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IR Spectra of Trifluoromethanesulfonamide and Its Self-Associates in the Gas Phase

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Abstract — A labile equilibrium between monomeric trifluoromethanesulfonamide and its trimer and cyclic dimers in the gas phase at 385–485 K was determined by IR spectroscopy and quantum-chemical calculations (B3LYP/6-31G*).

Methanesulfonamide and its N-monosubstituted derivatives exist mainly as self-associates stabilized by strong N–H···O hydrogen bonds and form in solutions cyclic dimers [1–3]. As determined by single crystal X-ray diffraction, the crystal structure of these compounds consists of dimers bound by intermolecular hydrogen bonds into infinite chains [4]. Substitution of the methyl group by a trifluoromethyl group increases the acidity and lipophilicity of these compounds, thus affecting their biological [5] and chemical activity. The geometric parameters of separate trifluoromethanesulfonamide molecule and its force field were calculated *ab initio*, and the normal modes of this molecule were fully analyzed [6]. Based on the calculated vibration frequencies, the IR and Raman spectra of the solid samples were assigned. However, this assignment should be considered as tentative, since no structural data for these compounds in the solid phase are reported. It is unclear whether this compound is associated in the solid state, what is the structure of its H complexes with other proton donors or proton acceptors, and how the trifluoromethyl group affects the supramolecular structure of this compound. Hence, the studies initiated by Fernandez *et al*. [6] should be continued. In this work we studied the state of trifluoromethanesulfonamide $CF_3SO_2NH_2$ (**I**) in the gas phase by IR spectroscopy and determined the structure of its self-associates by comparing the experimental and calculated data.

The IR spectra of gaseous amide **I** were recorded in the temperature range 458–385 K. At 399 K, several overlapped bands were observed in the range typical for absorption of NH_2 group (Fig. 1, *1*). The ratio of their intensities strongly depends on temperature (Fig. 1, *1*–*5*). Hence, equilibrium is attained in the gas phase between several forms of amide **I**. At 450 K, only two symmetric bands at 3501 and 3395 cm^{-1} with almost the same half-width ($\Delta\nu_{1/2}$ ~30 cm^{-1}) are registered in this range (Fig. 1, *5*). These bands are assigned, respectively, to antisymmetric (ν_{as}) and symmetric (ν_s) stretching vibrations of the NH_2 group of the monomeric form **Ia**. This assignment agrees with the spectroscopic data for structurally related compounds. The half-width of ν(NH) bands for monomeric *N*-phenylmethanesulfonamide is 36 and 38 cm^{-1}, and for its cyclic associate in CCl_4 and $CHCl_3$ it is 66 and 80 cm^{-1}, respectively [7]. The band of the free NH_2 group in the spectra of gaseous amides and their solutions in CCl_4 (or $CHCl_3$) lies in the range 3550–3400 cm^{-1} [8], and the NH_2 bands of monomeric methanesulfonamide $CH_3SO_2NH_2$ (**II**) in CCl_4 are at 3455 and 3360 cm^{-1} [7].

The IR spectra of a vapor of amide **I** at 458 K and of its crystals at room temperature in the range 400–4000 cm^{-1} are given in the table. The $\nu_{as}(NH_2)$ and $\nu_s(NH_2)$ bands in the spectrum of the gaseous com-

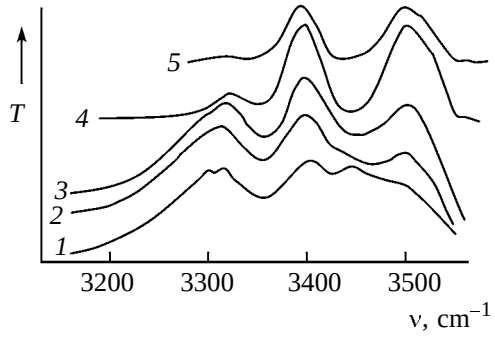

Fig. 1. IR spectra of a trifluoromethanesulfonamide vapor in the range 3200–3600 cm^{-1} at *T* (*1*) 399, (*2*) 408, (*3*) 426, (*4*) 435, and (*5*) 458 K.

