\beta_{\text{asym}}\text{Ph}(\text{d})$
	1596.5	$\beta_{\text{asym}}\text{Ph}(\text{f,g})$
1611	1597.1	$\beta_{\text{asym}}\text{Ph}(\text{f,g})$
	1614.8	$\beta_{\text{sym}}\text{Ph}(\text{d,f,g})$
1625	1615.5	$\beta_{\text{sym}}\text{Ph}(\text{d,f,g})$
1700	1684.9	$\nu\text{C}=\text{O}(\text{h})$
	1711.4	$\nu\text{C}=\text{O}(\text{e})$
1722	1715.4	anti-phase $\nu\text{C}=\text{O}(\text{e,h})$
1737	1718.2	in-phase $\nu\text{C}=\text{O}(\text{e,h})$
2861	2944.8	$\nu_{\text{asym}}\text{CH}_2(\text{b,c})$
	2945.3	$\nu_{\text{sym}}\text{CH}_2(\text{j})$
	2956.3	$\nu_{\text{asym}}\text{CH}_2(\text{j})$, $\nu_{\text{sym}}\text{CH}_3(\text{j})$
2878	2963.8	$\nu_{\text{sym}}\text{CH}_2(\text{b,c})$
	2964.8	$\nu_{\text{asym}}\text{CH}_2(\text{b})$, $\nu_{\text{asym}}\text{CH}_2(\text{j})$, $\nu_{\text{sym}}\text{CH}_3(\text{j})$
2936	3006.8	$\nu_{\text{sym}}\text{CH}_2(\text{b,c})$
2960	3016.5	$\nu_{\text{asym}}\text{CH}_2(\text{j})$
2976	3027.9	$\nu_{\text{asym}}\text{CH}_2(\text{j})$

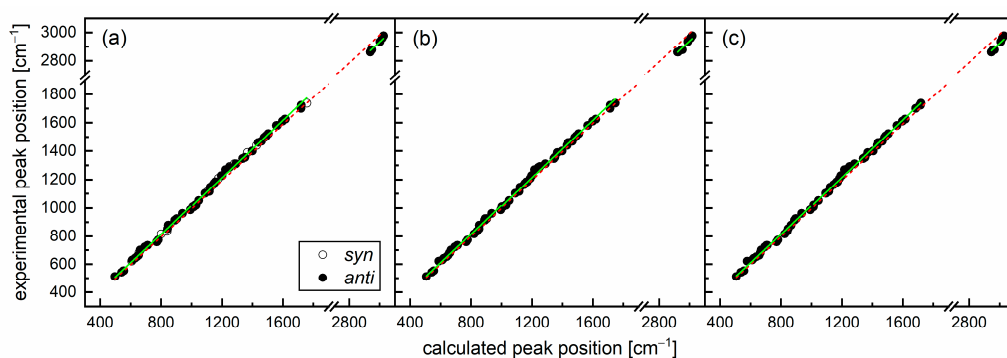


Figure 4. Experimental peak positions determined from the IR spectrum of 3F2HPhF6 in the crystal phase at 253 K vs. peak positions calculated for isolated molecules in two conformations: (a) head-to-head dimer (b) and head-to-tail dimer (c). Dashed and solid lines indicate linear fits in the whole spectral range and in the separate ranges, respectively.

As a next step with the molecular models, we built a periodic model of 3F2HPhF6 that esthetically represents one of its tilted smectic phases (see computational details and Figure 5a,b). Figure 5c,d show the overlaid discrete Fourier transforms of the evolutions of every respective C=O(h) (blue) and C=O(e) (red) bond distance in the system. Specifically, if the positions of the signal maxima are compared with the predicted C=O vibrational

frequency from an isolated monomer (indicated by the dashed lines in Figure 5c,d), the periodic models further support the key observations from the molecular cluster models about how the influences of intermolecular interactions cause a general decrease in and splitting of the observed frequencies. In addition, the xTB results indicate that the C=O(e) groups are particularly sensitive to the nature of the splitting. Although we are cautious to interpret the sources of the observed splitting without further exploring how the model setup and choice of methodology influence the splitting, we observed that the main difference between the “lowest” and “highest” frequency C=O(e) bonds were that the lowest frequency one (near 1700 cm^{-1}) engaged in mostly C=O...H-C contacts and some C=O...F contacts, whereas the highest frequency one (near 1740 cm^{-1}) was different in two ways: (I) it is bound to a F-substituted phenyl ring that rotated by 180° during pre-equilibration (the C=O(e) group rotated with it in such a way as to preserve its local *anti* symmetry with respect to the F substituent; this gave the molecule a distinct rotamer vs. all of the other molecules in the cell), and (II) it creates an intermolecular lone pair... π contact [34] ($\sim 3.0\text{ \AA}$) with a nearby biphenyl group.

