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Vibrational spectra of 1-methylthymine: matrix isolation, solid state and theoretical studies

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Abstract

The infrared spectra of 1-methylthymine (1-MeT) in argon and nitrogen cryogenic matrices are presented, for the first time. The molecular structure, conformations, vibrational frequencies, infrared intensities and Raman scattering activities of 1-MeT have been calculated by the DFT(B3LYP), MP2 and HF methods using the D95V** basis set. The theoretically predicted intensity pattern of the IR and Raman bands has proved to be of great help in assigning the experimental spectra. Rigorous normal coordinate analysis has been performed, at each level of theory. The unequivocal and complete vibrational assignment for 1-MeT has been made on the basis of the calculated potential energy distribution (PED). Comparison of the experimental matrix isolation spectra with the theoretical results has revealed that the B3LYP method is superior to both the MP2 and HF methods in predicting the frequencies of uracil derivatives. The MP2 method consistently underestimates the frequencies of the out-of-plane $\gamma(C=O)$ and $\gamma(C–H)$ bending modes, while the HF method yields the reverse order of the frequencies of two $\nu(C=O)$ stretching vibrations. Investigation of the frequency shift of several bands, on passing from matrix isolation to solid state spectra, has provided information on the strength of intermolecular hydrogen bonding in the crystal of 1-MeT. Several ambiguities in the earlier assignments of the vibrational spectra of polycrystalline 1-MeT have been clarified.
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1. Introduction

1-Methylthymine (1-MeT) can be considered as a model of thymidine, naturally occurring in DNA, because the methyl group adjacent to the N_1 atom simulates the deoxyribose moiety. 1-MeT has been applied as the protective group in the studies of "platination reactions" of trans-Pt(NH$_3$)$_2$(1-MeT)Cl with DNA oligonucleotides [1,2]. A clear understanding of the vibrational spectrum of 1-MeT is important for studying the spectral changes caused by the formation of metal complexes and of the hydrogen bonded complexes, in biological systems.

Recently, a comprehensive Raman and infrared matrix isolation study and the DFT(B3LYP)/6-31G** calculations have been reported for thymine [3]. The C=O stretching frequencies of the radical anions of monomers and dimers of thymine were calculated using the BLYP/6-31G* method [4]. In our earlier work we carried out a thorough ab initio study of the spectra of the N_3-deprotonated 1-MeT anion using the extended (6–31++G** and D95V**) basis sets [5]. The results obtained from normal coordinate analysis of 1-methylthyminate anion have proved to be of great help in the assignment of the vibrational spectra of its complexes with mercury(II) and potassium cations, in the solid state.

It should be emphasized that numerous experimental infrared matrix isolation studies and theoretical calculations have been performed for uracil [6–14], 1-methyluracil [10,11,14–17], 3-methyluracil [10,11,15], 5-methyluracil (thymine) [3,4,9,10,18,19], 1,3-dimethyluracil [11,15] and dihydrouracil [20]. Surprisingly, no vibrational spectra of 1-methylthymine (1,5-dimethyluracil) isolated in low-temperature matrices have been published, as yet.

An early study of the IR and Raman spectra of the polycrystalline 1-MeT was reported by Susi and Ard [21], but only a few bands corresponding to the in-plane fundamentals were assigned. Kirin et al. [22] studied the lattice vi-

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brations of 1-MeT single crystal, in the frequency range below $100\,cm^{-1}$. Lagant and coworkers [23,24] performed the semiempirical treatment of 1-MeT using the AM1 method and employed the calculated general valence force constants in normal coordinate analysis of this molecule. Unfortunately, the reported vibrational assignment [23] is inconsistent with that reported in reference [21], and it differs substantially from the assignment of crystalline 1-methyluracil [25]. Thus, there is a need to clarify ambiguities in the vibrational assignment of 1-MeT, in the solid state.

The aim of this work is to present, for the first time, the infrared spectra of 1-methylthymine isolated in low-temperature Ar and N_2 matrices. The experimental study has been combined with thorough theoretical calculations of the structures, conformations and vibrational spectra of 1-MeT, performed at the HF, MP2 (the second order Möller–Plesset perturbation) and the DFT(B3LYP) levels of theory. The calculated potential energy distribution (PED) enabled us to get a detailed insight into the nature of the normal modes and to make a clear-cut assignment of the vibrational spectra of the 1-MeT monomer. The theoretical results have also been used to revise an existing assignment of the vibrational spectra of solid 1-methylthymine.

