Vibrational Spectroscopy 57 (2011) 294–299

Contents lists available at SciVerse ScienceDirect

Vibrational Spectroscopy

journal homepage: www.elsevier.com/locate/vibspec

Detection of relative dimer and rotamer concentrations of diacetamide in different solvents by FT-IR spectroscopy and DFT calculations

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ARTICLE INFO

Article history:
Received 6 April 2011
Received in revised form 24 August 2011
Accepted 26 August 2011
Available online 16 September 2011

Keywords:
Diacetamide
Dimerization
Rotamerization
FT-IR
DFT
Relative equilibrium concentrations

ABSTRACT

The relative rotamer, dimer and tautomer concentrations of diacetamide have been studied by means of infrared spectroscopy, with the recorded spectra being analyzed employing results from density functional theory calculations. It is observed that the cis–trans monomeric form of diacetamide (**1**) is found to be the most stable isomer in all studied solvents, with trans–trans diacetamide (**2**) being found to be 20% of total diacetamide in methanol. While the dimer form of diacetamide (**3**) is present only in carbon-tetrachloride (about 34% of the total), its tautomeric forms (**4**, **5**) are not favorable in any of the studied solvents.

1. Introduction

Most of the organic molecules have different structural (dimeric, tautomeric or rotameric) properties in solvent media. It is well known that these structural differences induce different chemical properties and reactivity [1,2]. Thus, abundance and relative proportions of the species (dimers, tautomers, rotamers) that are in equilibrium in solution is very important [1,3].

Since tautomeric and rotameric interconvertions are quite fast processes, they are difficult to study. Nevertheless, the variety and importance of applications encompassing these phenomena continuously encourage researchers to undertake their investigations [2]. The NMR is one of the common method used to determine equilibrium constants [4,5] but inability of NMR time scale for the detection of fast interconversions is a common problem and in contrast to NMR spectroscopy, the time scale of vibrational spectroscopic measurements is suitable for simultaneous detection of coexisting species. In this respect, infrared spectroscopy is one of the most versatile spectroscopic methods in the chemical sciences allowing studying processes such as the keto-enol equilibrium [2,3,6].

Among the molecules that can show tautomerism, imides are strong candidates that may present structural features in solution differing from solid state ones thanks to the similarity with amides and the presence of two carbonyls attached to the –NH– group. For this reason, the absorption bands of acyclic imide rotamers in the crystalline state and in solution have been studied extensively by FT-IR spectra [7–11]. Besides, imides are very important molecules in molecular recognition. Imide hydrogen-bond rules can be also applied to chemical homologues and analogues such as uracils and barbiturates to investigate host–guest interactions where predictable aggregation patterns are very often observed [12].

Diacetamide is the simplest open chain molecules that contain a –CONHOC– functional group. While the two carbonyls and imide nitrogen are planar, there are three possible configurations according to the relative orientation of carbonyls and hydrogen on the nitrogen. It was concluded that both cis–trans (**1**) (named from the position of the carbonyl groups relative to the group attached to the nitrogen) and trans–trans (**2**) rotamers of diacetamide (Fig. 1) are present in the solid state, with the first one being the most stable conformation [13]. The less stable cis–cis (**6**) conformation of diacetamide (Fig. 1) has never been observed in solid state or in solution [14].

The conformations of diacetamide in CCl_4 were also studied and the existence of the dimer (**3**) and monomer$_{cis–trans}$ (**1**) (Fig. 1) geometry was reported [15,16]. Existence of dimeric structures in non-polar solvents was explained invoking a reduction of the dipole moment upon dimerization [16]. The effect on the geometry and bonding of diacetamide with metals (Mn (II), Fe (II), Co (II), Ni

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doi:10.1016/j.vibspec.2011.08.008

