



## Complexes of acetylene–fluoroform: A matrix isolation and computational study



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### HIGHLIGHTS

- Experimental evidence for the formation of 1:1 C–H... $\pi$  complex of C<sub>2</sub>H<sub>2</sub>–CHF<sub>3</sub> in Ar and N<sub>2</sub> matrices.
- The experimental vibrational frequencies agree well with the frequencies calculated using MP2/6-311++G(d,p) level of theory.
- The blue shift of the C–H stretching frequency increases in going from C<sub>2</sub>H<sub>2</sub>–CHCl<sub>3</sub> complex to C<sub>2</sub>H<sub>2</sub>–CHF<sub>3</sub> complex.
- Both 1:2 and 2:1 complexes of CHF<sub>3</sub> and C<sub>2</sub>H<sub>2</sub> are also characterized in this study.

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### ABSTRACT

Hydrogen-bonded complexes of C<sub>2</sub>H<sub>2</sub> and CHF<sub>3</sub> have been investigated using matrix isolation infrared spectroscopy and *ab initio* computations. The complexes were trapped in both solid argon and nitrogen matrices at 12 K. The structure of the complexes and the energies were computed at the B3LYP and MP2 levels of theory using a 6-311++G(d,p) basis set and at the MP2/aug-cc-pvdz level. Our computations indicated two minima for the 1:1 C<sub>2</sub>H<sub>2</sub>–CHF<sub>3</sub> complex, with the C–H... $\pi$  complex being the global minimum, where CHF<sub>3</sub> is the proton donor. The second minimum corresponded to a relatively less exothermic C–H...F complex, in which C<sub>2</sub>H<sub>2</sub> is the proton donor. Experimentally, we observed only the C–H... $\pi$  complex in our matrix, which was evidenced by the shifts in the vibrational frequencies of the modes involving the C<sub>2</sub>H<sub>2</sub> and CHF<sub>3</sub> sub-molecules. The increase in the blue shift of the C–H stretching frequency in going from CHCl<sub>3</sub>–acetylene complex to CHF<sub>3</sub>–acetylene complex with corresponding increase in the interaction energy helps to place these two complexes on the left hand end of the qualitative diagram (Fig. 1). We also performed computations to study the higher complexes of C<sub>2</sub>H<sub>2</sub> and CHF<sub>3</sub>. One minimum was found for the 1:2 C<sub>2</sub>H<sub>2</sub>–CHF<sub>3</sub> complexes and two minima for the 2:1 C<sub>2</sub>H<sub>2</sub>–CHF<sub>3</sub> complexes, at all levels of theory. Experimentally we observed the features corresponding to the 1:2 and 2:1 C<sub>2</sub>H<sub>2</sub>–CHF<sub>3</sub> complexes in the N<sub>2</sub> matrix. The computed vibrational frequencies of C<sub>2</sub>H<sub>2</sub>–CHF<sub>3</sub> complexes at B3LYP and MP2/6-311++G(d,p) level corroborated well with the experimental frequencies. Interestingly, no experimental evidence for the formation of higher complexes was observed in the Ar matrix.

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### 1. Introduction

Studies of hydrogen-bonded complexes, both experimental and theoretical, are of considerable interest [1–13]. The conventional hydrogen bond (H-Bond) where an X–H bond interacts with Y is represented by X–H...Y. Here X is an electronegative atom and Y with its electrons is a hydrogen bond acceptor and the formation of the H-Bond results in a red-shift of the X–H stretching fre-

quency. There are a number of experimental and theoretical studies on this subject. During the last fifteen years there has been an emphasis on the study of weak hydrogen bonds involving C–H...O, C–H... $\pi$  and O–H... $\pi$  interactions, as these serve as a driving force for many molecular phenomena and processes in chemistry, biology and material science [14]. Our interest in these weak hydrogen bonded systems led early studies on hydrogen bonded complexes formed by CHCl<sub>3</sub>, C<sub>2</sub>H<sub>4</sub> and C<sub>6</sub>H<sub>6</sub> with C<sub>2</sub>H<sub>2</sub>, using matrix isolation infrared spectroscopy in an Ar matrix [15–17]. The interactions in the C<sub>2</sub>H<sub>2</sub>–CHCl<sub>3</sub> complex was indicated, both by computations and experiments, to be of the C–H... $\pi$  type, where the C<sub>2</sub>H<sub>2</sub> acts as a proton acceptor and the CHCl<sub>3</sub> as the proton donor [15]. In addition, a secondary interaction between one of the