2. Methods

2.1. Experimental

1-Methylthymine (Sigma) was purified by vacuum sublimation prior to the matrix experiment. The matrix gases, argon (Linde AG) and nitrogen (Technische Gase, Leipzig), were of purity grade 6.0. The method of matrix preparation was the same as described earlier [26]. The vapors of 1-MeT were mixed with the matrix gas, Ar or N_2 (precooled in a liquid nitrogen trap), and deposited on a CsI window on the cold finger (10 K) of the cryostat. The matrix-gas/dopant ratio was experimentally adjusted to ensure that only the bands due to the monomer were recorded. No sign of thermal decomposition was observed during the experiment. The matrix-isolation IR spectra were recorded on a Perkin-Elmer Model 580B grating spectrophotometer operating at $1\,cm^{-1}$ resolution in the frequency range of $3600–600\,cm^{-1}$, and at $3\,cm^{-1}$ resolution in the range of frequencies below $600\,cm^{-1}$. Integral intensities of the absorption bands were measured by numerical integration.

The FT-IR spectra of solid 1-MeT, in the region $4000–400\,cm^{-1}$, were measured on a Nicolet–Nexus spectrometer using the KBr pellets. The far infrared spectra in the frequency range of $700–50\,cm^{-1}$ were recorded on a Perkin-Elmer 2000 FT-IR spectrometer using Nujol mull technique. The FT-Raman spectra were recorded on a Nicolet 2000 spectrometer equipped with a Nd-YAG laser. A maximum laser power of 100 mW was used and the spectra were measured at $2\,cm^{-1}$ resolution. The title compound was studied in the solid state in the capillary tubes.

2.2. Theoretical methods

The optimized geometry, harmonic frequencies, infrared intensities and Raman scattering activities of 1-MeT have been calculated by the three-parameter hybrid B3LYP functional [27,28] and the ab initio (MP2 and HF) methods (see supplementary material). In all calculations, the D95V** basis set (the Dunning/Huzinaga polarized valence double-ζ basis set) [29] was employed. This basis set has been successfully used in our previous calculations of the vibrational spectra of structurally similar 1-methyluracil [17], dihydrouracil [20] and glutarimide [26]. To verify the results obtained at the HF level of theory, the extended basis set 6–31++G** [30] was also used, for comparison (see supplementary material).

Full geometry optimization of 1-MeT has been performed for several initial conformations of two methyl groups in the molecule. This has yielded four stationary points on the potential energy surface of 1-MeT. Subsequently, vibrational frequencies were calculated to determine the nature of the stationary points (two conformers of the highest energy turned out to be the transition states). For two conformers of the lowest energies the theoretical infrared and Raman spectra were calculated. All the frequencies calculated by the MP2 and HF methods were scaled by 0.96 and 0.90, respectively, similarly as in our earlier studies [17]. The scaling of the frequencies computed by the B3LYP method deserves some comments. Rauhut and Pulay [31] have shown, for a number of molecules, that the unscaled B3LYP-calculated frequencies, in the range below $1000\,cm^{-1}$, show good agreement with the experimental data. However, in the range above $1500\,cm^{-1}$, the discrepancies between the experimental and theoretical harmonic frequencies systematically increase. This is mainly due to the fact that vibrations have different anharmonicity (for example, the NH and CH stretching vibrations are more anharmonic than the in-plane ring deformations). Pulay and co-workers [31,32] derived a set of transferable scaling factors for the DFT-calculated force constants. We have shown recently for aromatic molecules [33–35] that the B3LYP-calculated frequencies of the CH stretching vibrations, scaled by the factor of 0.958, almost reproduce the experimental data. It is worth mentioning that the scaling factor for the CH stretching frequencies (k_v) has been derived as the square root of the scaling factor for the valence CH stretching force constant, ($k_f = 0.918$), reported in reference [32]. A similar procedure has been used in this work. For the frequency of the "pure" NH stretching vibration, the scaling factor of 0.95 has been derived from the scaling factor applied for the corresponding NH stretching force constant by Szczepaniak et al. [3] ($0.95 = \sqrt{0.902}$). Thus, the B3LYP-calculated N–H and C–H stretching frequencies (modes Q1–Q9) were scaled by the factor of 0.95, the frequencies of modes Q9–Q25 were scaled by 0.98, and the other frequencies were left unscaled. This approach aimed at using the least possible number of scaling factors,

which can yield frequencies in good agreement with the experiment.

