

Discrimination between O-H...N and O-H...O=C Complexes of 3-Methyl-4-pyrimidone and Methanol. A Matrix-isolation FT-IR and Theoretical DFT/B3LYP Investigation

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ABSTRACT

FT-IR matrix-isolated spectra for 3-methyl-4-pyrimidone and its H-bonded complexes with methanol in Ar were studied with the aim of discriminating between O-H...N and O-H...O=C complexes. Theoretical calculations were carried out using the DFT/B3LYP/6-31+G(d) methodology in an attempt to predict the preferred interaction site of the 3-methyl-4-pyrimidone molecule with proton donors. The observed frequency decrease of the $\nu(\text{C}=\text{O})$ mode of 3-methyl-4-pyrimidone and the appearance of a broad $\nu(\text{OH}\dots\text{O})$ band in the spectrum of the complex with methanol suggest that H-bonding with methanol occurs at the carbonyl group. Computed binding energies of the hydrogen-bonded complexes (ΔE_b) and computed intermolecular distances ($r(\text{O}\dots\text{H})$) confirm that the O-H...O=C complex is preferred with methanol. However, for H-bonding with stronger acids such as HCl, the computational data suggest that the H-bonding occurs at the N₁ ring atom of 3-methyl-4-pyrimidone.

KEYWORDS

Matrix-isolation, 3-methyl-4-pyrimidone, methanol, FT-IR spectroscopy, DFT/B3LYP calculations.

1. Introduction

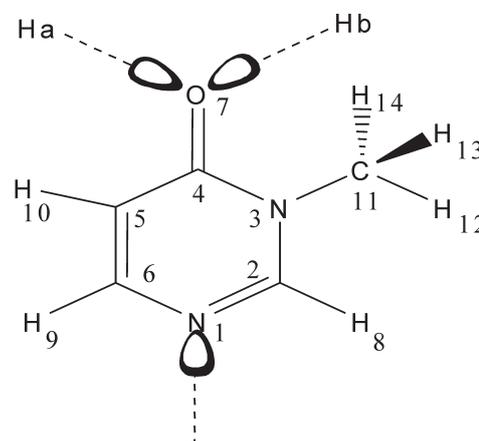
Much attention has been devoted to the properties of H-bonds of nucleic acid bases because of their involvement in the processes of reproduction and transmission of genetic information in nature. The nucleic acid bases are heterocyclic polyfunctional bases carrying carbonyl groups and nitrogen atoms as possible H-bond interaction sites. The stability of the H-bonding involving these carbonyl or nitrogen sites may be examined in a pyrimidine base such as 3-methyl-4-pyrimidone (3M4P, Scheme 1), in which one of the nitrogen sites is methylated, thus reducing the possibilities of interaction.

In one of our previous papers on the electron donating properties of 3M4P using IR spectrometry in solution as well as in the solid state, it has been demonstrated that phenol derivatives with pK_a values ranging from 4.3 to 10.3 form normal O-H...O=C bonds with 3M4P, while stronger acids ($\text{pK}_a = 0.4$ to -6.0) give rise to protonation occurring at the N₁ atom of the base molecular ring.¹⁻³ Additionally we have demonstrated that phenols with pK_a values around 3.5 have no preferred site of interaction and either O-H...O=C and O⁻...⁺HN bonds are formed in solution. These data suggest that in 3M4P the H-bonding site is not the preferred site for protonation but that the preferred site of interaction with a proton donor depends on its acidity in the solvent.

Therefore, since the acidity of a proton donor depends on the medium, it is interesting to check the selectivity of both interaction sites of 3M4P in inert medium such as a noble gas matrix. A combination of IR spectroscopy with theoretical calculations providing predictions for different interaction types, their physicochemical properties, their geometry and their stability is the most suitable approach.

As far as we know, theoretical and IR matrix-isolated investigations on 3M4P or its complexes have never been reported. Matrix-isolation FT-IR spectroscopy is without any doubt one of the most suitable experimental methods to study this problem. As a matter of fact, frequency shifts of H-bond sensitive modes such as $\nu(\text{C}=\text{O})$, $\delta(\text{C}=\text{O})$, $\gamma(\text{C}=\text{O})$ and $\nu(\text{N}_1=\text{C}_2)$ in a 3M4P-CH₃OH complex spectrum as well as the appearance of one of the broad bands, characteristic for either $\nu(\text{OH}\dots\text{O})$, $\nu(\text{OH}\dots\text{N})$, $\nu(\text{NH}^+\dots\text{O}^-)$ or $\nu(\text{OH}^+\dots\text{O}^-)$, are good arguments for a discrimination between O-H...N and O-H...O=C H-bonded complexes.

The comparison of computed H-bond interaction energies (ΔE_b) and internuclear as well as intermolecular distances for both O-H...N and O-H...O=C optimized complexes allows to predict the most stable interactions. The use of methanol as a proton donor simplifies the spectral analysis and allows for the



Scheme 1. 3-Methyl-4-pyrimidone.

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investigation of the influence of H-bond cooperativity on the stability and the geometry of the complexes.^{4–5}

In the first section of this paper, we present the results of DFT/B3LYP/6-31+G(d) theoretical calculations for 3M4P as well as its FT-IR spectrum in an argon matrix. We also compare these predicted results with available experimental data of similar molecules.^{6–9} In the following sections, we present the spectrum of methanol and its complex with 3M4P in an attempt to identify the H-bond site in the base. Since the IR spectrum of methanol is well known in the literature,^{10–17} we will restrict in this study to the H-bond sensitive vibrations of the OH and CO group in this proton-donor molecule. In the last section we compare the present predicted results for complexes between 3M4P and different proton donors such as methanol and HCl.

2. Methods

2.1 Experimental Method

The experimental equipment used for preparing the matrix sample has been described in detail in earlier papers.^{18–19} Briefly, the 3M4P compound was evaporated from a recently developed miniature oven mounted in the cryostat. The optimal sublimation temperature was found to be 304 K. The vapour of products was mixed with a large excess of argon gas. The low temperature matrix was prepared by depositing this gaseous mixture onto the cold CsI window kept at 16 K. This optimal temperature was high enough to yield matrices with a sufficient concentration of the isolated product(s), but still sufficiently low to prevent product decomposition. The IR spectra of these matrices were obtained by accumulating 32 interferograms with a Bruker IFS-66 Fourier-transform instrument and Fourier-transforming them in the range 4000–500 cm⁻¹ at a resolution of 2 cm⁻¹. The frequencies in Hz could be obtained by a multiplicative factor of 3.10¹⁰ of wavenumbers (in units of cm⁻¹).

3M4P was prepared by methylation of the (H₃)-4-pyrimidone precursor using the method described by Curd and Richardson for amino-halogeno-oxopyrimidine methylated derivatives.²⁰ (H₃)-4-pyrimidone was dissolved with NaH in ethanol and methyl iodide was added afterward. The reaction mixture was magnetically stirred for 14 hours at 70 °C. After completion of the reaction, which was monitored by thin-layer chromatography (TLC), the ethanolic solution was washed with water and a small amount of NaHCO₃ was added to neutralize the excess amount of the base. The ethanolic solution was dried with MgSO₄ and the solvent was evaporated by a rotavap under 40 °C and 750 mbar. The 3M4P solid obtained was purified by column chromatography with dichloromethane-methanol 95/5. The purity of the methylated compound as checked with mass, ¹H-NMR and ¹³C-NMR spectrometry appeared to be better than 99 %.

Most of the products used were purchased from Janssen Chimica. Their purities are 98 % ((H₃)-4-pyrimidone), 98 % (CH₃I), 98 % (MgSO₄) and 98 % (ethanol). The other compounds were obtained from different companies, i.e. NaH (UCAR, 98 %), NaHCO₃ (UCAR, 98 %), methanol (Chem-LabNV, 99 %+) and dichloromethane (Aldrich, 99 %+). The argon gas with purity of 99.9999 % was provided by Air Liquide.

