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Blue-shift of the C-H stretching vibration in CHF_3-H_2O complex: Matrix isolation infrared spectroscopy and *ab initio* computations

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ABSTRACT

As a result of hydrogen bonding in CHF_3-H_2O complex, *ab initio* computations exhibited a blue shift in the C-H stretching region of CHF_3 sub-molecule. In this work, we have investigated whether the blue-shifting in CHF_3-H_2O complex can be experimentally discerned using matrix isolation infrared spectroscopy. The 1:1 CHF_3-H_2O complex was therefore trapped and studied in argon and neon matrices. Experimentally a blue shift of 20.3 and 32.3 cm^{-1} in the C-H stretching region of CHF_3 sub-molecule for the CHF_3-H_2O complex was observed in argon and neon matrices. The structure of the complex and the energies were computed at MP2 level of theory using a 6-311++G(d,p) and aug-cc-pVDZ basis sets. Computations indicated only one minimum corresponded to a C-H···O interaction between the hydrogen of fluoroform and oxygen of water. AIM and NBO analyses were performed to understand the reasons for blue-shifting of the C-H stretching wavenumber in the complex.

1. Introduction

The role of hydrogen bonded (H-bonded) interaction in the molecular conformation, crystal packing in solid state [1–6], supramolecular chemistry [7,8], and biological networks [9,10] has been extensively studied. There are a large number of reports on the red-shifted H-bonding involving C-H···O, O-H···O, N-H···O, O-H···N, and N-H···N interactions [11–14]. Apart from these conventional H-bonds, there are weak, red-shifted hydrogen bonds involving π cloud as electron donors in complexes stabilized by C-H···π, O-H···π and N-H···π interactions [4].

The concept of blue-shifted H-bonds has gained momentum in recent times and the quantum of experimental and theoretical reports on these systems is rapidly growing [15–28]. In blue-shifted H-bonding with X-H···D moiety, the bond shortening of X-H result in blue-shifting of its vibrational wavenumber. The blue-shifted H-bonds have been reported in weakly acidic C-H group such as halomethanes and benzene ($CHCl_3$/CHF_3/C_6H_6). Among the varieties of blue-shifted hydrogen bonds, C-H···O H-bonding has attracted attention because these interactions play a crucial role in stabilizing a specific structure of molecules and molecular assemblies.

Matsuura et al. reported the first experimental evidence for the intramolecular blue-shifted H-bonding [29]. Using matrix-isolation IR spectroscopy, Ahokas et al. studied the blue-shifted H-bonding in formyl fluoride dimers [30]. Hobza et al. reported the first theoretical study on the blue shifted H-Bonds in the benzene dimer $(C_6H_6)_2$, C_6H_6-CH_4 and C_6H_6-$CHCl_3$ system using correlated *ab initio* computations [31]. Subsequently, numerous theoretical work on the blue-shifted H-bonds were reported in the literature [32–61].

Recently, we have reported using matrix isolation infrared spectroscopy, the experimental evidence for the formation of 1:1 hydrogen-bonded cyclic complex between fluoroform and hydrogen chloride, where a blue-shift in the C-H stretching mode of the CHF_3 sub-molecule was observed [62].

CHF_3 is a simple molecular model to observe blue-shifted H-bonding and several groups have performed computations on this system with various proton acceptors [63–71]. Paulson and Barnes using matrix isolation technique examined the infrared and Raman spectra of trifluoromethane and trichloromethane mixed with water and ammonia in argon or nitrogen matrices. Formation of the CHF_3-H_2O complex was evidenced from the vibrational analysis of the normal mode corresponding to the ν_1, ν_2 and ν_3 modes of H_2O sub-molecule but they could not observe a distinct blue-shifted feature in the C-H stretching region of CHF_3 sub-molecule in the complex [70]. Moreover, in their work, computation on the CHF_3-H_2O complex was not reported to correlate with the experimental vibrational wavenumbers. The structure of the CHF_3-H_2O was well studied by several theoretical groups [15–18,34,43,50,66,68,71,72]. All these studies showed that the complex has a near linear geometry (∠C-H···O = ∼175°) with C-H···O

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interaction. Anharmonic vibrational frequency calculation performed at MP2/6-311++G(d,p) level of theory showed a blue shift of 33 cm^{-1} in the C-H stretching wavenumber of the CHF_3-H_2O complex [15].