In normal coordinate analysis, a nonredundant set of 48 internal coordinates was defined, similar to that reported earlier for 1-MeU [17]. The vibrations of the methyl group have been designated as follows: $\nu(Me1)$ is the symmetric stretching; $\nu(Me2)$ and $\nu(Me3)$ are the antisymmetric stretchings; $\beta(Me1)$ is the symmetric bending (or umbrella vibration); $\beta(Me2)$ and $\beta(Me4)$ are the antisymmetric deformations; $\beta(Me3)$ and $\beta(Me5)$ are the rocking vibrations (parallel and perpendicular, respectively). At each level of theory, the PED was calculated. All computations have been carried out using Gaussian 98 [36].

3. Results and discussion

3.1. Conformations of 1-MeT

Full geometry optimization of 1-MeT has yielded four stationary points (A, B, C and D), which differ in the relative orientation of two methyl groups, as shown in Fig. 1. In A and B conformations, the CH_3 group at the C atom is oriented in such a way that one hydrogen atom is placed in the plane of the ring, in *trans* (*t*) orientation with respect to the carbonyl group. In C and D isomers, the in-plane H atom (connected to C) is in *cis* (*c*) orientation to the carbonyl group. The remaining two hydrogen atoms from the methyl group are located symmetrically above and under the molecular plane. Isomers A and B (as well as C and D) differ by the orientation of hydrogens in the N_1-methyl group. In the B and D forms, the in-plane hydrogen atom has *cis* orientation with respect to the nearby carbonyl group.

According to the results obtained at the three levels of theory (DFT, HF and MP2), the C and D conformations are unstable (both have one imaginary frequency for methyl torsion vibration). In the estimation of the relative stability of A and B forms, the calculated total electronic energies have been corrected for zero-point vibrational energies, ZPVE. In B3LYP calculations, form B is slightly more stable than A,
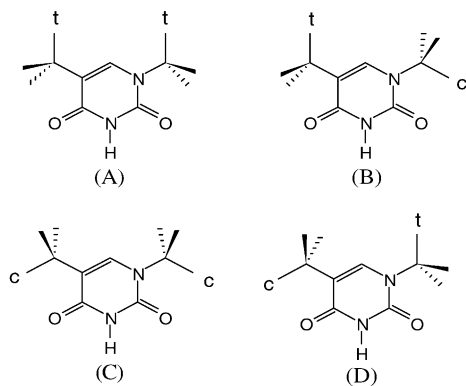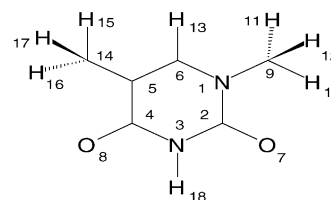

Fig. 2. Atom numbering of 1-methylthymine (B conformer).

by about $0.8\,kJ\,mol^{-1}$, and A has one imaginary frequency. According to the HF and MP2 methods, both isomers A and B are stable and have almost equal energy (in the HF calculations, the energy of B is lower than A by only $0.1\,kJ\,mol^{-1}$, whereas in MP2 calculations, A is more stable than B by $0.2\,kJ\,mol^{-1}$). Thus, it seems that both conformers (A and B) of 1-MeT may coexist in the gas phase.

It is worth mentioning that the position of the hydrogen atoms in the C-methyl group, in A and B conformers of 1-MeT, is analogous to that calculated for thymine [19]. In B isomer, the predicted orientation of the hydrogen atoms in the N_1-methyl group is similar to that in 1,3-dimethyluracil, which has been determined by NMR studies [37]. The numbering of atoms in the B conformer is shown in Fig. 2.

3.2. Vibrational spectra

The infrared spectra of 1-methylthymine measured in low-temperature argon and nitrogen matrices and the theoretical infrared spectra of B conformer (calculated by the B3LYP and MP2 methods) and of A conformer (MP2) are compared in Fig. 3. As follows from this comparison, the theoretical IR spectrum of B calculated by the B3LYP method is in the best overall agreement with the experiment. Table 1 lists the experimental wavenumbers and infrared intensities of the bands in the matrix-isolation spectra of 1-MeT, along with the theoretical results from the B3LYP calculations for B conformer. The remaining theoretical results (the harmonic frequencies, IR intensities and Raman scattering activities calculated for A and B isomers using the HF and MP2 methods) are available in supplementary information.

