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Hydrogen bond interactions in the binary solutions of formamide with methanol: FTIR spectroscopic and theoretical studies

P.P. Kannan [a], N.K. Karthick [b], G. Arivazhagan [c],*

[a] Postgraduate Department of Physics, Mannar Thirumalai Naicker College, Madurai 625004, Tamilnadu, India
[b] Department of Physics, The Madura College, Madurai 625011, Tamilnadu, India
[c] Department of Physics, Thiagarajar College, Madurai 625009, Tamilnadu, India

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ABSTRACT

FTIR spectroscopic studies on the binary solutions of formamide with methanol reveal the presence of "free" $O-H$ in methanol. These "free" $O-H$ groups are found in methanol tetramers which is confirmed from the DFT calculations. DFT calculations on the formamide dimers of five different geometries encompassing one or more of the $N-H\cdots O$, $C-H\cdots O$ and $N-H\cdots N$ hydrogen bonds tell that $N-H\cdots N$ bonds are the strongest. Dissociation of the.

$N-H\cdots N$ bonds of formamide in the binary solutions with methanol has a major impact on the NH_2 symmetric stretching mode of formamide in the FTIR spectra. In these solutions the formation of 1:4 (formamide:methanol), 1:5 and 2:4 complexes are possible. These complexes are more stable than the formamide dimers, methanol tetramer and pentamer investigated in the present work. Methanol methyl group plays no role in either the self-association or heterointeraction with formamide.

1. Introduction

The role of $N-H\cdots O=C$ interactions is very important in the structure and properties of biologically important molecules like DNA, RNA, proteins etc., [1,2]. Considering their significance, a deep understanding of this type of interactions may be extremely helpful in obtaining more information about the structure and properties of the bio molecules like DNA, RNA, proteins etc., But the large size of these molecules is a big barrier for carrying out highly accurate ab initio quantum chemical calculations on these molecules - an approach which can provide good amount of information about the $N-H\cdots O=C$ interactions [1]. Therefore, these interactions were investigated by some researchers in detail by subjecting the comparatively smaller formamide (FMD) molecules to ab initio calculations [1–5]. Since there is a possibility for the FMD molecules to involve in dimeric associations not only through the $N-H\cdots O=C$ interactions but also the $C-H\cdots O=C$ interactions, five different geometries of the dimers with these interactions were investigated by researchers [1,2]. Among all these dimers, the one with two $N-H\cdots O=C$ interactions is the most stable whereas the dimer with two $C-H\cdots O=C$ interactions is the least stable. Earlier works dealing with the H-bond interactions of FMD with various solvents including methanol (MeOH) can be found in the research article by Ojha et al. [6]. In a recent work, Abdelmoulahi et al. [7] have studied the H-bond interaction of the equimolar mixture of FMD with MeOH using neutron scattering experiment combined with DFT calculations and concluded that 2:1 (FMD:MeOH) and 2:2 complexes have been formed. In these complexes, the FMD dimer has been reported remaining intact.

MeOH, the simplest alcohol molecule, is highly self associative with strong $O-H\cdots O$ interactions [8–10]. But in methanol there is a methyl group which may also act as a proton donor. The possibility for this methyl group to contribute either to the self association or the heterointeractions was investigated by Keefe et al. [11] through Fourier Transform Infra Red (FTIR) and Raman spectroscopy. For this work the researchers [11] used the solutions of methanol in water, acetonitrile, carbon tetrachloride, deuterium oxide, and deuterated acetonitile. This investigation led Keefe et al. [11] to conclude that the blue shifts in the vibrational modes of methanol methyl group may not mandatorily be due to the involvement of the group in self association/heterointeraction. Instead, the blue shift may be the manifestation of the $O-H\cdots O$ interactions happening in methanol. So, the research work carried out by Keefe et al. [11] presented an inconclusive picture of the ability of methanol methyl group to participate in molecular interactions. A recent report [12] by our research group shows that MeOH methyl hydrogens participate neither in homo interaction nor

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* Corresponding author at: Thiagarajar College, Madurai 625009, Tamil Nadu, India.
E-mail addresses: arivuganesh@gmail.com, arivazhagan_physics@tcarts.in (G. Arivazhagan).

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in heterointeraction. In that study, it has been reported that neat MeOH is a mixture of more than one type of closed multimers, with the exception of tetramer which is a open multimer. The binary solutions of dibutyl ether and MeOH also consists of closed structures of H-bonded heteronetworks. These findings may be taken as to signify that MeOH prefers to form closed structures rather than open geometries in neat form as well as in solutions with other molecules.

Using Raman Spectroscopy and ab initio calculations, Ojha et al. [6] have investigated the H-bonding and self-association in neat FMD and its binary solutions with MeOH by varying the mole fraction from 0.1 to 0.9 insteps of 0.1. From the analysis of the change in the wavenumber position of the bands due to $C = O$ stretching, $N - H$ bending, $C - H$ bending and $C - N$ stretching vibrations of only FMD molecule, they have concluded that the binary mixtures consist of 1:1 (FMD:MeOH) and 1:2 (in which the two MeOH molecules are on either side of FMD) H-bonded complexes. Only the bond length profile obtained form ab initio calculations has been given as confirmative results. Stangret et al. [13] have also investigated the molecular interactions in FMD-MeOH binary mixtures, but using FTIR Spectroscopy. By the factor analysis and difference spectra method, they have proposed that 1:1 (FMD:MeOH), 2:1, 3:1, 1:3 and 1:5 complexes have been formed in the FMD-MeOH binary solutions and all these complexes, except 1:1, are open. Here, it should be noted that the MeOH molecules of the FMD-MeOH complexes proposed either by Ojha et al. or Stangret et al. interact with FMD molecules as separate units with no H-bond interaction among themselves as in the work by Abdelmoulahi et al. [7]. This possibility is certainly questionable at the concentration employed becuase MeOH is highly self-associative in nature. Therefore, in the present work we have decided to investigate again the nature of molecular interactions as well as the homo and heteroassociated networks using FTIR studies and DFT calculations. FTIR spectroscopy studies can give clue about the molecular interactions happening in any binary solution through the shifts in the vibrational modes of various functional groups present in the constituent compounds [14–16]. These experimental shifts can be coupled with the theoretical frequency calculations on the most probable structures and the existence of these structures in liquid state can be confirmed if the experimental and theoretical frequency shifts agree with each other [17,18].

2. Materials and methods

Formamide-puriss. p. a., (ACS reagent,≥99.5%) of GC/T grade and Methanol–anhydrous (99.8%) were procured from Sigma Aldrich, U. S. A. These chemicals were used as such without any purification.

2.1. FTIR spectroscopic studies

Sample Solutions (SS1, SS2, SS3 and SS4) of Formamide (FMD) with Methanol (MeOH) were prepared in the following composition: FMD 0.2 + MeOH 0.8 (SS1), FMD 0.4 + MeOH 0.6 (SS2), FMD 0.6 + MeOH 0.4 (SS3) and FMD 0.8 + MeOH 0.2 (SS4). In these solutions, the numbers 0.2, 0.4, 0.6 and 0.8 adjacent to FMD/MeOH refer to the mole fraction of respective component in the solutions. The FTIR spectra of pure FMD, MeOH and the solutions SS1,…,SS4 were recorded using a Perkin Elmer FTIR spectrophotometer (model: Spectrum Two) with the resolution of 1 cm^{-1} at room temperature.

