ISNN:2181-1296



SHAROF RASHIDOV NOMIDAGI
SAMARQAND DAVLAT UNIVERSITETI

САМАРКАНДСКИЙ ГОСУДАРСТВЕННЫЙ
УНИВЕРСИТЕТ ИМЕНИ ШАРОФА РАШИДОВА

SAMARKAND STATE UNIVERSITY NAMED
AFTER SHAROF RASHIDOV

ILMIY AXBOROTNOMA

НАУЧНЫЙ ВЕСТНИК
SCIENTIFIC JOURNAL

ANIQ VA TABIIY FANLAR SERIYASI

Matematika, Mexanika, Informatika
Fizika, Kimyo, Biologiya, Geografiya

№ 1/1 (149)
2025

ISSN 2181-1296

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Samarqand viloyat matbuot boshqarmasida ro‘yxatdan o‘tish tartibi 09-25.
Jurnal 1999-yildan chop qilina boshlagan va OAK ro‘yxatiga kiritilgan.

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tashkilot, korxonalar uchun **- 5584**

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UDC:542.452.1 https://doi.org/10.59251/2181-1296.2025.v1.149.1.3201

INVESTIGATION OF $CD_3Hall\cdots HCl$ (Hal = F, Cl, Br) COMPLEXES BASED ON IR SPECTRA AND DFT CALCULATIONS

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Received: 15.02.2025
Revised: 24.02.2025
Accepted: 28.02.2025
Published: 29.03.2025

Publisher: Samarkand State University named after Sharof Rashidov.

Abstract. Weakly interacting complexes of $CD_3Hal\cdots HCl$ (Hal = F, Cl, Br) have been investigated in a liquid argon environment using infrared (IR) spectroscopy and density functional theory (DFT) calculations. The structural and energetic properties of these complexes were analysed using the B3LYP functional with the 6–311++G(d,p) basis set. The effect of the weakly interacting argon medium on the stability and spectroscopic characteristics of the complexes was examined. Quantum theory of atoms in molecules (AIM) analysis confirmed the presence of van der Waals interactions and elucidated the nature of the interaction. The IR spectra showed characteristic red shifts in the HCl stretching vibrations, indicating van der Waals interactions formation. A detailed comparison between experimental and theoretical results provided insights into the influence of different halogens on the strength and geometry of van der Waals interactions. The findings contribute to a deeper understanding of weakly bound complexes in cryogenic environments and their spectroscopic signatures.

Keywords: AIM analysis, $CD_3Hal\cdots HCl$ complexes, DFT, IR spectroscopy, H-bonding, NCI analysis, RDG analysis.

$CD_3Hal\cdots HCl$ (Hal = F, Cl, Br) komplekslarini IQ spektrlari va DFT hisoblari asosida tekshirish

Annotatsiya. Ushbu tadqiqotda $CD_3Hal\cdots HCl$ (Hal = F, Cl, Br) komplekslarining xususiyatlari infraqizil spektroskopiya va DFT hisoblashlari yordamida o‘rganildi. Tadqiqot natijalari shuni ko‘rsatdiki, vodorod bog‘lanishining mustahkamligi galogen atomining turi va uning elektrmanfiyligiga bog‘liq. Infraqizil spektroskopiya ma’lumotlari va DFT hisoblashlari natijalari bir-birini tasdiqladi hamda komplekslarning tuzilishi, energetik xususiyatlari va Mulliken atom zaryadlari haqida muhim ma’lumotlar berdi. Olingan natijalar vodorod bog‘lanishiga ega tizimlarning o‘ziga xos xususiyatlarini chuqur tushunish va ularning fizik-kimyoviy reaktivligini oldindan bashorat qilish uchun foydali bo‘lishi mumkin.

Kalit so‘zlar: AIM tahlili, $CD_3Hal\cdots HCl$ komplekslari, DFT, IQ spektroskopiyasi, H-bog'lanish, NCI tahlil, RDG tahlil.

Исследование комплексов $CD_3Hal\cdots HCl$ (Hal = F, Cl, Br) на основе ИК-спектров и расчетов DFT

Аннотация. В данном исследовании свойства комплексов $CD_3Гал\cdots HCl$ (Гал=F, Cl, Br) были изучены с помощью инфракрасной спектроскопии и расчетов ТФП. Результаты показали, что прочность водородной связи зависит от типа галогенного атома и его электроотрицательности. Данные инфракрасной спектроскопии и результаты расчетов

ТФП взаимно подтверждали друг друга и предоставили важную информацию о структуре, энергетических свойствах и зарядах атомов по Мулликену в комплексах. Полученные результаты могут быть полезны для более глубокого понимания уникальных характеристик систем с водородными связями и прогнозирования их физико-химической реактивности.

Ключевые слова: анализ AIM, водородные связи, ИК-спектроскопия, ТФП, комплексы $CD_3Hal\cdots HCl$, NCI анализ, RDG анализ.