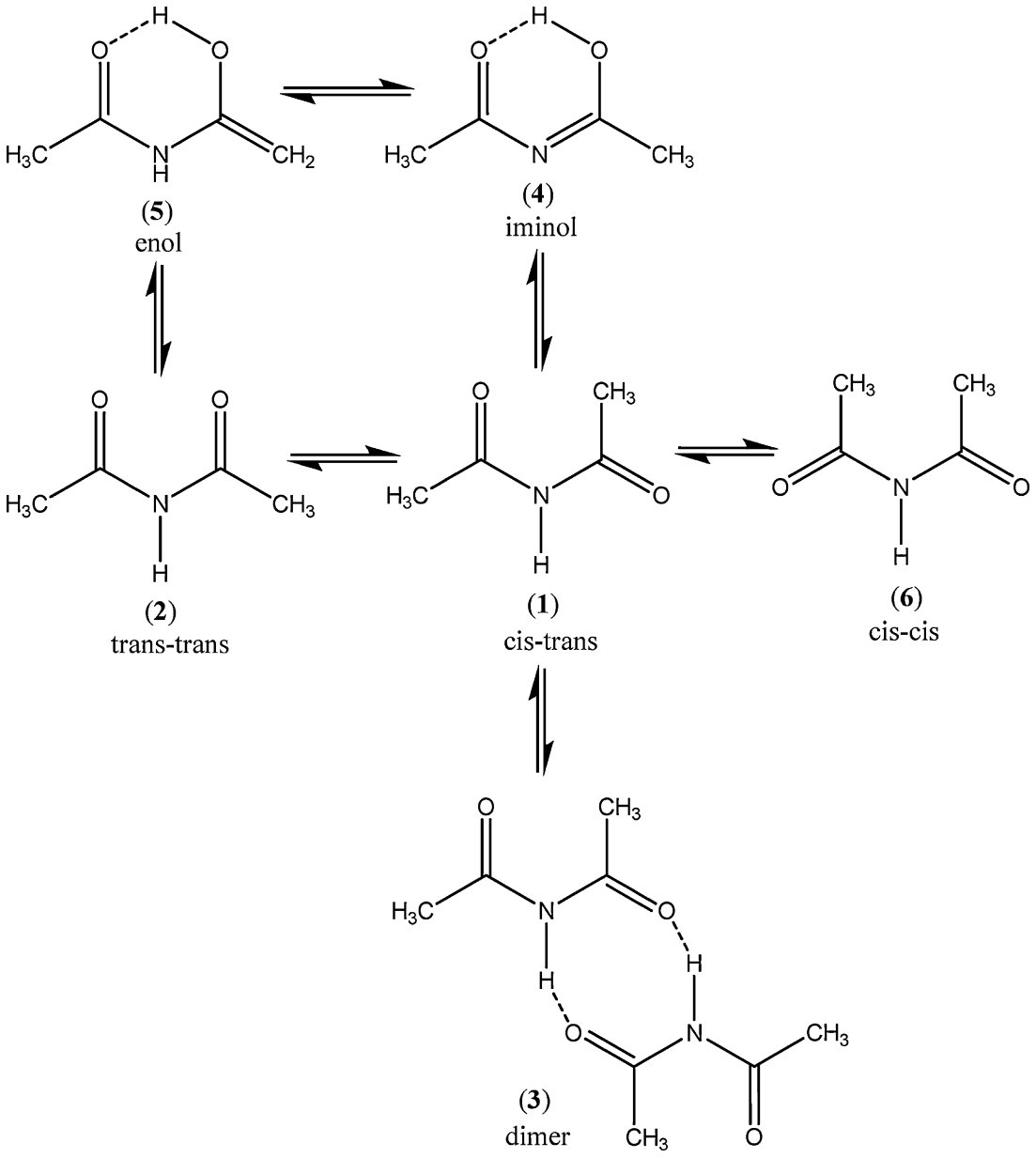

Fig. 1. All possible rotamer, tautomer and dimer structures of diacetamide.

(II), and Zn (II)) were also studied by FT-IR [17]. Infrared spectra of trans-cis diacetamide and its C- and N-deuterated compounds were compared and the vibrational assignments performed [18].

Diacetamide was also found to be a versatile cocrystallizing agent, forming at least ten different cocrystal pairs and crystallizes in two different polymeric forms, the stable form containing molecules having the cis–trans conformation. In the crystalline state, the molecules are held together by centrosymmetric NH···O hydrogen bonds. The cis–trans (**1**) conformer is also the most stable form in solution [12]. Besides, the lack of spectral features indicating tautomerism in the published study agrees well with theoretical relative energies showing that the iminol (**4**) tautomer (Fig. 1) of the 1,3-dicarbonyl imide structure is indeed not favorable [15].