The detailed vibrational assignment of 1-MeT has been made on the basis of the calculated PED, and is shown in Table 1.

3.2.1. Vibrations of N–H group

The assignment of the N_3–H stretching vibration in the infrared spectra of 1-MeT is straightforward. As is seen in Table 1 (and Fig. 3), a distinct band at $3434\,cm^{-1}$ in an argon matrix, which shifts to $3417\,cm^{-1}$ in a nitrogen matrix, is readily assigned to the mode Q1. The corresponding $\nu(N_3$–H) vibration in 1-methyluracil was observed at very similar frequencies, 3430 and $3416\,cm^{-1}$, in Ar and N_2 matrices, respectively [17]. In the recently reported infrared spectrum of thymine in an Ar matrix, the corresponding frequency was assigned at $3432\,cm^{-1}$ [3]. These results indi-

Fig. 1. Four conformers (A–D) of 1-methylthymine considered in theoretical study.

Table 1
Comparison of the experimental wavenumbers ($\tilde{\nu}$) and the relative intensities (I_∞) of the bands in the infrared spectra of 1-MeT in argon and nitrogen matrices and the theoretical wavenumbers, infrared intensities (A^{th}) and Raman scattering activities (S^{th}) calculated for B conformer of 1-MeT by DFT(B3LYP) method using D95V** basis set. Band assignment has been made on the basis of the calculated PED

Experimental				Calculated				
Ar matrix		N$_2$ matrix		B3LYP/D95V**				
$\tilde{\nu}$ (cm^{-1})	I_∞ rel.[a]	$\tilde{\nu}$ (cm^{-1})	I_∞ rel.	Mode number	$\tilde{\nu}^b$ (cm^{-1})	A^{th} (km mol^{-1})	S^{th} (Å^4 amu^{-1})	PED (%)
3434	114	3417	118	Q1	3444	72	78	ν(N3H) (100)
				Q2	3046	5	61	ν(C6H) (99)
2994		3001}		Q3	3031	1	34	ν(Me2)$_N$ (93)
2970		2988		Q4	2983	14	55	ν(Me2)$_C$ (100)
	74	2965	47	Q5	2969	21	68	ν(Me3)$_N$ (100)
2942		2940		Q6	2963	11	72	ν(Me3)$_C$ (100)
2911		2915		Q7	2902	51	196	ν(MeI)$_N$ (92)
				Q8	2899	21	145	ν(MeI)$_C$ (99)
1754		1762						
1748		1748		Q9	1757	593	9	ν(C2O) (74)
1744	1205	1735	1140					
1719		1723		Q10	1736	654	47	ν(C4O) (74)
1710								
1704		1705						
1665	26	1667	48	Q11	1669	43	41	ν(C5C6) (58)
