

# Isotope effects on the IR spectrum of the $CX_3Y \cdots HCl$ complex in liquefied argon: DFT calculations, topological analyses, and electronic properties

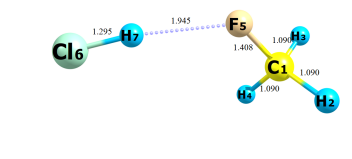
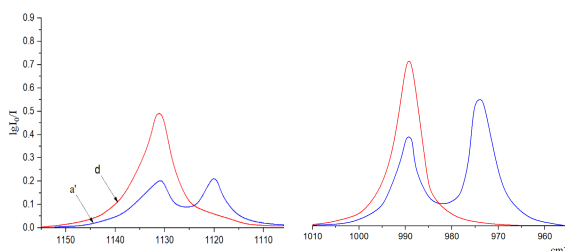
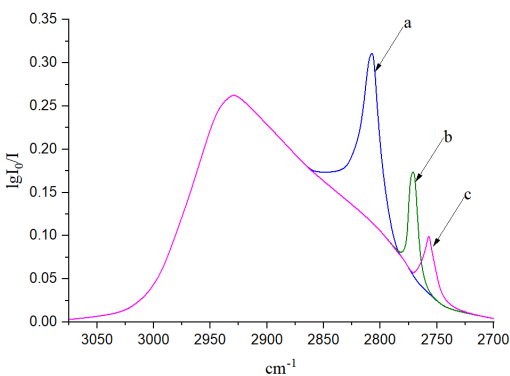
Abduvakhid Jumabaev, Gulomhon Murodov, Hakim Hushvaktov, Utkir Khujamov, Gulshan Nurmurodova  
Samarkand State University named after Sharof Rashidov, University blv.15, 140104, Samarkand, Uzbekistan

## MOTIVATION

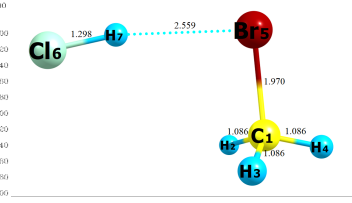
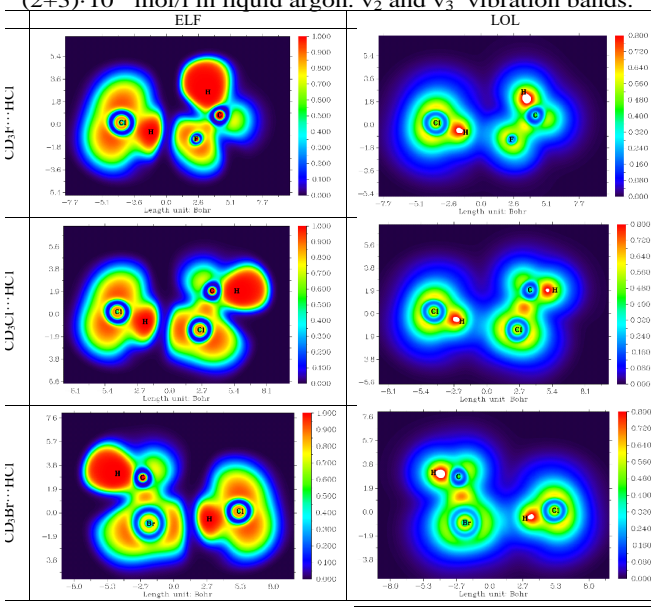
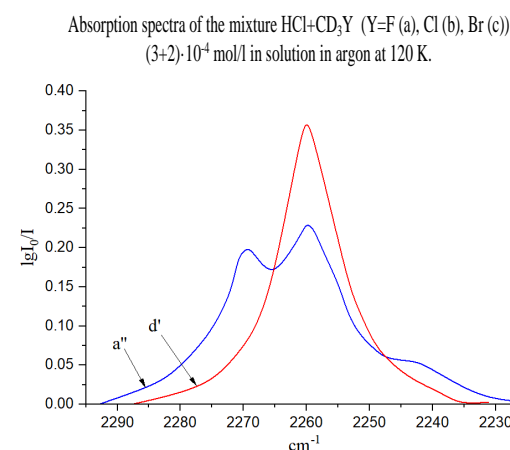
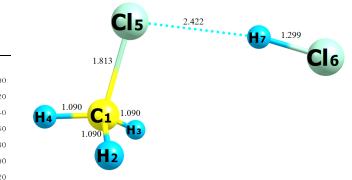
Infrared spectra ( $4000-400\text{ cm}^{-1}$ ) of free molecules  $CX_3Y$  ( $X=H, D, Y=F, Cl, Br$ ),  $HCl$ , and  $CX_3Y \cdots HCl$  mixtures in liquefied argon (90, 120 K) are recorded. The intermolecular interactions of the  $CX_3Y \cdots HCl$  complexes are studied using the DFT method based on the B3LYP/6-311++G(d,p) basis set. The effect of deuterium (D), an isotope of the hydrogen atom (H), on the vibrational spectra of hydrogen-bonded complexes is discussed. Harmonic and anharmonic vibration frequencies are determined in calculations. The intermolecular interactions in these complexes are studied for the first time using topological (AIM, NCI, RDG, ELF, and LOL) analyses. NBO analysis and Mulliken atomic charge distribution are used to study the mechanism of charge transfer in intermolecular interactions. The HOMO-LUMO gap and MEP are used to determine the electronic properties. Good agreement shows between the experimental and theoretical results.

