Characteristic redshift and intensity enhancement as far-IR fingerprints of the halogen bond involving aromatic donors†

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Six halogen-bonded cocrystals involving aromatic donors have been studied by far-IR spectroscopy. Characteristic redshift and intensity enhancement of the C–I stretching band have been observed, which provided a distinct signature of the halogen bond involving iodopentafluorobenzene.

In the late 1960s, a number of spectroscopic studies in the far-infrared (IR) region have regarded halogen-bonded complexes involving strong donors, such as I2 (ref. 1) and ICl,2 and various acceptors. These studies highlighted several common features such as red-shift and enhancement of the IR absorption bands of the covalent bonds the halogen-bond donor sites were involved in.3 These features were indicative of the charge-transfer component of the interaction and connected with the charge flux from the electron donor to the acceptor partner.4–6 Similar features were also observed when aliphatic iodoperfluorocarbons were used, e.g. CF3I.7–9 Various halogen-bonded complexes involving different trifluoromethyl halides and formed in cryo-matrices have been more recently investigated in detail by using IR and Raman spectroscopies.10–12 However, to the best of our knowledge, no study has regarded so far the far-IR investigation of halogen-bonded complexes involving haloperfluoroaromatic donors despite the fact that they are common and effective halogen-bond donor sites, frequently present also in molecular materials endowed with unique and useful properties.13

The performance of a halogen-bond donor largely depends on the degree of polarization of the halogen atom, i.e. the greater the positive electrostatic potential of the σ-hole, the more effective the halogen-bond donor will be.14 This means that the magnitude of the positive potential of the σ-hole depends on the ability of the halogen atom to be polarized as well as on the presence of electron-withdrawing moieties that cause a decrease in electron density on the halogen atom. In this respect, iodoperfluoroaromatics are very good halogen-bond donors, although weaker than I2 and iodoalkynes.15

On the other hand, iodopentafluorobenzene easily undergoes selective nucleophilic substitution at its para-positioned fluorine atom, allowing high-yield introduction of halogen-bond donor tectons on various molecular platforms.16 This prompted us to study the far-IR features of the C–X bond (X = Br and I) in model halogen-bonded complexes involving haloperfluoroaromatics in order to ascertain the fingerprint of the occurrence of the halogen bond.

In this paper, we report the experimental and theoretical far-IR studies of six prototypical halogen-bonded cocrystals, which were also fully characterized by single crystal and powder X-ray crystallography and calorimetry. Very simple

![Scheme 1](image-url)
starting tectons were chosen to be devoid of functional groups that could interfere with the occurrence of the halogen bonds or modify their features. Monodentate halogen-bond donors such as iodo pentfluorobenzene (IPFB) and bromopentafluorobenzene (BrPFB) were chosen in order to obtain dimeric and trimeric adducts with minimal crystal packing requirements with respect to those of multimeric adducts or the infinite chains formed by dihalotetrafluorobenzenes. As far as the halogen-bond acceptors are concerned, pyridine, 3-methylpyridine, 4-methylpyridine, and 3,5-dimethylpyridine were chosen, along with tetramethylethylene diamine as an example of an aliphatic acceptor (Scheme 1). Single crystal X-ray structures of the obtained adducts 1–6 confirmed that the X⋯N halogen bonds (X = I, Br) were, by far, the most important interactions in the crystals (Fig. 1). Other interactions being relatively long, i.e. weak, the studied IR characteristics are indicative of the inherent features of the halogen bonds rather than of halogen bonds heavily perturbed by crystal packing effects.

The six halogen-bonded cocrystals were synthesized by direct mixing of the liquid starting materials in either 1:1 (1, 2, 3, 4, and 5) and 1:2 (6) molar ratios, taking into account the pairing of the respective halogen-bond donor and acceptor sites. Crystallization of 2–4 and 6 occurred during blending, while 1 and 5 remained liquids at room temperature. The formation of new, discrete adducts and the absence of remaining starting compounds were confirmed by differential scanning calorimetry (DSC) measurements. New single melting and crystallization peaks were obtained, which dif- fered from the starting compounds. In particular, while all melting and crystallization peaks were obtained, which differential scanning calorimetry (DSC) measurements. New single cocrystal structures have never been reported before. Expectedly, the self-assembly of the starting compounds into dimers 1–5 and trimer 6 is driven by short X⋯N (X = I, Br) contacts, see Fig. 2. The I⋯N distance is in the range of 2.728(2)–2.841(9) Å, corresponding roughly to a 20% reduction in the sum of the vdW radii for I and N (3.50 Å).20 The Br⋯N distance found in 5 was 2.882(2) Å, which corresponds to a 15% reduction in the sum of the vdW radii for Br and N (3.40 Å).20 All crystal structures adopt the monoclinic P21/c or P21/n space group, showing strong similarities in their packing.