1. Introduction. Diluted inert gases, including argon (Ar), krypton (Kr), and xenon (Xe), play a crucial role in the spectroscopic study of hydrogen-bonded complexes. These gases are used as low-temperature solvents under thermodynamic equilibrium conditions [1, 2] and enable effective spectroscopic analysis of weakly bound complexes due to their high transparency in the infrared (IR) region. In particular, liquid argon is widely used as a solvent; however, its temperature range suitable for research is limited by its melting point (90 K).

In this study, spectroscopic experiments were conducted in a liquid argon environment, which allows for the investigation of complexes in the liquid phase under equilibrium conditions. Additionally, the spectroscopic properties of the complexes in the gas phase were compared with their characteristics in the liquid phase.

As a model system, $CD_3Hal\cdots HCl$ (Hal = F, Cl, Br) complexes, which exhibit weak van der Waals interactions, were selected. Previously, the spectroscopic manifestation of the $CH_3F\cdots HCl$ complex was studied in liquid argon and liquid krypton environments [3, 4]. Compared to CH_3F, the use of deuterated methyl fluoride (CD_3F) prevents the overlap of ν(HCl) absorption with ν(CH) bands. Furthermore, in addition to fluorine (F), the complexes containing chlorine (Cl) and bromine (Br) were also investigated.

In recent years, significant attention has been given to weak hydrogen-bonded complexes, particularly to the binding energies and structural analysis of $H_3CHal\cdots HHal$-type structures [5,6]. R. M. Badger and colleagues [7] demonstrated a direct proportionality between the binding energy (E) and the red shift (Δν) of the H-X stretching band in hydrogen-bonded complexes ($E \sim \Delta\nu$).

In this study, the optimal geometry of $CD_3Hal\cdots HCl$ complexes was determined using density functional theory (DFT) calculations, and their electrostatic and spectroscopic properties were analyzed in relation to their structure. The DFT method was employed to compute the structural parameters of the molecules, Mulliken atomic charges, molecular electrostatic potential (MEP) surfaces, atoms-in-molecules (AIM) interaction fields, reduced density gradient (RDG), non-covalent interactions (NCI), electron localization functions (ELF), and localized orbital locator (LOL) quantum-chemical parameters.

Furthermore, the binding energies of $CD_3Hal\cdots HCl$ complexes were determined while accounting for the basis set superposition error (BSSE). It was observed that the E-energy is not always directly proportional to Δν. The increase in the distance between the H-Cl nuclei upon complex formation, compared to the monomer, and its effect on vibrational frequency shifts were also analyzed in detail.

2. Methods.

2.1. Experimental method

An optical cuvette designed for liquid samples was used. Experimental results were obtained at a temperature of T = 90 K. The concentration for CD_3Hal + HCl complexes in liquid Ar was prepared in the range of $(2–3)\cdot10^{-4}$ mol/L.

The spectral range was determined using BaF_3 optics, covering the region from the UV to 800 cm^{-1}. For IR spectra measurements, a UR-20 spectrometer (with a resolution of 2 cm^{-1}) was used. Spectral measurements were performed in the range of 4000–800 cm^{-1}.

The experimental results were compared with the literature data [8].

2.2. Computational details

For the calculations, the 6–311++G(d,p) basis set was used, which includes diffuse and polarization functions, allowing for highly accurate calculations of hydrogen bonding. This approach

has been effectively applied to determine the energy and various physicochemical properties of systems with non-covalent interactions [9–14].

To visualize the computational results and assign the obtained vibrational frequencies to molecules, the GaussView 6.0 and Chemcraft programs were used [15]. All calculations were performed using the Gaussian 09 W software [16].

Additionally, scaling factors were applied to minimize systematic errors arising from anharmonic vibrational frequencies and the incomplete basis set. In this study, a scaling factor of 0.9668 was used for the B3LYP/6–311++G(d,p) method [17,18].

To further analyze intermolecular interactions, the topological properties of electron density were investigated using Bader's AIM (Atoms-in-Molecules) theory with the MULTIWFN software [19]. Non-covalent interactions (NCI) and reduced density gradient (RDG) analysis were carried out using VMD software, and the results were visualized graphically [20].

The binding energies for these complexes were calculated using Equation (1) (Table 1). These values do not include the zero-point vibrational energy (ZPE). To obtain a more accurate estimation of ZPE, anharmonic calculations were performed, and anharmonic constants as well as rovibrational interaction constants were determined [21].

The binding energy was calculated using the following formula:

$$E_{bind} = E_{comlex} - (E_{HCl} + E_{D_3CHal}) + E_{BSSE} \qquad (1)$$

Here: E — binding energy of complex formation, $E_{complex}$ — total energy of the complex, $(E_{HCl} + E_{D_3CHal})$ — sum of the energies of the constituent monomers, E_{BSSE} — correction term for the basis set superposition error (BSSE) in the calculation [22].

This approach enables an accurate evaluation of the binding properties of the complexes and allows for an in-depth analysis of their physicochemical characteristics.