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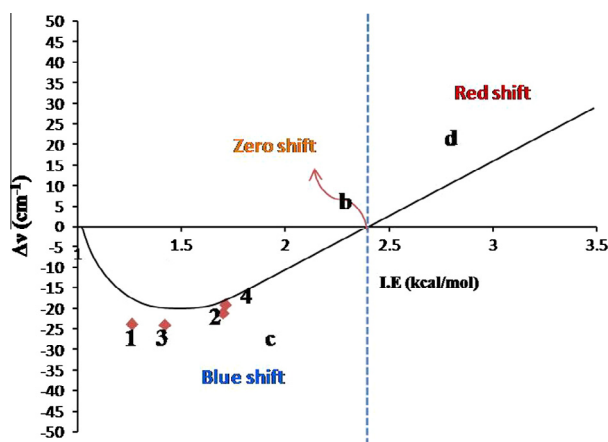
chlorine atoms of  $\text{CHCl}_3$  and hydrogen in  $\text{C}_2\text{H}_2$  was also indicated. Unlike the usual red shift observed in conventional hydrogen bonding, the blue-shift in the C–H stretching frequency of  $\text{CHCl}_3$  in the  $\text{C}_2\text{H}_2\text{-CHCl}_3$  complex, was corroborated by our computations. Similar computational studies on 1:1 and 1:2 complexes of  $\text{C}_2\text{H}_2$  with  $\text{CHCl}_3$ ,  $\text{CH}_2\text{Cl}_2$  and  $\text{CH}_3\text{Cl}$  indicated a blue-shift of the C–H stretching frequency [18]. There is a linear relation between frequency and interaction energy in the case of red-shifted hydrogen bonds. Our detailed analysis of hydrogen bonds with red and blue X–H shifts had shown that variation of interaction energy versus X–H frequency shift forms a continuous curve where blue-shifted hydrogen bonds form a nonlinear relation (Fig. 1) [19]. This is possible when there are opposing forces in deciding the weakening and strengthening of the X–H bond. In ordinary H-Bonds the factors that contribute to the weakening of the X–H-Bond and attendant red-shift dominates. Explanations for red shift have been around for a long time. As these are typically found for X–H bonds that have large ionic contribution, the electrostatic interaction between the  $\text{H}(\delta^+)$  and  $\text{Y}(\delta^-)$  dominates. The larger the positive charge on the hydrogen, the stronger is the electrostatic interaction. Elongation of the X–H bond increases the charge separation and this happens always in strong H-Bonds, leading to red-shift. Examples where the H-bond energy is very low, magnitude of the commonly observed weakening interaction is very low, and then the opposing interactions that stabilizes the X–H bond becomes relatively dominant. As the blue-shift is seen only in very weak H-Bonds, the forces that strengthen the X–H bond in H-Bond formation must be very weak. It is difficult to assign the contributors to very weak interactions. We had suggested the following possibility. Blue-shift is observed only in the case of covalent X–H bonds where the electron density corresponding to the X–H bond is evenly distributed around the bond. It is noticed from the variation of electron density distribution around X–H bond as a function of the  $\text{XH}\cdots\text{Y}$  distance that, at the equilibrium distance the electron density in between the X and H is increased in relation to the isolated molecule, as a result of the influence of the electrons on Y. While the exact mechanism of the redistribution of the electron density along the X–H bond can be debated, the enhancement of the electron density within the X–H bonding region increases the bond strength and leads to blue shift. This redistribution of electron density is helped by the substituents on X. In strong H-Bonds the X–H bond has a high ionic character with  $\text{H}(\delta^+)$  and