Once the occurrence of the halogen bond in all of the obtained cocrystals was ascertained, these were submitted to IR spectroscopy studies, in particular in the far-IR region at room temperature, in order to determine how the halogen bond affects vibrations of the involved molecular components. However, due to the limited literature on the topic, it was essential to first accurately assign the molecular vibration bands by calculations and then possibly predict the ones that should manifest a detectable change upon formation of the halogen bond. Therefore, we carried out a detailed vibrational analysis in the gas phase by density functional theory (DFT) calculations starting from the optimized geometry observed in the above described structures (see Table 1 and section S.5 of the ESI† for the detailed methodology).

Four vibrations of IPFB were located in the far-IR region, those being out of plane C–I bending at 80 cm⁻¹, in-plane C–I bending at 132 cm⁻¹, and in-plane C–I stretching at 204

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**Fig. 1** Halogen-bonded dimers in the crystal structures of 1 (top, left) and 5 (top, right) and trimer in 6 (bottom). Colours are as follows: C, grey; H, light grey; N, blue; F, yellow; Br, orange; I, magenta. The black dotted lines indicate the N⋯I and N⋯Br halogen bonds.

**Fig. 2** Normalized far-IR spectra of IPFB (red, top) and related cocrystal 4 (black, bottom). A clear redshift of ca. 12 cm⁻¹ and an intensity increase of about 25% were observed for the in plane C–I stretching band upon occurrence of the halogen bond (red dashed line).
 condemnation of pure IPFB shifted from 204 cm⁻¹ and the experimental spectra of the cocrystals involving IPFB, wavenumbers (blueshift) by approximately the same amount. Previously reported by N. F. Cheetham and A. D. E. Pullin for a characteristic change, undergoing a blueshift of –9 cm⁻¹, plus ring wagging at 212 cm⁻¹. The latter three are in very good agreement with the experimental ATR-FTIR spectroscopic measurements (132 cm⁻¹, 204 cm⁻¹ and 214 cm⁻¹), whereas the out of plane C–I bending, unfortunately, falls just outside our experimental range. Furthermore, the DFT calculations showed that a noticeable shift in the aforementioned vibrational modes should occur upon involvement of IPFB in the halogen bond. In fact, a redshift of around 15 cm⁻¹ was calculated for the C–I stretching vibration, whereas the C–I bending mode was shown to shift to higher wavenumbers (blueshift) by approximately the same amount.

Indeed, we observed clear shifts in the far-IR region of the experimental spectra of the cocrystals involving IPFB, i.e. 1–4 and 6 (Table 1). In particular, the in-plane C–I stretching vibration of pure IPFB shifted from 204 cm⁻¹ to 193 cm⁻¹ in 1 and up to 188 cm⁻¹ in 2 and 6 (Fig. 2). A similar redshift was previously reported by N. F. Cheetham and A. D. E. Pullin for the complex of trimethyamine and CF₃I.

The observed redshift is perfectly consistent with the weakening and lengthening of the C–I bond upon halogen bonding with pyridine nitrogen. Alongside the above-discussed shift, we also observed a remarkable intensity increase in the same vibration band of IPFB when involved in cocrystals, see Fig. 2. This intensity increase was also reproduced by DFT calculations (Table 1) and may find an explanation in the intrinsic charge-transfer characteristics of the halogen bond. In fact, according to Torii et al., the intensity increase of IR vibrations occurs in halogen-bonded cocrystals as a consequence of the intermolecular charge flux from the electron donor to the acceptor counterpart, thus affecting the dipole moment derivative of the C–I stretching mode. This leads to an increase in IR intensity, since the latter is proportional to the square of the dipole moment derivative with respect to the normal mode of vibration.

