PAPER

The electronic structure of perfluorodecalin studied by soft X-ray spectroscopy and electronic structure calculations†

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Fluorine and carbon K absorption and emission spectra of liquid perfluorodecalin are presented and analyzed in terms of density functional calculations–configuration interaction. A comprehensive view of the electronic structure is given, and site-specific intramolecular interactions are investigated in detail. It is found that, while the outer fluorine atoms have excess charge in the ground state, the lowest excitations must be associated with charge transfer towards the inner carbon atoms.

1 Introduction

Perfluorocarbons have unusual properties, which make them interesting for applications in biomedicine, physical chemistry and polymer science.[1,2] As their C–F bond is strong and their intermolecular interaction weak, they are often chemically and biologically inert. At ambient conditions they are liquids with remarkably low surface tension, dielectric constant and refractive index, very high density, viscosity and gas solubility.[3,4] Out of the numerous applications their use in biomedicine is probably the most important, where their ability to dissolve O_2 together with their biological inertness is exploited in fluids for tissue oxygenation.[5–7]

The fundamental mechanisms governing the properties of the perfluorocarbons have been investigated using nuclear magnetic resonance (NMR),[3,8,9] inner-shell electron energy loss (ISEEL)[10] and photoelectron spectroscopy.[11–13] It is acknowledged that the polarity of the chemical bonds, due to the large electronegativity of the fluorine atoms, is important for the electronic structure. Attention has also been given to the so-called perfluoro effect, *i.e.* the observation that substitution of hydrogen by fluorine in planar molecules has a larger stabilizing effect on the σ orbitals than on the π orbitals.[11,12]

The introduction of techniques which enable core level spectroscopy on liquids gives new opportunities to investigate the geometry and the electronic structure of liquid systems.[14,15] In this work we apply these techniques to investigate the origin of the unusual properties of PFD, which are still under debate.

We have investigated perfluorodecalin (PFD) in the liquid phase. The PFD molecule, $C_{10}F_{18}$, consists of two combined carbon rings, fully saturated with fluorine (Fig. 1). We present the total fluorescence yield (TFY) spectra mirroring the X-ray absorption (XA) process at the fluorine and carbon K edges and thus the local unoccupied states and X-ray emission (XE)[16] spectra at the same edges reflecting local occupied states.

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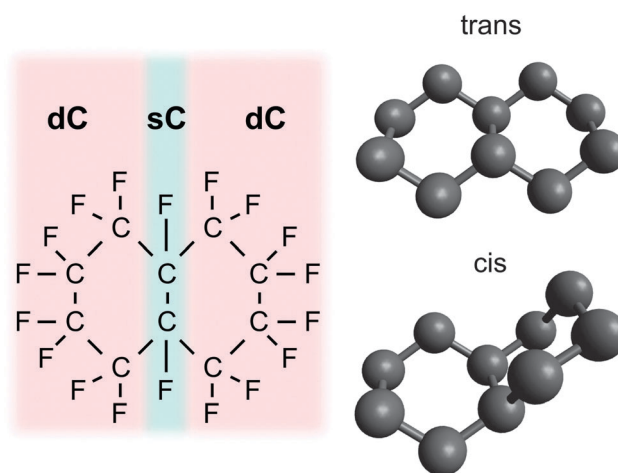
Fig. 1 Schematic picture of perfluorodecalin depicting the different carbon sites sC (one fluorine as nearest neighbour) and dC (two fluorine as nearest neighbours). Additional schematics (without fluorine atoms) depict the chiral character of perfluorodecalin.

Resonant excitation enables enhanced site-selectivity and gives information about the dynamics in the resonant inelastic X-ray scattering (RIXS)[17] process. The microjet technique was used, ensuring fast sample replenishment, crucial for X-ray studies of large molecular systems, and avoiding influence due to any interactions with a membrane.[16,18]

We interpret the spectra by comparing them to fluorocarbon spectra in the literature and by *ab initio* density functional theory. A theoretical electronic structure is also presented.