Table 4. The scaling coefficients between experimental and calculated IR absorption peak positions and the corresponding coefficients of determination R^2 of the linear fits (*in italics*).

Model	Full Range	<1000 cm^{-1}	1000–2000 cm^{-1}	>2000 cm^{-1}
Isolated molecule	0.994(2) <i>0.99961</i>	1.019(4) <i>0.99966</i>	1.011(2) <i>0.99988</i>	0.978(1) <i>0.99999</i>
Head-to-head dimer	0.998(3) <i>0.99962</i>	1.020(4) <i>0.99964</i>	1.011(2) <i>0.99986</i>	0.980(2) <i>0.99998</i>
Head-to-tail dimer	0.996(3) <i>0.99953</i>	1.018(5) <i>0.99955</i>	1.012(2) <i>0.99991</i>	0.975(2) <i>0.99998</i>

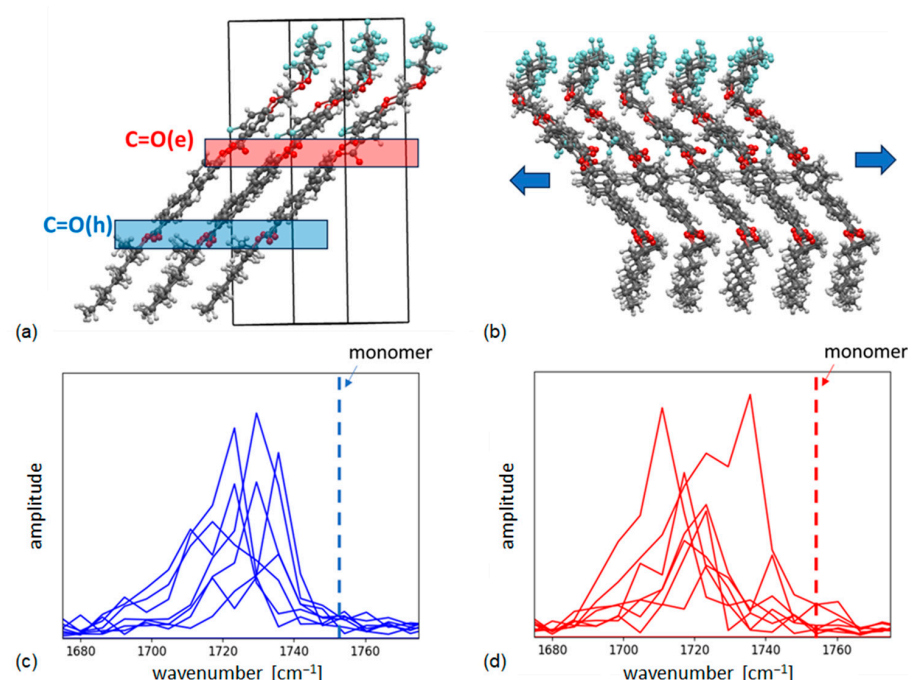


Figure 5. (a) A side view of the 7-molecule simulation cell that was used to model periodic layers of a tilted smectic phase for 3F2HPhF6; all of the molecules were initially assigned the *anti* configuration and the initial distribution of the C=O(h) and C=O(e) carbonyl groups is indicated. (b) A different perspective of the model that shows deviation after optimization from the underlying hockey-stick shape. (c,d) The overlaid discrete Fourier transforms of every C=O(h) (c) and C=O(e) (d) type of carbonyl group in the molecular dynamics simulations; the wavenumber of the C=O vibration from a normal mode analysis on an individual molecule is indicated by the dashed line.