2.2. DFT calculations

Geometry optimization, frequency calculation and Natural Bonding Orbital (NBO) analysis for the structures investigated in the present work were done using the B3LYP functional [19] with the basis set 6-311++G (d, p). Gaussian 09W programme package [20] bought from Scube Scientific Software Solutions Pvt., Ltd.- New Delhi was utilized for these DFT calculations. All the calculations have been carried out on gas phase structures and the reason for not using the Polarizable Continuum Model (PCM) has been given in our earlier article [12].

3. Results and discussion

3.1. FTIR spectroscopic studies

The peaks at 3402.4, 2886.6, 1686.7 and 1309.6 cm^{-1} in the FTIR spectrum of pure FMD are assigned to the stretching modes of NH_2 (symmetric), $C - H$, $C = O$ and $C - N$, respectively (Fig. 1a, Table 1). As far as pure MeOH is concerned, two peaks at 3653.5 and 3383.3 cm^{-1} are observed for the $O - H$ stretching mode in the FTIR spectrum (Fig. 1b, Table 1). The former peak can be attributed to the vibrations corresponding to the free $O - H$ whereas the latter is due to the hydrogen bonded $O - H$ in MeOH. This could be the consequence of the presence of self associated MeOH structures of various orders of cyclic geometry, except the open tetramer, in neat form as reported in our earlier article [12]. This phenomenon can be held responsible for the appearance of three peaks for the $C - O$ stretching mode of MeOH at 1053.2, 1032.6 and 1019.1 cm^{-1}. The methyl asymmetric and symmetric stretching vibrations of MeOH produce a peak at 2966.7 and 2866.4 cm^{-1}, respectively.

In the FTIR spectrum of solution SS1 (Fig. 1c, Table 1), the free and bonded $O - H$ stretching modes of MeOH undergo blue and red shifts, respectively. Since MeOH is self associative in nature [21], the shifts in the $O - H$ stretching modes in the solution may be reasoned out to the perturbations in the $O - H \cdots O$ contacts that exist among the MeOH molecules and the heterointeractions involving the hydroxyl hydrogen. These inferences in the present work are based on the explanations given by Elangovan et al. [17] and Zhou et al. [22] for the blue shifts observed in the bonded $O - H$ stretching mode of ethanol in the binary solutions with acetonitrile. The investigators [17,22] concluded that these blue shifts are the evidence for the domination of $(ethanol)$ $O - H \cdots O$ $(ethanol)$ interactions over the $(ethanol) O - H \cdots N$ $(acetonitrile)$ interactions. In other words, the ethanol $O - H$ stretching mode shifts to higher wavenumbers when the heterointeraction involving the hydroxyl hydrogen is weaker than the homointeractions existing among the ethanol networks. In the present work, the forces that are operative in the $(MeOH) O - H \cdots O$ $(MeOH)$ contacts may be weakened by the presence of FMD in the solution SS1. And the hydroxyl hydrogen of MeOH may involve in interaction with the nitrogen and/or the oxygen of FMD. The contribution from these heterointeractions may outweigh that of the $(MeOH) O - H \cdots O$ $(MeOH)$ interactions, therein resulting in the red shift in the bonded $O - H$ stretching mode of MeOH in the solution SS1. The possibility for these heterointeractions is well supported by the shifts in the $C = O$ and $C - N$ stretching modes of FMD in the solution SS1. These shifts could also happen if the oxygen and nitrogen in FMD prefer to interact with the methyl hydrogen of MeOH in the solution. Chances for the $(MeOH\ methyl)$ $C - H \cdots O$ (FMD) and $(MeOH\ methyl) C - H \cdots N$ (FMD) interactions are strongly supported by the red shift in the methyl asymmetric stretching mode of MeOH in the solution SS1. The disturbances in the $(MeOH)$ $O - H \cdots O$ $(MeOH)$ contacts and the heterointeractions involving the MeOH hydroxyl hydrogen in the solution SS1 may also be correlated to the shifts in the $C - O$ stretching modes of MeOH.

While discussing the shifts in the MeOH vibrational bands in solution SS1 it has been mentioned that the disturbances in self association among the MeOH- MeOH molecules may be one among the factors responsible for the shifts. The same analogy may be used to explain the shifts in the vibrational modes of FMD, in which the self association happens through the $N - H \cdots O$ interactions [1–5,23,24]. The molecular forces that are operative in these interactions may be affected by the majority of MeOH in the solution SS1. These perturbations may be accountable for the shifts in the NH_2 symmetric, $C = O$ and $C - N$ stretching modes of FMD in the solution SS1, as observed in Table 1. The shifts have been discussed based on the notion that the presence

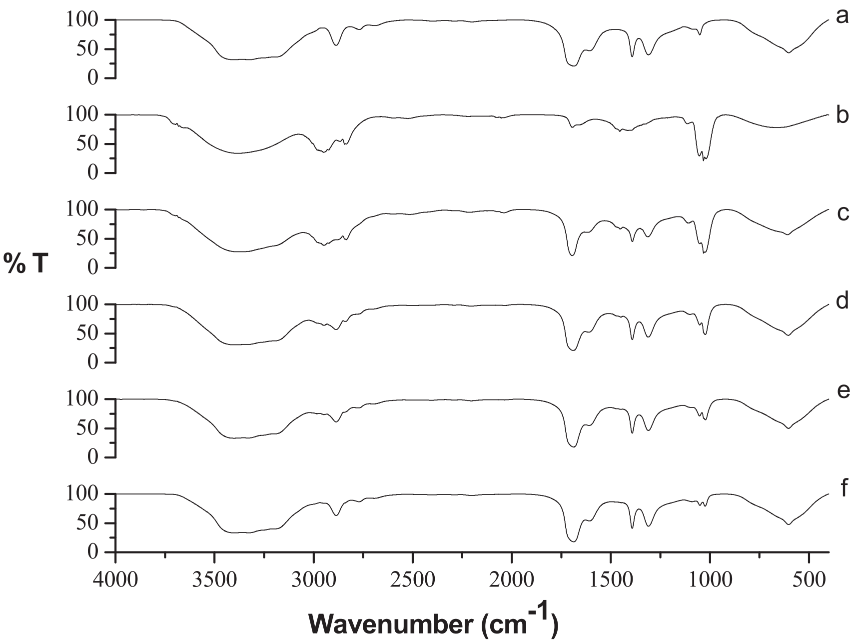

Fig. 1. FTIR spectrum of a) pure FMD, b) pure MeOH, c) binary solution SS1 (FMD 0.2 + MeOH 0.8), d) binary solution SS2 (FMD 0.4 + MeOH 0.6), e) binary solution SS3 (FMD 0.6 + MeOH 0.4) and f) binary solution SS4 (FMD 0.8 + MeOH 0.2). In the binary solutions the numbers 0.2, 0.4, 0.6 and 0.8 adjacent to FMD and MeOH indicate their mole fraction in the solutions.