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IR bands (ν, cm^{-1}) of gaseous and crystalline trifluoromethanesulfonamide $CF_3SO_2NH_2$

Experimental IR spectrum		Separate molecule, calculation		Assignment [6]
gas (458 K)	crystal [6]	B3LYP/6-31G*	HF/6-31G** [6]	
3501 w	3392 v.s	3633 (61)[a]	3921 (3529)[b]	$\nu_{as}(NH_2)$
3395 w	3280 v.s	3516 (53)	3787 (3408)	$\nu_s(NH_2)$
1537 w	1522 s	1613 (46)	1730 (1557)	$\delta(NH_2)$
1428 v.s	1357 v.s	1380 (240)	1527 (1374)	$\nu_{as}(SO_2)$
1238 s	1235 s	1216 (76)	1403 (1262)	$\nu_s(CF_3)$
1200 v.s	1190 v.s	1264 (268)	1426 (1284)	$\nu_{as}(CF_3)$
1150 s	1153	1117 (215)	1258 (1132)	$\nu_s(SO_2)$
1065 v.w	1046 v.w	1093 (0.1)	1177 (1060)	$\rho(NH_2)$[c]
888 m	957 m	876 (159)	993 (894)	ν(SN)
–	767 v.v.w	758 (10)	854 (769)	$\delta_s(CF_3)$
605 m	628 s	617 (220)	684 (616)	$\omega(SO_2)$[d]
–	568 m	562 (118)	621 (559)	$\delta_{as}(CF_3)$
496 w	495 s	550 (12)	549 (495)	$\delta(SO_2)$

[a] The relative intensity is in parentheses. [b] Frequencies calculated with the scaling factor of 0.9 are in parentheses [c] (ρ) Rocking vibrations. [d] (ω) Wagging vibrations.

pound are weaker and are shifted by 110 and 113 cm^{-1}, respectively, to high frequencies as compared to those in the spectrum of the solid sample. The similar high-frequency shift ($\Delta\nu$ ~100 cm^{-1}) was observed with primary amides in going from the crystal to gas or solution [8]. The high-frequency shift of $\nu_{as}(NH_2)$ and $\nu_s(NH_2)$ bands in going from crystalline methanesulfonamide **II** to its solutions in CCl_4 is 115 and 95 cm^{-1}, respectively [7]. By the analogy with crystalline amide **II**, this spectral transformation can be assigned to association of trifluoromethansulfonamide **I** in the solid phase. The high-frequency shift of the band of antisymmetric stretching vibrations of the SO_2 groups confirms dissociation of associates of amide **I** at high temperatures with rupture of the NH···O=S bond to form monomeric species. It should be noted that the difference in $\nu_{as}(SO_2)$ in the spectra of gaseous and crystalline amide **I** (71 cm^{-1}) is substantially larger than that in the spectra of its closest analog, amide **II**, recorded in the solid state and in a solution in CCl_4 (33 cm^{-1} [7]). The $\nu_s(SO_2)$ band of amides **I** and **II** is slightly shifted ($\Delta\nu$ 3 and 7 cm^{-1}, respectively) upon phase transition. In addition, the band of S–N stretching vibrations of amide **I** is shifted from 957 to 888 cm^{-1} upon vaporization. Similar low-frequency shift of the band of C–N stretching vibrations of carboxylic acid amides is observed upon rupture of the NH···O=C homomolecular hydrogen bonds [8]. The NH_2 bending band in the spectra of amide **I** is shifted from 1522 to 1537 cm^{-1} and weakens in going from the crystal to the gas phase.

When a vapor of amide **I** is cooled to 435 K, new broader bands appear in the range of NH_2 stretching vibrations. On further cooling, the intensity of these bands increases and the relative intensity of the band of monomeric amide **Ia** decreases (Fig. 1, *1–4*). The band at 3320 cm^{-1} and the low-frequency shoulder of the band at 3500 cm^{-1}, appearing in the temperature range 435–425 K (Figs. 1, *3*, *4*) can be due to overlapping of the bands of symmetric and antisymmetric NH_2 stretching vibrations of associated amide **I** with the monomer bands. The additional bands of associated amide **I** at 3280–3300 and ~3450 cm^{-1} are observed at lower temperatures (410–390 K) (Fig. 1, *1*, *2*). These spectral transformations are reversible and are typical for mobile equilibria between monomeric molecules and their self-associates. Thus, on heating self-associates of amide **I** dissociate in the gas phase into the monomeric species. The NH···O=S hydrogen bonds are completely ruptured at $T \geq 540$ K (Fig. 1, *5*).

