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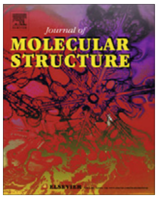

The S–H···N versus O–H···N hydrogen bonding in the ammonia complexes with CH_3OH and CH_3SH

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ABSTRACT

The methanol and methanethiol complexes with ammonia were studied by means of infrared matrix isolation spectroscopy and ab initio MP2/6-311++G(3df,3pd) calculations. The calculations resulted in the stability of two similar structures for each of the two complexes: $CH_3OH–NH_3$, $CH_3SH–NH_3$, and in addition, in the third structure for the latter complex. In the argon matrices the most stable complexes stabilized by the O–H···N or S–H···N bond were formed. The OH, SH stretching frequencies exhibited 266, 84 cm^{-1} red shifts in the complexes with respect to the monomers which correlate well with the calculated frequency shifts for the most stable $CH_3OH–NH_3$, $CH_3SH–NH_3$ structures and their energies of interactions ($\Delta E = -18.8$ kJ mol^{-1} for $CH_3OH–NH_3$ and $\Delta E = -7.1$ kJ mol^{-1} for $CH_3SH–NH_3$). Both theoretical and experimental spectra demonstrate the large increase of the intensity of the SH stretching vibration after formation of the complex (more than 300 times), as compared to the OH stretching vibration (less than 20 times). The small intensity of the SH band in the CH_3SH spectrum and its large growth in $CH_3SH–NH_3$ one are explained by atypical behavior of the dipole moment function of the SH proton donor.

1. Introduction

Among the various hydrogen bonded complexes the most interest has been traditionally focused on the more common and stronger H-bonds with the O-H, N–H groups as the proton donors and the oxygen or nitrogen atoms as the proton acceptors. However, recognition of the role of weaker interactions in nanostructural chemistry or biology recently inspired an increasing number of studies on the weaker hydrogen bonded systems, and among them on the complexes in which the S–H group acts as a proton donor or the sulfur atom acts as a proton acceptor.

The S atom provides, in terms of hydrogen bonding, an interesting point of reference to the closely related oxygen atom. Sulfur is a biologically abundant element and is a well established constituent of the therapeutic agents and agrochemicals, it is also present in atmospheric systems. There is growing appreciation of the influence exerted by the H-bonds involving sulfur. A number of experimental [1–7] and theoretical studies [8–14] on the A–H···S hydrogen bonds, with the sulfur atom playing a role of proton acceptor, have been published recently. The information on the S–H···B bonds is scarce and, particularly, there are only a few experimental data for these type of interaction. An early infrared spectroscopic study concerned thiophenol dissolved in acetonitrile [15]. The methanethiol and ethanethiol aggregates, the methanethiol complexes with dimethyl sulfide and SO_2, were studied by means of infrared matrix isolation spectroscopy [16–18]. The studies of the H_2S complexes with indole or 3-methyl indole were performed by supersonic jet expansion technique and laser-induced fluorescence [19]. In terms of the computational studies, the early reports dealt with the methanethiol aggregates [20–22]. The very recent literature data concern the complexes pairing HSN with aliphatic amines and phosphines [23], H_2S and HS with various nitrogen bases [24], and H_2S with azulene [25]. Moreover, the computational data on the methanethiol complexes with various bases [26] and on the complexes of H_2S and three related thiols with water molecule have been also recently published [27]. In the latter two reports the intensities of the SH stretching modes, in addition to their wavenumbers, are also presented. The calculations on the MP2/6-311++G(d,p) level result in the intensity ratio, I_{comp}/I_{mon}, as large as 60.18 when the methanethiol complex with $(CH_3)_3N$ is formed; however, the ratio varies in the range 1.83–4.34 for much weaker complexes of CH_3SH with $(CH_3)_3P$, $(CH_3)_2O$ and $(CH_3)_2S$ [26]. The ratio, I_{comp}/I_{mon}, strongly depends on the calculation method applied as shown for the H_2S and thiol complexes with water [27]. For the $CH_3SH–H_2O$ complex the MP2/6-311++G(2df,2pd) method results in $I_{comp}/I_{mon} = 168$ and the B3LYP/6-311++G(2df,2pd) method in $I_{comp}/I_{mon} = 20$ [27].