of MeOH affects the $N-H\cdots O$ interactions. It is also possible that MeOH affects the $C-H\cdots O$ contacts [1,2] existing in FMD dimers which can be inferred from the shift in the $C-H$ stretching mode of FMD in the solution SS1. The red shifts in the $C-H$ and NH_2 (symmetric) stretching modes of FMD may be attributed to the dominance of heterointeractions $(FMD)C-H\cdots O$ $(MeOH)$ and $(FMD)N-H\cdots O$ $(MeOH)$ over the $N-H\cdots O$ and $C-H\cdots O$ interactions in FMD dimers. The heterointeractions $(FMD)C-H\cdots O$ $(MeOH)$ and $(FMD)N-H\cdots O$ $(MeOH)$ could be an another factor in inducing the shifts in the $C-O$ stretching modes of MeOH in SS1 (Fig. 1c, Table 1). All the homo/heterointeractions prevailing in the solution SS1 may result in the creation of molecular structures that consist MeOH with both free and bonded $O-H$ groups. This prediction is substantiated by the appearance of peaks separately for the stretching modes of both types of $O-H$ in the solution SS1. In the previous paragraphs, the possible factors for the shifts in the bonded $O-H$ vibrational modes of MeOH in the solution have been discussed. As far as the shifts in the free $O-H$ stretching mode of MeOH is concerned, it is absolutely not mandatory for the $O-H$ to engage in any interaction for the shifts to be produced. All the other interactions happening in its vicinity may be sufficient to cause the shift in the FTIR spectral bands of SS1. We are giving this interpretation based on the results of our earlier research work on the binary solutions of acetone with ethanol [25]. In that work, we had observed FTIR spectral shifts in the methyl and methylene stretching modes of ethanol in the binary solutions prompting us to believe that the interactions $(ethanol\ methyl)C-H\cdots O=C\ (acetone)$ and $(ethanol\ methylene)C-H\cdots O=C\ (acetone)$ take place in the solutions. But the NBO analysis on the acetone-ethanol complexes investigated in that work proved otherwise. Inspite of this, the theoretical frequency shifts of the ethanol methyl and methylene stretching modes in those complexes agreed well with the experimental FTIR spectral results. From these findings, we concluded [25] that the other hydrogen bond interactions in the acetone-ethanol complexes can produce shifts in the ethanol methyl and methylene stretching modes even without the active participation of these groups in any hydrogen bond interactions. On these lines, the shifts in the peak values corresponding to free $O-H$ streching vibrations of MeOH in the solution SS1 may be attributed to the influence of other hydrogen bond interactions on this group.

Table 1
FTIR spectral band assignments for FMD, MeOH and their binary solutions SS1,…,SS4.

Vibrational modes	Wavenumber (cm^{-1})				
	Pure liquid	FMD 0.2 + MeOH 0.8 (SS1)	FMD 0.4 + MeOH 0.6 (SS2)	FMD 0.6 + MeOH 0.4 (SS3)	FMD 0.8 + MeOH 0.2 (SS4)
FMD					
NH_2 s str	3402.4	3381.5	3398.2	3400.2	3406.1
$C-H$ str	2886.6	2882.1	2886.7	2886.2	2886.1
$C=O$ str	1686.7	1694.5	1687.6	1687.3	1687.1
$C-N$ str	1309.6	1312.1	1310.9	1310.1	1309.6
MeOH					
$O-H$ str	3653.5	3680.9	3694.8	3680.7	Not observed
	3383.3	3373.1	3388.5	3396.3	3396.9
CH_3 as str	2966.7	2948.5	2948.3	2948.4	2946.8
$C-O$ str	1053.2	1051.6	1051.2	1051.5	1050.1
	1032.6	1031.7	1030.7	1030.3	Not observed
	1019.1	1023.7	1023.2	1022.5	1024.1

as- asymmetric; s- symmetric; str- stretch.

In the FTIR spectrum of solution SS2 the FMD NH_2 (symmetric) stretching mode (Fig. 1d, Table 1) has undergone a blue shift relative to its value in SS1 but red shift in comparison to the value in pure FMD. This may be the consequence of decrease in the strength of heterointeractions $(FMD)N-H\cdots O$ $(MeOH)$ in SS2 as compared to SS1. With further increase in the concentration of FMD in solution SS3 the wavenumber corresponding to NH_2 (symmetric) stretching vibrations increases in the FTIR spectrum (Fig. 1e, Table 1) implying the further weakening of the heterointeractions $(FMD)N-H\cdots O$ $(MeOH)$. When the mole fraction of FMD reaches 0.8 in SS4 there is a further blue shift in the NH_2 (symmetric) stretching mode (Fig. 1f, Table 1) and most importantly this is a blue shift relative to its value in pure FMD. In this solution, the magnitude of forces that bridge the FMD molecules through the $(FMD)N-H\cdots O$ (FMD) contacts may be greater than the forces that prevail in the heterointeractions $(FMD)N-H\cdots O$

$(MeOH)$. The variations in the strengths of these homo/heterointeractions in the solutions SS2, SS3 and SS4 may be the reason for the shifts in the $C=O$ and $C-N$ stretching modes of FMD, $C-O$ stretching modes of MeOH in these solutions. In all these solutions, the $C-H$ stretching mode of FMD absorbs the IR radiation at almost the same frequency as in pure FMD. This is due to the same $C-H$ bond strength of FMD in the solutions as in pure FMD. Any one of the following factors may account for this result: 1) complete absence of the heterointeractions $(FMD)C-H\cdots O\ (MeOH)$ and the lack of any disturbance to the FMD dimers that possess $C-H\cdots O$ interactions 2) an equilibrium created by the coexistence of the interactions $(FMD)\ C-H\cdots O\ (FMD)$ and $(FMD)C-H\cdots O\ (MeOH)$.

With the dilution of MeOH by FMD in solution SS2, the IR absorption frequency pertaining to bonded $\nu\ (O-H)$ mode of MeOH increases sharply relative to its magnitude in the FTIR spectrum of both SS1 and pure MeOH. This blue shift suggests the superiority of the $(MeOH)\ O-H\cdots O\ (MeOH)$ contacts over the bridging of MeOH-FMD through the hydrogen bonds $(MeOH)O-H\cdots O\ (FMD)$ and/or the $(MeOH)\ O-H\cdots N\ (FMD)$. These heterointeractions may become more feeble in FMD rich solutions SS3 and SS4 in which there is the largest blue shift in the bonded $\nu\ (O-H)$ mode of MeOH.

In solutions SS2 and SS3 there is not much shift in the CH_3 stretching mode of MeOH with respect to the solution SS1. The increase/decrease in the concentration of FMD/MeOH in the solutions SS2 and SS3 may not drastically affect the strength of heterointeractions $(MeOH\ methyl)\ C-H\cdots O\ (FMD)$ and/or $(MeOH\ methyl)C-H\cdots N\ (FMD)$ which may be correlated to the no shift in the MeOH CH_3 stretching mode. But, in solution SS4 a huge red shift in this mode is observed and this may be due to the enhancement in the strength of forces operative during the heterointeractions of the methyl hydrogen with the oxygen and/or the nitrogen of FMD.