Despite all the qualitative characterization carried out in the past, there is substantial lack of quantitative information on the solution equilibria afforded by diacetamide, a gap that we strive to fill in this study. The main idea behind this work is that different compounds (tautomers, dimer–monomer, and rotamers) should be expected to have different FT-IR spectra. Thus, an experimental FT-IR spectrum of a compound in dynamical isomeric equilibrium in an appropriate solvent should be the sum of the spectra of all components in the equilibrium thanks to the difference in time scale between isomeric conversion and internal vibrations. Obviously, absorption band intensities ought to be proportional to their relative concentrations. For most of the equilibrium systems, it is clearly impossible to isolate each compound in order to investigate its individual spectral properties. It is instead possible to calculate their theoretical FT-IR spectrum with electronic structure methods such as Density Functional Theory made available in, e.g., Gaussian 03 [19]. We thus decided to exploit such possibility in order to obtain semi-quantitative information.

In this study, we have thus employed a matching approach between the diacetamide FT-IR spectra obtained with theoretical means and experimentally. For this purpose, calculations on all possible species (**1**, **2**, **3**, **4** and **5**) in solution (Fig. 1) have been carried out with a suitable method and basis set. The assignment of the absorption bands, supplemented with calculated electronic and thermal free energies, allowed us to determine the existence

or absence of any species in equilibrium system. Theoretical intensities of species likely to be present in solution were scaled with appropriate constants (the sum of the constants being equal to 1) and added together to generate the "best matching synthetic spectrum" to the experimental FT-IR spectra as a way to extract relative concentrations and equilibrium constants.

2. Materials and methods

All solvents and diacetamide were purchased from Aldrich or Fluka as analytical purity and no further purification has been done. The vibrational absorption spectra of diacetamide in all solutions were measured using a Perkin Elmer 1600 BX 2 FT-IR spectrophotometer. The resolution and the interval values were chosen as 4 and 2 in all FTIR measurements. The spectra of pure solvents were recorded as a background and stored on the computer for each measurement. Solution spectra were measured using a 0.015 mm path length in CaF_2 cell with an average 32 scans. In all FT-IR measurements, the concentrations of the diacetamide were 0.0100 mol/L, except in carbon tetrachloride. To get more information about the monomer–dimer equilibrium, three different concentrations (0.0100, 0.0050, 0.0025 mol/L) of diacetamide have been studied.

The Gibbs free energy of all possible molecules (**1**, **2**, **3**, **4** and **5**) in each solvent has been separately calculated and these energies were used to assign the existence of these species in equilibrium. These existing assignments were also supported by matching the experimental and calculated FT-IR spectra. While the frequencies of the FT-IR absorption bands gives clue for the existence, the comparison of the intensities also provide valuable information about the relative concentrations of these species in the equilibrium system.

Calculations for all possible structures; tautomers (**4**, **5**), dimer (**3**) and rotamer (**1**, **2**) (Fig. 1) were carried out with the Gaussian 03 [19] set of programs. All the input files generated with ChemDraw 2008 and potential energy surface calculations were done with semi-empirical AM1 method to prepare the best input geometry. The geometry optimizations and frequency calculations of tautomers, dimers and rotamers of diacetamide were carried out at the DFT B3LYP/6-311G ++ (2d, 2p) level [20–24] in different solvents, employing the conductor-like polarizable continuum model (CPCM) [25]. Thus, all stationary points of the different species involved in this study were optimized both in the gas phase and using the CPCM model with the appropriate dielectric constants.

3. Results and discussion

To obtain the relative stabilities between rotamers, dimers and tautomers of diacetamide a theoretical study has been performed for all possible keto and enolic forms of diacetamide (Fig. 1) in 7 different solvents. Energy differences between all possible structures and the most stable conformer (**1**) were obtained subtracting the energy of the latter from the one of the other molecules (**2**, **3**, **4** and **5**). Thus, the most stable conformer (**1**) is used as reference and given zero energy value with all solvents. The results are summarized in Table 1. Species with a energy difference less or equal 5 kcal/mol are considered to dynamically convert between each other at ambient temperature [2]. Species with an energy difference higher than 5 kcal/mol have not been taken into account in our discussion. As it can be seen from Table 1, the energy difference of molecules **4** and **5** from the most stable molecule **1** is higher than 5 kcal/mol. Thus, the effects due to **4** and **5** could be neglected in all studied solvents [15,26].