1486	66	1488	57	Q12	1479	89	17	β(Me2)$_N$ (60), β(Me3)$_N$ (14)
1481								
1468	13	1473	8	Q13	1476	13	13	β(Me4)$_N$ (92)
1463		1466	6	Q14	1466	7	10	β(Me2)$_C$ (76)
		1456	15	Q15	1437	9	3	β(Me4)$_C$ (92)
1448	77	1438	78	Q16	1432	91	9	β(Me2)$_N$ (18), ν(C4C5) (15), ν(N1C2) (11)
1441		1430						
1419	42			Q17	1419	31	5	β(MeI)$_N$ (78)
1391	9	1392	15	Q18	1394	10	7	β(MeI)$_C$ (91)
1381	4	1386		Q19	1378	1	4	β(N3H) (42), β(C6H) (19)
1371	66	1371	53	Q20	1363	55	35	ν(ring) (35) β(N3H) (15), β(C6H) (19)
1366								
1320	82	1326	85	Q21	1311	122	7	ν(C6N1) (32), β(C6H) (18), β(N3H) (10)
1229	6	1232	5	Q22	1231	5	8	ν(C2N3) (30), β(R1) (17), ν(C5C14) (16)
1194	37	1197	44	Q23	1201	35	1	β(C6H) (20), ν(N3C4) (18), ν(N1C9) (16)
1137	16	1140	20	Q24	1135	14	3	ν(N3C4) (27), ν(C5C14) (18), ν(C2N3) (13)
				Q25	1125	0	3	β(Me5)$_N$ (91)
1064	40	1068	43	Q26	1071	28	9	β(Me3)$_N$ (42), ν(C6N1) (15), ν(N1C9) (10)
1047	1	1048	2	Q27	1062	4	1	β(Me5)$_C$ (79), γ(C5C14) (10)
1006	3	1009	1	Q28	1016	7	5	β(Me3)$_C$ (61)
895	17	901	18	Q29	916	18	1	γ(C6H) (99)
891		895						
				Q30	860	1	4	ν(N1C2) (25), ν(C5C14) (14), ν(N1C9) (13)
773	9	775	5	Q31	780	9	12	β(R1) (41), ν(C4C5) (16)
764	38	768	51	Q32	767	33	2	γ(C4O) (72)
756	11	759	7	Q33	754	13	0.3	γ(C2O) (93)
692	8	694	9	Q34	695	7	7	β(R2) (51), ν(C5C14) (11), ν(N1C9) (11)
658	56	681	43	Q35	677	62	2	γ(N3H) (90), τ(R1) (10)
641	2			Q36	639	2	1	β(CO)$_{rock}$ (57), β(C5C14) (11)
518	3	520	2	Q37	520	4	14	β(R2) (46), ν(N3C4) (13), ν(C2N3) (10)
439	23	443	25	Q38	437	26	3	β(R3) (79)
				Q39	413	5	1	τ(R3) (44), τ(R1) (26), γ(C4O) (13)
395	20	396	13	Q40	396	22	0.7	β(CO)$_{sciss}$ (60)
				Q41	337	0	0.8	β(N1C9) (63), β(CO)$_{rock}$ (14)
				Q42	314	1	0.6	γ(C5C14) (73), γ(N1C9) (14)
270	0.4			Q43	264	4	0.6	β(C5C14) (69)
				Q44	201	7	0.4	τ(R1) (51), γ(N1C9) (49)
				Q45	144	1	0.3	τ(Me)$_C$ (39), τ(R2) (23), γ(N1C9) (11)
				Q46	133	0	0.5	τ(Me)$_C$ (57), τ(R3) (17), γ(N1C9) (15)
				Q47	97	0	0.1	τ(R2) (61), τ(R3) (31)
				Q48	77	0	0.4	τ(Me)$_N$ (85), γ(N1C9) (14)