2.3. **Results and discussions.** Structural parameters of complexes

The results of the optimized geometry calculated using the DFT method **(**Figure 1**)** indicate that the presence and intensity of hydrogen bonding in $CD_3Hal\cdots HCl$ (Hal = F, Cl, Br) complexes depend on the nature of the halogen atom**.**

In the optimized structures of these complexes, the main focus was on the bond distance between the CD_3Hal and HCl molecules, as well as the changes in bond angles.

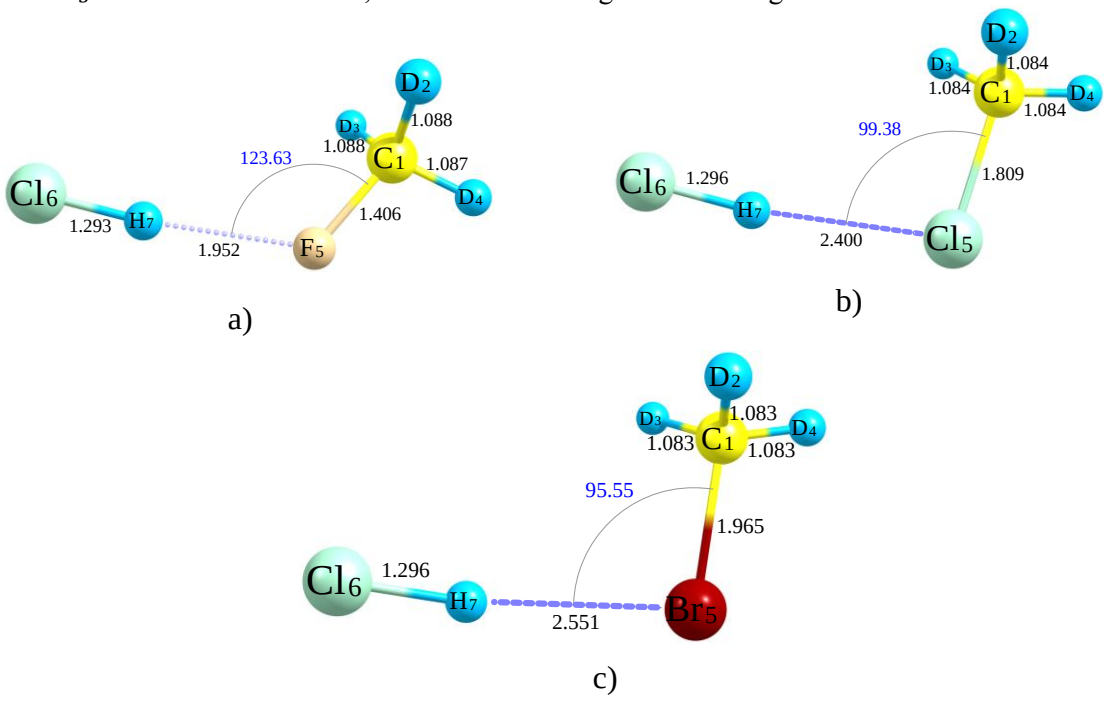


Fig. 1. Optimal geometries of the complexes $CD_3F\cdots HCl$ (a), $CD_3Cl\cdots HCl$ (b), and $CD_3Br\cdots HCl$ (c).

According to the computational results, the van der Waals interaction distance (r(H···Hal)**)** is the shortest in the $CD_3F\cdots HCl$ complex (r(H···F)=1.952 Å), and this distance slightly increases as the

nuclear charge of the halogen atom increases. In other words, the strongest van der Waals interaction is observed in $CD_3F\cdots HCl$ **(**E(H···F)=-2.97 kcal/mol), while in $CD_3Cl\cdots HCl$**,** the bond distance **(**r(H···Cl)=2.4 Å) is slightly longer, and the binding energy (E(H···Cl)=-2.33 kcal/mol**)** is lower. In the $CD_3Br\cdots HCl$ complex, the longest interaction distance (r(H···Br) =2.551 Å) is observed, indicating a weaker bond (E(H···Br) = -2.24 kcal/mol**).**

This trend is related to the decrease in electronegativity and the increase in atomic radius**.** Since fluorine (F) has the highest electronegativity, it forms the most stable complex with the HCl molecule.

The analysis of the main bond angles in the molecules shows that complex formation leads to slight changes in the C-Hal bond angles within the CD_3Hal molecule, with the most significant deformation occurring in the $CD_3F\cdots HCl$ complex. Additionally, the HCl molecule is slightly tilted relative to the CD_3Hal molecule, reflecting the complex nature of electrostatic interactions**.**

2.4. Spectral Characteristics of HCl in Monomeric and Complexed Forms

The vibrational properties of HCl in monomeric form and in complexes with D_3CF, D_3CCl, and D_3CBr were analyzed using infrared (IR) spectroscopy and density functional theory (DFT) calculations. The experimental results obtained at 90 K in liquid argon (Ar) and theoretical calculations performed at 298.15 K in an Ar solvation environment provided valuable insights into the spectral behavior of HCl under different conditions.