For the sake of comparing theoretical and experimental frequencies and intensities in the spectrum matching method employed in this work, the recorded experimental data were exported as data tables. Scaling factor for the theoretical vibrational bands in the experimentally scanned frequency range were determined by least square fit of selected frequencies against experimental results in order to allow a direct comparison also from the visual point of view. Obtained R^2 values were an indication for frequency regression. With the theoretical frequencies appropriately scaled to match the experimental ones, a linear regression between theoretical and experimental intensities can be carried out to extract relative concentration. In other words, assuming good accuracy for the theoretical absorption coefficients, the linear regression provides one with the relative fractions to be assigned to all species in order to reconstruct the experimentally recorded spectra.

Table 1
The energy difference between the possible structures in solvents. (For the dimer structure, the obtained energy from theoretical calculation divided by two.)

Solvents	δΔGf values for possible species (kcal/mol)				
	1 ref.	**2**	**3**	**4**	**5**
MeOH	0.0	1.6	6.2	14.6	18.4
DMSO	0.0	0.4	5.0	12.4	17.3
CH_3CN	0.0	0.9	5.0	13.4	17.3
THF	0.0	3.0	5.7	12.8	18.2
DCM	0.0	1.5	5.5	12.6	18.9
$CHCl_3$	0.0	2.2	4.5	13.6	18.3
CCl_4	0.0	3.3	2.7	11.6	18.1
Gas Phase	0.0	4.8	0.4	7.7	17.9

From the experimental FT-IR spectra (Fig. 2) and theoretical energy calculations of diacetamide (Table 1), it is obvious that there are no indications for the presence of enol (**5**) and iminol (**4**) tautomers in any solvent. Since tautomerization seems not to occur, dimerization and rotamerization should be held responsible for the differences between the FT-IR spectra of diacetamide in different solvents, especially in the region 1660 cm^{-1}–1800 cm^{-1} (Fig. 2). Thus, we aim to obtain semi-quantitative information on the relevant equilibria with the aforementioned spectrum matching approach. In this respect, we chose to discuss in details the approach for the cases represented by diacetamide in carbon tetrachloride and methanol. These are good representative model systems thanks to the fact that CCl_4 is the only solvent where the dimer structure (**3**) has been detected while methanol is the solvent that contains the highest amount (20%) of trans–trans (**2**) configuration. The method was identically applied to the case of the other solvents and results are summarized in Table 2.

The calculated gas phase IR frequencies of existing molecules (**1**, **2** and **3**) have been compared with the IR frequencies in solvent. It is observed that the stretching bands of highly polarized bonds (C=O, N–H) shift considerably more than those of less polarizable bonds comparing gas phase and solvent media. This kind of shifts has also been observed by the increase in polarity of the

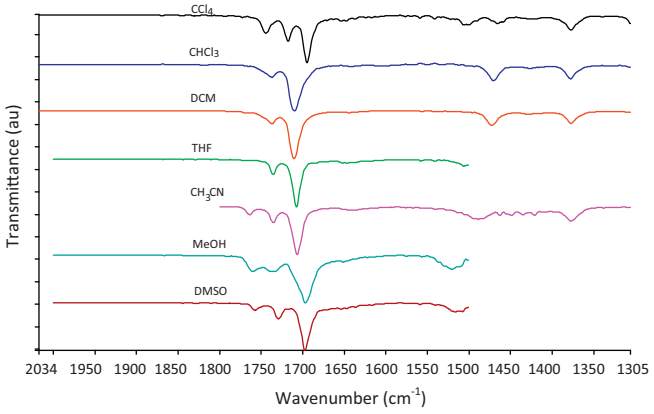

Fig. 2. Experimental FT-IR spectra of diacetamide in solvents.

Table 2
Selected experimental (V_{exp}) and related theoretical (V_{theo}) frequencies, correlation coefficient between V_{exp} and V_{theo} (R_V^2), experimental absorbances (A_{exp}) and related theoretical intensities(A_{theo}) (multiplied with appropriate relative concentration values), correlation coefficient between A_{exp} and A_{theo} (R_A^2), relative concentration of **1** (%cis–trans), **2** (%trans–trans) and **3** (%dimer).