2 Experimental and theoretical details

2.1 Materials and methods

Perfluorodecalin was obtained from Alfa-Aeser in a 50/50 *cis*/*trans* mixture with >95% purity. XA, RIXS and XE spectra at the carbon and fluorine K-edges were recorded using a liquid microjet setup[14,19] at the U41-PGM undulator beamline of BESSY II at Helmholtz-Zentrum Berlin[15] with a microjet-diameter of around 14 μm. Detailed information about the end-station (LiXEdrom) is presented elsewhere.[19,20] The XA measurements were taken using a GaAs-diode from Hamamatsu. The RIXS and XE measurements were performed using a Rowland-circle geometry spectrometer with two gratings for different energetic ranges. The first grating of 5 m radius of curvature and 1200 lines per mm was used for the carbon K emission and a grating with 7.5 m radius of curvature and 1200 lines per mm was used for the fluorine K emission. The detector, which is operated at a pressure of 10^{-8} mbar, consists of an MCP-stack, phosphorescent screen and a CCD camera. The pressure in the experimental chamber is generally around 10^{-5} mbar. The beamline U41-PGM provides an excitation energy bandwidth of 0.1 eV at the energy of 300 eV for carbon excitations and 0.4 eV at 700 eV for fluorine excitations. The energy calibration of the RIXS and XE spectra was performed using the elastic scattering features.

2.2 Theoretical methods

The presented theoretical calculations were carried out with the ORCA program package.[21] Molecular geometry optimizations were performed using the B3LYP[22,23] density functional method with the def2-TZVP(-f) basis set[24,25] implying suitable symmetries for the *cis* and *trans* configurations. Transition energies and moments for K-edges were calculated with DFT/CIS (configuration interaction singles) and the electron population was calculated with a Löwdin population analysis using the same basis set and functional method. During the optimization calculations, the resolution of identity approximation[26–30] was used employing the def2-TZV/J basis set.[31] K-edge absorption spectra were obtained from the calculated transition moments by applying a Gaussian type broadening of 0.8 eV.

We find that introduction of nearest-neighbour molecules does not appreciably change the prediction of the spectra, showing that the intermolecular interactions are too small to be addressed in the present core-level study. Possible effects of conformational fluctuations in the liquid would add a new level to the analysis, but we believe that they will not influence the

discussion appreciably at the present level of accuracy. The theory does not predict any significant difference between the X-ray spectra of *cis* and *trans* forms of the molecule.

3 Results and discussion

The C K XA spectrum (Fig. 2a) of perfluorodecalin shows a rich structure with an isolated peak at 290 eV, followed by a broad band exhibiting at least 6 intensity maxima up to 300 eV. The spectrum shows some similarities to spectra of other sp^3 hybridized fluorocarbons,[32] with the C K-edge situated at unusually high energy. This can be mainly attributed to the large core-level chemical shift, due to the electronegativity of the fluorine neighbors. The spectrum differs substantially, however, from XA spectra of fluorobenzenes, which are dominated by an intense peak at lower energies, assigned to a π* excitation with respect to C–C bonds. Seemingly, the core hole in the PFD double ring cannot localize the lowest unoccupied molecular orbital (LUMO) in the same way as in fluorobenzene and therefore the oscillator strength for the first absorption transition is much lower.

The XA spectrum comprises transitions of many non-equivalent carbon sites and one may have suspected most spectral fine structures to be washed out. Note, however, that most carbon atoms have a similar chemical environment, with the same sp^3 hybridization and two fluorine atoms and two carbon atoms (dC) as nearest neighbours (Fig. 1). One could consequently expect the spectra associated with the core levels
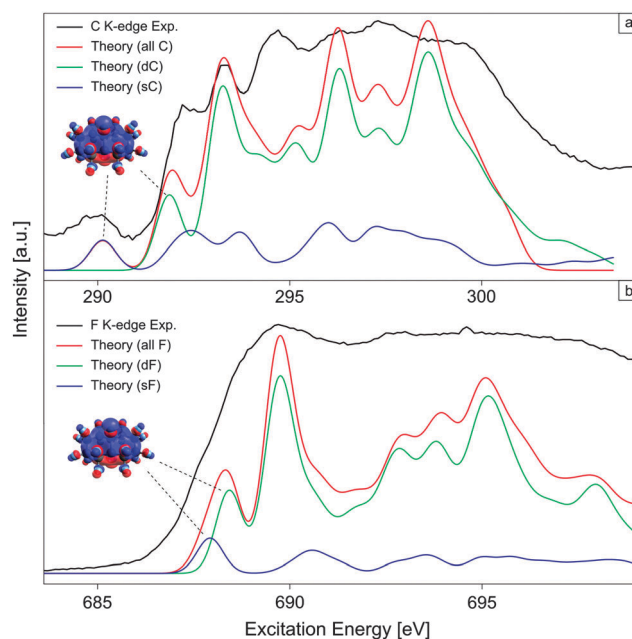

Fig. 2 Experimental carbon and fluorine K FY spectra of PFD, and theoretical XA spectra based on DFT calculations. DFT shows distinctly different spectra for various carbon or fluorine sites (sF and sC are associated with carbons having one C−F bond, whereas dF and dC are associated with carbons having two C−F bonds). This gives the opportunity for site selective excitation.