The bond lengths of the free $O-H$ groups in MeOH present in the molecular networks that emerge out of the various interactions in solution SS2 undergo compression. As a result the $O-H$ stretching mode is blue shifted in the solution with respect to both SS1 and pure MeOH. When the number of MeOH molecules decrease further in solution SS3 the bond length of the free $O-H$ group becomes almost the same as in solution SS1, due to the molecular interactions. Therefore,

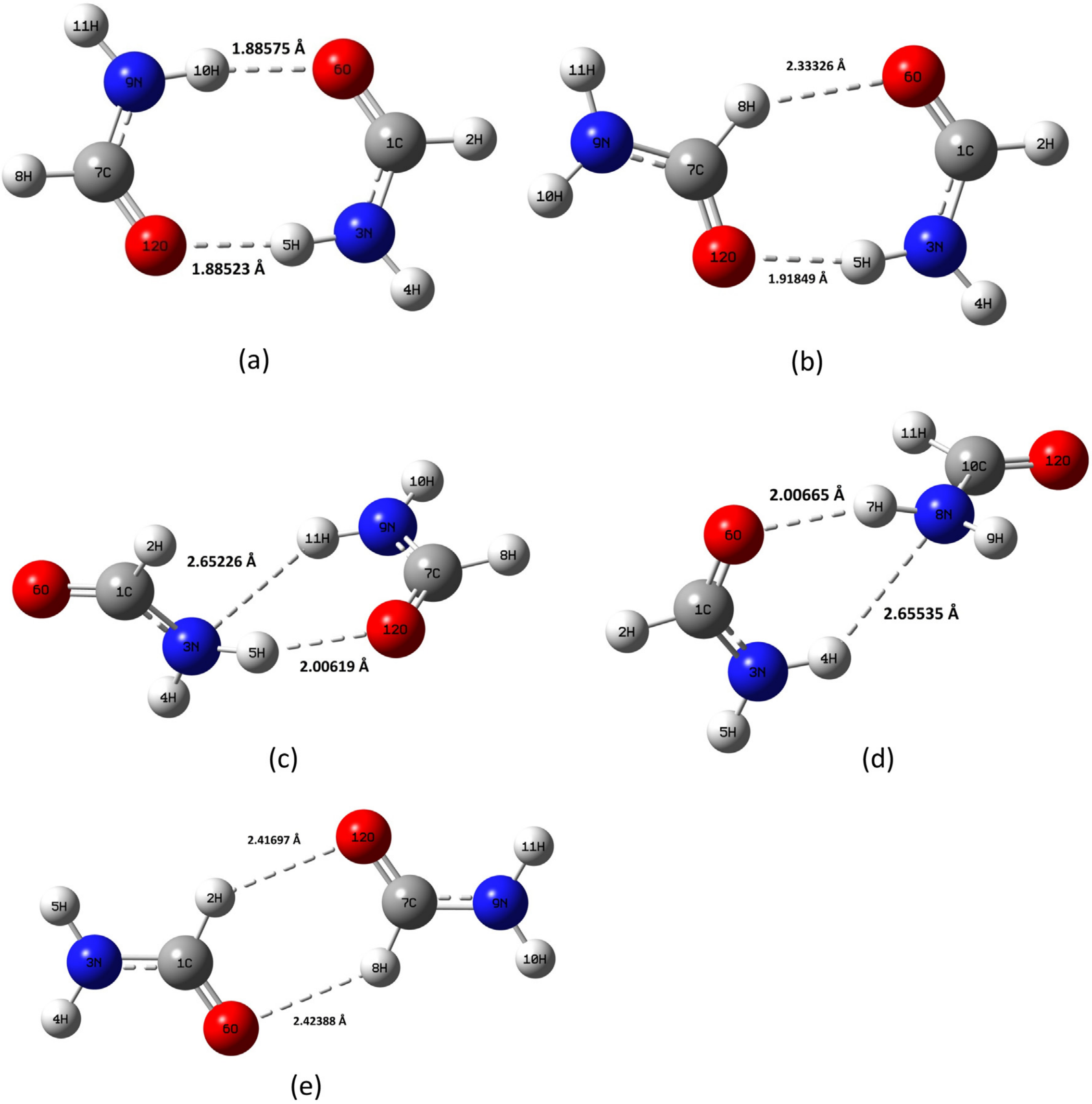

Fig. 2. Optimized structure of (a) FMD dimer1, (b) FMD dimer2, (c) FMD dimer3, (d) FMD dimer4 and (e) FMD dimer5. In all these structures, the major interactions are shown by dashed lines along with the proton- proton acceptor distances. Panel d is an open dimer and the dotted line between 4H and 8N is to show the presence of relatively weak interaction as suggested by the second order perturbation energy (E(2)) value.

the wavenumber corresponding to its vibrational mode is same in the solution SS3 as in SS1. In the solution SS4 with the lowest MeOH concentration among the other binary solutions, the free $O-H$ vibrational mode is not observed. May be in this solution the molecular moieties created out of the molecular interactions may not have any free $O-H$. All the molecular interactions in solutions SS2, SS3 and SS4 affect the MeOH $C-O$ stretching modes, as evident from their shifts in these solutions. As in our earlier report [12], the triplet of $C-O$ stretching band of MeOH continues to exist in all the solutions (except in SS4 in which doublet appears) indicating the presence of more than one type of heteroassociated FMD-MeOH complexes.

3.2. DFT calculations

In the previous section, FTIR spectral shifts have been discussed based on the variations in the strengths of not only the heterointeractions (between FMD and MeOH) but also the homointeractions (in both FMD and MeOH) in the binary solutions SS1,…,SS4. Therefore, it becomes imperative to investigate the self associating multimeric forms of both FMD and MeOH on par with the FMD-MeOH heteromolecular complexes through theoretical calculations. The existence of FMD dimers with five different geometries was already proved through high level theoretical calculations in which the researchers [1,2] analyzed the stabilities of these dimers based on their interaction energies. For these dimers, we decided to calculate the theoretical frequencies in the present work. But carrying out the theoretical frequency calculations on these dimers at those high levels of theory [2] is computationally difficult which prompted us to restrict our calculations at the B3LYP/6-311++G(d,p) level in the present work. Moreover, the theoretical frequency calculations are important in the present work in order to correlate with the experimental FTIR spectral studies to identify the molecular structures existing in the liquid phase. So, we optimized the geometries of these 5 different types of FMD dimers (labeled as FMD dimer1, FMD dimer2, FMD dimer3, FMD dimer4 and FMD dimer5 in Fig. 2) and calculated the frequencies (unscaled).