a redistribution of electron density that increases the covalent character is not possible. For this reason blue-shift is not observed for strong H-Bonds. Even in the Blue-shifted H-Bonds further increase of  $\text{XH}\cdots\text{Y}$  distance to infinite separation must lead to eventual zero interaction where obviously there is no shift. Therefore there will be a point in the curve for H-Bonds with relatively covalent X–H bonds where the opposing forces balance each other which could result in a hydrogen bonded species with a zero-shift, but with non-zero interaction energy [19]. It is possible to envisage specific examples of weak H-Bonds with appropriate X and Y such that the opposing forces contributing to the X–H frequency cancel out each other, leading to an H-Bond with zero X–H shift (Fig. 1). It is interesting to see the blue-shift region of the curve in Fig. 1 [19]. Depending on the increasing or decreasing part of the curve, an increase in the H-Bond strength may increase or decrease the blue shift. We plan to explore this behavior further from the studies of  $\text{C}_2\text{H}_2$  and  $\text{CHF}_3$ . There has been many studies on  $\text{C}_2\text{H}_2$  and  $\text{CHF}_3$  interacting with different molecules [20,21]. Oliveira et al. varied the  $\pi$  component keeping  $\text{CHF}_3$  as the constant C–H bond donor [22]. Studies on  $\text{C}_6\text{H}_6$  with  $\text{CH}_3\text{Cl}$ ,  $\text{CH}_2\text{Cl}_2$ ,  $\text{CHCl}_3$  and  $\text{CHF}_3$  also showed the C–H... $\pi$  interaction with a blue-shifted C–H bond of halomethanes [23]. There have been several recent spectroscopic studies of weak interactions involving haloforms [24–30]. Vincent and Hillier studied the structure and interaction energies of the weak complexes of  $\text{CHClF}_2$  and  $\text{CHF}_3$  with  $\text{C}_2\text{H}_2$  using different density functional approaches and compared the results with high resolution microwave data [31]. Melikova et al. studied the interaction of  $\text{C}_2\text{H}_2\cdots\text{BY}$  and  $\text{F}_3\text{CH}\cdots\text{BY}$  ( $\text{BY} = \text{N}_2, \text{CO}, \text{CD}_3\text{CN}, (\text{CD}_3)_2\text{CO}, \text{NH}_3, \text{C}_5\text{D}_5\text{N}$  and  $(\text{CD}_3)_3\text{N}$ ) in liquid Ar,  $\text{N}_2$  and CO [32]. In  $\text{CHF}_3$  complexes they observed blue shifting in the C–H stretching vibration accompanied by decrease in the infrared intensity of the  $\nu_1$  band of the  $\text{CHF}_3$  whereas in the case of  $\text{C}_2\text{H}_2$  complexes, they observed a red shift and an increase in the infrared intensity of the  $\nu_3$  C–H stretching mode. Peebles et al. identified the four isotopomers of the  $\text{C}_2\text{H}_2\text{-CHF}_3$  complex by FTMW spectroscopy [33]. Calculations performed at MP2/6-311++G(2d,2p) levels for the  $\text{C}_2\text{H}_2\text{-CHF}_3$  complex show that the structure of  $\text{C}_s$  symmetry exhibiting C–H... $\pi$  and C–F...H–C interaction corroborates well with the experiments.

To our knowledge there is no matrix isolation infrared work on the  $\text{C}_2\text{H}_2\text{-CHF}_3$  system. The present work is carried out with an aim to explore the possibility of forming 1:1 complexes between  $\text{C}_2\text{H}_2$  and  $\text{CHF}_3$  in Ar and  $\text{N}_2$  matrices and to corroborate with the computational results. Further, we would like to compare the results between the H-Bonds in  $\text{C}_2\text{H}_2\text{-CHCl}_3$  and in the corresponding  $\text{CHF}_3$  complex and to see where they fit in the qualitative scheme (Fig. 1). We also report the formation of 1:2 and 2:1  $\text{C}_2\text{H}_2\text{-CHF}_3$  complexes computationally and experimentally by matrix-isolation infrared spectroscopy.

## 2. Experimental and computational methods

Matrix isolation experiments were performed using a RDK-408D2 (Sumitomo Heavy Industries Ltd.) closed cycle helium compressor cooled cryostat. The cryostat was housed in a vacuum chamber where the base pressure was <1 mPa.  $\text{C}_2\text{H}_2$  (Commercial Grade, Asiatic Oxygen Limited, India) and  $\text{CHF}_3$  (Air products, USA, Electronic Grade) were used as such, without further purification.  $\text{N}_2$  and Ar (IOLAR Grade 2) were used as matrix gases, in which  $\text{C}_2\text{H}_2$  and  $\text{CHF}_3$  were premixed to obtain the desired matrix-to-sample ratios. The  $\text{C}_2\text{H}_2/\text{CHF}_3/\text{matrix}$  gas mixture was then deposited onto a KBr substrate maintained at 12 K. We used typical matrix-to-sample ratios ranging from 1000:0.15 to 1000:1 for  $\text{C}_2\text{H}_2$  and 1000:0.25 to 1000:2 for  $\text{CHF}_3$ . The matrix was deposited at a



**Fig. 1.** A schematic diagram of plot between interaction energy (I.E.) in kcal/mol and frequency shift in  $\text{cm}^{-1}$  of the C–H stretch of  $\text{CHX}_3$ . The nonlinear distribution of blue shifts of the C–H stretching frequency in going from  $\text{C}_2\text{H}_2\text{-CHF}_3$ (restricted) (1),  $\text{C}_2\text{H}_2\text{-CHCl}_3$ (restricted) (2),  $\text{CHCl}_3\text{-acetylene}$  complex (3) and  $\text{CHF}_3\text{-acetylene}$  complex (4) with corresponding increase in the interaction energy helps to place these complexes on the left hand side (blue-shift region) of the qualitative diagram.

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