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of these atoms to be similar. The chemical environment of the two carbon atoms (sC) connecting the rings is similar, but significantly different from the dC atom environment, as they have three carbon atoms and only one fluorine atom as nearest neighbour. Thus, the fluorine influence is smaller than for the dC atoms and a correspondingly smaller core-level chemical shift suggests that the resonance at lowest energy may be associated with excitations at the sC sites.

A comparison to the XA spectra of simple fluoromethanes is helpful for the general understanding of the PFD spectra.[32] In these compounds the valence is typical of C sp^3 hybridization and, like for sC carbons, there is one C–F bond in CH_3F, whereas, like for dC carbons, there are two C–F bonds in CH_2F_2. Therefore we expect the local electronic structure to show similarities. Indeed the LUMO transition in the C K absorption spectrum of CH_3F is found just below 289 eV, whereas the corresponding transition in CH_2F_2 appears around 292 eV. The Rydberg series, which are prominent for the small molecules, have no correspondence in liquid PFD.

This picture is fully in line with the theoretical predictions (Fig. 2). In general the theory predicts the overall spectrum qualitatively well with the pre-peak and a broad structure with six maxima at appropriate energy positions, albeit with differing intensities. The theoretical spectrum is constructed as the sum of spectra of the ten non-equivalent carbon sites. The theory predicts distinctly different spectra for these sC and dC atoms, and the separate theoretical spectra are shown in Fig. 2a with the statistical weight (1/4). Thus, the theory indeed assigns the first peak to transitions to the lowest unoccupied orbital (LUMO) from core levels of the sC atoms. The predicted difference in chemical shift between dC and sC atoms is 1.1 eV and judging from the FY spectra the difference may be a little larger.

Note also that the relative weight of the LUMO is larger in the theoretical sC spectrum than in the dC spectrum. As we shall see later also excitonic effects must be taken into account for a full understanding of the spectrum.