The experimental FTIR spectroscopic studies of the present work strongly support the coexistence of some free hydroxyl groups in addition to the hydrogen bonded ones in pure MeOH and also in the binary solutions of MeOH with FMD (Section 3.1). Therefore, we created the structures of some MeOH multimers with free $O-H$ groups and fed them as input for the geometry optimization. After the successful optimization of these structures, we found that their final geometry didn't seem to contain any free $O-H$ groups. We got the same result even after attempting several times with the free $O-H$ groups in the initial geometries of MeOH multimers. Therefore, we proceeded with the theoretical frequency (unscaled) calculations for these multimers. While analyzing the theoretical frequencies in these structures we took the average of the frequencies of all the $O-H$ stretching vibrations in each structure. The same strategy was followed with respect to the theoretical frequencies (unscaled) of the optimized structures of FMD-MeOH complexes because a casual look at their final geometries didn't reveal the presence of any free $O-H$ groups in them too. We tried to optimize the open 1:2 complex, but obtained the closed structure. Since MeOH, of course any of the alcohols, is highly associative in nature, the FMD-MeOH complexes with higher number of MeOH molecules need to have closed geometries which are more stable than open structures. All these mean that all the $O-H$ groups of MeOH may be involved in hydrogen bonds in the MeOH multimers and the heteromolecular complexes. Since oxygen in this group is bonded to carbon on the other side of MeOH, all the $C-O$ bonds of MeOH may be more or less similar in bond strength due to the probable closed geometry of the optimized structures of MeOH multimers and the heteromolecular complexes. Due to these, we didn't segregate the frequencies for the $C-O$ stretching modes of MeOH in those structures which have many $C-O$ bonds. In other words, for each of the MeOH multimers and the FMD-MeOH complex, we considered only the resultant of the stretching frequencies of all the $C-O$ bonds in a multimer or complex.

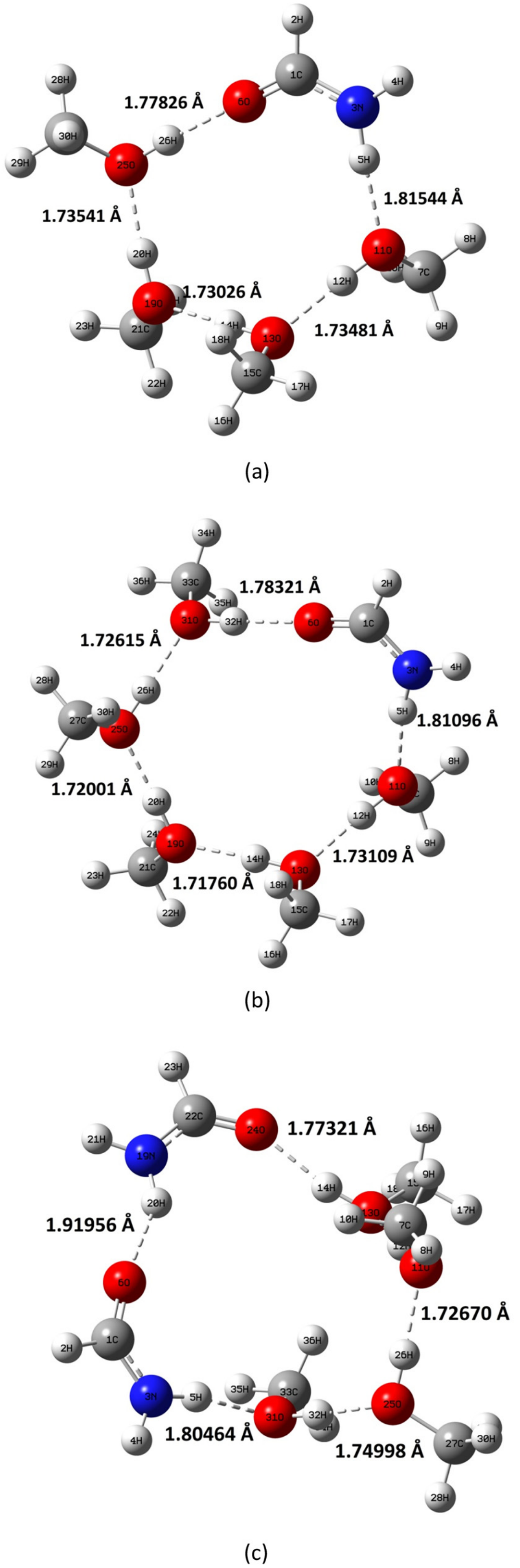

Fig. 3. Optimized structure of (a) 1:4 (FMD:MeOH) complex, (b) 1:5 (FMD:MeOH) complex and (c) 2:4 (FMD:MeOH) complex. In all these structures, the major interactions are shown by dashed lines along with the proton-proton acceptor distances.

