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Spectroscopic evidence of weak complex formation between *N*,*N*-dimethylformamide and fluoroform in the gas phase

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ABSTRACT

The interactions between *N*,*N*-dimethylformamide (DMF) and fluoroform (CHF_3) in the gas phase are studied with the help of FTIR spectroscopy. Temperature changes observed in the region of the CO stretching mode of DMF suggest a weak complex formation that results in a red wavenumber shift of the ν(CO) band. Series of van Hoff plots obtained by means of temperature and concentration spectroscopic measurements give the energy of the complex formation $\Delta E \sim -19.6$ kJ/mol. Ab initio calculations performed at the MP2/6–311++G(df,pd) level are in good agreement with the experimental results.

1. Introduction

The amide linkage is one of the most studied functional groups [1]. Structural characteristics and the ability for the molecular recognition through hydrogen bonding are the highly important aspects of the amide linkage for understanding of properties and biological functions of proteins [2]. *N*,*N*-dimethylformamide (DMF) can be considered as one of the simplest models for the chain proteins. It is also one of the most widely used solvents employed in organic and medicinal chemistry. For those reasons both self-association and hetero-association of DMF with a variety of molecules have been extensively studied. Much interest was focused on crystal and liquid structure of DMF in mixtures with water or alcohols [3–8]. The DMF heteroassociates with amino acids [9,10], phosphoric acid [11], sulfonamides and thioamides [12] were also examined. Theoretical studies on hydrogen bonded complexes between glycine, alanine or leucine and *N*,*N*-dimethylformamide [9] indicated three stable isomerical structures for each system. The most stable structure of the complex contains both OH⋯O and CH⋯O bonds with the carbonyl oxygen of DMF playing a role of proton acceptor and the OH/NH group of amino acid acting as a proton donor. The strong O/N–H⋯O contacts are indicated by short H⋯O distance (lying in the range from 1.74 to 2.14 Å) and their near linear arrangements. The weaker bonding stabilizing those complexes is formed between the formyl or methylene C–H group of DMF and the carbonyl oxygen or nitrogen atoms of amino acid. The calculations predict the blue shift of the C–H stretching wavenumber in the C–H⋯O and C–H⋯N bonds after complex formation. In the last published work, the research on the complexes of *N*,*N*-dimethylformamide with the molecules of different proton acceptor abilities, namely with N_2, CO, NH_3 and H_2O [13] was performed. Both infrared matrix isolation spectroscopy and ab initio calculations were applied. The results indicated that the DMF-N_2, DMF-CO complexes identified in solid argon were stabilized by (C =)O⋯N and (C =)O⋯C van der Waals interactions. In turn, in the DMF-H_2O, DMF-NH_3 complexes the (C =)O⋯H(OH) and (C =)O⋯H(NH_2) hydrogen bonds were formed. The C–H⋯X (X = N, C, O) bonding was the second intermolecular force stabilizing the planar complexes. For DMF-H_2O, DMF-NH_3 the nonplanar structures with the C=O⋯H interaction were also present.

In this paper the results on molecular complex formation in the gaseous mixture of DMF and fluoroform (CHF_3) are presented for the first time. Fluoroform belongs to the so called CH donors often involved in blue shifting H – bond formation [14–17]. The experimental infrared spectroscopic data are compared with results of ab initio calculations performed on the MP2/6–311++G(df,pd) level.