The F K XA spectrum (Fig. 2b) shows saturation effects, as the fluorine K absorption totally dominates the absorption cross section above the edge. When the yield of secondary particles is used to monitor absorption cross sections, the contrast relies on the self-absorption of the emitted radiation. When the investigated absorption transition is totally dominating the cross section, the secondary photons, which have energy below the edge are not reabsorbed and the contrast is lost,[33,34] so that strong features are suppressed and weak features are relatively enhanced. The F K spectrum is more saturated than the C K spectrum because the fluorine K absorption cross section is more dominating at its edge. Thus, the stronger peaks are
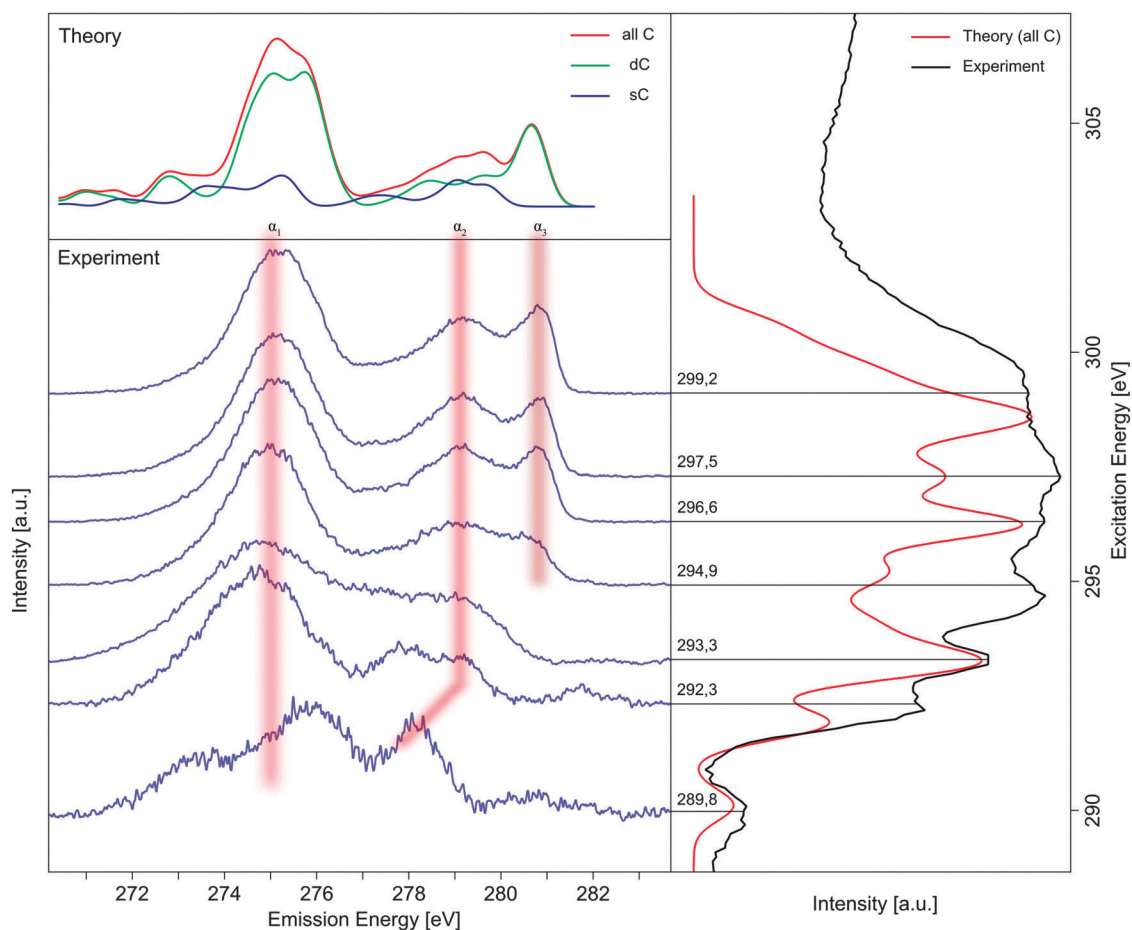

Fig. 3 Carbon K RIXS spectra of PFD (bottom, left) excited at the XA resonances (right). The theory (top, left) shows site selected XE spectra.

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relatively suppressed and the XA spectrum is not proportional to the transition probability. However, the overall spectral shape, with a first peak at around 690 eV followed by a broad band extending up to 700 eV, can be compared to predictions and we note that two of the fluorine atoms (sF) differ from the others (dF) in that they bind to the sC atoms, resulting in their next-nearest neighbour not being another fluorine atom. The theory predicts for the core-level of the sF atoms a different chemical shift than for the dF core levels by 0.7 eV, which leads to a corresponding shift, when comparing the sF and dF absorption spectra, shown in Fig. 2b with their statistical weight (1/8). In the experimental spectrum there is a faint low-energy shoulder at around 688 eV, which may be attributable to the sF sites.

The theory predicts that the sF and dF spectra are completely different, with respect to their intensity ratios and feature positions. In the former, transitions to the LUMO seem to dominate the spectrum, giving little intensity in the region of the most intense dF peak. This suggests that the local character of the unoccupied orbitals varies over the molecule and, as we shall see below, also excitonic effects are important.

C K XE spectra are compared to predictions in Fig. 3. The spectra excited at the highest energies show a broad band around 275 eV (α_1), a sharper high-energy peak at around 281 eV (α_3), and a local maximum in-between at 279 eV (α_2). Again, the overall shape can be understood by comparing to the XE spectra of gas-phase fluoromethanes.[35] As dC PFD carbon atoms, the CH_2F_2 carbon valence show sp^3 hybridization and the carbon atom binds two fluorine atoms, and one may expect corresponding similarities in the local electronic structure. Indeed, the C K emission spectrum of the CH_2F_2 molecule shows, like PFD, a three-peak structure: a broader peak at lower energies (277 eV), typical for sp^3 hybridized carbon, a sharper high-energy (283 eV) peak, due to a mixed C–F orbital, and a peak at intermediate energies (281 eV), where the orbitals predominantly have fluorine character. The similarities between the two spectra suggest an overall assignment, accordingly.