2.2. Theoretical Method

Molecular properties such as geometries, energies and vibrational frequencies of the different monomers and H-bonded complexes were calculated by the Density Functional Theory (DFT) using the hybrid of Becke's non-local three-parameter exchange and correlation functional with the Lee-Yang-Parr

functional (B3LYP).^{21–23} DFT methods provide an adequate compromise between the desired chemical accuracy and the computational cost. DFT/B3LYP methods have been demonstrated in former studies to produce quite accurate results for isolated molecules modeling heterocyclic bases.^{24–30} Although it is well established that H-bonding involving acid nucleic bases is not fully correctly described by DFT methods, these methods remain useful. The reason is that interactions due to H-bonding are principally electrostatic and they are reasonably well accounted for by DFT or MP2 methods.³¹

In H-bond studies, the standard 6-31+G(d), 6-31++G(d), 6-31++G(d,p) and 6-311++G(d,p) basis sets have frequently been used.^{32–35} For the molecular orbital expansion we have initially used the 6-31++G(d,p) basis set in this work. The choice of this basis set was based on the consideration that in order to obtain reliable properties for hydrogen-bonded systems, it is essential to employ basis sets of orbitals which possesses sufficient diffuseness and angular flexibility.³⁶ Since it appeared for methanol and its homo-associates that the calculated values of the electronic energies and vibrational frequencies with the basis set 6-31+G(d) were similar to those with the larger basis set 6-31++G(d,p), we have only used the former set in the further study.

Since it has been demonstrated by one of us that for larger molecules such as nucleic acid base derivatives, selective frequency scaling allows a reliable assignment of vibrational modes,³⁷ the harmonic DFT frequencies were scaled with variable scaling factors, i.e. 0.95 for $\nu(\text{X-H})$, 0.98 for out-of-plane modes and 0.975 for all other modes. The use of different scaling factors for DFT predicted frequencies has been proposed by several authors in the past.^{37–40} The IR frequencies, intensities, and the zero-point vibrational energy (ZPE) were subsequently computed using the analytical derivatives procedure incorporated in the Gaussian 03 program.

Following these calculations, the total energies E_T of the optimized structures were calculated as the sum of the electronic energy $E_{(\text{DFT})}$ and 0.975 ZPE (ZPE determined with the DFT methodology). The H-bond interaction energy of each complex was computed as the difference between the energy of the complex (cluster) and the sum of the energies of the monomer 3M4P and the proton donor. These results were corrected for the basis set superposition error (BSSE),⁴¹ by recalculating the monomer energies in the basis set of the hetero-dimers using the Boys-Bernardi counterpoise correction.⁴² The corrected H-bond interaction energy of each complex (ΔE_c) was finally computed as

$$\Delta E_c = [E_{(\text{cluster})} + (0.975 \text{ ZPE}_{(\text{cluster})})] - \sum_i [E_{i(\text{monomer})} + (0.975 \text{ ZPE}_{i(\text{monomer})})] \quad (1)$$

All calculations were performed using the Gaussian 03 *ab initio* software package.⁴³

The H-bond cooperativity effect in the (methanol)₃, the (methanol)₄ and the 3M4P-(methanol)_n complexes was quantitatively measured by the ratio A_b between the relative frequency shift of the bridged OH in these complex structures, $\nu_{\text{O-H}, \dots}$, and the shift in the homodimer or heterodimer, $\nu_{\text{O-H}, \dots}$, as earlier defined by one of us:⁴⁴

$$A_b = \frac{(\nu_{\text{O-H}} - \nu_{\text{O-H}, \dots})}{(\nu_{\text{O-H}} - \nu_{\text{O-H}, \dots})} \quad (2)$$

The cooperative factor (A_b) defined in this way is always larger than 1.

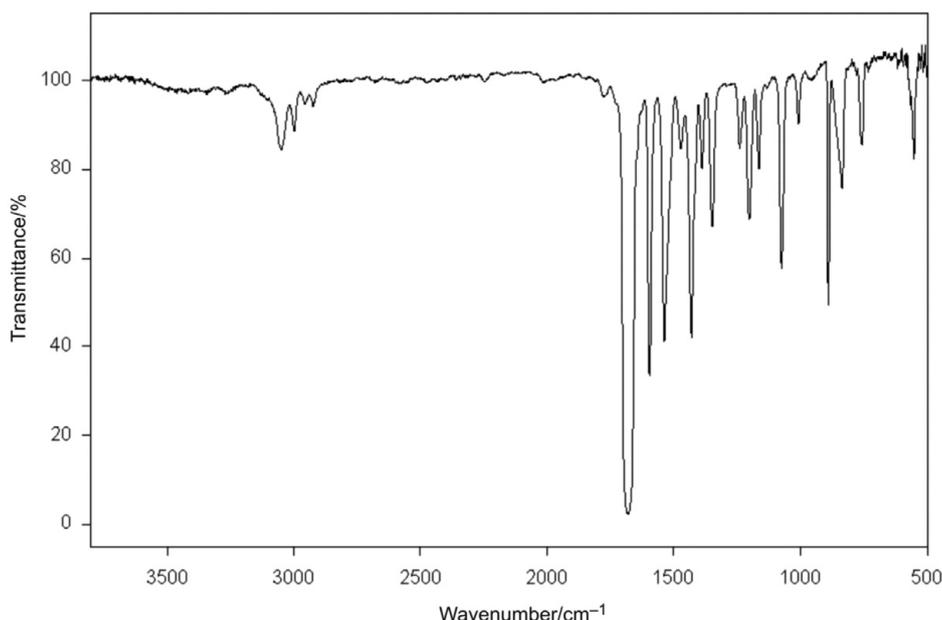


Figure 1 FT-IR spectrum of 3-methyl-4-pyrimidone in Ar at 16 K

3. Results and Discussion

We first discuss the FT-IR spectra of 3M4P and methanol isolated in Ar separately in order to assign these vibrational modes which are expected to be sensitive to H-bond interactions. In the next step, these data serve as a reference frame for spectral perturbation caused by H-bonding between both molecules. Analysis of the bonded O-H... vibrational modes of methanol at larger concentration will also allow us to evaluate the H-bond cooperativity in the dimer, trimer and tetramer, respectively.⁴⁴

In some of the spectra weak bands between 3750 and 3550 cm^{-1} as well as around 2350 cm^{-1} are present, which are due to absorption of water and CO_2 , respectively.⁴⁵ However, the impurities concentration is very small because no band reflecting the formation of a complex of water or CO_2 with 3M4P or methanol is observed near the respective monomer frequencies. This implies that these impurities do not perturb the spectral analysis.

3.1. FT-IR Spectrum of 3M4P

Although matrix spectral data for 3M4P have not yet been published in the literature, the IR spectrum of this compound has been obtained earlier in KBr dispersion and in dichloroethane solution.^{1–3} In addition, the FT-IR spectra of similar molecules such as 4-pyrimidone, 1-methyl-2-pyrimidone and 1-methyl-uracil isolated in argon matrix have been reported.^{6–9}

The 3M4P molecule belongs to the C_s symmetry group and has 36 predicted active vibrational modes. However its IR spectrum can be complicated by additional bands due to frequency combinations or Fermi resonance, which has been reported for similar molecules.⁴⁶

Figure 1 shows the overall spectrum while Figs 2a, 2b and 2c show the different spectral ranges (3400–2600 cm^{-1} , 1900–1000 cm^{-1} and 1000–400 cm^{-1}) for 3M4P isolated in Ar at 16 K. In order to perform the assignments of the observed bands, DFT/B3LYP/6-31+G(d) calculations have been performed to obtain the predicted values of the frequencies and their intensities. The available literature data for similar molecules were also exploited for the assignment. The experimental and theoretical frequencies and intensities of 3M4P compared with available literature frequencies for similar molecules are summarized in Table 1.