[a] rel.: relative values (infrared absorption bands normalized in such a way that the observed intensity sum of all bands is equal to the B3LYP-calculated intensity sum of the corresponding modes).

[b] B3LYP frequencies of modes Q1–Q8 were scaled by 0.95; the frequencies of modes Q9–Q25 scaled by 0.98; the frequencies of modes Q26–Q48 were left unscaled (see text).
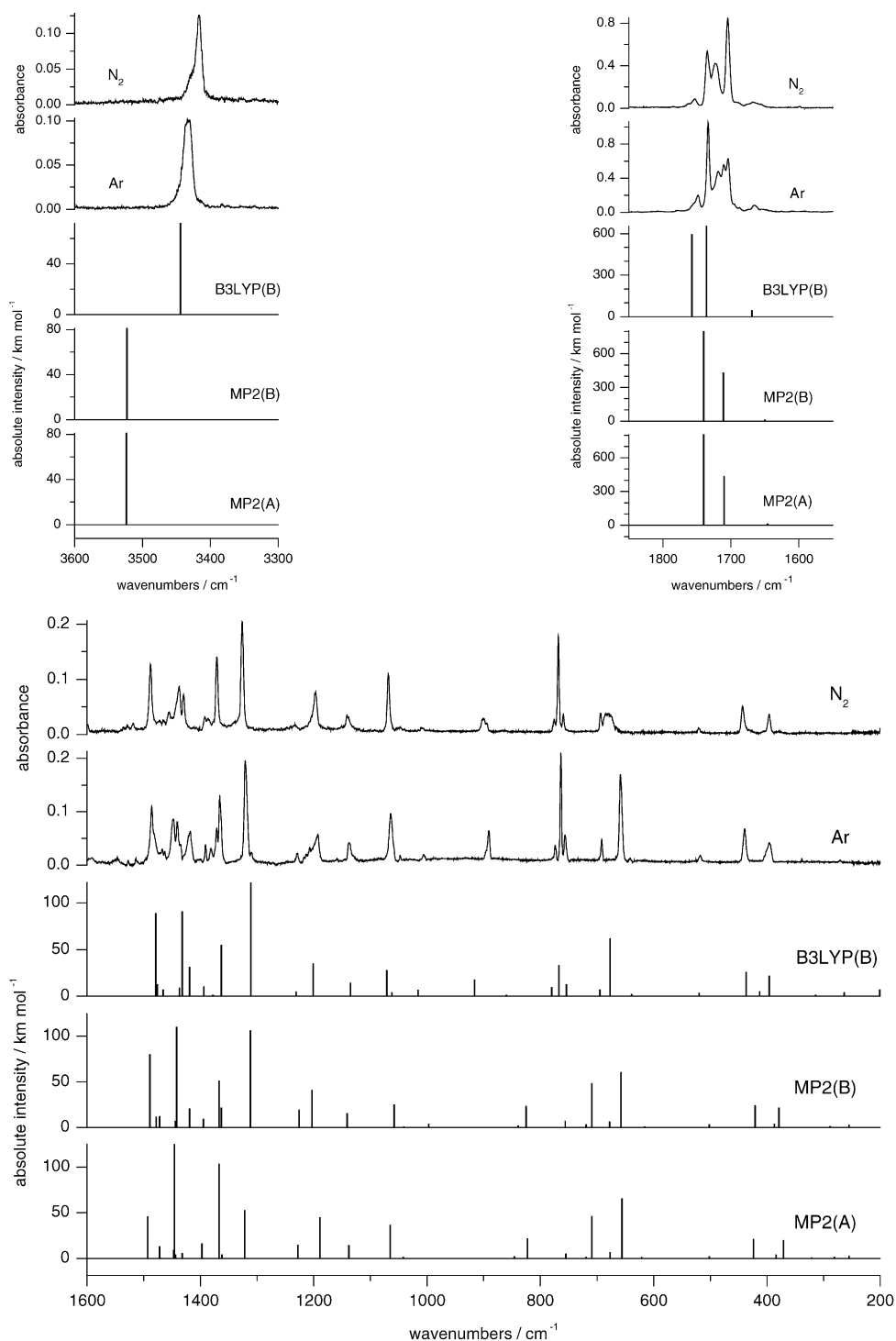
Fig. 3. Comparison of the IR spectra of 1-methylthymine isolated in N_2 and Ar matrices with theoretical harmonic frequencies and IR intensities calculated by DFT(B3LYP) and MP2 methods. The D95V** basis set was used in calculations. Theoretical MP2 frequencies were scaled by a factor of 0.96. The scaling factors for B3LYP-frequencies are shown in Table 1. The conformers (A or B) are indicated in parentheses.

cate that the polarity of the N_3H bond, in the monomers of 1-MeT, 1-MeU and thymine, is very similar.

It has been shown that the anharmonicity correction for the NH stretching frequency is of about 5% [3]. Indeed, as follows from Table 1, the scaling factor of 0.95 employed for

the B3LYP-calculated frequency of this mode, reproduces very well the experimental frequency (measured in Ar matrix).

Examination of Table 1 shows that the N_3H in-plane bending vibration, $\beta(N_3H)$, is extensively coupled with the C_6–H

in-plane bending vibration and ring deformations, and contributes to the modes Q19, Q20 and Q21. The predominant contribution of $\beta(N_3H)$ is noted in the mode Q19, calculated at 1378 cm^{-1}. Since the predicted IR intensity of this mode is very low, therefore, it can be assigned to the weak band at 1381 cm^{-1} (Ar matrix) and 1386 cm^{-1} (N$_2$ matrix). Such a shift towards higher frequency in N$_2$ matrix (with respect to Ar matrix) is typical for the bands arising from the bending vibrations of NH group [18]. The next two strong bands, at 1371 and 1320 cm^{-1} (Ar) can be assigned to the modes Q20 and Q21, respectively, and they arise from the ring stretching vibrations coupled with $\beta(N_3H)$ and $\beta(C_6H)$, as revealed by the calculated PED (Table 1).