As noted above, excitation at the pre-peak mainly selects sC atoms, i.e., carbon atoms which bind only one fluorine atom, and the corresponding emission spectrum differs radically from the high-energy excited spectra. The low-energy feature (α_1) seems to split into a double structure peaking at 273.5 eV and 276 eV, the intensity of the high-energy feature (α_3) is suppressed and the local maximum at intermediate energies (α_2) is shifted from 279 eV to 278 eV. Assuming that the coupling to the excited electron is small and that the emission is typical for ionization at sC sites, one would expect a local electronic structure that simulates the carbon site in CH_3F.[35] Indeed, the CH_3F C K emission spectrum is lacking the high-energy peak of the CH_2F_2 spectrum and comprises two rather broad features at 276.5 eV and 280 eV, the first again, reminiscent of sp^3 hybridized carbon and the second peak being due to an F–C antibonding orbital. Although the PFD spectrum is more complex, with a splitted low energy peak, the similarities in the phenomenology are striking. Like for the small molecules the overall spectral shape depends on extensive vibronic excitations.

We note that there is a steep excitation-energy dependence for the spectra excited in the range of 292.3–294.9 eV. The main changes comprise a gradual high-energy shift and intensity-increase of the high-energy flank so that the high-energy excited spectrum is retrieved at an excitation energy of 296.6 eV. The shift of the high-energy flank from the lowest to the highest excitation energy can be explained by the difference in the core-level chemical shift and the appearance of an additional feature when going from sC to dC atom sites. However, site-selective excitation cannot fully explain the details in the excitation-energy dependence. The three-peak structure with the most intense peak at 275.5 eV in the spectrum excited at the lowest excitation energy is not predicted by sC site XE theory, whereas the double structure at 278–279 eV in the spectrum excited at 292.3 eV seemingly corresponds to a feature in the theoretical sC spectrum. The XE theory does not support any appreciable site selectivity for excitation energies in the 292.3–296 eV, where the XE spectrum is excitation-energy dependent. Instead, we attribute the observed excitation-energy dependence to excitonic effects, i.e., and that the electron excited in the first step influences the emission spectrum.

The high-energy excited F K emission spectrum (Fig. 4) shows a main peak at 675 eV, with an asymmetry towards higher energies and a low-energy feature at 672 eV. This is rather well reproduced by the theoretical prediction and we also note that the overall shape resembles the F K emission spectrum of CH_2F_2.[35] In analogy, one would assign the low-energy feature with the orbitals mixed with the carbon sp^3 valence and the main peak to states that are dominated by local F p character. At low-energy excitation the relative intensity of the low-energy peak decreases and the main peak becomes sharper and shifts towards lower energies. To some extent we anticipate increased contributions from the sF sites at low-energy excitation, although the site-selectivity is not as clear-cut as at the carbon edge. The observed trends upon decreasing the excitation energy can, to some extent, be explained by comparing the predicted XE from sF and dF sites. A shift towards lower emission energies and a narrowing of the main feature is in line with increasing relative emphasis on sF sites. Note, however, that the site selectivity predicted by the calculations is not as pronounced as at the carbon edge. In addition, we see that the main emission peak has a low-energy shift also for excitation as high as 689.7 eV, where we find it unlikely that sF sites are dominating. Therefore, we believe that the coupling with the excited electron must also be important at these energies. Such an influence of the core hole potential is indeed supported by the calculations.