2. Experimental and computational methods

The spectra were recorded with a Bruker IFS 125 HR spectrometer in the interval 4500–750 cm^{-1} at a resolution of 0.5 cm^{-1}. The spectrometer was equipped with a KBr beam splitter and a LN

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-MCT detector. The experimental setup for temperature measurements was close to that presented earlier [18]. Briefly: the stainless cell of 8.5 cm path length equipped with BaF_2 windows and a water jacket was used to record spectra of DMF, CHF_3 and their mixture in $+5 - +50$ °C temperature interval. The water jacket was connected to a Lauda RE 1050 S thermostat and filled up with antifreeze (water + ethylene glycol mixture). To reduce the heat exchange with the environment the cell was mounted inside the evacuated box of the spectrometer. The pressure of DMF in the range of 1.0–3.6 mbar was measured with a MKS Baratron capacitance manometer (upper limit: 100 mbar; declared accuracy: 0.1% of displayed value). The pressure of CHF_3 and total pressure of mixtures in the range 600–1500 mbar were determined with a Swagelok gauge (range: -1–0.6 bar; accuracy class 1.0). N,N-dimethylformamide and fluoroform were commercially available. The mixtures of DMF/CHF_3 were prepared at room temperature ($T = +24$ °C) directly in the cell. The initial pressure of the compounds in the mixtures varied in the range: $p(\mathrm{DMF}) = 1$–3.6 mbar: $p(\mathrm{CHF_3}) = 500$–1500 mbar. The IR spectra of pure gases with pressure close to that used in the mixtures were recorded first. Then analogous measurements at the same temperatures were performed for the mixtures. Prior to the spectroscopic measurement of the DMF/CHF_3 mixture or only single component, the gaseous sample was allowed to stand for 10–20 min at each temperature. Information on the relative stability (ΔE) was obtained by studying the behavior of selected bands as a function of temperature. The data were averaged over a set of measurements, using the integrated intensities of selected bands of monomers and of the complexes studied.

Theoretical calculations were run using the GAUSSIAN 09 Rev. D.01 package [19]. The local minima of DMF + CHF_3 system were searched starting from several initial configurations. The local minimum found was fully optimized using ab initio second order Møller-Plesset perturbation (MP2) frozen core method [20] with a set of the Pople type basis sets. The final basis set 6–311++G(df,pd) and harmonic approximation have been chosen as a compromise between the accuracy of calculations and available computing resources. The equilibrium geometries, interaction energies and harmonic vibrational frequencies of the complexes were obtained using CP-corrected gradient techniques [21,22]. The structures were characterized as those local minima having all real frequencies. The AIM2000 program [23,24] was used to analyze the topology of the electron density in the vicinity of the bond critical points (BCP).

3. Results and discussion

3.1. Infrared spectra

The room temperature vapor pressure of DMF does not exceed ca. 3 torr (5 mbar). Moreover, this value decreases with lowering the temperature. Additionally, noticeable adsorption of DMF on the walls of the cell should be taken into account. Thus, the gas phase temperature spectroscopic studies of complex formation between DMF and CHF_3 face some difficulties. To carry out the research, a very strong stretch $\nu(\mathrm{CO})$ band of DMF has been chosen (see Table 1). The measurements have been performed with large excess of CHF_3. A typical example of the gas phase spectrum of the monomers and DMF + CHF_3 mixture is shown in Fig. 1. The $\nu(\mathrm{CO})$ band of DMF is registered on the high wavenumber wing of a very intense $\nu_5 + \nu_6$ combination band of CHF_3. Both bands consist of the central Q-type peak surrounded by relatively wide shoulders. Nevertheless, the band of the complex can be resolved with reasonable accuracy by subtraction from the spectrum of the mixture (line 1) the appropriately scaled spectra of the CHF_3 (line 2) and DMF (line 3) monomers. Fig. 2 shows temperature changes observed for the band of the complex. Accepting the known dependence of the equilibrium constant on temperature [25], one could expect that the integrated intensity of this band will increase with lowering the temperature. However, this band becomes weaker due to the effect of adsorption decreasing the DMF content in the cell. Such behavior, together with inaccuracy of the subtraction procedure in the region of Q-type peak marked by an ellipse, might be a source of an additional error in evaluation of temperature changes of the integral intensity of the bands interested. The result of subtraction gives the band of the complex with a hole in the region of this peak. The most plausible explanation of this undesirable effect is noticeable broadening of Q branch of DMF monomer by large excess of fluoroform.