Solvents	V_{exp}	V_{theo}	Source of band	R_V^2	A_{exp}	A_{theo}	R_A^2	% (**1**)	% (**2**)	% (**3**)
CCl_4	1376	1412	**3**	0.99	0.020	79	0.98	32	0	34
	1464	1506	**1**		0.012	65				
	1506	1556	**3**		0.014	87				
	1694	1702	**3**		0.063	598				
	1716	1730	**1**		0.034	246				
	1744	1770	**3**		0.024	143				
$CHCl_3$	1426	1466	**1**	0.99	0.003	99	0.99	100	0	0
	1470	1508	**1**		0.011	193				
	1710	1714	**1**		0.031	688				
	1736	1756	**1**		0.008	198				
CH_3CN	1378	1406	**1**	0.99	0.028	84	0.99	99	1	0
	1448	1466	**1**		0.017	56				
	1706	1698	**1**		0.099	936				
	1736	1742	**1**		0.031	199				
	1764	1774	**1**		0.016	84				
DCM	1428	1464	**1**	0.99	0.006	88	0.99	96	4	0
	1472	1512	**1**		0.021	245				
	1710	1706	**1**		0.071	849				
	1736	1752	**1**		0.019	196				
	1768	1786	**2**		0.004	45				
THF	1708	1722	**1**	0.99	0.097	865	0.99	96	4	0
	1736	1764	**1**		0.032	202				
	1770	1804	**2**		0.008	35				
DMSO	1508	1512	**1**	0.99	0.010	248	0.95	90	10	0
	1698	1698	**1**		0.052	856				
	1730	1746	**1**		0.018	197				
	1758	1776	**2**		0.009	92				
MeOH	1522	1524	**2**	0.99	0.009	184	0.99	80	20	0
	1696	1698	**1**		0.041	714				
	1738	1748	**1**		0.012	172				
	1760	1776	**2**		0.012	217				

different solvents. For example the C=O stretching band of **1** is calculated as 1762 cm^{-1}, 1730 cm^{-1} and 1698 cm^{-1} in gas phase, CCl_4 and CH_3CN respectively. In trans–trans form (**2**) same band has been calculated as 1834 cm^{-1}, 1806 cm^{-1} and 1774 cm^{-1}. This shift in frequency has been obtained as 1718 cm^{-1}, 1702 cm^{-1} and 1686 cm^{-1} for dimeric structure. The N–H stretching bands of **1** and **2** are significantly different from gas phase to solution but this is not true for dimeric structure (**3**). There is only 2 cm^{-1} difference between the calculated N–H stretching band frequency of **3** in gas phase (3338 cm^{-1}) and CCl_4 (3340 cm^{-1}). Even in polar solvents the frequency of the stretching of N–H is about the same (3346 cm^{-1} for CH_3CN). On the determination of the N–H