Table 1 presents the experimental and theoretical vibrational frequencies of the ν(HCl) stretching mode in different environments. In the experimental spectra, the ν(HCl) vibration appears at 2869 cm for the monomeric HCl, whereas for the $D_3CF\cdots HCl$, $D_3CCl\cdots HCl$, and $D_3CBr\cdots HCl$ complexes, the corresponding IR absorption bands shift to 2804, 2770, and 2756 cm, respectively. These results indicate a systematic redshift of the ν(HCl) stretching mode upon complexation, suggesting van der Waals interactions that weaken the H-Cl bond [23-25].

Table 1. The experimental (90 K, in Ar solvent) and theoretical (298.15 K, in Ar solvation environment) spectral parameters of ν(HCl) in monomer HCl and $D_3CHal\cdots HCl$ complexes**.**

$D_3CHal\cdots HCl$	ν_{HCl} (cm^{-1})		$\Delta\nu$ (cm^{-1})		$-E_{bind}$ (kcal/mole)		$r_{H\text{-}Cl}$ (Å)
	Exp.	Theo.	Exp.	Theo.	Exp.	Theo.	Theo.
HCl	2869	2930.35					1.2839
$D_3CF\cdots HCl$	2804	2813.65	65	116.70	-	2.97	1.2932
$D_3CCl\cdots HCl$	2770	2764.82	99	165.53	-	2.33	1.2957
$D_3CBr\cdots HCl$	2756	2749.13	113	181.22	-	2.24	1.2965

The DFT calculations further support this trend, predicting the monomeric HCl stretching frequency at 2930.35 cm. For the $D_3CF\cdots HCl$, $D_3CCl\cdots HCl$, and $D_3CBr\cdots HCl$ complexes, the computed ν(HCl) values are 2813.65, 2764.82, and 2749.13 cm, respectively. These theoretical values are in good agreement with the experimental results, confirming the influence of halogen substitution on the strength of the van der Waals interactions and the corresponding vibrational shifts [26].

2.4.1. Influence of Halogen Substitution on Vibrational Frequencies

Figures 2a–d illustrate the IR absorption bands associated with ν(HCl) in different molecular environments. The observed redshift of ν(HCl) upon complexation follows the trend: $D_3CF\cdots HCl > D_3CCl\cdots HCl > D_3CBr\cdots HCl$. This shift can be attributed to differences in the electronegativity of the halogen atoms, which influence the electron density around the interacting HCl molecule [27,29]. The stronger the interaction, the greater the shift in vibrational frequency.

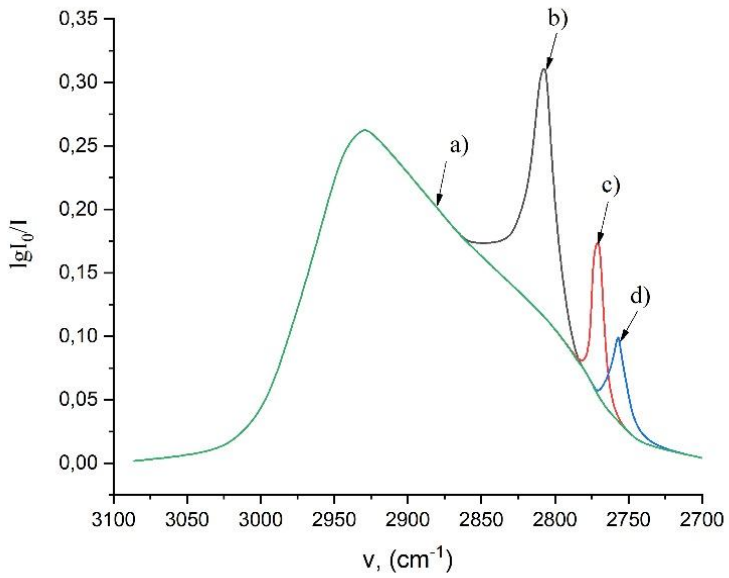


Fig. 2. a) IR absorption bands attributed to n(HCl) in monomeric HCl, b) $D_3CF\cdots HCl$, c) $D_3CCl\cdots HCl$, and d) $D_3CBr\cdots HCl$ complexes.

Additionally, Figures 3 and 4 provide insights into the vibrational behavior of the $D_3CF\cdots HCl$ complex. In Figure 3, the ν(CD) stretching vibrations for the monomeric D_3CF and the $D_3CF\cdots HCl$ complex are compared, demonstrating minor shifts due to complexation. Similarly, Figure 4 highlights the deformations in the ν(CD) modes upon van der Waals interactions, further confirming the interaction between HCl and D_3CF [28,30].