3.2. Temperature Evolution of Vibrational Spectra and Structure

The XRD patterns and IR spectra were registered in the same temperatures to facilitate their comparison (Figure 6) and their selected fragments were analyzed closely (Figures 7–9). The XRD results are in agreement with the phase sequence obtained in [10] by differential scanning calorimetry (DSC). At 253–323 K, the diffraction patterns consisting of the sharp peaks are typical for the crystal phase (Figure 6a). Above the Cr $\rightarrow$ SmC_A* transition, at 333–373 K, there are only three sharp diffraction peaks—the main peak at $2\theta = 3.2^\circ$ and its second and third harmonics at 6.4° and 9.6° —related to the smectic layer order, while at higher angles, with a middle at $2\theta \approx 18^\circ$, there is a wide maximum arising from the short-range order in the smectic layers [15–19]. The SmC_A* and SmC* phases are characterized, respectively, by the anticlinic and synclinic order of the tilt angle in the neighbor smectic layers [15]. This structural change at the SmC_A* $\rightarrow$ SmC* transition does not lead to qualitative changes in the conventional XRD patterns (only the resonant XRD method gives different patterns for SmC*, SmC_A* and various sub-phases [35]). The sharp peaks from the smectic layers are absent at the patterns collected at 383 and 393 K, which signals the occurrence of the SmC* $\rightarrow$ Iso transition. The position of the first diffraction peak appearing in the XRD patterns at low angles is related by the Bragg equation $d = \lambda / 2 \sin \theta$ [15] to the layer spacing d in the crystal and smectic phases. The decrease in the tilt angle of the molecules in the SmC*, SmC_A* phases [8] leads to the increasing smectic layer spacing upon heating. Another important parameter is the integrated intensity of the low-angle peak. The abrupt changes in the layer spacing and integrated intensity indicate the phase transitions [17,18]. For 3F2HPhF6, the Cr $\rightarrow$ SmC_A* transition can be noticed in the $d(T)$ plot as a decrease in the layer spacing, while the SmC* $\rightarrow$ SmC_A* transition is not accompanied by any significant change in d . However, both transitions are clearly visible in the temperature dependence of the integrated intensity (Figure 8a).

The phase transition which influences the IR spectrum to the most extent is the melting of the crystal phase, which leads to a change in the shape and positions of some absorption bands (Figure 6b). Further transitions are not clearly visible in the IR spectra, which look practically the same for the SmC_A*, SmC* and Iso phases. As reported in other publications [1,2,5,6,9], the absorption bands in the $1700\text{--}1750\text{ cm}^{-1}$ range, assigned to the $\nu\text{C=O}$ vibrations, show a noticeable sensitivity to changes in temperature, phase transitions, intermolecular interactions and molecular conformation; therefore, they are investigated as a function of temperature (Figures 7 and 8b,c). The $\nu\text{C=O}$ bands are designated as I, II and III in order of their increasing wavenumber. According to the assignments presented in Tables 1–3 and the computational results from [9], band I is related to the stretching of the C=O bond close to the chiral center, while bands II and III are more likely related to the stretching of the C=O bonds located within the aromatic core. We consider this a sound guiding principle, but we further highlight that the results from the periodic models (in Figure 5) suggest that the shifts in the $\nu\text{C=O}$ frequencies that are induced by non-homogeneous intermolecular interactions can overlap with the magnitudes of the shifts that are induced by intramolecular effects. The Cr $\rightarrow$ SmC_A* transition is connected with the change in the integrated intensity of all the $\nu\text{C=O}$ absorption bands, while the significant change in the wavenumber occurs only for band I. There is no certain signature of the SmC_A* $\rightarrow$ SmC* transition, probably because the surroundings of the C=O groups do not differ in both smectic phases. In the isotropic liquid phase at 393 K, bands I and III decrease and band II increases in intensity; a decrease in the wavenumber of band II and an increase in the wavenumber of band III is also visible. At 383 K, the parameters of the $\nu\text{C=O}$ bands are not very different to the values for the SmC* phase, despite the XRD results confirming that 3F2HPhF6 is in the isotropic liquid phase at this temperature. The explanation for this could be the presence of small domains with a preserved smectic order in the sample, which survived a few degrees above the SmC* $\rightarrow$ Iso transition temperature (resembling the so-called cybotactic clusters reported for the nematic phase [36]).