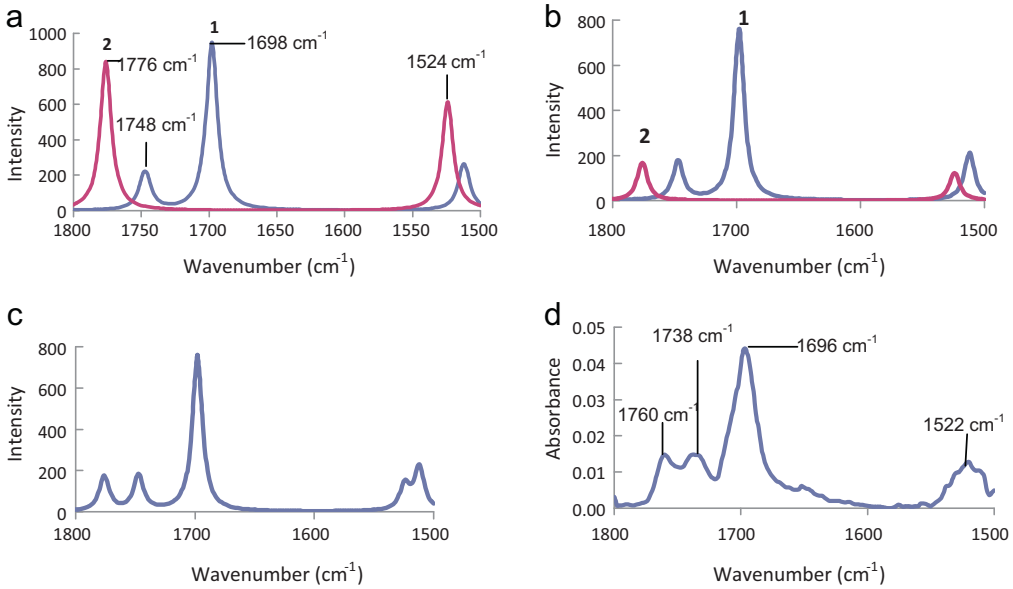

Fig. 3. (a) Theoretical IR spectra of cis–trans (**1**) and trans–trans (**2**) rotamers of diacetamide between 1500 cm^{-1} and 1800 cm^{-1} in methanol. (b) IR spectra of **1** (0.80) and **2** (0.20). (c) Representation of final theoretical spectrum by addition of multiplied intensities of **1** and **2**. (d) Experimental FT-IR spectrum of diacetamide in MeOH.

stretching band frequency, the C═O···H–N hydrogen bond is very effective so the solvent cannot interact with the protic hydrogens as much as monomeric structures **1** and **2**.

3.1. The equilibrium in methanol

Table 1 shows the energy difference between **2** and **1** (1.6 kcal/mol), and **3** and **1** (6.2 kcal/mol); thus, we excluded **3** from our model spectrum. The theoretical IR frequencies for **1** and **2** in methanol are shown in Fig. 3a. The calculated intensities for **1** and **2** were overlaid with equal weight on the same frequency axis for a direct comparison with the experimental data (experimental data are shown in Fig. 3d).

Focusing on the 1800–1650 cm^{-1} region, the overlaid spectrum (Fig. 3a) shows three absorption bands, the latter being assigned as asymmetric and symmetric C═O stretching bands of **1**, at 1698 cm^{-1} and 1748 cm^{-1}, and symmetric C═O stretching of **2** at 1776 cm^{-1}. The experimental spectrum (Fig. 3d) also has three absorption bands in the related region supporting our suggestion for the presence of the equilibrium between **1** and **2** (Fig. 1) in methanol. The absorption band at 1760 cm^{-1} in the experiment relates to the symmetric C═O stretching of **2** (theoretically at 1776 cm^{-1}).

A least square fit of selected experimental and theoretical frequencies (Table 2), shows a strong linear relationship with an R^2 value of 0.99 (Fig. 4a) without applying any scaling factor.

Although the calculated frequencies of these two molecules (**1** and **2**) appear in a good harmony with the experimental frequencies (Fig. 4a), the intensities do not for relative concentrations of 50% (Fig. 4b).

Since it is well known that the absorption band intensities of different molecules in the same FT-IR measurement are directly related to the relative concentrations, a better matching between spectra can be obtained modifying the relative weight of the two species. We begin noticing that, while the experimental absorption bands at 1738 cm^{-1} and 1760 cm^{-1} (Fig. 3d) have similar in intensity, it is not so for the related theoretical absorption bands at 1748 cm^{-1} and 1776 cm^{-1} (Fig. 3a) for a 1:1 ratio between **1** and **2**. Since the latter has higher intensity, it is clear that the relative concentration of **2** should be decreased. Reducing the relative concentrations of **2** while increasing the one of **1** should therefore increase the correlation coefficient between the theoretical and experimental intensities (R^2). At the right relative concentrations, R^2 for the intensities should be at maximum. We found that multiplying the intensities of **1** and **2** respectively by 0.80 and 0.20 (Fig. 3b) R^2 reaches its maximum of 0.99 (Fig. 4c)