The theoretical density of states (DOS), projected on sC, dC, sF and dF sites, is shown in Fig. 5. We see that the theoretical XE spectra shown in Fig. 3 and 4 are very similar to the occupied DOS, although the core-level chemical shift influences the XE spectra, so that they cannot be taken as a direct measure of the DOS. We see e.g., that the states of lowest binding energy are predicted to have some contribution from sC atomic sites, although the first peak in the C K XE spectrum is totally dominated by dC contributions. The outermost states are predicted to have about the same contribution from dC and
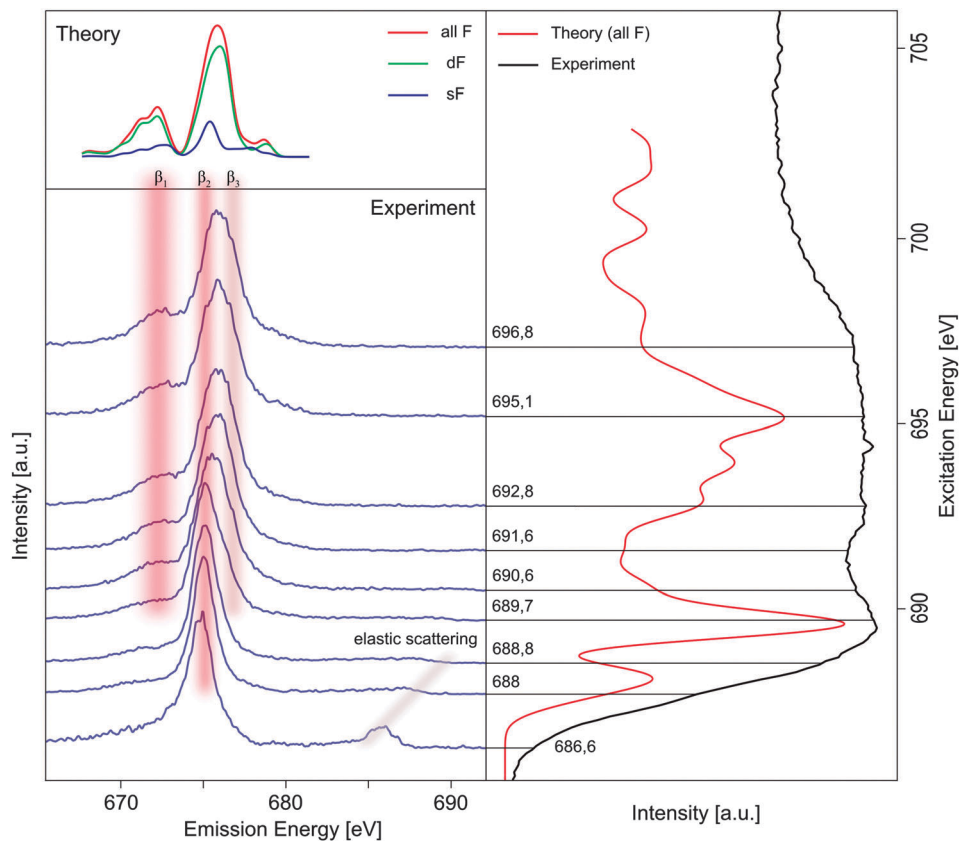
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Fig. 4 Fluorine K RIXS spectra of PFD (bottom, left) excited at the XA resonances (right). The theory (top, left) shows site selected XE spectra.
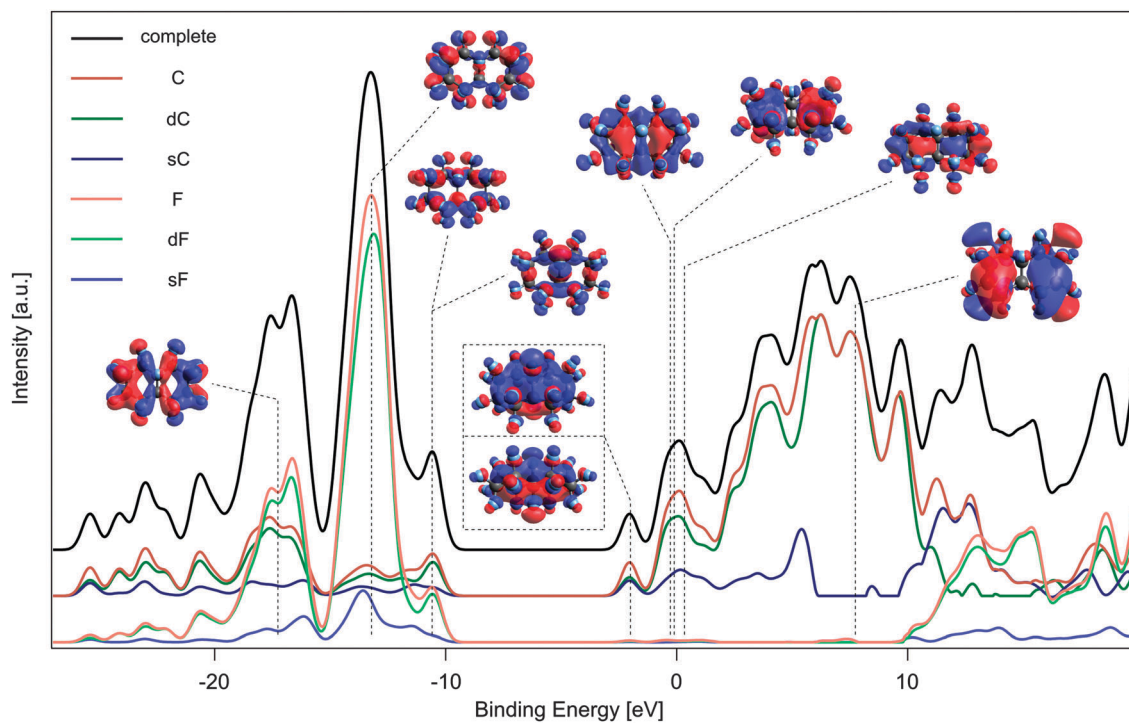