Since the computational results indicate that intermolecular interactions influence the wavenumbers of the $\nu\text{C=O}$ bands, it is reasonable to compare their values with the average

distance w between the long axes of molecules in the smectic layers and in the isotropic liquid. The w value is determined from the position of the wide maximum at $2\theta \approx 18^\circ$ in the XRD patterns [15,16]. For 3F2HPhF6, w equals 4.8–4.9 Å in the smectic phases and 5.0–5.1 Å in the isotropic liquid phase, increasing with increasing temperature. In the temperature range of 333–373 K in the smectic phases, there is a roughly linear increase in the wavenumbers of the $\nu\text{C}=\text{O}$ bands with an increasing intermolecular distance, with the slope equal to 11–15 $\text{cm}^{-1}/\text{\AA}$ (Figure 9). The larger the distances between the molecules in the smectic layers, the weaker the intermolecular interaction. The computational results show that the proximity of the $\text{C}=\text{O}$ group and the F atom shifts the $\nu\text{C}=\text{O}$ band towards higher wavenumbers [9]. However, according to the literature [4,37–39], the presence of the hydrogen bonds involving the O atom from the $\text{C}=\text{O}$ group has an inverse effect and shifts the $\nu\text{C}=\text{O}$ band towards lower wavenumbers. This means that the intermolecular interactions have various effects on the $\nu\text{C}=\text{O}$ bands, depending on the arrangement of the molecules. In our computational results, the theoretical positions of the $\nu\text{C}=\text{O}$ bands calculated for the *anti/syn* set of isolated molecules (1718.5–1756.5 cm^{-1}) are higher than those obtained for the head-to-head (1712.0–1747.3 cm^{-1}) and head-to-tail (1684.9–1718.2 cm^{-1}) dimers. The theoretical $\nu\text{C}=\text{O}$ band with the lowest position of 1684.9 cm^{-1} is related to the stretching of the $\text{C}=\text{O}(\text{h})$ group making a short contact with the $\text{C}-\text{H}$ atoms from the $\text{CH}_2(\text{b})$ group of the neighbor molecule; this is curiously similar to what we observed for the lowest frequency $\text{C}=\text{O}(\text{e})$ contribution in Figure 5d, which also involved a contact with a nearby $\text{CH}_2(\text{b})$ group. The $\text{H}(\text{b})\dots\text{O}(\text{h})$ and $\text{C}(\text{b})\dots\text{O}(\text{h})$ distances in the molecular model are 2.2 Å and 3.2 Å, respectively, and the $\text{C}-\text{H}(\text{b})\dots\text{O}(\text{h})$ angle equals 155.2° . These parameters are similar to the experimental values obtained for the $\text{C}-\text{H}\dots\text{O}$ hydrogen bonds in the crystal structures of other liquid crystals [40,41]. Taking this all into account, we conclude that the blueshift of the $\nu\text{C}=\text{O}$ bands with the increasing intermolecular distance w and increasing temperature is caused by the decreasing amount of hydrogen bonds between molecules. In the isotropic liquid phase, the positions of the $\nu\text{C}=\text{O}$ absorption bands show various dependences on w : band III still blueshifts with increasing w , while bands I and II slightly redshift. The explanation of their relationship is not as straightforward as for the smectic phases because the orientational disorder in the isotropic liquid enables much more configurations of neighboring molecules.