Table 1
MP2/6–311++G(df,pd) predicted geometric (distances r of the corresponded bond) and spectroscopic (harmonic frequencies ω and intensities I) parameters and their changes upon complex formation ($\Delta^{\mathrm{c\text{-}m}}$) of the most stable structure of DMF·CHF_3 complex and monomers.

Parameter	DMF	Complex	$\Delta^{\mathrm{c\text{-}m}}$ ($I^{\mathrm{c}}/I^{\mathrm{m}}$)
r(CH), Å	1.10476	1.10346	−0.0013
ω(CH), $\mathrm{cm^{-1}}$ I, (km/mol)	3000.1 (80.4)	3020.5 (54.2)	+20.4 (0.67)
r(CO), Å	1.21826	1.22257	+0.0043
ω(CO), $\mathrm{cm^{-1}}$ I, (km/mol)	1777.7 (494.9)	1770.2 (585.4)	−7.5 (1.18)
r(CN)[a], Å	1.36022	1.35464	−0.0056
r(CN)[b], Å	1.44532	1.44665	+0.0013
r(CN)[c], Å	1.44262	1.44437	+0.0018
Parameter	CHF_3	Complex	$\Delta^{\mathrm{c\text{-}m}}$ ($I^{\mathrm{c}}/I^{\mathrm{m}}$)
r(CH), Å	1.09009	1.08800	−0.0021
ω(CH), $\mathrm{cm^{-1}}$ I, (km/mol)	3175.9 (36.3)	3212.0 (5.84)	+36.1 (0.16)
r(CF)[d], Å	1.33770	1.33418	−0.0035
r(CF)[e], Å	1.33770	1.33064	−0.0071
r(CF)[f], Å	1.33770	1.33066	−0.0070
ω(CHF), $\mathrm{cm^{-1}}$ I, (km/mol)	1425.6 (57.2 × 2)	1456.3 (60.8)	+30.7 (1.06)
		1440.0 (19.0)	+14.4 (0.33)

[a] C_{10}-N1 (see Fig.5 for the numbering of atoms).
[b] C2-N1.
[c] C6-N1.
[d] C13-F17.
[e] C13-F15.
[f] C13-F6.

Despite the mentioned difficulties, the temperature measurements of integrated intensities of monomer and complex were performed and then used for drawing the well known Van't Hof plots [26]. Fig. 3 presents typical example of such a plot for the DMF + CHF_3 gaseous system. Note that the data used in the plot were obtained both with lowering the temperature and with increasing the temperature of the sample. Because the measurements were performed at a constant volume of the sample cell the slope of the van't Hoff plot gives an evaluation of the complexation energy ΔE [25]. The result averaged over a set of temperature measurements with different ratios of DMF to CHF_3 is: $\Delta E = -(19.6 \pm 0.9)$ kJ/mol.

The complex formation results in a low wavenumber shift $\Delta\nu(\mathrm{CO})^{\mathrm{c\text{-}m}}$ of ca. $-(9 \pm 1)\ \mathrm{cm^{-1}}$, measured between Q-type peak of the $\nu(\mathrm{CO})$ band of the DMF monomer and the maximum of a relatively broad $\nu(\mathrm{CO})$ band of the complex. This shift is comparable with the shift of the carbonyl group wavenumber upon hydrogen bond formation in the gas phase (HF·Acetone, shift 19 $\mathrm{cm^{-1}}$, energy 39 kJ/mol [27]), in cryosolution (Pentafluoroethane·Acetone, 21.3 $\mathrm{cm^{-1}}$, 20 kJ/mol [28]), and in low temperature matrices (DMF·H_2O, 9 $\mathrm{cm^{-1}}$, 19 kJ/mol; DMF·NH_3, 5.5 $\mathrm{cm^{-1}}$, 12 kJ/mol [13]).

3.2. Theoretical studies

The MP2/6–311++G(df,pd) calculations performed with the option opt = tight predict that the most stable heterodimer