To determine the structure of the most probable self-associates of amide **I**, we calculated the vibrational spectrum of its molecule and the heats of formation and normal mode frequencies of its dimer and trimer by DFT procedure (B3LYP/6-31G*) with full geometry optimization. The total energy minimum corresponds to the following structures: centrosymmetrical (**Ib**) and noncentrosymmetrical (**Ic**) cyclic dimers, cyclic trimer **Id**, acyclic trimer **Ie** with the free SO_2 group, and chain-like dimer **If** with free and associated NH_2 and SO_2 groups (Fig. 2). The acyclic trimer with the free NH_2 groups is unstable

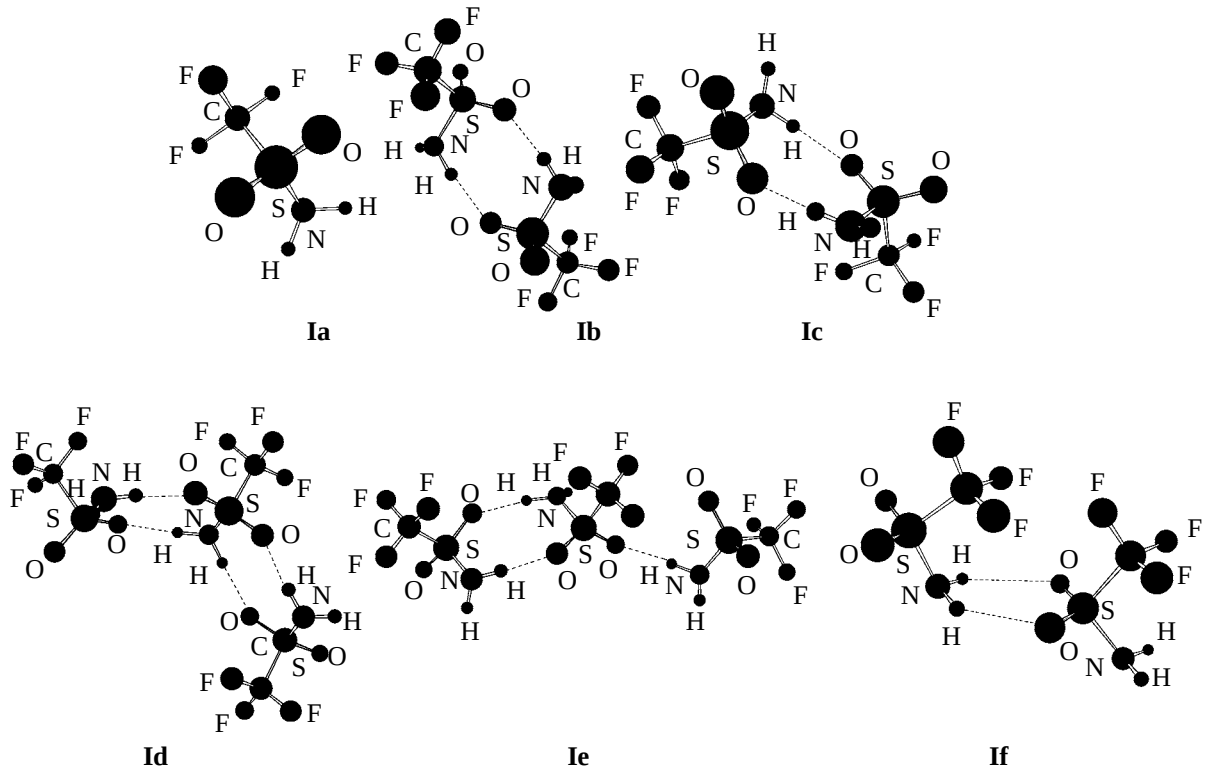
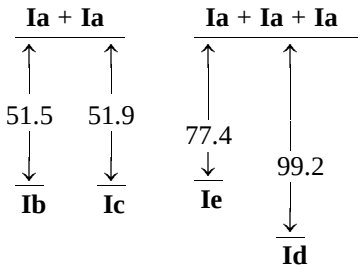


Fig. 2. Structures of monomeric trifluoromethanesulfonamide **Ia**, its centrosymmetrical **Ib**, nonsymmetrical **Ic**, and cyclic dimers, cyclic **Id** and acyclic trimer **Ie**, and linear dimer **If**.

and transforms into the cyclic form **Id** after geometry optimization.

The relative energies of formation of the most stable associates with respect to the sum of the energies of the monomers (ΔE, kJ mol^{-1}) are presented in the scheme.