Initially, 1:1 (FMD:MeOH), 1:2, 1:3, 1:4, 1:5, 2:2, 2:3, 2:4 and 2:5 complexes, each with two different interaction schemes leading to a total of 18 FMD-MeOH heteroassociated structures, which include all the interaction possibilities suggested by experimental frequency shifts have been optimized. Theoretical frequencies of all the optimized structures were used for validating the results obtained from FTIR spectroscopic studies. This type of validation is not straightforward because we have to take into account the shifts in the experimental wavenumbers corresponding to various vibrational modes of FMD and MeOH in all the solutions SS1,…,SS4. Moreover, for the solutions and pure MeOH we took an average of the peak values corresponding to $O-H$ and $C-O$ stretching modes, separately. Then for each vibrational mode, the experimental shift relative to pure FMD/MeOH is calculated based on the average of the experimental wavenumbers in all the 4 binary solutions. These experimental shifts are compared with the overall theoretical frequency shifts in the FMD-MeOH complexes relative to the average of the frequencies in the self associating structures of FMD and MeOH optimized in the present work. This analysis reveals that the FMD dimers (Fig. 2), MeOH tetramer and pentamer (Fig. S1), 1:4 (FMD: MeOH), 1:5 and 2:4 complexes (Fig. 3), all are of closed geometries, are possible. The theoretical vibrational spectra for these structures are presented as supplementary files Fig. S2. Neat MeOH may also consist of monomer, dimer, trimer etc. as reported in our earlier work [12]. Out of the 18 interaction schemes, the frequency shift for the 15 complexes do not concord with the experimental shifts and therefore, their existence has been ruled out even though they are energetically possible structures. So, the agreement of theoretical frequency shift with the experimental one is an important requirement for the realization of the theoretical H-bonded heterostructures in practice and Ojha et al. [6] or Stangret et al. [13] or Abdelmoulahi et al. [7] failed to arrive at the agreement. As far as the structures given in Figs. 2, 3 and S1 are concerned, the theoretical results (Table 2) are in good agreement with the experimental findings for all the vibrational modes in FMD and MeOH, except the carbonyl stretching mode of FMD. Experimentally, a blue shift in this vibrational mode can be inferred which is in contradiction with the red shift observed in the theoretical frequencies in the complexes. This disagreement in just one vibrational mode may not be a reason to rule out the existence of these complexes. Because in the recent work by our research group on the hydrogen bond interactions in the ethyl acetate – nitrobenzene binary solutions [26], we observed this kind of disagreement with respect to two vibrational modes, one each of ethyl acetate and nitrobenzene in the heteromolecular complexes investigated in that work. But still we confirmed the existence of various interactions predicted from the experimental studies with the help of second order perturbation energies (E(2)) in that work [26]. Therefore, in the present work we extracted the E(2) profiles of FMD dimers (Table 3), MeOH tetramer and pentamer (Table 4), 1:4 (FMD:MeOH), 1:5 and 2:4 complexes (Table 5) through the NBO analyses of these structures. These profiles describe that all the hydrogen bond interactions in these structures happen via the $n \rightarrow \sigma^*$ transitions. In all these hydrogen bonds except the $O24\cdots H14$ in 2:4 complex, lone pair 2 of oxygen interacts more strongly with the hydrogen than the lone pair 1. This conclusion can be drawn out of the larger E(2) values for the interactions involving lone pair 2 compared to that of lone pair 1 of oxygen. Apart from this information, the types of hydrogen bond interactions in the FMD dimers can be understood from their E(2) profiles which are explained as follows: Two $N-H\cdots O$ interactions in FMD dimer1 (Fig. 2a), one $N-H\cdots O$ and one $C-H\cdots O$ interaction in FMD dimer2 (Fig. 2b), one $N-H\cdots O$ and one $N-H\cdots N$ interaction in FMD dimer3 (Fig. 2c), one $N-H\cdots O$ and $N-H\cdots N$ interaction in FMD dimer4 (Fig. 2d), two $C-H\cdots O$ interactions in FMD dimer5 (Fig. 2e). Among all these interactions the $N-H\cdots N$ interaction in FMD dimer3 with the E(2) value 224.22 kJ/mol is the strongest. This is followed by the $N-H\cdots O$ interaction in FMD dimer2 with the E(2) value 199.12 kJ/mol. The next strongest interaction is found in FMD dimer5 in the form of $C-H\cdots O$ interaction with the E(2) value 174.77 kJ/mol. The stability of the FMD dimers is in the following order: FMD dimer1 > FMD dimer2 > FMD dimer3/FMD dimer4 > FMD dimer5 which can be disseminated from their interaction energies in Table 3. The results regarding the stability of these dimers are in good agreement with the earlier reports [1,2]. But these dimers are highly unstable in comparison to the MeOH tetramer (Fig. S1a) and pentamer (Fig. S1b) whose interaction energies (Tables 3 and 4) are appreciably lesser than that of the FMD dimers. In terms of strengths of hydrogen bond interactions the following interactions $O5\cdots H25$, $O11\cdots H24$, $O17\cdots H6$, $O23\cdots H18$ and $O26\cdots H12$ with E(2) values 222.92, 223.72, 222.30, 222.88 and 224.76 kJ/mol, respectively in MeOH pentamer are stronger than any of the $O-H\cdots O$ interactions in the tetramer. In terms of stability too, MeOH pentamer scores over the tetramer. In tetramer, the distance between O5 and H20 is notably lesser than that of the $O7\cdots H6$ and $O13\cdots H8$ distances (Fig. S1a). Despite this, the $O7\cdots H6$ and $O13\cdots H8$ interactions are possible with appreciable E(2) values (Table 4). The absence of any E(2) values with respect to $O5\cdots H20$ interaction indicates that this interaction is absent in the tetramer. This inference leads to the belief that the hydroxyl hydrogen $H20$ is completely free from any hydrogen bond interaction. Stretching motions of the hydroxyl group containing this hydrogen may absorb the IR radiation at higher wavenumbers in the FTIR spectrum of pure MeOH. This may be the reason for the free $O-H$ peak in the FTIR spectrum and also more than one $C-O$ stretching peaks. Because the influence of the asymmetry with respect to this free hydroxyl hydrogen may be felt on the adjacent $C-O$ stretching modes. Therefore, just a look at the optimized structures may not be sufficient to declare whether they are of open or closed geometry, as in case of MeOH tetramer here. There are no interactions between the methyl hydrogen and hydroxyl oxygen of MeOH in both tetrameric and pentameric forms.

In 1:4 complex (Fig. 3a), the $(MeOH)O-H\cdots O\,(MeOH)$ interactions, which are $O25\cdots H20$, $O19\cdots H14$ *and* $O13\cdots H12$ with E(2) values 225.10, 207.19 and 203.18 kJ/mol, respectively, are stronger than the $(MeOH)$ $O-H\cdots O\,(FMD)$ interactions, the $O6\cdots H26$, which are with the energies 70.17 and 140.12 kJ/mol (Table 5). Apart from these interactions, the hydroxyl group of MeOH takes part in another heterointeraction ($O11\cdots H5$) through the $(FMD)N-H\cdots O\,(MeOH)$ contacts with the energies 11.30 and 199.83 kJ/mol. There is a weak $(MeOH)O-H\cdots N\,(FMD)$ interaction $N3\cdots H9$ in this complex. From the overall analysis of the E

Table 2
Theoretical wavenumbers (unscaled, in cm^{-1}) for the optimized structures of FMD dimers, MeOH tetramer and pentamer, and FMD-MeOH complexes.

Vibrational mode	FMD					MeOH		FMD:MeOH complexes		
	Dimer1	Dimer2	Dimer3	Dimer4	Dimer5	Tetramer	Pentamer	1:4	1:5	2:4
NH_2 s str	3318.7	3468.4	3497.1	3497.7	3578.3			3233.2	3248.0	3347.7
$C-H$ str	2971.0	2978.5	2964.6	2964.4	2998.7			2957.6	2955.0	2960.3
$C=O$ str	1755.1	1753.6	1772.5	1772.5	1758.9			1764.0	1762.7	1755.9
$C-N$ str	1330.6	1296.3	1279.0	1278.9	1261.7			1327.8	1322.1	1317.9
$O-H$ str						3434.3	3402.5	3492.4	3456.3	3461.9
CH_3 as str						3103.1	3100.7	3099.5	3099.3	3091.7
$C-O$ str						1059.2	1061.0	1060.6	1062.1	1059.0

as- asymmetric, s- symmetric, str- stretch.

Table 3
Second order perturbation energy (E(2)) profiles and interaction energy for FMD dimers. Both these energies are expressed in kJ/mol. The atom labels and symbols in this table should be correlated with Fig. 2. In this table σ and LP stand for bonding orbital and lone pair, respectively. The presence of asterisk symbol (*) adjacent to σ denote the anti bonding orbital.

FMD dimer1		FMD dimer2		FMD dimer3		FMD dimer4		FMD dimer5	
Interaction type	E(2)	Interaction type	E(2)	Interaction type	E(2)	Interaction type	E(2)	Interaction type	E(2)
$n_{O6LP(1)} \rightarrow \sigma^{*}_{N9-H10}$	60.75	$n_{O6LP(1)} \rightarrow \sigma^{*}_{C7-H8}$	57.03	$n_{N3LP(1)} \rightarrow \sigma^{*}_{N9-H10}$	0.25	$n_{O6LP(1)} \rightarrow \sigma^{*}_{N8-H7}$	10.56	$n_{O6LP(1)} \rightarrow \sigma^{*}_{C7-H8}$	31.84
$n_{O6LP(2)} \rightarrow \sigma^{*}_{N9-H10}$	135.94	$n_{O6LP(2)} \rightarrow \sigma^{*}_{C7-H8}$	153.43	$n_{N3LP(1)} \rightarrow \sigma^{*}_{N9-H11}$	224.22	$n_{O6LP(2)} \rightarrow \sigma^{*}_{N8-H7}$	24.35	$n_{O6LP(2)} \rightarrow \sigma^{*}_{C7-H8}$	174.77
$n_{O12LP(1)} \rightarrow \sigma^{*}_{N3-H5}$	56.94	$n_{O12LP(1)} \rightarrow \sigma^{*}_{N3-H5}$	30.21	$n_{O12LP(1)} \rightarrow \sigma^{*}_{N3-H5}$	45.73	$n_{N8LP(1)} \rightarrow \sigma^{*}_{N3-H4}$	3.98	$n_{O12LP(1)} \rightarrow \sigma^{*}_{C1-H2}$	33.72
$n_{O12LP(2)} \rightarrow \sigma^{*}_{N3-H5}$	132.26	$n_{O12LP(2)} \rightarrow \sigma^{*}_{N3-H5}$	199.12	$n_{O12LP(2)} \rightarrow \sigma^{*}_{N3-H5}$	156.40			$n_{O12LP(2)} \rightarrow \sigma^{*}_{C1-H2}$	174.01
Interaction energy (kJ/mol)									
−46.1		−29.0		−19.2		−19.2		−12.8	