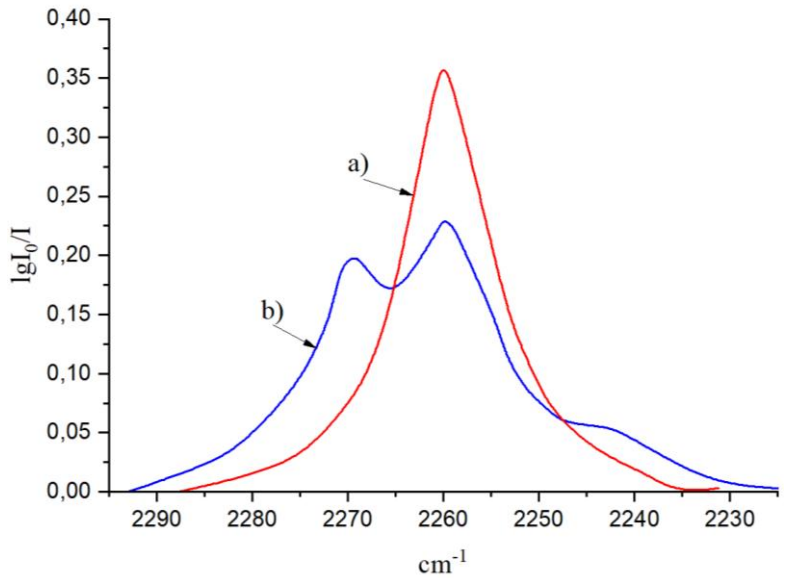


Fig. 3. a) Bands corresponding to ν(CD) valence vibrations in the monomer D_3CF and b) the $D_3CF\cdots HCl$complex.

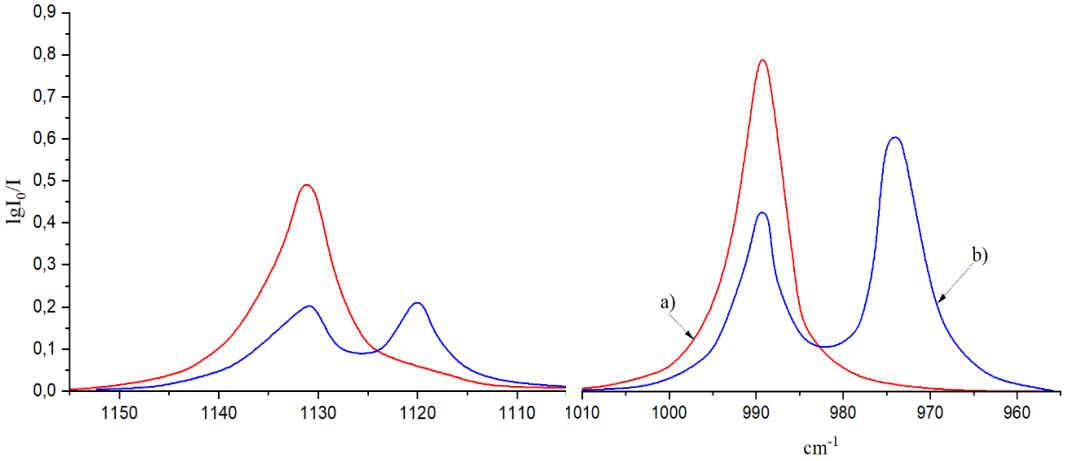


Fig. 4. a) Bands corresponding to the ν(CD) deformation vibrations in the monomer D_3CF and b) $D_3CF\cdots HCl$ complex.

2.4.2. Comparison of Experimental and Theoretical Findings

The consistency between experimental and theoretical spectral parameters indicates the reliability of the computational approach used in this study. While small deviations exist between the experimentally observed and DFT-predicted frequencies, these differences can be attributed to temperature effects, solvent interactions, and the level of theory employed in the calculations.

Overall, the findings demonstrate that the interaction strength between HCl and halogenated compounds affects the vibrational characteristics of the molecule. The decreasing shift in ν(HCl) with increasing halogen size (F>Cl>Br) suggests that the electronegativity of the substituent plays a significant role in determining van der Waals interactions strength [24-26]. These results provide a deeper understanding of the spectral behavior of HCl in complex systems and pave the way for further investigations into molecular interactions in halogenated environments.

2.5. AIM analysis: $CD_3F\cdots HCl$, $CD_3Cl\cdots HCl$ and $CD_3Br\cdots HCl$ complexes

A topological analysis based on AIM theory was performed to determine the nature and strength of hydrogen bonding in the $CD_3F\cdots HCl$, $CD_3Cl\cdots HCl$, and $CD_3Br\cdots HCl$ complexes. This analysis allows for the evaluation of the electron density distribution between the complexes, the electron density ρ(r) at the bond critical points (BCP), its Laplacian $\nabla^2\rho(r)$, and bonding energy parameters.

The results of the AIM analysis showed that all complexes exhibit bond critical points (BCP) at the H···X (X = F, Cl, Br) interaction sites (Figure 1). The electron density values ρ(r) were distributed as follows: In the $CD_3F\cdots HCl$ complex, the highest electron density (ρ(r) = 0.0212 a.u.) was observed, indicating a stronger hydrogen bond.

In the $CD_3Cl\cdots HCl$ complex, the electron density decreased slightly to ρ(r) = 0.0176 a.u., suggesting a weaker hydrogen bond.

In the $CD_3Br\cdots HCl$ complex, the lowest electron density (ρ(r) = 0.0162 a.u.) was found, indicating the weakest interaction.