The main aim of the present work, therefore, is to discern experimentally the blue-shifted feature in the C-H stretching region of CHF_3 sub-molecule in the CHF_3-H_2O complex in Ar and Ne matrices. *Ab initio* computations were carried out for the CHF_3-H_2O complex to compare the results with the experimental observation.

2. Experimental and computational methods

Matrix isolation experiments were performed using a RDK-408D2 (Sumitomo Heavy Industries Ltd.) closed cycle helium compressor cooled cryostat. Experiments were carried out with a base pressure better than 1×10^{-6} mbar. CHF_3 (Air products, USA, Electronic Grade) was used as such without further purification. Deionized water was purified by first chilling it to temperatures of $\approx$170 K, and then pumping on it to eliminate volatile impurities. High purity Argon (Inox, 99.998%) and Neon (Chemtron, 99.995%) were used as matrix gases. A twin-jet nozzle system was used to co-deposit CHF_3 and H_2O by streaming them separately onto the cold KBr substrate. CHF_3 with Ar/Ne gas mixture in the required ratio is prepared, in the mixing chamber, and this gas mixture was subsequently allowed to pass through the nozzle and deposited onto the substrate through a fine needle valve. A temperature range of ~ -80 to -75 °C kept for water in the bulb to control its concentration in the matrix and deposited through a second nozzle. The matrix to solute ratio varied between 1/0.5/1000 to 2/1/1000 for $CHF_3/H_2O/Ar$ or $CHF_3/H_2O/Ne$. The gas mixture deposited for about $\sim$80 min with a typical rate of $\sim$3 mmol/h.

Infrared spectra of the matrix isolated samples were recorded in the range 4000 to 400 cm^{-1}, using a Vertex 70 FTIR spectrometer, operated at a resolution of 1 cm^{-1}. The temperature of the matrix is slowly increased to 35 K (Ar) and 9 K (Ne) and kept for 15 min and then re-cooled to 12 K (Ar) and 4 K (Ne). During the annealing process the precursors diffuse into the matrix and form complex. Infrared spectra again recorded for the annealed matrix. All the spectra shown in this report were those recorded after annealing the matrix.

Computations were carried out for the CHF_3-H_2O complex using GAUSSIAN 09 suite of programs [73]. Monomer geometries were first optimized at MP2 level of theory using 6-311++G(d,p) and aug-cc-pVDZ basis sets. The geometry of the 1:1 complex was obtained without imposing any constraints in the structural parameters. Vibrational wavenumber calculations gave all positive values, which helped us to assign the observed vibrational wavenumbers in our matrix isolation infrared experiments. Stabilization energies were computed for the complexes, corrected separately, for both Zero point energy (ZPE) and BSSE (basis set superposition errors) using the method outlined by Boys and Bernadi [74].

Atoms in Molecules (AIM) theory was employed to understand the nature of the interaction between the CHF_3 and H_2O sub-molecules [75]. A $(3,-1)$ bond critical point (BCP) was searched between the two sub-molecules and the following properties at this BCP were examined: the electron density ($\rho(r_c)$), Laplacian of electron density ($\nabla^2\rho(r_c)$) and the ratio of the eigenvalues $|\lambda_1|/\lambda_3$. The small values of $\rho(r_c)$ and $\nabla^2\rho(r_c) > 0$ are characteristic of weak interactions [76]. Identification and analysis of the critical points was done using AIM package [77]. NBO (version 3.1) analysis invoked through Gaussian09 [78] was employed to understand the blue-shifting in the CHF_3-H_2O complex.

3. Results and discussion

3.1. Experimental details

When CHF_3 with varying concentrations of H_2O was co-deposited and annealed, new features were produced in the ν_1 C-H stretching mode of CHF_3 at 3064.7 cm^{-1} in Ar matrix and the corresponding feature in Ne matrix was observed at 3066.1 cm^{-1} (Fig. 1b-c block A and block B). Fig. 1a (block A and B) shows the uncomplexed CHF_3 spectra in Ar and Ne matrices. The feature observed at 3058.4 and 3064.4 cm^{-1} in Ar and Ne matrices, respectively is due to the aggregates of CHF_3 [70].