In the earlier studies of thymine in argon matrix, the N$_3$H out-of-plane bending mode was assigned to the band at 662 cm^{-1} [3,9,18]. In the infrared spectrum of 1-MeT in Ar, a similar strong band is observed at 658 cm^{-1} (Fig. 3). However, in the IR spectrum of 1-MeT in a nitrogen matrix, the corresponding broad absorption consists of three components, shifted to higher frequencies, with the maximum at 681 cm^{-1} (Fig. 3). This effect clearly indicates that these bands can be assigned to the out-of-plane vibration, $\gamma(N_3H)$, mode Q35. Barnes and coworkers [7] have suggested that such an upward shift of $\gamma(NH)$ frequency, on passing from Ar to N$_2$ matrix, is due to interactions between nitrogen molecules and the NH group. The splitting of the $\gamma(N_3H)$ band, in the IR spectrum of 1-MeT in a nitrogen matrix, is attributed to the fact that this out-of-plane vibration is very sensitive to intermolecular interactions. In this case, the complicated character of this band has demonstrated interactions of 1-MeT with the nitrogen molecules (matrix splitting). It is worth mentioning that in the infrared spectrum of 1-MeU in an Ar matrix, the corresponding $\gamma(N_3H)$ vibration was observed at 659 cm^{-1}, whereas in a nitrogen matrix, it was assigned to the broad and split band with the maximum at 682 cm^{-1} [17].

3.2.2. Vibrations of two C=O groups

A complicated pattern of the infrared spectrum near 1700 cm^{-1} is observed for 1-MeT in Ar and N$_2$ matrices (Fig. 3). This can be attributed to the presence of combination bands, which are enhanced in intensity *via* Fermi resonance with two strong fundamentals corresponding to C=O stretching vibrations. It should be emphasized that a similar complicated absorption, in this frequency region, was reported earlier for the six-membered cyclic imides containing two carbonyl groups: uracil and thymine [3,6–15,18,19]; 1-MeU [17]; dihydrouracil [20] and glutarimide [26].

As can be seen in Fig. 3, the infrared intensities of these bands are dependent on the matrix. In an Ar matrix, the band at 1734 cm^{-1} is the strongest, while in a N$_2$ matrix the broad band at 1705 cm^{-1} is the most intense.

Both the B3LYP and MP2 methods consistently indicate that the frequency of the $\nu(C_2=O_7)$ stretching vibration is higher than that of $\nu(C_4=O_8)$. This is in agreement with the assignment of two C=O stretching vibrations

in 1-methyluracil [17] and thymine [3]. However, the HF method yields the reverse order of these frequencies, in both A and B conformers, regardless of the basis set used (see supplementary materials). In the B3LYP and MP2 calculations, a lower frequency of $\nu(C_4=O_8)$ vibration is consistent with a slightly longer C$_4$=O$_8$ distance (1.235 Å, MP2) in comparison to C$_2$=O$_7$ (1.231 Å, MP2). It should also be noted that the O$_7$ atom is slightly more basic (Mulliken charge of -0.473 e) than the O$_8$ atom (-0.440 e). In 1-MeT (and in other uracil derivatives), a conjugation between the C$_5$=C$_6$ and C$_4$=O$_8$ bonds should lead to a slight lengthening of the bonds, as compared to those in the non-conjugated systems. Correlation energy plays important role in conjugation, therefore the HF method (which neglects the correlation energy) yields too short C$_4$=O$_8$ bond length, and it overestimates the $\nu(C_4=O_8)$ stretching frequency. This deficiency of the HF method leads to the reverse order of the predicted frequencies of two C=O stretching vibrations in 1-MeT. It should be emphasized that in our earlier calculations on 1-methyluracil [17] we have also noted a similar failure of the HF method in predicting the correct order of the two carbonyl stretching frequencies.

Thus, in the matrix-isolation spectra of 1-MeT, the $\nu(C_2=O_7)$ vibration should be assigned at higher frequency than $\nu(C_4=O_8)$. However, it is impossible to recognize unequivocally which component of the complicated absorption is the fundamental, and which is the combination tone. Probably, the very strong band at 1734 cm^{-1} in Ar, and the band at 1735 cm^{-1} in a nitrogen matrix originate from the $\nu(C_2=O_7)$ fundamental, whereas the very strong band at 1705 cm^{-1} in a nitrogen matrix (1704 cm^{-1} in Ar) is due to the $\nu(C_4=O_8)$ fundamental vibration. Among the possible combinations are the following: $\nu_{21} + \nu_{38} = 1759$, $\nu_{26} + \nu_{34} = 1756$, $\nu_{21} + \nu_{40} = 1715$ and $\nu_{23} + \nu_{37} = 1712$ cm^{-1} (Ar frequencies). It should be noted that the components of the combination tones have slightly different frequencies in Ar and N$_2$ matrices, therefore the position of the corresponding combination bands in the infrared spectra, is also slightly different.