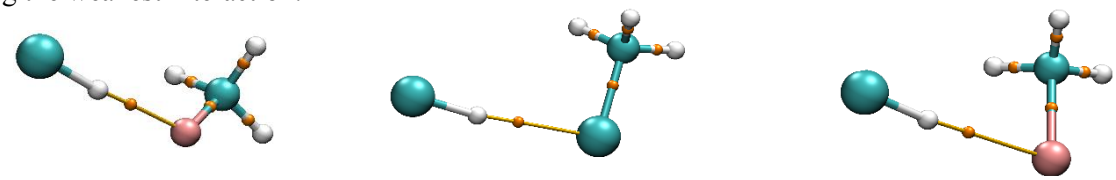


Fig. 5. Critical points of binding of $CD_3F\cdots HCl$ (a), $CD_3Cl\cdots HCl$ (b), and $CD_3Br\cdots HCl$ (c).

The decrease in electron density is associated with the increase in the halogen atomic radius, following the trend F > Cl > Br**.**

The positive values of the Laplacian $\nabla^2\rho(r)$ ($\nabla^2\rho(r) > 0$) were determined for all complexes, confirming that the hydrogen bonds are electrostatically dominant. The highest $\nabla^2\rho(r)$ value was

recorded in the $CD_3F\cdots HCl$ complex, indicating a strong electrostatic interaction due to the high electronegativity of fluorine. In the $CD_3Cl\cdots HCl$ and $CD_3Br\cdots HCl$ complexes, the $\nabla^2\rho(r)$ value decreases, reflecting a weakening of the bond strength**.**

In the AIM analysis, the potential energy density (V) and kinetic energy density (G) are used to evaluate bond stability**.** The highest V value was observed in the $CD_3F\cdots HCl$ complex, confirming its most stable bond. In the $CD_3Cl\cdots HCl$ and $CD_3Br\cdots HCl$ complexes, the V values decrease, indicating a weakening of the bond strength (Table 2). The G/V ratio being greater than 1 further confirms that the hydrogen bonding is electrostatically dominant**.**

Table 2. AIM analysis results.

Complex	Bond	ρ(r) (a.u)	$\nabla^2\rho(r)$ (a.u)	G(r) (a.u)	V(r) (a.u)	H(r) (a.u)	$E_{int.}$ (kcal/mol)
$D_3CF\cdots HCl$	F···H	0.0212	0.0804	0.0182	-0.0163	0.0019	
$D_3CCl\cdots HCl$	Cl···H	0.0176	0.0440	0.0106	-0.0102	0.0004	
$D_3CBr\cdots HCl$	Br···H	0.0162	0.0352	0.0087	-0.0086	0.0001	

In the $CD_3F\cdots HCl$ complex, the strongest hydrogen bond is formed, characterized by the shortest bond length and the highest electron density. In the $CD_3Cl\cdots HCl$ and $CD_3Br\cdots HCl$ complexes, the bond strength gradually decreases, which is attributed to the electronegativity and atomic radius of the halogen atom.

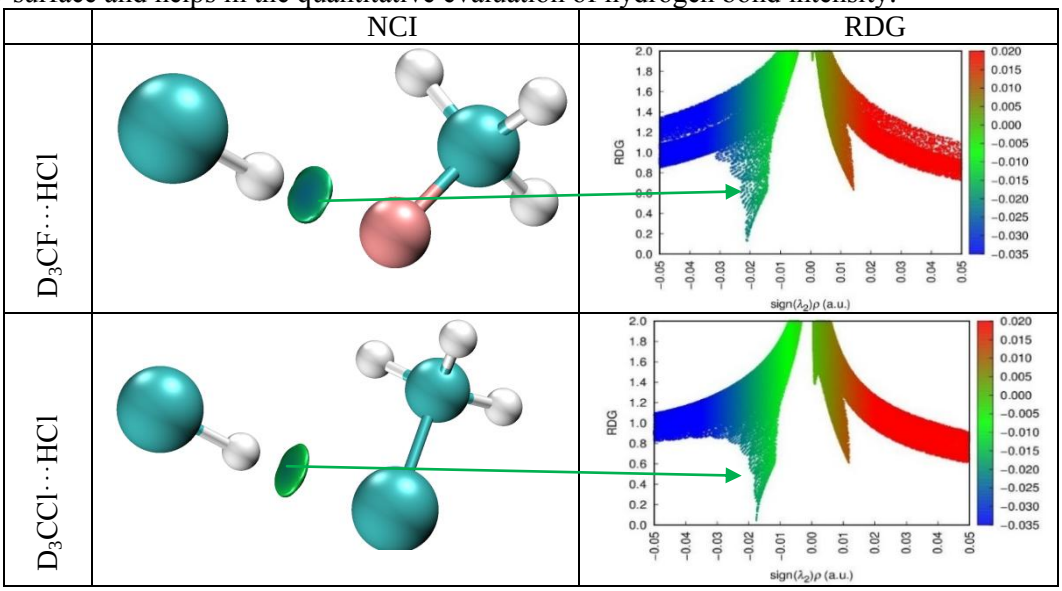
The results of the AIM analysis indicate that hydrogen bonds are primarily electrostatic in nature, with bond strength decreasing in the order of fluorine > chlorine > bromine. These findings are discussed in correlation with the spectroscopic properties of the complexes and DFT calculations**.**

2.6. RDG and NCI analyses

NCI and RDG analyses were used to study van der Waals interactions and other non-covalent interactions in the $CD_3F\cdots HCl$, $CD_3Cl\cdots HCl$, and $CD_3Br\cdots HCl$ complexes (Figure 6).