## Computational methods

The Density Functional Theory (DFT) method was used to optimise the molecular structures of  $CX_3Y$  and complexes of  $CX_3Y \cdots HCl$ . The B3LYP/6-311++G(d,p) basis set was used in the calculations to account for intermolecular interaction as accurately as possible. The energies and other physicochemical characteristics of several noncovalently interacting systems have been successfully calculated using this collection of techniques and bases. Calculations were determined using the Gaussian 09 W package. Calculated wavenumbers were assigned to molecules and the calculation results were graphically shown using the GaussView 6.0 molecular visualisation program. Additionally, the MULTIWFN software was used to acquire the topological features of the electron density distribution in the most stable structure in order to gain a greater knowledge of intermolecular interactions based on Bader's AIM theory. Non-covalent interaction (NCI) and reduced density gradient (RDG) studies were carried out using VMD software, and the outcomes were shown.

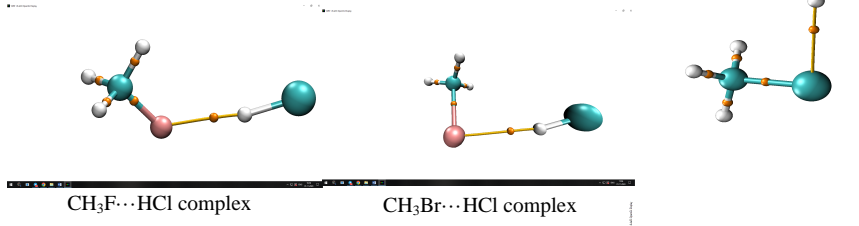


Absorption spectra of  $CD_3F$  (d) and a mixture of  $CD_3F+HCl$  (a')  $(2+3) \cdot 10^{-4}$  mol/l in liquid argon.  $\nu_2$  and  $\nu_3$  vibration bands.

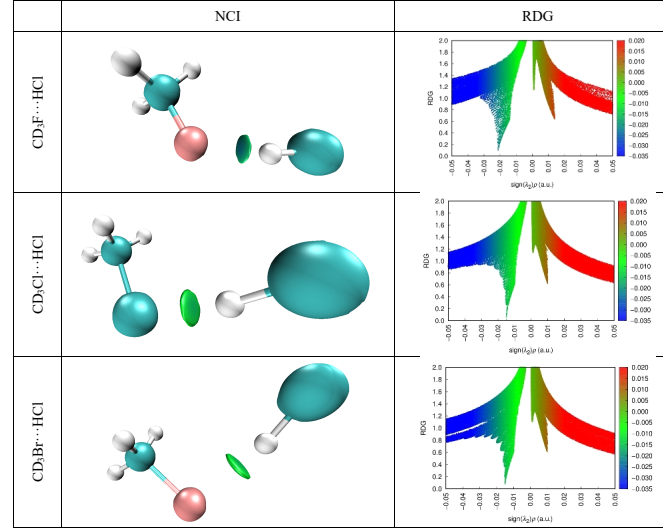


Optimal geometric structures of free molecules  $CX_3Y$  and  $CX_3Y \cdots HCl$  complexes

Absorption spectra of  $CD_3F$  (d) and a mixture of  $CD_3F+HCl$  (a')  $(2+3) \cdot 10^{-4}$  mol/l, in argon, vibration band at 90 K.



Complexes	$\rho$ (a.u.)	$\nabla^2\rho$ (a.u.)	$G(r)$ (a.u.)	$V(r)$ (a.u.)	$H(r)$ (a.u.)	$E_{HB}$ (kcal/mol)
$CD_3F \cdots HCl$	0.021	0.079	0.018	-0.016	0.002	5.02
$CD_3Cl \cdots HCl$	0.008	0.041	0.0093	-0.0083	0.001	2.60
$CD_3Br \cdots HCl$	0.015	0.036	0.0076	-0.0062	0.0014	1.94



## CONCLUSION

Among the partners of hydrogen halides in the formation of weak hydrogen bonds, fluoromethane, a very weak proton acceptor, occupies a special place as one of the first objects of study. The most detailed study in cryogenic solutions was carried out for the  $CH_3F \cdots HCl$  complex. In this section, in addition to the previously obtained results, the characteristics of the  $HCl$  band of the  $CD_3Y \cdots HCl$  complex in the series  $CD_3F, CD_3Cl, CD_3Br$  are analyzed, and the spectral manifestations of the hydrogen bond on the bands of interacting vibrations of the proton acceptor are studied.