In the high frequency region (3600–3000 cm^{-1}), weak bands are observed which can be attributed to $\nu(\text{C-H})$ stretching vibrations following the sequence $\nu(\text{C}_5\text{H}) > \nu(\text{C}_6\text{H}) > \nu(\text{C}_2\text{H})$. The weak bands found between 3000 and 2910 cm^{-1} can be attributed to $\nu(\text{CH}_3)$. An intense absorption band with a splitting at 1705/1691 cm^{-1} is, without doubt, ascribable to the stretching mode $\nu(\text{C=O})$ of the carbonyl group. This mode is known to be very sensitive to H-bonding. The splitting can be due to Fermi resonance between the $\nu(\text{C=O})$ mode and a combination involving the $\delta(\text{C=O})$ and $\delta(\text{C-H})$ modes as has been demonstrated in the solid state.^{1–3} The $\nu(\text{C=O})$ band of 1-methyl-2-pyrimidone also showed a splitting at 1712/1704 cm^{-1} attributed to Fermi resonance.^{7,8} The $\nu(\text{C=O})$ frequency of 3M4P is lower than that of 4-pyrimidone at 1725 cm^{-1} , 2-pyridone at 1728 cm^{-1} and 1-methyl-2-pyrimidone at 1712/1704 cm^{-1} .^{6–8} This suggests that the electronic density of the 3M4P carbonyl group is the highest among these similar molecules.

The in-plane bending vibrations $\delta(\text{C-H})$ are located near 1420 cm^{-1} , between 1345–1320 cm^{-1} and at 1162–1150 cm^{-1} . The bands at 1601, 1541, 1387, 1234, 764 and 756 cm^{-1} are assigned to ring stretching modes. The corresponding in-plane bending modes δ_r are found at 937, 619 and 548 cm^{-1} . It may be mentioned that the absorption band at 1601 cm^{-1} ascribed to $\nu(\text{C}_5=\text{C}_6)$ is intense, probably because of the electronic delocalization between the $\text{C}_5=\text{C}_6$ and C=O double bonds. The $\delta(\text{CH}_3)$ mode is situated between 1476 and 1410 cm^{-1} , whereas the rocking modes $\rho(\text{CH}_3)$ are observed between 1120 and 1050 cm^{-1} . The $\nu(\text{N}_1=\text{C}_2)$ mode absorbs at 1197 cm^{-1} . Some authors assign bands located at 1541 and 1387 cm^{-1} also with an important vibrational contribution of the $\nu(\text{N}_1=\text{C})$ mode.^{7, 47–49} Therefore, all three bands observed at 1541, 1387 and 1197 cm^{-1} are useful for evaluation of H-bonding at the N_1 ring atom of 3M4P.

The in-plane bending mode of the carbonyl group $\delta(\text{C=O})$ is found at 568 cm^{-1} . As far as out-of-plane modes are concerned, the $\gamma(\text{C-H})$ vibrations are close to 1004 cm^{-1} , 980 cm^{-1} and 838 cm^{-1} following the sequence $(\text{C}_2\text{H}) > (\text{C}_6\text{H}) > (\text{C}_5\text{H})$, respectively. The out-of-plane mode of the carbonyl group $\gamma(\text{C=O})$ is found at 888 cm^{-1} .

Special care was taken for a correct assignment of the modes $\nu(\text{C=O})$, $\delta(\text{C=O})$, $\gamma(\text{C=O})$ and $\nu(\text{N}_1=\text{C}_2)$ modes of 3M4P, because these are sensitive to H-bonding allowing to discriminate

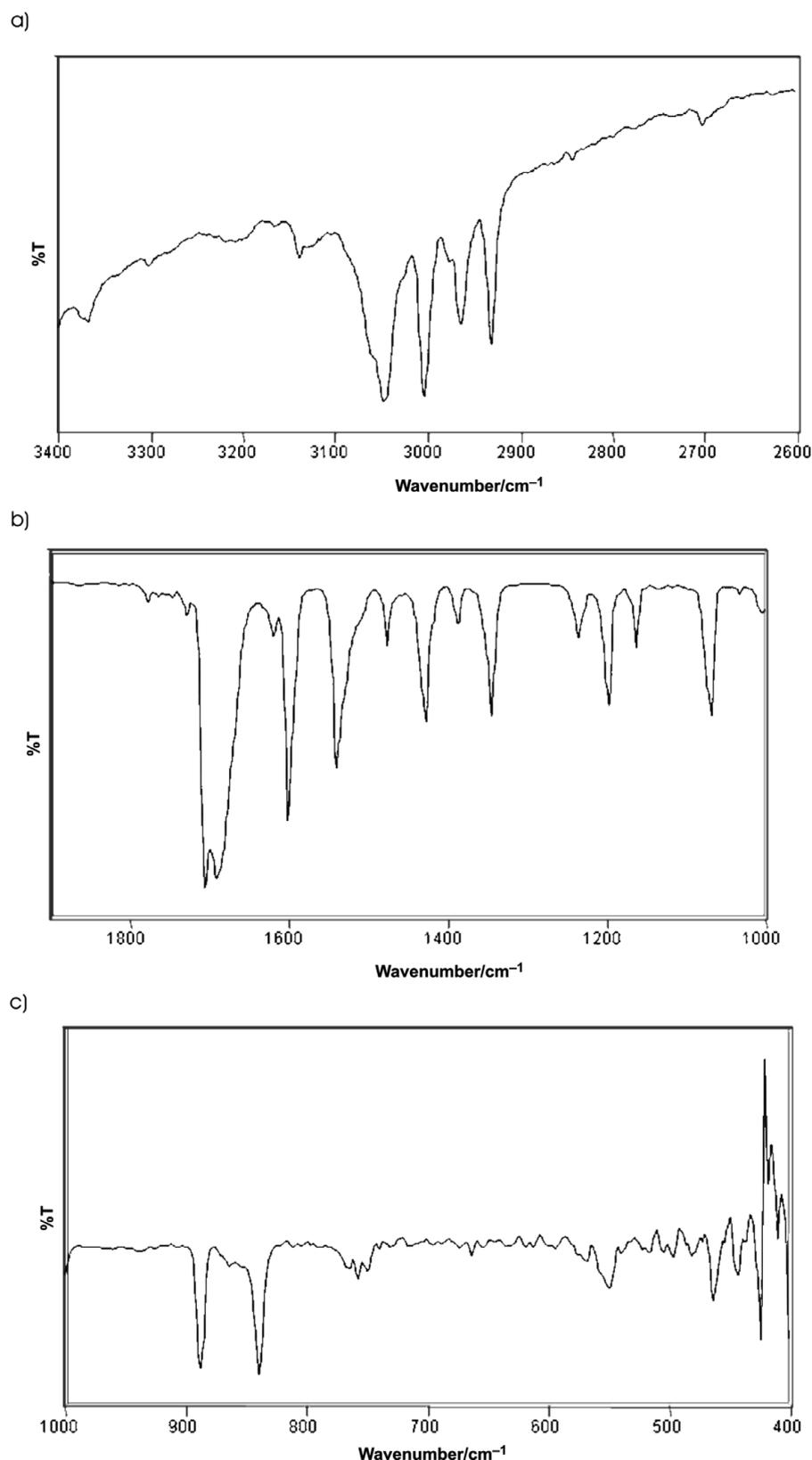


Figure 2 Different spectral ranges of the FT-IR spectrum of 3-methyl-4-pyrimidone in Ar at 16 K: (a) 3400–2600 cm⁻¹; (b) 1900–1000 cm⁻¹; (c) 1000–400 cm⁻¹.

between O-H...N and O-H...O=C complexes of 3M4P and methanol. A good mean precision of 10.9 cm⁻¹ is obtained by comparing the values of experimental and predicted frequencies, which confirms the reliability of the theoretical methodology used.