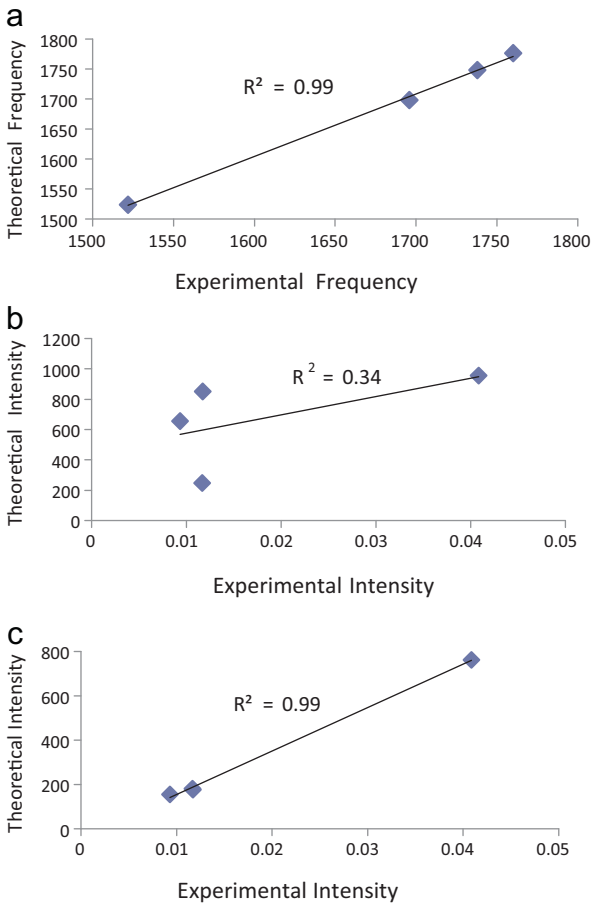

Fig. 4. (a) Correlations of selected experimental and theoretical frequencies for **1** and **2** in MeOH. (b) Correlations of selected experimental and theoretical intensities for **1** and **2** in MeOH. (c) Correlations of selected experimental and theoretical intensities for **1** and **2** in MeOH (relative concentration values of **1** (0.8) and **2** (0.2)).

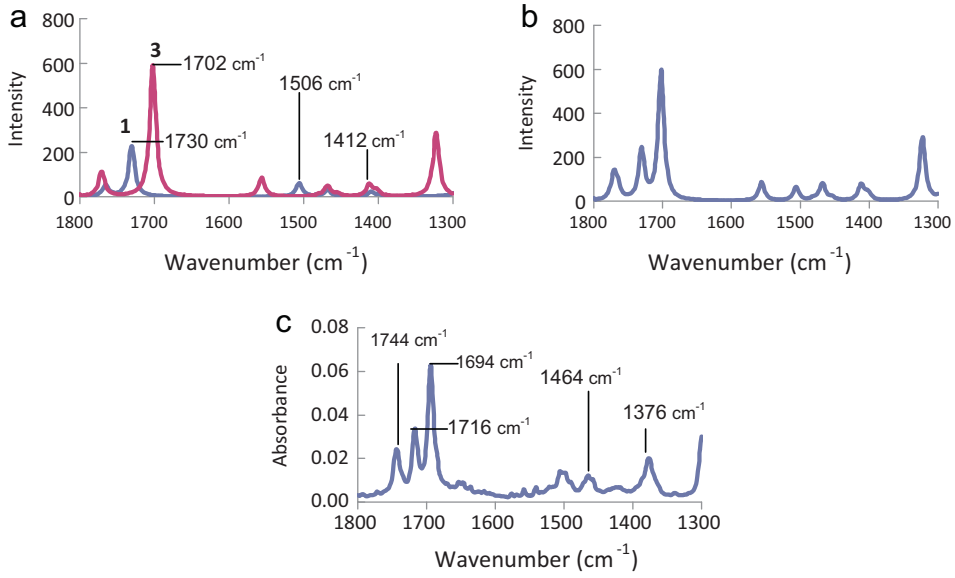

Fig. 5. (a) Multiplied intensities of **1** with 0.32 and **3** with 0.34. (b) Addition of multiplied intensities of **1** and **3**. (c) Experimental FT-IR spectrum of diacetamide in CCl_4.

