



Raman study of the effects of solvent Lewis basicity on halogen bonding for short-chain primary and secondary iodo-perfluoroalkanes

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ABSTRACT

Raman spectroscopy is used to investigate vibrational frequency shifts in two specific normal modes of 1-iodo-perfluorobutane, 1-iodo-perfluorohexane, and 2-iodo-perfluoropropane when each is mixed with 21 distinct solvents. The two normal modes studied each red-shift upon halogen bonding. The degree of the red-shift is in some sense a measure of the strength of the halogen bond. The shift is correlated with the Lewis base strength of the solvent compound. Data presented here show that the two normal modes respond differently to the basicity of the solvent and hence provide some insight into the halogen bond interaction.

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1. Introduction

The concept of halogen bonding had its origins in the mid-1800s [1]. Later, in the mid-1900s, Hassel [2] and Mulliken [3] studied the interaction of halogen molecules with electron donors; the spirit of that exists in the current paper. In the past 20 years there has been increasing investigation of halogen bonding reported in the literature [4–6], particularly led by Resnati and Metrangolo. Applications in materials science, chemistry, and biology have been explored. Halogen bonding is pervasively utilized in many areas of materials chemistry [6–12]. It is currently being actively investigated for its use in chiral recognition [13,14]. Halogen bonding has recently been used to develop a high performance liquid chromatography separation of chiral compounds [13]. It is seen that halogen bonding mediates organic chemistry reactions such as perfluoroalkylation [15], amination of ether/thioether [16] and other reactions that specifically involve iodo-perfluoroalkanes [17,18]. In biochemistry, halogen bonding provides an avenue for development of possible new drugs in which halogen bonding is involved in drug-protein interactions [19–21]. Halogen bonding between halogenated base pairs in DNA has been investigated [22]. An understanding of the fundamental physics and chemistry of halogen bonding is developing [23–26].

The current study is focused on exploring the role of lone-pair electrons on halogen-bond acceptor molecules. Specifically, conventional Raman spectroscopy is used to directly monitor shifts in the C–I stretching mode in three short-chain iodo-perfluoroalkane molecules: 1-iodo-perfluorobutane, 1-iodo-perfluorohexane, and 2-iodo-perfluoropropane. Each of these compounds exists as a liquid at room temperature. A variety of solvents are used to form a collection of iodo-perfluoroalkane/solvent binary mixtures. The solvents were chosen to represent a broad range of Lewis basicity.

Characteristic of halogen-bond donors, which are the iodo-perfluoroalkanes for this work, is the presence of a positively charged σ -hole on the halogen atom that is engaged with the lone pair of the halogen-bond acceptors. In the case of iodo-perfluoroalkanes, the σ -hole appears on the distal side of the iodine atom relative to the σ bond to the connecting carbon atom [5,27,28]. Politzer et al. have done considerable work to map out the electronic surface of the halogen in halogen-bond donors using natural bond order population analysis [27,29,30]. More recently Head-Gordon et al. have applied correlated energy decomposition analysis to halogen bonding [31,32]. Because of their high electronegativity, the constituent fluorine atoms significantly enhance the positive charge of the σ -hole. The resulting σ -hole is comparable to a hydrogen atom on a traditional hydrogen bond donor molecule. Consequently, the halogen bond with iodo-perfluoroalkanes and traditional hydrogen bond acceptors is comparable in strength to hydrogen bonds.

The halogen bond strength between iodo-perfluoroalkanes and traditional hydrogen bond acceptors has led to their extensive use

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in materials science [11,12,33]. Specifically, di-iodo-perfluoroalkanes are used as linker molecules via their ability to halogen bond from both ends of the molecules. In this work, only mono-iodo-perfluoroalkanes are considered as a matter of simplicity.

The current work especially complements the work of Metrangolo et al. [34], Messina et al. [35], Cabot and Hunter [36], Messina et al. [37], Hawthorne et al. [38], and Fan-Hagenstein et al. [39]. The first three of these papers report shifts in F^{19} NMR peaks when di-iodo-perfluoroalkanes are mixed with a variety of different Lewis bases. The fourth reports upon the utilization of both Raman and IR spectroscopy to investigate the effects of halogen bonding on stretching modes in di-iodo-perfluoroalkanes/diazabicyclooctane mixtures. The fifth of these papers presents F^{19} NMR and IR studies of 1- and 2-(mono) iodo-perfluoroalkanes when mixed with several neutral and halogen-bond acceptor solvents. Finally, the sixth of these papers reports upon a noisy light version of coherent Raman spectroscopy used to investigate the effects of halogen bonding from 1- and 2-(mono) iodo-perfluoroalkanes on the ring breathing mode of pyridine. In the current work, Raman spectroscopy was employed to directly monitor shifts in two specific normal modes of the iodo-perfluoroalkanes when mixed with a variety of solvents. The pool of solvents was large enough to reveal correlation of peak shifts with various measures of Lewis basicity. These include the one-parameter measures of Gutmann donor number [40,41] and pK_b values [42], as well as the two-parameter measures of the Laurence scale [43] and the solvatochromic model [44,45]. Further, correlations between normal mode frequency shifts and shifts reported from the above F^{19} NMR studies are explored. It should be noted that Webb et al. studied shifts in C-NMR peaks for normal (non-fluorinated) iodo-alkanes [46].