3.2. FT-IR Spectrum of Methanol

The FT-IR spectrum of methanol at low concentration isolated in Ar at 16 K is illustrated in Fig. 3 and the assignments for the OH and CO modes are summarized in Table 2. These assignments were performed in comparison with B3LYP/6-31+G(d) calcula-

Table 1 Vibrational analysis of 3-methyl-4-pyrimidone.

Experimental frequencies	Corrected calculated frequencies ^a /cm ⁻¹	Experimental Intensities ^b /km mol ⁻¹	Calculated intensities /km mol ⁻¹	4-Pyrimidone frequencies ^[7] /cm ⁻¹	1-Methyl-2-pyrimidone ^[6-8] /cm ⁻¹	1-Methyluracil frequencies ^[6-7] /cm ⁻¹	Assignment
3062	3063	shoulder ^c	13	3053	very weak	3090	$\nu(\text{C}_5\text{-H})$
3047	3030	11	16	3047	3020	3024	$\nu(\text{C}_6\text{-H}) + \nu(\text{C}_2\text{-H})$
3026	3023	shoulder ^c	4	3031	–	–	$\nu(\text{C}_2\text{-H}) + \nu(\text{C}_6\text{-H})$
3003	3007	5	4	–	2983	2956	$\nu^{\text{as}}(\text{CH}_3)$
2965	2990	4	6	–	2962	2945	$\nu^{\text{as}}(\text{CH}_3)$
2931	2917	4	21	–	2883	2822	$\nu^{\text{s}}(\text{CH}_3)$
1705/1691	1712	457	583	1725/1713/1680	1712/1704	1721	$\nu(\text{C}=\text{O})$
1601	1603	71	71 ^d	1601	1636	1650	$\nu(\text{C}_5=\text{C}_6) + \nu(\text{N}_1\text{C}_2)$
1541	1533	87	144	1545/1541	1530	1482	$\nu_{\text{R}} + \nu(\text{N}_1\text{C}_2)$
1476	1478	8	8	–	1479	1461	$\delta^{\text{as}}(\text{CH}_3)$
1427	1438	10	42	–	1435	1446	$\delta^{\text{as}}(\text{CH}_3)$
	1430	20		–	1414	1433	$\delta^{\text{s}}(\text{CH}_3)$
1419	1415	shoulder ^c	4	1414	^s	1420	$\delta(\text{C}_2\text{H})$
1387	1385	7	3	1366	1386	1386	$\nu_{\text{R}} + \gamma(\text{N}_1\text{C}_2)$
1345	1339	35	42	1314/1312	1365: $\delta(\text{C}_4\text{H})$	1320	$\delta(\text{C}_6\text{H}) + \nu(\text{N}_3\text{C}_4) + \nu(\text{N}_3\text{C}_5)$
1234	1210	12	5	1226	1239	1224	$\nu_{\text{R}} + \nu(\text{N}_1\text{C}_6)$
1197	1191	27	53	–	1200: $\nu(\text{N}_1\text{C})$	1188: $\nu(\text{N}_1\text{C})$	$\nu(\text{N}_3\text{C})$
1162	1151	9	5	1160	1165	1150	$\delta(\text{C}_5\text{H}) + \nu(\text{C}_4\text{C}_5)$
Very weak	1120	very weak	0	–	1106	1126	$\rho(\text{CH}_3)$
1067	1059	39	36	1025	1051	1028	$\rho(\text{CH}_3)$
1004	1001	7	7	very weak	991		$\gamma(\text{C}_2\text{H})$
980	981	1	<1	980	952	990	$\gamma(\text{C}_6\text{H})$
937	925	1	1	972	928	963	δ_{R}
888	870	20	16	–	793	790	$\gamma(\text{C}=\text{O})$
838	831	29	38	839	762	760	$\gamma(\text{C}_5\text{H})$
764	744	11	5	–	756	746	ν_{R}
756	742	11	9	754	649	710	ν_{R}
619	609	1	0	651	569	619	δ_{R}
568	553	3	3	–	552	548	$\delta(\text{C}=\text{O})$
548	541	9	13	–	508	514	δ_{R}
463	451	7	7	454	461	461	τ_{R}
^f	372	^f	2	–	^s	352	$\delta(\text{N}_3\text{C})$
^f	321	^f	5	–	^s	269	$\gamma(\text{N}_3\text{C})$
^f	223	^f	<1	390	^s	190	τ_{R}
^f	141	^f	10	149	^s	108	τ_{R}
^f	127	^f	<1	–	^s	75	$\tau(\text{CH}_3)$

^a Calculated frequencies are corrected in order to fit with experimental frequencies by scaling with variable scaling factors, i.e. 0.95 for $\nu(\text{X-H})$, 0.98 for out-of-plane modes and τ and 0.975 for all other modes.

^b Experimental intensities were adjusted to calculated intensities using 71 km mol⁻¹ for the $\nu(\text{C}_5=\text{C}_6)$ mode at 1601 cm⁻¹.

^c Shoulder for which the intensity cannot be estimated by integration of the band area.

^d This band has been used for the adjustment of intensities.

^e Only main contributions are listed.

^f Bands situated below the accessible region.

^g Frequencies not assigned in reference [35].

tions and with several literature reports for methanol vibrational spectra in the gas phase and the solid state.¹⁰⁻¹⁷

In the high frequency region of the FT-IR spectrum of methanol at low concentration, three bands due to the rotation-vibration structure (RQP) of the ν_{OH} mode are observed at 3724 cm⁻¹ (R-branch), at 3653 cm⁻¹ (P-branch) and at 3687 cm⁻¹ (Q-branch). The R-branch of the monomer is accompanied by some additional bands at 3758 and 3712 cm⁻¹ and the P-branch with an additional band at 3627 cm⁻¹. At lower frequencies, the bands at 3504, 3333 and 3228 cm⁻¹ are ascribable to the dimer, the cyclic trimer and the cyclic tetramer respectively (see further). In the $\nu(\text{C-O})$ region, three bands at 1077, 1046 and 1031 cm⁻¹ are assigned to the rotation-vibration structure (RQP), the Q branch being observed as the strongest band. Bulgarevich et al have found the R-branch as the strongest absorption in this region for supercritical methanol at 523 K and 1.3 MPa.¹² The absorption band at 1341 cm⁻¹ is assigned to the in-plane bending mode

$\delta(\text{OH})$. Finally, the weak bands found between 760 and 500 cm⁻¹ can be tentatively ascribed to the $\gamma(\text{OH})$ mode of the dimer, trimer or tetramer, respectively. The monomer $\gamma(\text{OH})$ mode is most probably situated below 400 cm⁻¹, since the predicted value is 318 cm⁻¹.