Table 4
Second order perturbation energy (E(2)) profiles and interaction energy for multimeric forms of MeOH. Both these energies are expressed in kJ/mol. The atom labels and symbols in this table should be correlated with Fig. 3. In this table σ and LP stand for bonding orbital and lone pair, respectively. The presence of asterisk symbol (*) adjacent to σ denote the anti bonding orbital.

MeOH tetramer		MeOH pentamer	
Interaction type	E(2)	Interaction type	E(2)
$n_{O7LP(1)} \rightarrow \sigma^{*}_{O5-H6}$	8.75	$n_{O5LP(1)} \rightarrow \sigma^{*}_{O26-H25}$	8.28
$n_{O7LP(2)} \rightarrow \sigma^{*}_{O5-H6}$	205.60	$n_{O5LP(2)} \rightarrow \sigma^{*}_{O26-H25}$	222.92
$n_{O13LP(1)} \rightarrow \sigma^{*}_{O7-H8}$	8.03	$n_{O11LP(1)} \rightarrow \sigma^{*}_{O23-H24}$	8.16
$n_{O13LP(2)} \rightarrow \sigma^{*}_{O7-H8}$	218.11	$n_{O11LP(2)} \rightarrow \sigma^{*}_{O23-H24}$	223.72
$n_{O19LP(1)} \rightarrow \sigma^{*}_{O13-H14}$	8.24	$n_{O17LP(1)} \rightarrow \sigma^{*}_{O5-H6}$	7.70
$n_{O19LP(2)} \rightarrow \sigma^{*}_{O13-H14}$	203.80	$n_{O17LP(2)} \rightarrow \sigma^{*}_{O5-H6}$	222.30
		$n_{O23LP(1)} \rightarrow \sigma^{*}_{O17-H18}$	7.91
		$n_{O23LP(2)} \rightarrow \sigma^{*}_{O17-H18}$	222.88
		$n_{O26LP(1)} \rightarrow \sigma^{*}_{O11-H12}$	8.16
		$n_{O26LP(2)} \rightarrow \sigma^{*}_{O11-H12}$	224.76
Interaction energy (kJ/mol)			
−104.5		−136.9	

(2) profile of this complex, it can be stated that the homointeractions $(MeOH)O - H \cdots O\ (MeOH)$ plays a major role over all the other interactions in this complex. Same is the case with the 1:5 complex – Fig. 3b and 2:4 complex – Fig. 3c. Among all the 3 complexes the strongest $(MeOH)O - H \cdots O\ (MeOH)$ interactions are found in 1:5 complex between $O31$ and $H26$ with energy 230.37 kJ/mol. Hence, the dominance of $(MeOH)O - H \cdots O\ (MeOH)$ interactions over the $(MeOH)O - H \cdots O\ (FMD)$ interactions in all the 3 complexes and the $(MeOH)O - H \cdots N\ (FMD)$ interaction in 1:4 complex is proved. This supports the overall blue shift in the $O - H$ stretching mode of MeOH in the binary solutions and also the presence of these heteromolecular complexes in the solutions. In the solutions SS1,…,SS3 the appearance of free $O - H$ stretching mode and more than one $C - O$ stretching mode of MeOH is due to the presence of MeOH tetramers. These tetramers may completely dissociate in the FMD rich solution SS4 which is the causative factor behind the disappearance of free $O - H$ and one of the $C - O$ stretching modes (Fig. 1f, Table 1).

The earlier theoretical investigations on the FMD dimers by Frey and Leutwyler [1] predicted that the $N - H \cdots N$ interactions are weaker than the $N - H \cdots O$ interactions in FMD dimer3. But in the present work the $N - H \cdots N$ interactions ($N3 \cdots H11$) in FMD dimer3 identified through the E(2) profile (Table 3) are found to be stronger than the $N - H \cdots O$ and $C - H \cdots O$ interactions in other dimers. This fact implies that any variations in the strengths of $N - H \cdots N$ interactions in FMD dimer3 in the environment of MeOH may exert major impact on the NH_2 symmetric and $C - N$ stretching modes of FMD in the binary solutions SS1,…, SS4. The red shift undergone by the NH_2 symmetric stretching mode in the solution SS1 is not due to the predominance of heterointeractions $(FMD)N - H \cdots O\ (MeOH)$ over the self association of FMD as mentioned in Section 3.1. This strong statement is inferred from the E(2) profiles of the heteromolecular complexes investigated in the present work. The heterointeractions $(FMD)N - H \cdots O\ (MeOH)$ in 1:4 complex ($O11 \cdots H5$), 1:5 complex ($O11 \cdots H5$) and 2:4 complex ($O31 \cdots H5$) are weaker than the $N - H \cdots N$ interactions in FMD dimer3. These $N - H \cdots N$ interactions are broken by the rapid dissociation of the FMD dimer3 in solutions SS1,…,SS3 which may be the main reason for the red shift in the FMD NH_2 symmetric stretching mode in these solutions. However, the magnitude of red shift decreases as we move from SS1 to SS3. This may be due to the reduction in the dissociation of FMD dimer3 with the increasing mole fraction of FMD from SS1 to SS3. In the solution SS4, there may not be any more dissociation of the FMD dimer3 which could be the reason for the blue shift observed in the NH_2 symmetric stretching mode.

The $(FMD)C - H \cdots O\ (FMD)$ interactions are found only in FMD dimer2 and FMD dimer5 (Table 3). Apart from these, the FMD $C - H$ doesn't involve in any homo/heterointeraction in the 3 complexes.

Table 5
Second order perturbation energy (E(2)) profiles and interaction energy for FMD-MeOH complexes. Both these energies are expressed in kJ/mol. The atom labels and symbols in this table should be correlated with Fig. 3. In this table σ and LP stand for bonding orbital and lone pair, respectively. The presence of asterisk symbol (*) adjacent to σ denote the anti bonding orbital.