In addition, the C–I bending vibration of IPFB experienced a characteristic change, undergoing a blueshift of ca. 10 cm⁻¹ in co-crystals 1–4, and 6. However, no intensity variations were either predicted or observed for this specific vibration.

On the other hand, cocrystal 5, the only one containing bromine as a halogen-bond donor site, showed neither appreciable C–Br band shift nor intensity increase. The slightly worse agreement between gas-phase calculated and solid-state measured wavenumbers (Table 1) in 5 is probably due to the different constrains in the solid state. The smaller dimensions of Br, in fact, allows for a better packing, increasing the differences between the solid-state and the gas-phase IR frequencies, due to interactions with the neighbouring atoms.

Clearly, iodine causes changes in the IR spectra of the corresponding complexes greater than those of bromine, this difference being related to the more positive σ-hole on IPFB compared to BrPFB. Higher polarizability of iodine compared to bromine enhances the electropositive cap on the electrostatic potential surface of the halogen atom allowing for the occurrence of stronger intermolecular interactions.

This is consistent with a general trend of the halogen bond strength, which decreases in the order I > Br > Cl.

All of the above discussed findings prove the successful formation of charge-transfer complexes driven by the I⋯N halogen bond. However, neither I⋯N nor Br⋯N vibration bands were detected in our experimental set-up, which might be due to either the band residing out of the range measured (i.e. <100 cm⁻¹) or its intensity being very weak to be detected, both hypotheses being in line with the recently calculated interaction vibrations.

In summary, six cocrystals assembled through the halogen bond were fully characterized via XRD, DSC, and IR analyses. C–X (X = Br and I) normal modes of vibration of halo-perfluoroaromatic donors C₆F₅X, directly involved in the intermolecular halogen bond, were assigned by both experimental analysis and ab initio theoretical calculations for all of the studied cocrystals. We have demonstrated that the C–I vibration band undergoes a clear redshift and intensity increase upon occurrence of the halogen bond. This new spectroscopic fingerprint of the halogen bond involving iodo-perfluoroaromatics may be developed as a routine tool to

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<th>Compound/cocrystal</th>
<th>In plane C₆F₅–X bending (cm⁻¹)</th>
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* Calculated intensity increase. ^ Experimental intensity increase. * Very low intensity to be detected.

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Table 1: Experimental (exp.) and calculated (calc.) values of selected far-IR vibration bands associated to the C–X bond in pure compounds and related cocrystals. The calculated intensity increase is the ratio between the C–X stretching band and the C–F out of plane wagging mode in both the cocrystal and the pure compound (see section S.5 in the ESI). For the calculation of the experimental intensity increase, please see section S.4 in the ESI.
detect its occurrence in materials when alternative methods are not available. This is clearly the case for amorphous materials, polymers, liquid crystals, and fibrils where more complex and advanced methods, such as Raman spectroscopy and X-ray photoelectron spectroscopy (XPS) have been used. Due to the availability of modern instruments at reasonable cost, far-IR spectroscopy may nowadays be developed as a powerful and sensitive technique for the fast and easy study of intermolecular interactions. IR spectroscopy typically allows for the halogen bond formation to be detected in the solid state via the blueshift and intensity decrease of the C–H stretching shown by the halogen-bond pyridine acceptors or the redshift of the C–F stretching shown by iodoperfluoroalkanes (see section S.4 in the ESI†). The new fingerprint here reported complements these possibilities and affords the first vibrational tool to detect the direct occurrence of the interaction via changes in the IR features of iodoperfluoroaromatics, common moieties in halogen-bonded molecular materials.

Furthermore, the present study also contributes to the ongoing discussion on the nature of the halogen bond demonstrating a charge-transfer contribution in the studied systems evidenced by the band intensity increase associated to the C–I bond. A more systematic study is currently under way in our laboratories to ascertain the generality of the findings described in this paper, by also studying a series of complexes involving iodoperfluoroalkanes, a well-known class of halogen-bonded tectons. The full results will be reported elsewhere.

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Notes and references

18 CSD search (ConQuest Version 1.17, 2015).