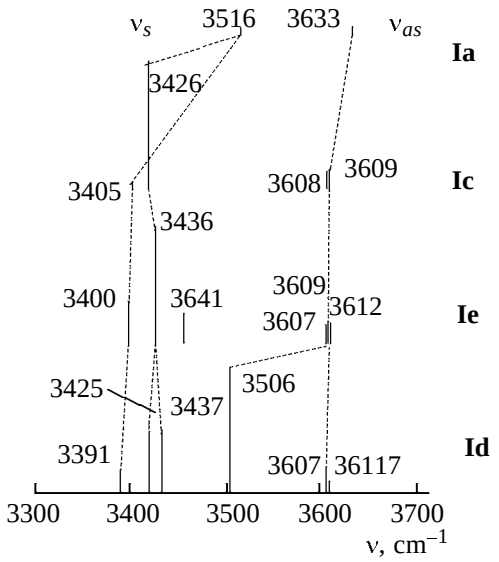


The association energy is mainly determined by the number of hydrogen bonds. The average energy of formation of single H-bond is ~25 kJ mol^{-1}. Thus, the concept of the additivity of the hydrogen bond energies is valid for homomolecular H-complexes of amide **I**. The energy of chain-like dimer **If** is higher by ΔE 21.8 kJ mol^{-1} than that of the cyclic species. In this case, the average energy of each of six hydrogen bonds of the six-membered ring is as low as ~11 kJ mol^{-1}.

Additional information on the structure of amide **I** associates in the gas phase was obtained from its vibrational frequencies. The ν(NH) frequencies of monomer **Ia**, calculated by the B3LYP/6-31G* procedure, are slightly higher than the experimental values. This is also the case for the other bands except for $\nu(SO_2)$ and ν(SN) (see table). The calculated $\nu_s(SO_2)$ and, to a lesser extent, ν(SN) are, on the contrary, underestimated. This is probably due to the fact that the calculated distance between the hydrogen atoms of the NH_2 groups and the oxygen atom of the SO_2 groups is short (2.556 Å), suggesting formation of an N–H···O intramolecular hydrogen bond.

The changes in calculated $\nu_{as}(NH_2)$ and $\nu_s(NH_2)$ bands upon association of monomer **Ia** to form homomolecular H-complexes **Ic**–**Ie** (Fig. 3) and estimated intensities of these bands allowed us to adequately assign the experimental spectra of gaseous amide **I**. The band at 3320 cm^{-1} observed at 435–420 K and shifted with respect to the band of monomer **Ia** (3395 cm^{-1}) (Fig. 1, *4*, *5*) is due to formation of cyclic dimers and acyclic trimer **Ie** in the gas phase. Broadening of the high-frequency band at ~3500 cm^{-1} is also the result of the association.

We failed to obtain reliable data on dimer **If** from



Theoretical vibrational spectrum of monomeric trifluoromethanesulfonamide (**Ia**) and its self-associates **Ic**–**Ie** in the region of NH stretching vibrations. Vertical intercepts correspond to the relative transition intensities.

its IR spectra. The calculated frequencies of its free and associated amino group differ from those in monomer **Ia**: 3648 (63), 3524 (60) cm^{-1} (ν_{as}) and 3603 (46), 3493 (110) cm^{-1} (ν_s) (the relative intensities of the bands are in parentheses). The difference in the frequencies of ν_{as} and ν_s bands in the spectrum of **Ia** and **If** is as high as 30 and 23 cm^{-1}, respectively, whereas the intensities of these bands are similar (see table). If the fraction of dimer **I** in the vapor phase is high, two groups of resolved bands should appear in the spectrum, which is not confirm experimentally.

Our calculations show that appearance of the band at 3450 cm^{-1} and complication of the shape of the band at 3300 cm^{-1} on cooling (Fig. 1, *1*, *2*) are due to formation of cyclic trimer **Id**. One of the calculated NH_2 antisymmetric bands is strong and is appreciably shifted toward lower frequencies (3450 cm^{-1}) as compared to the band of the monomer, cyclic dimer, and acyclic trimer (Fig. 3).

Thus, gaseous trifluoromethanesulfonamide exists mainly in the monomeric form at $T > 440$ K. At lower temperature (435–385 K), an equilibrium mixture of monomer, cyclic dimers, and trimers is formed.

EXPERIMENTAL

$CF_3SO_2NH_2$ **I** was prepared from trifluoromethanesulfonyl fluoride and ammonia by the procedure in [9] and was purified by double sublimation and recrystallization from benzene. The IR spectra of amide **I** vapor were recorded at 458–385 K on a Specord IR-75 spectrophotometer in a temperature-controlled 1-cm cell.

The quantum-chemical calculations were performed with full geometric optimization using GAUSSIAN 98 software [10].

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