An increase of the methanol concentration in the Ar matrix brings about spectral modifications, mainly in the OH and C-O absorption regions, causing the rotation-vibration structure RQP to disappear. A slight, progressive increase of the methanol concentration splits the monomer band located at 3687 cm⁻¹ into two bands, one at 3701 and the other at 3665 cm⁻¹ (spectrum Fig. 4, b), which convert into a single band at 3790 cm⁻¹ at very high methanol concentration (spectrum Fig. 4, c). The weak bands due to the methanol H-bonding observed in the monomer spectrum ascribed to the bonded OH stretching mode are regrouped in only one large band including two shoulders, roughly at 3487 and 3223 cm⁻¹, with a maximum near 3287 cm⁻¹

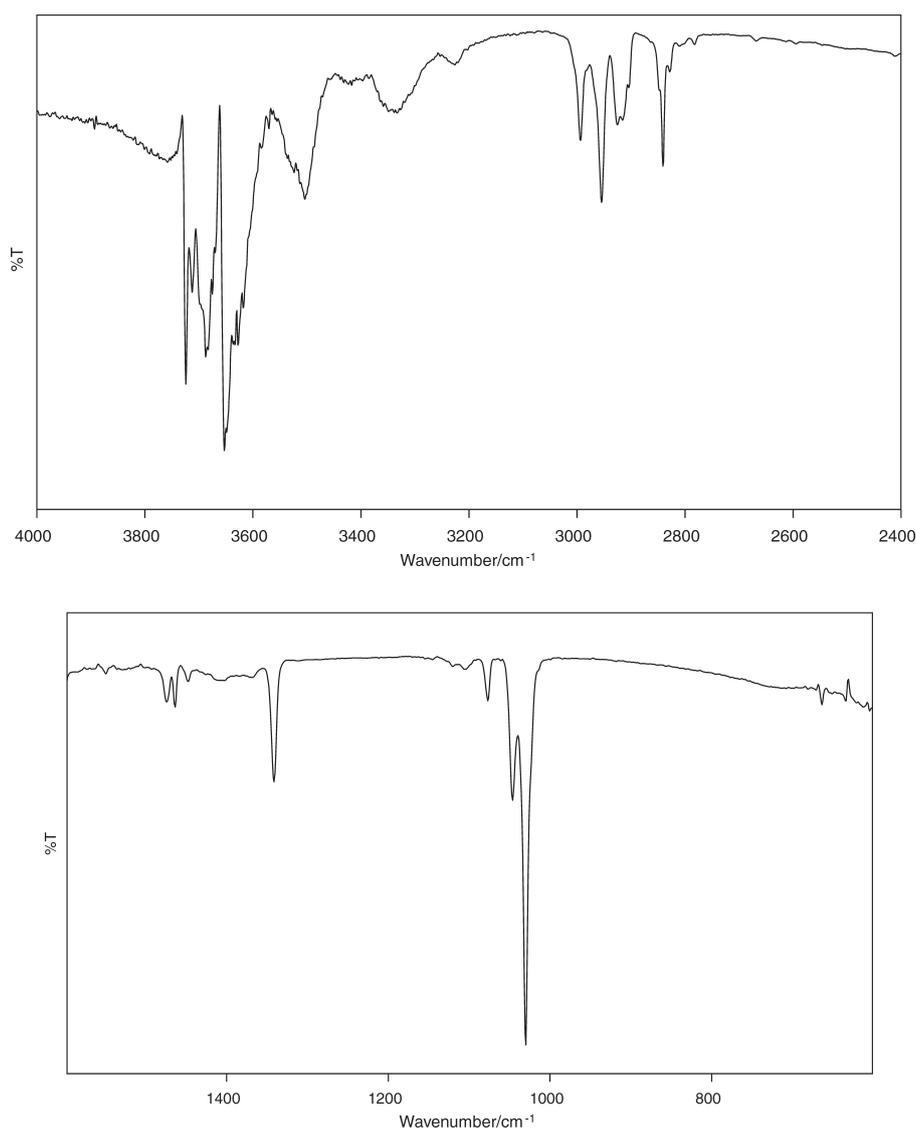


Figure 3 Ar-matrix FT-IR spectrum of monomer methanol at 16 K

Table 2 IR spectral analysis of methanol isolated in Ar at 16 K

Species	Experimental frequencies/cm ⁻¹	Calculated frequencies		Relative intensities	Assignment
		Not corrected/cm ⁻¹	Corrected/cm ⁻¹		
Monomer	3758/3724/3712				ν OH(R)
	3687	3765	3690	23.70	ν OH(Q)
	3653/3627				ν OH(P)
	1341	1370	1343	22.87	δ OH
	1077	1077	1077	0.20	δ C-O
	1046	1052	1031		ν C-O(R)
	1031			134.27	ν C-O(Q)
	1003 (shoulder)				ν C-O(P)
^a		324	318		γ OH _(monomer)
^a				145.62	γ C-O
Homo-associates	3504	3613		b	ν OH _(dimer)
	3333	3402/3485		b	ν OH _(trimer)
	3228	3246/3394		b	ν OH _(tetramer)
	753/667			b	γ OH _(tetramer)
	727/630			b	γ OH _(trimer)
	610/510			b	γ OH _(dimer)

^a Bands below the accessible region (<400 cm⁻¹).

^b Not separately measurable because of overlapping, broad structure.

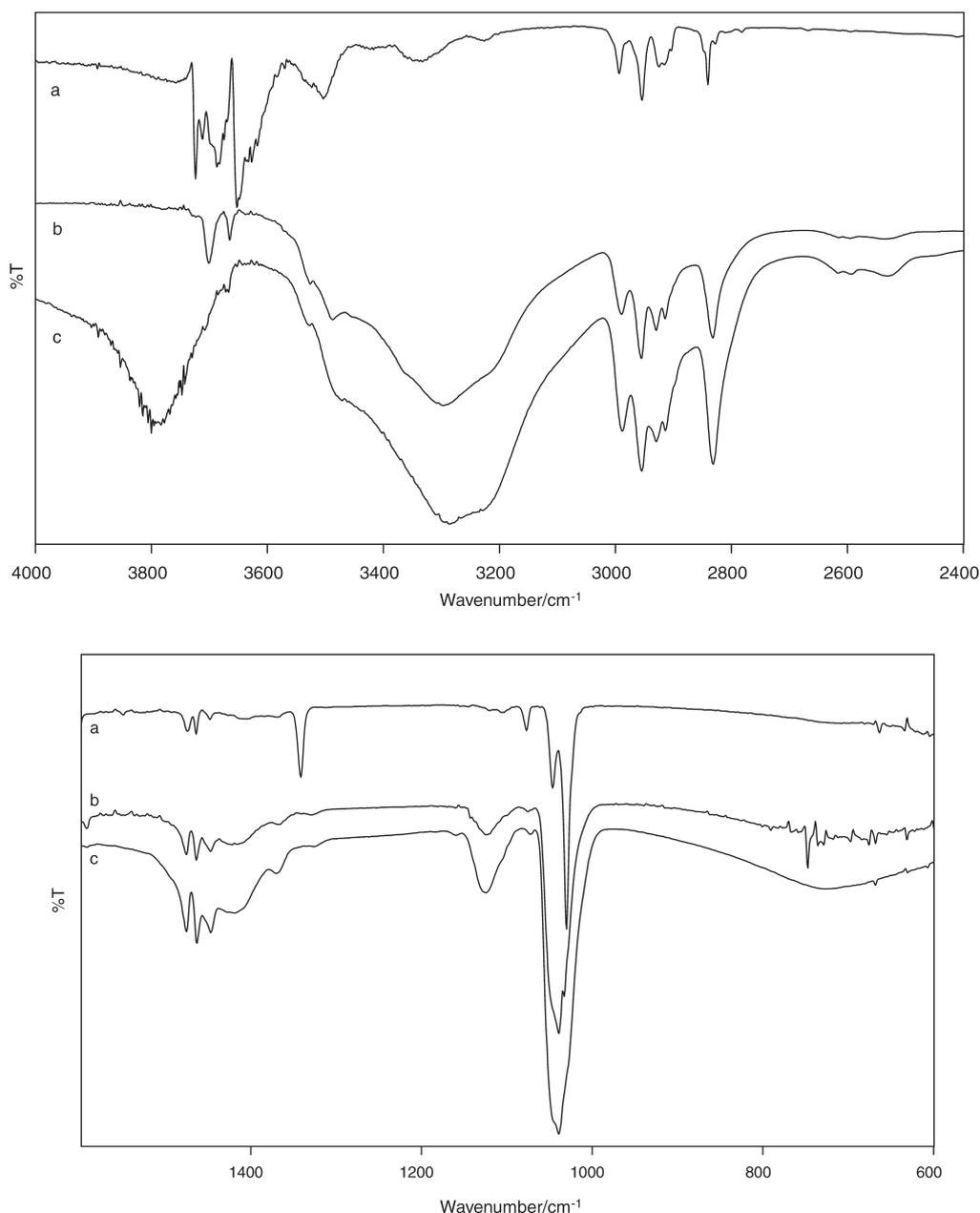


Figure 4 FT-IR spectra of methanol in Ar-matrices at 16 K: monomer (a); homo-associates at low concentrations (b) homo-associates at high concentrations (c).