The site split features found at 1148.0/1145.5 cm^{-1} are due to the doubly degenerate ν_5 mode of CHF_3 in Ar matrix, and the corresponding peak was observed at 1151.1 cm^{-1} in Ne matrix (Fig. 2a block A and block B). Co-deposition of CHF_3 and H_2O and subsequent annealing showed an increase in intensity of the doublet feature observed at 1138.3, 1135.6 cm^{-1} in Ar matrix and at 1139.0 cm^{-1} in Ne matrix (Fig. 2b-c block A and block B). Further, a new feature observed at 1146.0 cm^{-1} increase in intensity on annealing in Ne matrix (Fig. 2b-c block B). CHF_3 multimeric feature was observed at 1138.3 and 1139.0 cm^{-1} in Ar and Ne matrices, respectively [70].

The feature observed at 1135.6 cm^{-1} and 1137.8 cm^{-1} is due to the ν_2 mode of CHF_3 in Ar and Ne matrices, respectively (Fig. 2a block A and block B). In the annealed matrix, a new feature in the ν_2 mode of CHF_3 sub-molecule appears at 1127.7 cm^{-1} and 1133.9 cm^{-1} in Ar and Ne matrices, respectively. In the ν_2 mode, the CHF_3 aggregate feature is observed at 1129.6 cm^{-1} in Ar and 1126.0 cm^{-1} in Ne matrix [70].

Fig. 3 shows the IR absorption spectrum in the ν_4 C-H bending region of CHF_3 in Ar matrix covering the region 1420-1350 cm^{-1}. The feature observed at 1376.2 cm^{-1} is due to the doubly degenerate ν_4 mode in an Ar matrix. Co-deposition and subsequent annealing of the precursors produced a new feature in the ν_4 mode of CHF_3 at 1387.6 cm^{-1}. In the ν_4 C-H bending region of CHF_3 sub-molecule in Ne matrix, new feature could not be observed. Fig. 4 show the ν_3 antisymmetric O-H stretching region of H_2O in Ar matrix covering the region 3800–3680 cm^{-1}. In Ar matrix, the three intense features for rotating H_2O molecule observed at 3776.8 ($1_{01} \rightarrow 2_{02}$), 3756.0($0_{00} \rightarrow 1_{01}$), 3711.0 ($1_{01} \rightarrow 0_{00}$) cm^{-1}. The proton acceptor and donor band for the H_2O dimer were found in Ar matrix at 3724.4 and 3699.3 cm^{-1}, respectively. The monomer and dimer features observed for the H_2O in Ar and Ne matrices agreed well with the reported literature [79–81] . When CHF_3 and H_2O were co-deposited and annealed, new feature was observed at 3727.8 cm^{-1} in Ar matrix. In the ν_3 antisymmetric O-H stretching region of H_2O sub-molecule in Ne matrix, new feature could not be discerned for the complex.

Fig. 5 block A (1650–1580 cm^{-1}) and block B (1640–1590 cm^{-1}) shows the O-H bending region of H_2O in Ar and Ne matrices. The three most intense features observed at 1607.9 ($1_{01} \rightarrow 1_{10}$), 1624.1 ($0_{00} \rightarrow 1_{11}$), and 1635.6 ($1_{01} \rightarrow 2_{12}$) cm^{-1} are due to rotating H_2O molecule in Ar matrix and the corresponding feature observed in Ne matrix at 1614.6, 1631.3 and 1649.9 cm^{-1} (not shown in the figure). The feature found at 1590.1 and 1596.1 cm^{-1} in Ar and Ne matrix, respectively is due to the non-rotating monomer for the ν_2 bending mode of H_2O. The features observed at 1593.2, 1607.9 cm^{-1} in Ar matrix and 1599.2 and 1616.8 cm^{-1} are due to proton acceptor and proton donor of H_2O dimer, respectively [79,80]. Co-deposition of CHF_3 and H_2O and subsequent annealing the matrix, produced new feature at 1594.9 and 1600.9 cm^{-1} in Ar and Ne matrices, respectively.