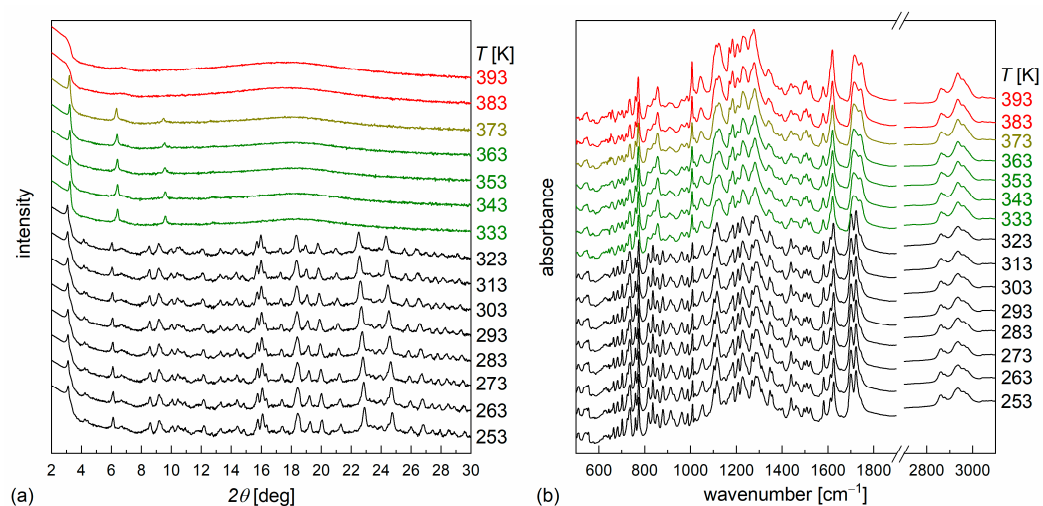


Figure 6. XRD patterns (a) and IR spectra (b) of 3F2HPhF6 collected upon heating. The phase sequence is as follows: 253–323 K—crystal (black), 333–363 K— SmC_A^* (green), 373 K— SmC^* (yellow), 383–393 K—liquid (red).

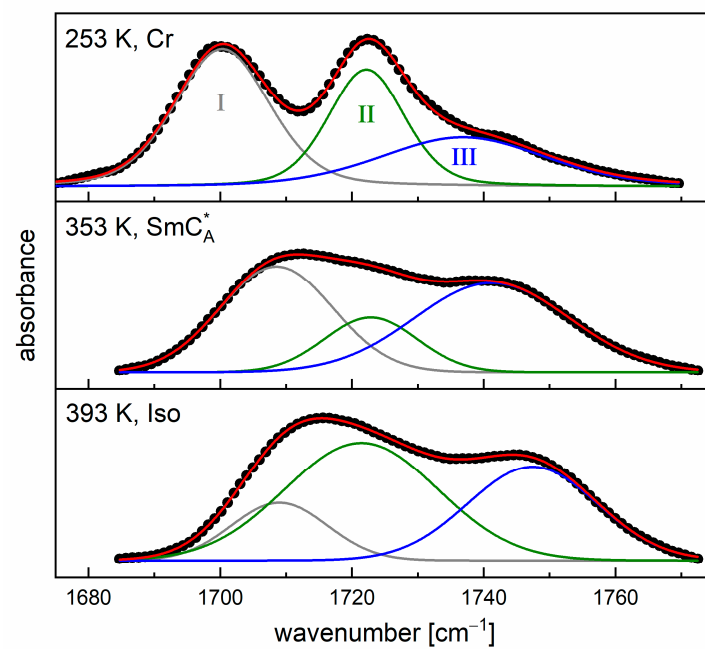


Figure 7. IR absorption bands related to the C=O stretching with the representative fitting results of the pseudo-Voigt (crystal phase) and Gaussian (smectic and isotropic liquid phases) peak functions after background subtraction.