(Fig. 4, c). Comparison with the predicted frequencies for monomer and homo-associated methanol (Table 2) allows to assign $\nu_{\text{O-H}\dots}$ (dimer) at 3504 cm^{-1} , $\nu_{\text{O-H}\dots}$ (cyclic trimer) at 3333 cm^{-1} and $\nu_{\text{O-H}\dots}$ (cyclic tetramer) at 3228 cm^{-1} .

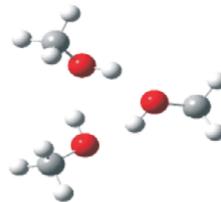
The $\nu(\text{C-O})$ band also loses its rotation-vibration RQP structure and only one band is present at 1038 cm^{-1} . At these higher concentrations it is also interesting to note the appearance of a set of bands at 753 and 667 cm^{-1} , confirming the presence of tetramers, at 727 and 630 cm^{-1} indicating trimers, and at 610 cm^{-1} reflecting the formation of dimers. These bands, which can be ascribed to librational modes of cyclic entities of methanol, have also been observed by Larsen and Suhm.¹³ The self-association capability of methanol can extend as far as nine entities, as has been demonstrated by Buck and Huisken.¹⁶

Using the $\nu_{\text{O-H}}$ frequencies of monomer methanol at 3687 cm^{-1} , the dimer at 3504 cm^{-1} , the trimer at 3333 cm^{-1} and the tetramer at 3228 cm^{-1} the strength of the H-bonds in these homo-associates can be evaluated through the cooperativity factors as follows:⁴⁴

$$(A_b)_{\text{tr}} = \frac{\nu_{\text{OH}}^{\text{M}} - \nu_{\text{OH}}^{\text{T}}}{\nu_{\text{OH}}^{\text{M}} - \nu_{\text{OH}}^{\text{A}}} = \frac{3687 - 3333}{3687 - 3504} = 1.93 \quad (3)$$

$$(A_b)_{\text{te}} = \frac{\nu_{\text{OH}}^{\text{M}} - \nu_{\text{OH}}^{\text{Te}}}{\nu_{\text{OH}}^{\text{M}} - \nu_{\text{OH}}^{\text{D}}} = \frac{3687 - 3228}{3687 - 3504} = 2.51 \quad (4)$$

$$(A_b)_{\text{tr-te}} = \frac{\nu_{\text{OH}}^{\text{M}} - \nu_{\text{OH}}^{\text{Te}}}{\nu_{\text{OH}}^{\text{M}} - \nu_{\text{OH}}^{\text{T}}} = \frac{3687 - 3228}{3687 - 3333} = 1.30 \quad (5)$$



Cyclic trimer



Cyclic tetramer

Table 3 Computed B3LYP/6-31+G(d) energetic and structural parameters of the H-bonded complex of 3-methyl-4-pyrimidone (3MP4) with methanol or with HCl at the C=O or the N₁ interaction site of the base.

	3M4P	MeOH...O=C _{anti}	MeOH...N _{1anti}	ClH...O=C _{anti}	ClH...N _{1anti}
E _T	-378.89186	-494.628644	-494.627324	-839.703010	-839.703168
μ	2.51	3.94	1.16	6.01	3.26
ZPE	0.110180	0.163531	0.163403	0.119304	0.119081
ΔE _c		-25.18	-22.56	-28.20	-29.20
Δ(ΔE _c)		0.00	2.62	1.00	0.00
r(C=O)	1.2287	1.2387	1.2270	1.2419	1.2249
r(C ₅ -C ₆)	1.3648	1.3661	1.3636	1.3671	1.3621
r(C ₄ -C ₅)	1.4457	1.4416	1.4465	1.4384	1.4476
r(N ₃ -C ₂)	1.3617	1.3639	1.3566	1.3637	1.3532
r(N ₃ -CH ₃)	1.4648	1.4659	1.4661	1.4676	1.4669
r(N ₁ -C ₂)	1.3027	1.3015	1.3066	1.3022	1.3059
r(N ₁ -C ₆)	1.3734	1.3726	1.3736	1.3703	1.3742
rN ₃ -C ₄)	1.4253	1.4141	1.4279	1.4102	1.4316
r(O...H)		1.8797	1.9800	1.7319	1.7315
r(O/Cl...O)		2.8326		3.0593	
r(O/Cl...N)			2.9005		3.0791
Δr(C-O)		-0.0056	-0.0047	0.0384	0.0572
Δr(O-H)		0.0186	0.0183		
Δr(Cl-H)				0.0132	-0.0038
Δr(C=O)		0.0100	-0.0017	0.0132	-0.0038
θ(OH...O)		163.46	155.67	176.53	179.91
ν(OH...)		3575	3572		
ν(O-H ⁺ ...) or ν(N-H ⁺ ...)				2410	2149
Δν(OH)		-190	-193		
Δν(ClH)				-511	-772
ν(C=O)	1757	1730	1762	1713	1767
Δν(C=O)		-27	+5	-43	-10

E_T: total energy (au); ZPE: zero-point vibrational energy (au); ΔE_c: H-bond interaction energy (kJ mol⁻¹); Δ(ΔE_c): relative energy (kJ mol⁻¹), μ: dipole moment (Debye); ν: frequency (cm⁻¹) and Δν: frequency shift (cm⁻¹); R or r: distances (Å); θ: angle (degree).

The cooperativity factor (A_b)_{tr}, evaluated by comparison of the bonded ν(O-H...) mode in the dimer and the same H-bond in the cyclic trimer, is an estimate of the fortification of the H-bond O-H...O-H by addition of a second H-bond ...O-H in the trimer, compared to the dimer. The factor (A_b)_{te} reflects the fortification of the H-bond O-H...O in the dimer by formation of two additional OH...O H-bonds in the cyclic tetramer. At last, the factor (A_b)_{tr-te} represents the fortification effect of one additional H-bond O-H...O in the cyclic tetramer compared to the cyclic trimer. These three parameters can be used to evaluate the H-bond strengths in the various clusters of methanol. The ratio for trimer and dimer is 1.93, the ratio for tetramer and dimer is 2.51, and the ratio for tetramer and trimer is 1.30. These cooperativity factors in addition to the observed relative intensities of tetramers in comparison to trimers, dimers and monomers, allow for the confirmation of the larger abundance of the most stable tetramers at the exploited methanol concentrations. This stability of the cyclic tetramer has been demonstrated by Buck and Huisken's energy calculations.¹⁶ They have found a minimal energy of -26.8 kJ mol⁻¹, -67.0 kJ mol⁻¹ and -132 kJ mol⁻¹ for the linear dimer, the cyclic trimer and the cyclic tetramer, respectively. The A_b cooperativity factor of about 1.9 for the methanol trimer is superior to that found for the water trimer (1.73),⁵⁰ which suggests that there is a stronger cooperativity or mutual fortification of the three H-bonds in methanol than in water. It has been shown that the geometry of the complex, especially the

deviation of the H-bond angle from linearity, has an appreciable influence on the cooperativity.⁵¹ Addition of a fourth, extra O-H...O bond to the trimer to form the cyclic tetramer again leads to a fortification of the H-bonds O-H...O, but the effect (2.51 - 1.93 = 0.58) compared to the trimer (1.93 - 1.00 = 0.93) decreases, which can be explained because the fortification is now divided over a larger amount of existing H-bonds. As a matter of fact, the ratio of 0.58/0.93 almost equals the ratio of existing H-bonds in the dimer (2) compared to the trimer (3). Inspection of the (A_b)_{tr-te} value of 1.30 indeed reveals that the addition of one extra H-bond O-H...O brings about a mean fortification of the existing H-bonds of about 0.3.