The computational results indicate that the primary stabilization factors in these complexes are related to van der Waals interactions.

NCI analysis confirms the presence of van der Waals interactions, providing a visual representation of their weak nature. RDG analysis, on the other hand, reflects changes in the potential energy surface and helps in the quantitative evaluation of hydrogen bond intensity.



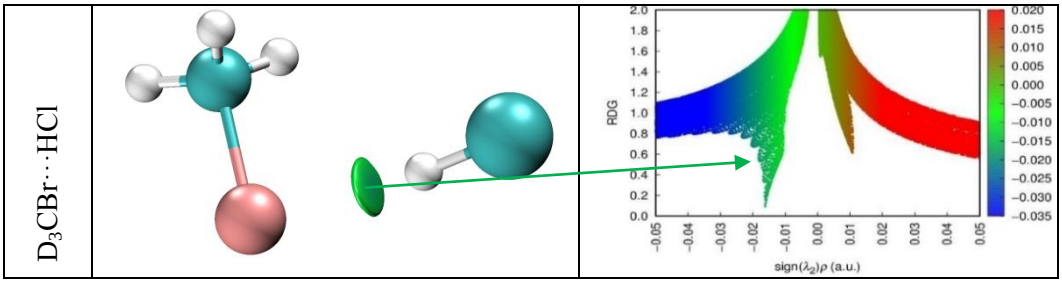


Fig. 6. NCI and RDG indices in intermolecular interactions.

The identified bonding regions indicate that van der Waals interactions are strongest in the $CD_3F\cdots HCl$ complex, which is attributed to the high electronegativity of the fluorine atom. In the $CD_3Cl\cdots HCl$ and $CD_3Br\cdots HCl$ complexes, the strength of these interactions gradually decreases, which can be explained by the increase in halogen atomic radius and polarizability**.**

Overall, NCI and RDG analyses demonstrate that the nature of the halogen atom has a significant influence on van der Waals interactions in these complexes.

2.7. **Mulliken atom charges.** The results of the Mulliken charge distribution show that the hydrogen atom in the HCl molecule is partially positively charged, and as it approaches the halogen atom, its electron density slightly decreases. In particular, in the $CD_3F\cdots HCl$ complex, the proton-donating ability of HCl increases, leading to a significant strengthening of the bond. This phenomenon can be explained by changes in charge distribution and the increase in bond strength.$CD_3Hal\cdots HCl$ kompleksida quyidagi Mulliken atom zaryadlari kuzatildi (Table 3):

Table 3. Mulliken atom charges

1	-0.367434	C1	-0.513649	C1	-0.621590
2	0.254957	H2	0.250111	H2	0.241098
3	0.261332	H3	0.250527	H3	0.241092
4	0.242516	H4	0.224356	H4	0.219765
5	-0.423679	Cl5	-0.221019	Br5	-0.088067
l6	-0.224824	Cl6	-0.228330	Cl6	-0.228697
7	0.257133	H7	0.238003	H7	0.236399

These results indicate that the nature of the halogen significantly affects the electron density distribution in $CD_3Hal\cdots HCl$ complexes. Since fluorine is the strongest electron-withdrawing atom, the electron density in the $CD_3F\cdots HCl$ complex is considerably higher compared to other complexes, leading to the strengthening of the hydrogen bond through the HCl molecule. Figure 7 presents the Mulliken charge distribution scheme of H and Cl atoms in $D_3CHal\cdots HCl$ complexes. This scheme visually illustrates how the electron density of HCl varies depending on the type of halogen.

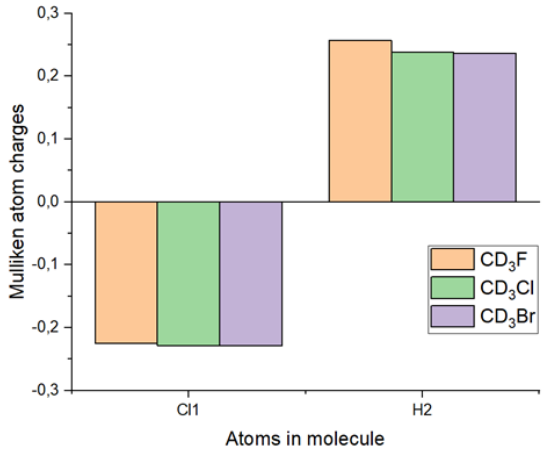


Fig. 7. Mulliken charge distribution diagram of H and Cl atoms in $D_3CHal\cdots HCl$ complexes.