It is important to address the issue of a normal mode versus local mode description of observed peaks. In the literature a local mode description has often been used [37,38]. The vibrational motion of the modes discussed in this paper and in the literature is actually not very local for the peaks of interest. The low frequency mode for the iodo-perfluoroalkanes that appears in the mid to high 200 cm^{-1} range is referred to as “low frequency C–I stretching” [37,38]. It, however, involves two similar full-frame bending motions—a good portion of each is an I–C–C bend. The length of the C–I bond does not change very much for this mode. This is consistent with results for regular iodo-alkanes [47]. In the current work, this mode will be referred to as “normal mode 1” and abbreviated NM1. This mode is shown in cartoon form in Fig. 1 and an animation is contained in the Supplementary Material.

The second mode of interest for the current work is the mode appearing at approximately 1100 cm^{-1} for iodo-perfluoroalkanes.

This mode has been referred to in the literature as “C–F” stretching as a local mode description. The motion of this mode again involves much of the full-frame and it includes C–I and C–C stretching to a large degree. Again, this is consistent with results for regular iodo-alkanes [47]. In the current work, this mode will be referred to as “normal mode 2” and abbreviated NM2. This mode is shown in cartoon form in Fig. 1 and an animation is contained in the Supplementary Material.

Both NM1 and NM2 are sensitive to halogen bonding, and this sensitivity varies with basicity of the halogen-bond acceptor. However, their responses to halogen-bond acceptors are different which provides some insight into halogen bonding of iodo-perfluoroalkanes. This is the primary contribution of this work.

2. Experiment

Halogen-bond donors, 1-iodo-perfluorobutane, 1-iodo-perfluorohexane, and 2-iodo-perfluoropropane, were obtained from Sigma-Aldrich. These compounds readily undergo a radical-based reaction to produce a small amount of I_2 among other products. This gives the solutions a mild purple color from the bottle. While the Raman signal is insensitive to these small amounts, the solutions were scrubbed of I_2 by placing clean copper wire into the solutions and letting them stand in the dark for two days. When used for the Raman studies, the solutions were clear (the copper does not remove other organic impurities). The solvents listed in Tables 1 and 2 were also procured from Sigma-Aldrich and used as received.

Mole fraction solutions of approximately $X = 0.2$, where X is the mole fraction of the particular iodo-perfluoroalkane in each solvent, were prepared by weight on an analytical grade balance. While this method made it impossible to prepare the nominal $X = 0.2$ exactly, the actual mole fractions could be determined very precisely. The measured mole fractions for each solution are given in Table 1. Solutions were prepared by difference in the same vials that were placed in the Raman spectrometer. Table 1 includes a shorthand reference to identify each binary mixture. The solvents are labelled with numbers while 1-iodo-perfluorobutane, 1-iodo-perfluorohexane, and 2-iodo-perfluoropropane are labelled **a**, **b**, and **c**, respectively. A particular mixture is referred to as #**x** (e.g., **18b** means a $X = 0.1893$ solution of pyridine and 1-iodo-perfluorohexane).

Spectra were acquired with a Snowy Range Sierra 2.0 Raman spectrometer with a 100 mW, 785 nm source laser. Spectra were collected over a range from 200 cm^{-1} to 2000 cm^{-1} . The instrument response function was estimated to give a resolution of approximately 4.5 cm^{-1} . This was determined using the 800 cm^{-1}

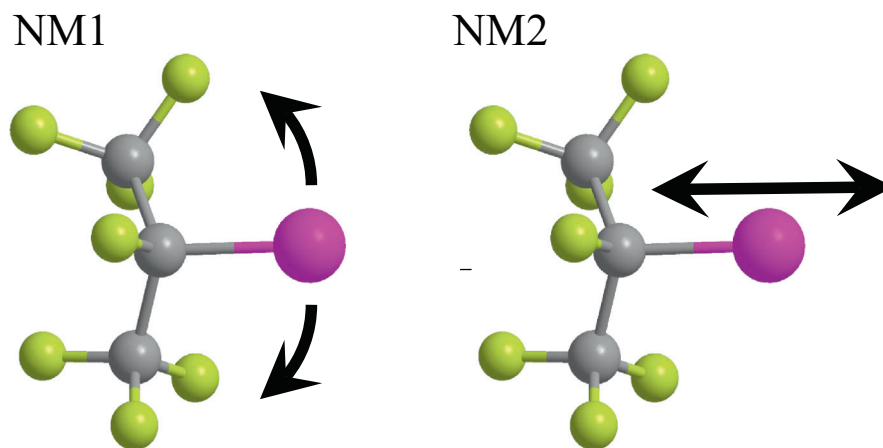


Fig. 1. Diagrams showing a cartoon representation of the normal vibrational modes of 2-iodo-perfluoro-propane studied in the present work. Both NM1 and NM2 are shown. Directions of motion are indicated by arrows on the diagrams (Animations of NM1 and NM2 can be found in the Supplementary Material). The C–I bond length changes very little in NM1, but changes significantly in NM2 during a vibrational period. All iodo-perfluoroalkanes used have similar normal modes.

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