3.3. The Methanol/3-methyl-4-pyrimidone Complex

3.3.1. Theoretical Predictions

The structural and energetic parameters for the methanol-3M4P H-bonded complex computed at the DFTB3LYP/6-31+G(d) level are summarized in Table 3. We should mention that, in principle, two different configurations of the H-bonded complex at the C=O site are possible, i.e. with the anti and the syn orientation of the ...H-O group with respect to the CH₃ group attached to the N₃ atom of 3M4P. Since it has been demonstrated that the anti orientated complex is more stable than the syn complex and that the differences are extremely small (0.3 kJ mol⁻¹),⁵² only the most stable anti complex is included in Table 3

Table 4 NBO atomic charges (e) in 3-methyl-4-pyrimidone.

Atom	N ₁	C ₂	N ₃	C ₄	C ₅	C ₆	O ₇	H ₈	H ₉	H ₁₀	C ₁₁	H ₁₂	H ₁₃	H ₁₄
NBO charge/e	-0.510	0.330	-0.427	0.635	-0.320	0.064	-0.613	0.172	0.187	0.221	-0.347	0.190	0.209	0.208

for the C=O...H-O interaction. The H-bond interaction energy (ΔE_c) for the H-bonded complex at the C=O site is $-25.18 \text{ kJ mol}^{-1}$, which is superior to the ΔE_c value for the complex at the N₁ site ($-22.56 \text{ kJ mol}^{-1}$). This suggests a preferential complexation on the carbonyl site, the H-bond interaction energy difference ($\Delta(\Delta E_c)$) being 2.63 kJ mol^{-1} . The formation of a relatively strong H-bond between the two molecules is also reflected by a considerable reduction of the distance between both molecules. The computed values of the distance $r(\text{O}\dots\text{H})$ of 1.8797 \AA compared with $r(\text{N}\dots\text{H})$ of 1.9800 \AA , as well as the H-bond distances $r(\text{O}\dots\text{O})$ of 2.8326 compared with $r(\text{O}\dots\text{N})$ of 2.9006 , also suggest that the H-bond is shorter and therefore stronger on the C=O compared to the N₁ site. Both H-bonded complexes are also characterized by different distance variations of the base acceptor sites, i.e. $r(\text{C}=\text{O})$ increases for the C=O...HO-Me whereas it decreases for the N...HO-Me complex and the opposite is true for $r(\text{N}_1\text{-C}_2)$.

Because the aim of the present study was to investigate the difference between the C=O and the N₁ proton-acceptor sites in 3M4P, the structural and energetic data for the 3M4P-HCl complexes at both interaction sites are also summarized in Table 3 for sake of comparison. It appears that the H-bond interaction energy on the N(1) site ($-29.20 \text{ kJ mol}^{-1}$) is slightly superior to that on the C=O site ($-28.20 \text{ kJ mol}^{-1}$), which suggests an preferential complexation of the stronger proton donor at the N₁ acceptor site, the relative energy $\Delta(\Delta E_c)$ being 1 kJ mol^{-1} . A very important result in Table 3 is the predicted frequency of either $\nu(\text{OH})$ or $\nu(\text{NH})$, at 2410 and 2149 cm^{-1} , respectively. These values exclude a normal H-bonded complex of the type Cl-H...O=C or Cl-H...N₁ in case of the proton donor HCl. As a matter of fact, in a large vibration correlation diagram for ClH...base complexes involving a large number of different bases of varying strength, it has been demonstrated that for normal, so-called type I complexes, the bonded mode $\nu(\text{Cl-H}\dots)$ is situated in the range $2000\text{--}1400 \text{ cm}^{-1}$.⁵³ This means that the frequencies at 2410 and 2149 cm^{-1} must be due to the proton-transfer modes $\nu(\text{Cl}\dots\text{H}^+\text{-O}=\text{C})$ or $\nu(\text{Cl}\dots\text{H}^+\text{-N}_1)$. The fact that proton transfer should occur with HCl is also supported by the considerably larger dipole moments, e.g. about 6 D for the complex of HCl with the C=O group, and by a much larger $\Delta\nu(\text{C}=\text{O})$ shift compared to the normal H-bonded complex O-H...O=C with methanol.

It also appears from the calculations that in 3M4P, the N₁ atom with sp^2 hybridization is more basic than the N₃ atom with sp^3 hybridization. As a matter of fact, from the NBO (Natural Bond Orbitals) atomic charges listed in Table 4, it is clear that the N₁ atom has a larger negative charge (-0.510 e) than the N₃ atom (-0.427 e). It appears also from a comparison of the NBO atomic charges that the negative charge at the carbonyl O atom (-0.613 e) is superior to that at N₁ (-0.510 e), which is in accordance with the predicted and experimentally observed (see further) preference of H-bonding at the carbonyl group in the case of methanol. The preference for the N₁ atom in the case of the stronger proton donor HCl can be explained by a proton-transfer interaction at shorter distances. The presence of two lone-pair orbitals at oxygen appears more hindering than the single one at nitrogen in the case of a proton transfer.

3.3.2. FT-IR Spectrum of the Complex

In order to discriminate between the two possible O-H...N₁ and O-H...O=C complexes of 3M4P with methanol, special attention has been paid to the shifts of the 3M4P modes $\nu(\text{C}=\text{O})$, $\delta(\text{C}=\text{O})$, $\gamma(\text{C}=\text{O})$ compared with the $\nu(\text{C}_2=\text{N}_1)$ mode, as well as to the modes $\nu(\text{OH})$, $\delta(\text{OH})$ and $\gamma(\text{OH})$ of methanol. Shifts of the 3M4P vibrational modes are best observed for matrices with an excess of methanol relative to 3M4P.

These spectral perturbations are illustrated in Fig. 5, which has been restricted to the H-bond sensitive spectral regions. The analysis is based on the theoretical DFTB3LYP/6-31+G(d) predictions.

Table 4 lists the observed IR frequencies for the H-bonded complex in comparison with the respective monomer frequencies of methanol and 3M4P. As far as the spectrum of 3M4P is concerned, the observed, weak frequency decrease of the $\nu(\text{C}=\text{O})$ mode (-22 cm^{-1}) as well as the small frequency increases of the $\delta(\text{C}=\text{O})$ ($+8 \text{ cm}^{-1}$) and $\gamma(\text{C}=\text{O})$ mode ($+7 \text{ cm}^{-1}$) in contrast to the very weak sensitivity of the $\nu(\text{C}_2=\text{N}_1)$ mode (-5 cm^{-1}) at weak methanol concentration (Fig. 5) undoubtedly demonstrate that methanol is H-bonded to the C=O group of 3M4P (Fig. 5, b). The frequency shifts observed in this work indicate that the H-complex methanol-3M4P is of intermediate strength, which is consistent with the theoretically obtained H-bond interaction energy of about 25 kJ mole^{-1} .

At increasing concentrations of methanol/Ar mixed with the sublimated 3M4P (Fig. 4), a very strong frequency shift of the carbonyl group $\Delta\nu(\text{C}=\text{O}) = -63 \text{ cm}^{-1}$ is observed, due to formation of a complex $\text{C}=\text{O}\dots\text{H-O}-(\text{H-O}\dots)_n$. The much larger frequency shift of the base C=O group is due to an increased cooperativity. The presence of an intense absorption band of methanol polymers between 3720 and 3200 cm^{-1} suggests that 3M4P is no longer H-bonded by a single methanol molecule, but rather by methanol associates. The structure of this complex may eventually be cyclic, involving the C-H bond of 3M4P or the C₍₅₎-H bond of methanol, as has been suggested elsewhere.⁵⁴⁻⁵⁵

From the above computed and experimental results it is obvious that the carbonyl group is the preferential site for H-bond complexation of 3M4P with methanol.