Additionally, Figure 8 presents the correlation graphs between various parameters in $D_3CHal\cdots HCl$ complexes. It was observed that as the internuclear distance (r) in the HCl molecule increases, the Mulliken atomic charge (q) on the Cl atom also increases (Figure 8a). In these complexes, as the van der Waals interaction energy (E) increases, r decreases, or vice versa (Figure 8b). A similar relationship was observed between the frequency shift (Δν) and E (Figure 8c). From the graph of Δν versus r, it can be seen that as the frequency shift increases, the internuclear distance also increases (Figure 8d).

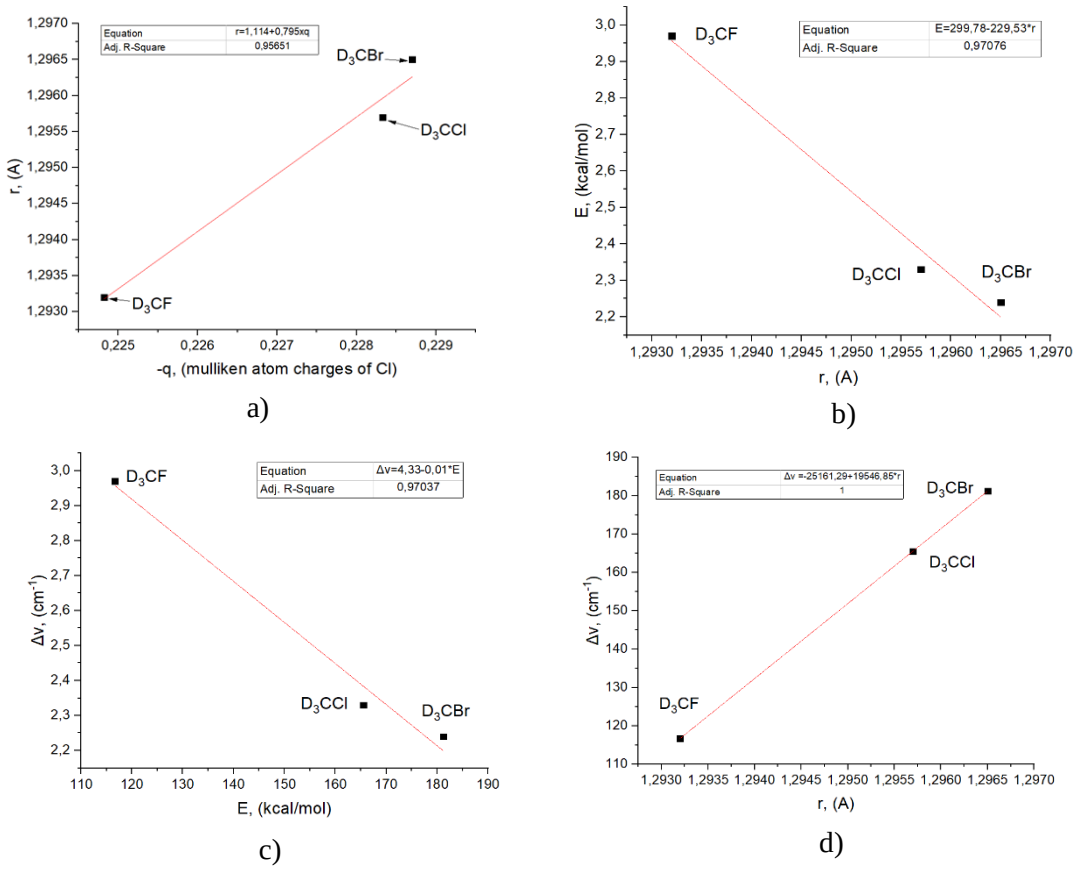


Fig. 8. In the $D_3CHal\cdots HCl$ complex, graphs are presented of the dependence of a) the distance between the nuclei of the HCl molecule (r) on the Mulliken atomic charge (q) on Cl, b) the binding energy (E) on r, c) the frequency difference (Δν) on E, and d) Δν on r.

These graphical results show that the distance between the nuclei of the HCl molecule increases with the increase in the electron density of Cl. In addition, the bond energy and frequency changes change in accordance with the hydrogen bonding ability of HCl. In particular, the largest bond energy and frequency difference is observed in the $CD_3F\cdots HCl$ complex, which indicates that it is the most stable complex. Overall, the results of this study confirm that the charge distribution and bonding properties of the $CD_3Hal\cdots HCl$ complexes depend on the nature and electron-withdrawing ability of the halogen.

3. Conclusion. In this study, the properties of $CD_3Hal\cdots HCl$ (Hal = F, Cl, Br) complexes were investigated using infrared spectroscopy and DFT calculations. The results showed that the strength of the hydrogen bond depends on the type of halogen atom and its electronegativity. The infrared spectroscopy data and DFT calculation results supported each other and provided important insights into the structure, energetic properties, and Mulliken atomic charges of the complexes. The obtained results may be useful for gaining a deeper understanding of the unique characteristics of hydrogen-bonded systems and predicting their physicochemical reactivity.

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