1:4 (FMD:MeOH) complex		1:5 (FMD:MeOH) complex		2:4 (FMD:MeOH) complex	
Interaction type	E (2)	Interaction type	E (2)	Interaction type	E (2)
$n_{N3LP(1)} \rightarrow \sigma^{*}_{C7-H9}$	0.42	$n_{O6LP(1)} \rightarrow \sigma^{*}_{O31-H32}$	63.97	$n_{O6LP(1)} \rightarrow \sigma^{*}_{N19-H20}$	29.04
$n_{O6LP(1)} \rightarrow \sigma^{*}_{O25-H26}$	70.17	$n_{O6LP(2)} \rightarrow \sigma^{*}_{O31-H32}$	125.81	$n_{O11LP(1)} \rightarrow \sigma^{*}_{O25-H26}$	9.67
$n_{O6LP(2)} \rightarrow \sigma^{*}_{O25-H26}$	140.12	$n_{O11LP(1)} \rightarrow \sigma^{*}_{N3-H5}$	11.51	$n_{O11LP(2)} \rightarrow \sigma^{*}_{O25-H26}$	81.21
$n_{O11LP(1)} \rightarrow \sigma^{*}_{N3-H5}$	11.30	$n_{O11LP(2)} \rightarrow \sigma^{*}_{N3-H5}$	201.42	$n_{O13LP(1)} \rightarrow \sigma^{*}_{O11-H12}$	8.03
$n_{O11LP(2)} \rightarrow \sigma^{*}_{N3-H5}$	199.83	$n_{O13LP(1)} \rightarrow \sigma^{*}_{O11-H12}$	8.83	$n_{O13LP(2)} \rightarrow \sigma^{*}_{O11-H12}$	74.39
$n_{O13LP(1)} \rightarrow \sigma^{*}_{O11-H12}$	8.45	$n_{O13LP(2)} \rightarrow \sigma^{*}_{O11-H12}$	205.56	$n_{O24LP(1)} \rightarrow \sigma^{*}_{O13-H14}$	36.32
$n_{O13LP(2)} \rightarrow \sigma^{*}_{O11-H12}$	203.18	$n_{O19LP(1)} \rightarrow \sigma^{*}_{O13-H14}$	8.20	$n_{O24LP(2)} \rightarrow \sigma^{*}_{O13-H14}$	21.67
$n_{O19LP(1)} \rightarrow \sigma^{*}_{O13-H14}$	7.70	$n_{O19LP(2)} \rightarrow \sigma^{*}_{O13-H14}$	205.98	$n_{O25LP(1)} \rightarrow \sigma^{*}_{O31-H32}$	11.97
$n_{O19LP(2)} \rightarrow \sigma^{*}_{O13-H14}$	207.19	$n_{O25LP(1)} \rightarrow \sigma^{*}_{O19-H20}$	7.20	$n_{O25LP(2)} \rightarrow \sigma^{*}_{O31-H32}$	66.15
$n_{O25LP(1)} \rightarrow \sigma^{*}_{O19-H20}$	6.95	$n_{O25LP(2)} \rightarrow \sigma^{*}_{O19-H20}$	216.77	$n_{O31LP(1)} \rightarrow \sigma^{*}_{N3-H5}$	11.80
$n_{O25LP(2)} \rightarrow \sigma^{*}_{O19-H20}$	225.10	$n_{O31LP(1)} \rightarrow \sigma^{*}_{O25-H26}$	7.00	$n_{O31LP(2)} \rightarrow \sigma^{*}_{N3-H5}$	64.35
		$n_{O31LP(2)} \rightarrow \sigma^{*}_{O25-H26}$	230.37		
Interaction energy (kJ/mol)					
−136.9		−167.7		−162.7	

Therefore, the red shift of the FMD $C-H$ stretching mode in the solution SS1 can solely be due to the dissociation of FMD dimer2 and FMD dimer5 (Table 1). No shift in this mode in the other binary solutions may be due to the equilibrium created by the other interactions like $(MeOH)O-H\cdots O\ (FMD)$, $(FMD)N-H\cdots O\ (MeOH)$ and $(MeOH)O-H\cdots N\ (FMD)$ happening nearer to the FMD $C-H$ in the heteromolecular complexes and the changes in the homointeractions among the FMD dimers. Similarly, the MeOH CH_3 is not hydrogen bonded to any of the electronegative atoms of FMD in the complexes. But still the CH_3 stretching vibrations result in IR absorption peaks at lower wavenumbers in the solutions. The red shift may be a manifestation of the dissociation of MeOH tetramers/pentamers and the $(MeOH)O-H\cdots O\ (FMD)$, $(FMD)N-H\cdots O\ (MeOH)$, $(MeOH)O-H\cdots N\ (FMD)$ and the $(MeOH)O-H\cdots O\ (MeOH)$ interactions in the complexes. The shifts in the FMD $C=O$ and MeOH $C-O$ stretching modes in the solutions are the resultant of all the interactions discussed in this section. The interaction energy values (Tables 3 and 4) clearly indicate that closed MeOH tetramer and pentamer are many fold stronger than FMD dimers. Therefore, there is no possibility for the formation of 1:1 (MeOH:FMD), 1:2 and 1:3 complexes as proposed by Stangret et al. [13] at the concentrations studied. A mismatch in the experimental and theoretical frequency shifts for the 1:1 (MeOH:FMD) and 3:1 complexes has been noticed and this also rule out the presence of these complexes.

4. Conclusions

FMD dimers with 5 different geometries are possible. Among all these dimers, the $N-H\cdots N$ interactions in FMD dimer3 are more stronger than the $N-H\cdots O$ and $C-H\cdots O$ interactions prevailing in the other dimers. But the FMD dimer1 which is stabilized by two $N-H\cdots O$ interactions is the most stable among all these dimers.

The interaction forces that operate in the pentamers are more stronger than those in the tetramers. In tetramers, there is a possibility for the existence of free $O-H$ whose vibrational modes result in higher peak values in the FTIR spectrum than the hydrogen bonded hydroxyl groups present in both tetramers and pentamers. The interaction energies imply that pentamers are more stable than tetramers.

In the binary solutions of FMD with MeOH, 1:4 (FMD:MeOH), 1:5 and 2:4 complexes with closed structures have been formed which are more stable than the self associated structures of FMD and MeOH. Therefore, the dissociation of these self associated structures is the more prominent effect in the solutions than the heterointeractions $(MeOH)O-H\cdots O\ (FMD)$ and $(FMD)N-H\cdots O\ (MeOH)$ identified in the complexes. These interactions are weaker than the $(MeOH)O-H\cdots O\ (MeOH)$ interactions existing in the complexes.

The $C-H$ in FMD and CH_3 in MeOH don't participate in any heterointeractions in the solutions. Therefore, the shifts in the vibrational modes of the MeOH CH_3 group in the solutions is solely due to the other interactions involving the MeOH because the methyl group doesn't contribute to the self association of MeOH. The shifts in the $C-H$ stretching mode of FMD in the solutions is due to the disturbances in the $(FMD)C-H\cdots O\ (FMD)$ interactions existing in the FMD dimers.

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Author contributions

Mr. P.P. Kannan Writing - Original draft, Investigation.

Dr. N.K. Karthick Writing - Review and Editing.

Dr. G. Arivazhagan Conceptualization, Writing - Review and Editing, Supervision.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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