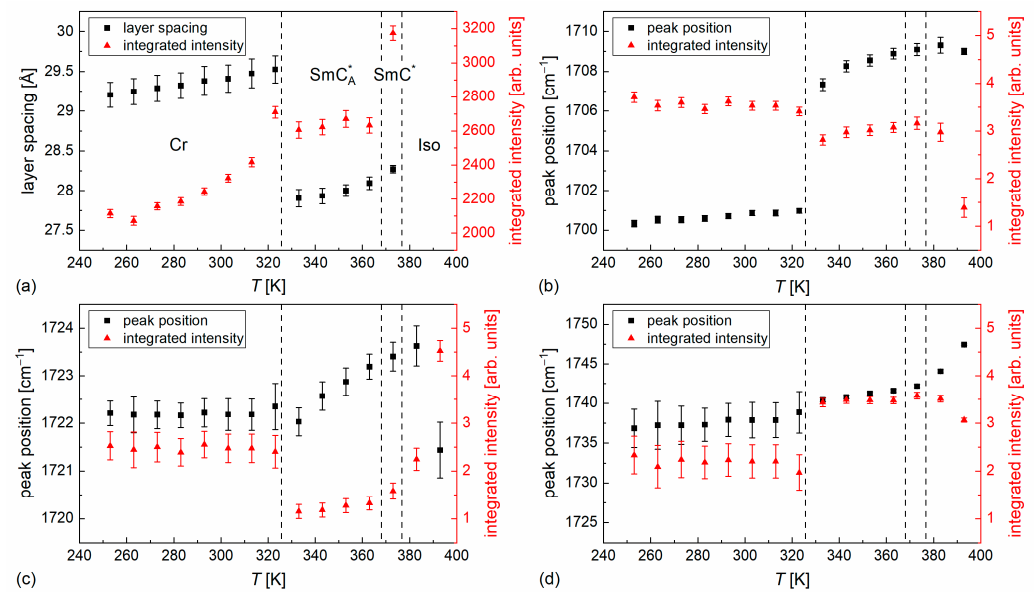


Figure 8. Layer spacing in the crystal and smectic phases of 3F2HPhF6, and the integrated intensity of the low-angle diffraction peak (a) combined with the positions and integrated intensities of the ν C=O bands I (b), II (c), III (d). The vertical lines indicate the phase transition temperatures from [10], determined by DSC.

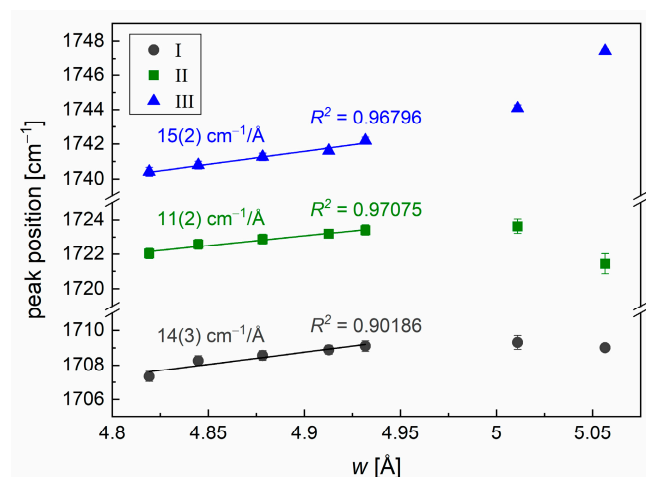


Figure 9. Relationship between the average distances between molecules within the smectic layers and in isotropic liquid determined by XRD, and the positions of the $\nu\text{C}=\text{O}$ bands obtained from experimental IR spectra. For the results in the smectic phases, the linear fits are performed and the slopes and coefficients of determination are given.

4. Conclusions

The intramolecular vibrations of the 3F2HPhF6 compound were investigated by FT-IR spectroscopy and density functional theory calculations for the isolated molecule, dimers and periodic model. The detailed band assignments in the wavenumber range of $500\text{--}3000\text{ cm}^{-1}$ show that the introduction of dimers into the DFT+D3 calculations gives a better agreement between the experimental and calculated spectra, i.e., the scaling factor is closer to 1. However, the calculations for isolated molecules are also sufficient, as long as they include two possible positions of the fluorine substituent in the aromatic core and the neighboring $\text{C}=\text{O}$ group (*syn* and *anti* conformations). The results for the periodic model obtained with the xTB method provide additional support for three key observations: (1) how the inclusion of non-covalent interactions directly influences the predicted $\text{C}=\text{O}$ stretching frequencies, (2) a major origin of the shifts in frequencies relates with the influences of the shortest non-covalent contacts that the $\text{C}=\text{O}$ groups participate in, and (3) it is important how the molecules ultimately position themselves vs. their neighbors (concerning both their relative orientations and their adopted rotamers). This is similar in spirit to the influence of the *anti* vs. *syn* monomer isomers, but rather points out the (dynamic) intermolecular aspect of this effect. The blueshift of the absorption bands related to the $\text{C}=\text{O}$ stretching upon heating, correlated with the increase in the average intermolecular distances obtained from the XRD patterns, indicates the decreasing amount of weak $\text{C}-\text{H} \cdots \text{O}=\text{C}$ hydrogen bonds in the smectic C_A^* and smectic C^* phases. The shift of the $\text{C}=\text{O}$ stretching band towards lower wavenumbers upon hydrogen bond formation is confirmed by one of the dimer models, and the calculated parameters of the $\text{C}-\text{H} \cdots \text{O}=\text{C}$ bond are in agreement with the experimental results reported for other liquid crystalline compounds.

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