Fig. 5 Total and local density of states, projected on various atomic sites (see text). Density maps of selected orbitals show that while all orbitals are delocalized over the whole molecule demonstrate that the C sp^3 hybridized orbitals mix appreciably with fluorine (−17 to 18 eV), there are fairly pure fluorine orbitals (−13 eV) while the HOMO has fairly equal dC and dF weight (−11 eV). The lowest unoccupied orbitals in a wide range (−2 to 10 eV) are totally dominated by C DOS, and the LUMO has particularly much sC weight.

dF sites, whereas the occupied states are dominated by fluorine weight as expected and even the states associated with C sp^3 hybridized states around -18 eV have more fluorine than carbon weight.

The core-level chemical shifts are also important when interpreting the XA spectra. Indeed, theory shows that the LUMO is not, as the first peak in the C XA spectrum, only due to sC sites, but has about the same sC and dC weights. In addition, there is a large difference between the predicted XA spectra and the unoccupied DOS, far beyond what can be explained by core-level chemical shifts. Although similar features appear both in the unoccupied DOS and the XA spectra, the latter have much more relative weight for the states of lower energy. This shifting of spectral weight is attributed to the influence of the core hole potential on the electronic states. As the excited electron localizes in the core hole potential the coupling with the remaining electrons results in excitation-energy dependence in the RIXS spectra, in line with the observations described above.

We note that the unoccupied states are totally dominated by carbon over a 10 eV range, before the F DOS increases appreciably. Thus, the F near-edge XA spectrum comprises transitions to states which are dominated by carbon and the excitonic effects are obvious since the F XA spectrum, both in theory and experiment, lacks a sharp edge around 10 eV above threshold where the F weight increases.

We believe that this peculiar electronic structure is the key to the unusual properties of PFD. The difference in electro-negativity gives a slight negative net charge on the outermost fluorine atoms (around 0.13–0.14), according to calculations, and a net positive charge on the carbon atoms (0.26–0.27 for dC and 0.16 for sC). The relative inertness of the molecule can be understood within the frontier orbital model.[36] Both the HOMO and especially the LUMO orbitals are largely localized on the carbon atoms and therefore have limited overlap with potentially reacting molecules. The molecular geometry dictates that the surrounding first sees the fluorine atoms which have little HOMO–LUMO weight.

The first energy-loss peak in the RIXS spectra, which corresponds to the first hole–electron excitation, is situated at an energy loss of 11.8 eV for selective excitation at the sC site (Fig. 3), and the lowest energy loss is similar in the F K RIXS spectra (Fig. 4). Thus, we conclude that theory somewhat underestimates the HOMO–LUMO gap (around 9.5 eV in Fig. 5). Note also, that most low-energy excitations involve transfer of electrons from fluorine to carbon.

4 Conclusions

Based on experimental XA, XE, and RIXS spectra and on DFT theory we have presented a comprehensive picture of the electronic structure of the PFD molecule. In spite of the absence of one dominating XA resonance it is demonstrated that the lowest core excited states are highly excitonic. Site selective excitation gives access to specific carbon and fluorine sites in the RIXS spectra, showing that, while there is excess charge on the fluorine atoms, there is strong fluorine–carbon covalency in the occupied states. The lowest unoccupied states are completely dominated by carbon, so that the lowest excitations, over a large (11.8 eV) energy gap, are associated with charge transfer from fluorine to carbon atom sites. The weak intermolecular interaction in the liquid and the relative inertness of a molecule with this electronic structure can be understood within the frontier orbital model.

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