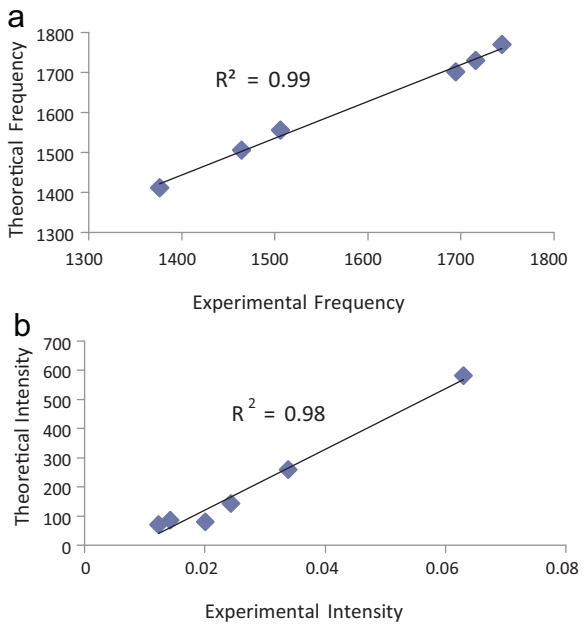

Fig. 6. (a) Correlations of selected experimental and theoretical frequencies for **1** and **3** in CCl_4. (b) Correlations of selected experimental and theoretical intensities for **1** and **3** in CCl_4 relative concentration values of **1** (0.32) and **3** (0.34).

with a nearly perfect match between synthetic and experimental spectra.

3.2. The equilibrium in CCl_4

The absence of the peculiar symmetric C=O stretching band of **2** at 1750 cm^{-1}–1800 cm^{-1} (Fig. 5) and low energy difference between **1** and **3** (2.7 kcal/mol in Table 1) allows us to assume that the equilibrium in CCl_4 includes only **1** and **3**. In this respect, the low polarity and aprotic nature of CCl_4 make advantageous for diacetamide to form intermolecular H-bonds and to dimerize. As a result of this, the diacetamide dimer **3** attains its highest concentration in CCl_4 with respect to other solvents as shown by the experimental spectra. The same procedure applied in the methanol case was followed to obtain the relative concentrations of diacetamide dimer (**3**) and monomer (**1**) in CCl_4, the latter being found 34% and 32% in 0.0100 mol/L solutions respectively. However, the concentration of the solution affects the relative dimer ratios, dilution of the solution to 0.0050 and 0.0025 mol/L causes decrease in relative ratios of the dimeric structure to 27% and 20%. Notice that relative concentrations must take into account that dimer contains two monomer molecules. This result supports the presence of dimeric structure in CCl_4 because in a non-polar solvent diacetamide prefers to interact with itself [27] which is the only chance to form hydrogen bonds.

The linear relationship between selected experimental and theoretical frequencies for diacetamide in its **1** and **3** forms are shown in Fig. 6a. After scaling the intensities, good agreement between spectra is found (Fig. 6b).

As seen from Table 2, the concentrations of monomer trans–trans (**2**) were changed according to the solvent properties. The high polarity of DMSO (7.2) and the protic hydrogen effect of MeOH should be responsible for the high concentration of monomer trans–trans (**2**) in related solvents. Although the polarity of methanol (5.1) is relatively lower than DMSO, the protic hydrogen effect prevails and the concentration of **2** is obtained as 20% in MeOH. The polarity of CH_3CN (5.8) is not as high as DMSO and quite similar to the MeOH. Since it does not have any protic hydrogen the concentration of **2** is obtained as 1%.

4. Conclusions

The presence and relative concentrations of possible diacetamide tautomers, dimer and rotamers were investigated in 7 organic solvents using both IR experiments and theoretical methods. Equilibria were fully characterized in a semi-quantitative manner using a spectra- matching method. For the latter task, theoretical IR spectra were obtained at the DFT B3LYP/6-311++ G(2d, 2p) level; the good part of doing this is that the latter results provided the molar absorption coefficients for the different species investigated. As it should perhaps be expected, it is found that diacetamide prefers to form hydrogen bonds with polar protic solvents like methanol and prefers cis–trans or trans–trans conformations.

In non-polar solvents, diacetamide tends to dimerize by intermolecular hydrogen bonding and giving rise to a dimer (**3**) – monomer (**1**) equilibrium. We consider the improved stability of the dimer with respect to the monomer in CCl_4 as due to two hydrogen bonds and additionally two $n-\pi^*$ transition from the nitrogen atoms to the carbonyls. The planar geometry of –CONCO–, shorter C–N and longer C=O bond distances are evidences for the $n-\pi^*$ transition. With respect to the possible tautomerization, the transition and the hydrogen bonds seem to be an acceptable explanation for the preferential formation of dimer (**3**) instead of a tautomer (**4**, **5**) since they reduce the potential energy of the system despite the fact that an intramolecular hydrogen bond and conjugate double bonds may represent an advantage for a tautomeric (**4**) structure (Fig. 1).

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