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The integrated IR intensity of ν_{AH}, I, is as important characteristic of H-bonding as the low wavenumber shift of the A–H stretching band, $\Delta\nu = \nu_{A-H\cdots B} - \nu_{A-H}$ (or the relative shift $\Delta\nu_{A-H\cdots B}/\nu_{A-H}$) [28–30]. The intensity increases with the strength of the H-bonding. The empirical relations between the relative intensity enhancement I_{comp}/I_{mon} and $\Delta\nu$ have been also published; the one for isothiocyanic acid bonded to various acceptors showed linear dependence in the $\Delta\nu$ range from 0 to 1000 cm^{-1} [31]. For some weak H-bonds, like those formed by chloroform as a proton donor, the integrated intensity is even more sensitive than the ν(AH) frequency [32–34]. It has been shown that chloroform [34,35] similarly like fluoroform [36,37] belongs to atypical proton donors whose dipole moment function, and more precisely, the Cartesian components of the dipole moment vector do not show the usually observed regular growth with respect to an increase of dimensionless normal coordinate of the AH (A = Cl, F) stretching vibration. The available literature data [26,27] suggest that the SH group in CH_3SH exhibits similar properties like the CH groups in $CHCl_3$ or CHF_3.

In this paper we present the comparative studies of the properties of the S–H···N and O–H···N bonds in the complexes of ammonia with methanethiol and methanol, respectively, by means of infrared matrix isolation spectroscopy and ab initio calculations on MP2 level utilizing the advanced 6–311++G(3df,3pd) basis set. The attention is particularly focused on the intensities of the νAH (A = O, S) vibration in the two systems.

2. Experimental

2.1. Infrared matrix isolation studies

The CH_3SH/Ar, CH_3OH/Ar, NH_3/Ar and CH_3SH/NH_3/Ar, CH_3OH/NH_3/Ar mixtures were prepared by the standard manometric technique; the concentration of ternary mixtures varied in the range from 1/1/100, 1/1/200 to 1/1/1000. The gas mixtures were sprayed onto gold-plated copper mirror held at 17 K by a closed cycle helium refrigerator (Air Products, Displex 202A). Infrared spectra (resolution 0.5 cm^{-1}) were recorded at 11 K in a reflection mode with Bruker 113v FTIR spectrometer using liquid N_2 cooled MCT detector. The spectra were recorded directly after matrix deposition and after its annealing to 33 K for 10 min.

CH_3OH and CH_3SH were commercially available (Aldrich), CH_3OH was distilled and degassed before the mixtures were prepared. Gaseous ammonia was obtained by dropping a 50% water solution of NaOH into a bulb containing solid NH_4Cl; the liberated gaseous ammonia was dried by passing through the tube filled with $CaCl_2$.

2.2. Computational details

The Gaussian 09 program [38] was used for the geometry optimization and harmonic vibrational calculations. The structures of the monomers (CH_3SH, CH_3OH and NH_3) and the structures of the $CH_3OH–NH_3$, $CH_3SH–NH_3$ complexes were fully optimized at the MP2 level of theory with the 6-311G++(3df,3pd) basis set. The harmonic vibrational frequencies were computed both for the monomers and for the complexes. The absence of imaginary frequencies for the optimized structures of the complexes confirmed that they correspond to the real minima on PES. Interaction energies were corrected by the Boys–Bernardi full counterpoise procedure [39], and the zero point vibrational energy corrections were also calculated. One-dimensional potential energies and dipole moment functions of dimensionless normal coordinates Q, corresponding to the SH stretch mode of CH_3SH, $CH_3SH–NH_3$ and OH stretch mode of CH_3OH, $CH_3OH–NH_3$ have been obtained in a series of single point calculations using 'freq = Hpmodes' option for determination of Cartesian displacements of all atoms engaged in the vibration of interest. The option 'density = current' was applied to account for electron correlation effects in dipole moment calculations.