4. Conclusion

Theoretical (DFT-B3LYP/6-31+G(d)) and experimental (matrix-isolation FT-IR spectroscopy) investigations have been performed to discriminate between O-H...N and O-H...O=C complexes of 3-methyl-4-pyrimidone and methanol. Attention has been paid to the $\nu(\text{C}=\text{O})$, $\delta(\text{C}=\text{O})$, $\gamma(\text{C}=\text{O})$ and $\nu(\text{N}_1=\text{C})$ modes of 3-methyl-4-pyrimidone which are sensitive to H-bonds. A substantial frequency decrease of the $\nu(\text{C}=\text{O})$ mode of 22 cm^{-1} contrary to that of the $\nu(\text{C}_2=\text{N}_1)$ mode of 5 cm^{-1} , as well as small frequency increases of the $\delta(\text{C}=\text{O})$ mode of 8 cm^{-1} and the $\gamma(\text{C}=\text{O})$ mode of 7 cm^{-1} suggest that methanol is H-bonded to 3-methyl-4-pyrimidone preferentially by the carbonyl group. Nevertheless, the relatively weak values of the frequency shifts indicate that the formed complex is not too strong. The values of the H-bond interaction energy (ΔE_c) and the internuclear and intermolecular distances computed at the DFTB3LYP/6-31+G(d) level of theory show that the complex of methanol on the carbonyl site of 3-methyl-4-pyrimidone is more stable than that

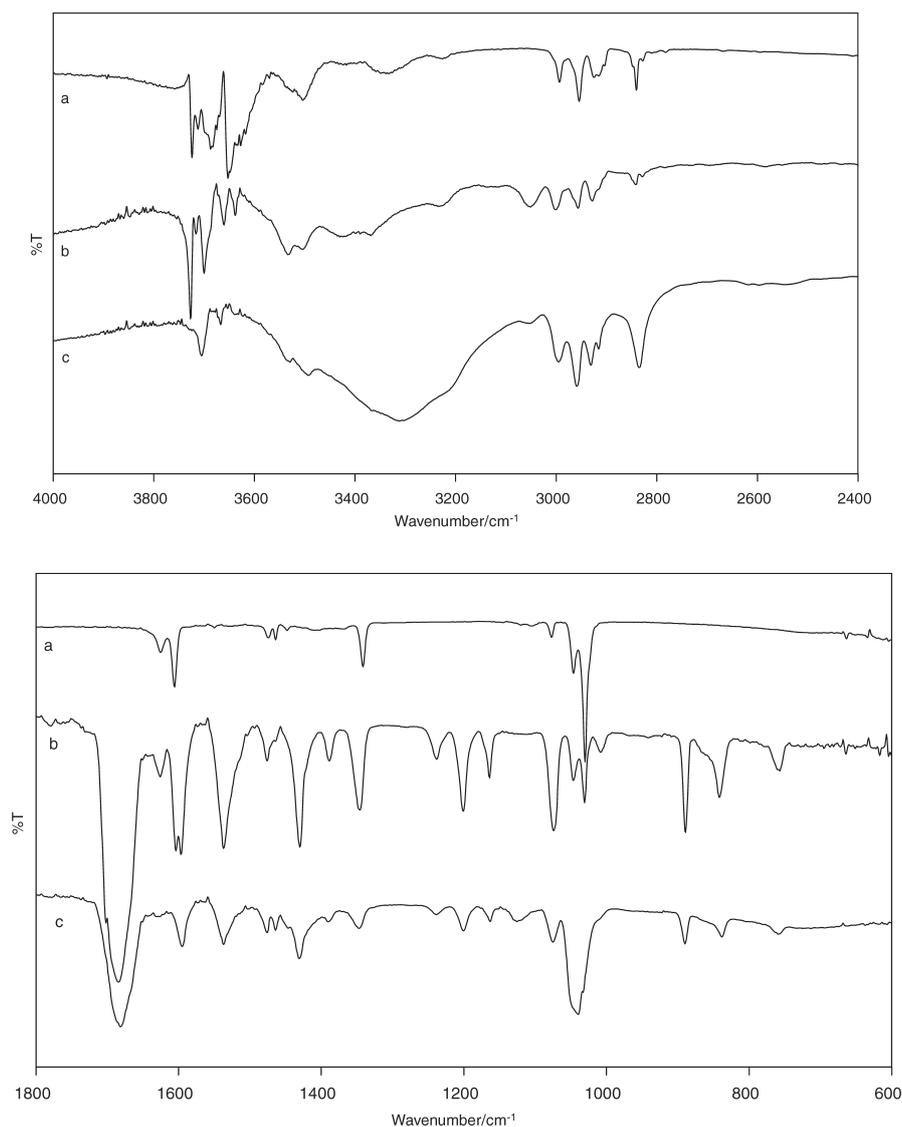


Figure 5 FT-IR spectra of methanol and methanol-3-methyl-4-pyrimidone complex in Ar at 16K: methanol in monomer concentrations (a); complex with methanol at relatively low methanol concentration (b); complex with methanol at relatively high methanol concentration (c).

Table 5 Experimental frequencies of 3-methyl-4-pyrimidone (3M4P) and methanol in the H-bonded complexes compared to the monomer frequencies; frequency shifts ($\Delta\nu$) of 3M4P or methanol due to the complexation

Experimental frequencies of methanol (a) or 3M4P (b)/cm ⁻¹	Experimental frequencies of methanol or 3M4P in the complex/cm ⁻¹	$\Delta\nu$ /cm ⁻¹	Assignment
(a) 3687	3662	-27	ν_{OH} methanol
1341		-	δ_{OH}
1046	1031	-15	$\nu_{\text{C-O}}$
(b) 3047	3055	+8	$\nu(\text{C}_6\text{H}) + \nu(\text{C}_2\text{H})$
1705/1691	1683	-22	$\nu(\text{C}=\text{O})$
1601	1596	-5	$\nu(\text{C}_5=\text{C}_6) + \nu(\text{N}_1\text{C}_2)$
1541	1537	-4	$\nu_{\text{R}} + \nu(\text{N}_1\text{C}_2)$
1387	1388	+1	$\nu_{\text{R}} + \nu(\text{N}_1\text{C}_2)$
1345	1347	+2	$\delta(\text{C}_2\text{H}) + \delta(\text{C}_6\text{H})$
1234	1239	+5	ν_{R}
1197	1201	+4	$\nu(\text{N}_3\text{C}) + \delta(\text{C}_6\text{H})$
1162	1164	+2	$\delta(\text{C}_5\text{H})$
1004	1008	+4	$\gamma(\text{C}_2\text{H})$
888	895	+7	$\gamma(\text{C}=\text{O})$
838	841	+3	$\gamma(\text{C}_5\text{H})$
764	767	+3	$\nu_{\text{R}} + \nu(\text{N}_3\text{C}_4)$
568	576	+8	$\delta(\text{C}=\text{O})$
548	550	+2	δ_{R}

at the N₁ atom of the ring. On the other hand, the interaction of HCl at the N₁ atom of the ring is predicted to be stronger than the interaction on the carbonyl site. Therefore, it may be concluded that H-bonds between weak acids such as methanol are formed preferentially at the carbonyl group, whereas for stronger acids such as HCl the complexation occurs on the N₁ atom of the ring.

The cooperativity factors in addition to the relative intensities observed for methanol tetramers compared to trimers, dimers and monomers, allow for the confirmation of the most stable tetramers for the exploited methanol concentrations. The comparison of cooperativity factors of associated methanol and water suggests that there is a stronger cooperation or an intense mutual fortification of H-bonds in methanol than in water.

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