3. Results

3.1. Infrared spectra

The infrared spectra of the CH_3OH/Ar, CH_3SH/Ar and NH_3/Ar matrices agree well with those reported in the literature [40–45]. In the spectra of the $CH_3SH(CH_3OH)/NH_3$/Ar matrices a set of new absorptions appeared in the vicinity of the CH_3SH or CH_3OH and NH_3 bands that can be safely assigned to the complexes formed between methanethiol or methanol and ammonia. The product bands which appeared already in the spectra of diluted matrices can be safely assigned to the 1:1 $CH_3SH–NH_3$ and $CH_3OH–NH_3$ complexes. The spectra of the CH_3SH/NH_3/Ar and CH_3OH/NH_3/Ar matrices are shown in Fig. 1. The wavenumbers of all observed product bands and their assignment, the wavenumbers shifts, $\Delta\nu = \nu_{comp} - \nu_{mon}$, and the relative integrated intensities are collected in Table 1. The assignment of the product bands was straightforward as they appear in close proximity to the absorptions of the parent molecules. The band that appeared at 2548 cm^{-1} in the spectra of the CH_3SH/NH_3/Ar matrices (indicated by hash in Fig. 1A) and was not observed in the spectra of the CH_3SH/Ar and NH_3/Ar matrices is attributed to the $CH_3SH–H_2O$ complex. Its intensity was dependent on the concentration of the H_2O impurity in the matrices.

As can be seen in Table 1 the identified product bands of the $CH_3SH–NH_3$, $CH_3OH–NH_3$ complexes belong to the perturbed methanethiol or methanol vibrations; only one perturbed ammonia vibration was identified for the $CH_3SH–NH_3$ complex. In addition to the bands due to the complexes between CH_3SH or CH_3OH and NH_3, the absorptions due to the CH_3SH, CH_3OH monomers and dimers were also observed in the spectra of the CH_3SH/NH_3/Ar, CH_3OH/NH_3/Ar matrices. In some regions they coincide with the product bands. For example, the band due to the ν_sCH_3 vibration of the $CH_3SH–NH_3$ or $CH_3OH–NH_3$ complex partly overlaps with the corresponding bands due to the CH_3SH and $(CH_3SH)_2$ in the spectra of the CH_3SH/NH_3/Ar matrices or with the corresponding absorptions of CH_3OH and $(CH_3OH)_2$ in the spectra of the CH_3OH/NH_3/Ar matrices. In order to estimate the relative intensities of the product bands the spectra of the CH_3SH/Ar, CH_3OH/Ar matrices were subtracted from the spectra of the CH_3SH/NH_3/Ar, CH_3OH/NH_3/Ar matrices, respectively. The two spectra (the spectrum for subtraction and the spectrum to subtract) corresponded to matrices with the same CH_3SH or CH_3OH concentrations, so, the relative intensities of the absorptions due to CH_3SH and $(CH_3SH)_2$ or to CH_3OH and $(CH_3OH)_2$, were the same or very close. The integrated intensities of the product bands in the difference spectra were measured and their relative ratios with respect to the most intense band were estimated. For the monomeric species the relative integrated intensities were estimated from the spectra of the CH_3SH/Ar or CH_3OH/Ar matrices. In Table 1 the averaged values of the relative intensities obtained from the measured spectra of the CH_3SH/Ar, CH_3SH/NH_3/Ar matrices and from the spectra of the CH_3OH/Ar, CH_3OH/NH_3/Ar ones are presented. The ratio $I_{comp}(SH)/I_{mon}(SH)$ was calculated on the basis of the two estimated experimental intensity ratios: $I_{comp}(SH)/I_{comp}(CH_3) = 1/0.11$, $I_{mon}(SH)/I_{mon}(CH_3) = 0.04/0.97$, and assuming, on the basis of theoretical spectra, that $I_{comp}(CH_3)/I_{mon}(CH_3) = (26/19)$ (see Table 1). The ν_sCH_3 band was selected as a reference because it is relatively intense and has a characteristic shape in the spectra of both CH_3SH