As revealed by the calculations, the frequencies of the two out-of-plane bending vibrations, mode Q32 ($\gamma C_4 O$) and Q33 ($\gamma C_2 O$) are very similar, 767 and 754 cm^{-1}, respectively, whereas the theoretical infrared intensity of the former is about three times higher than that of the latter. Therefore, the two closely spaced bands at 764 cm^{-1} (strong) and 756 cm^{-1} (weak), in the IR spectrum of 1-MeT in an argon matrix, can be assigned to the modes Q32 and Q33, respectively. In a nitrogen matrix, the corresponding modes are observed at 768 and 759 cm^{-1}, respectively. It is worth mentioning that in the infrared spectrum of thymine in an Ar matrix, the corresponding bands are observed at very similar frequencies, 763 and 754 cm^{-1}, respectively [3].

It should be emphasized that the MP2 calculations consistently underestimate the frequencies of the out-of-plane $\gamma(C=O)$ bending vibrations, by about 40–50 cm^{-1}, for both A and B conformers of 1-MeT (Fig. 3 and supplementary

information). A similar deficiency of the MP2 method in predicting the frequencies of $\gamma(C=O)$ bending vibrations has been observed in our earlier calculations of pyrimidine bases, 1-methyluracil [17] and dihydrouracil [20]. Recently, we have demonstrated that the MP2 method also fails in predicting the frequency of the out-of-plane ring puckering vibration in phenol [33] and in aniline [35]. It has been concluded that the MP2 method, with the inherent single-reference wave function, is inadequate for a proper description of different electron configurations that should be considered in some out-of-plane ring deformation vibrations of aromatic molecules [33]. This can also be the reason of the underestimated frequencies of the $\gamma(C=O)$ vibrations in uracil derivatives, calculated by the MP2 method. Thus, it is really remarkable that the density functional method overcomes this problem and predicts the frequencies of these modes in excellent agreement with experiment.

3.2.3. Vibrations of C6–H and methyl groups

The C–H stretching fundamentals are known to be very weak in matrix-isolation spectra of cyclic imides. Furthermore, the C–H stretching region (near 2900 cm^{-1}) in the infrared spectra of cyclic imides is strongly affected by Fermi resonances with a number of combination tones. The possible combinations and overtones for 1-MeT, in this frequency range, are the following: $\nu_{17} + \nu_{16}$ (1419 + 1448 = 2867 cm^{-1}); $\nu_{18} + \nu_{12}$ (1391 + 1486 = 2877); $\nu_{17} + \nu_{12}$ (1419 + 1486 = 2905); $\nu_{16} + \nu_{13}$ (1448 + 1468 = 2916); $\nu_{16} + \nu_{12}$ (1448 + 1486 = 2934); $2\nu_{12}$ (2 × 1486 = 2972); $2\nu_{13}$ (2 × 1468 = 2936); $2\nu_{16}$ (2 × 1448 = 2896 cm^{-1}) in Ar matrix. Under such circumstances, it is difficult to assign unambiguously the modes Q2–Q8 in the matrix-isolated infrared spectra of 1-MeT. In the Raman spectrum of solid 1-MeT, the overtones and combination bands have lower intensities, in comparison to those in IR spectra, therefore, the bands arising from C–H stretching fundamentals are better resolved, as illustrated in Fig. 4. The frequencies observed in the spectra of solid 1-MeT are listed in Table 2.

According to our calculations at the three levels of theory, of all ν(C–H) stretching vibrations, mode Q2 has the highest frequency. Thus, in the Raman spectrum of solid 1-MeT, the highest frequency band at 3064 cm^{-1} can be assigned to ν(C$_6$–H) stretching vibration. It should be noted that this band is also observed in the IR and Raman spectra of the N$_3$-deprotonated 1-methylthyminate complexes with metal ions [5], which confirms that this band is due to CH vibration. For comparison, the corresponding ν(C$_6$–H) stretching has been assigned at 3078 cm^{-1} in the matrix-isolated Raman spectrum of thymine [3].

Examination of the results in Table 1 indicates that the stretching and deformation vibrations in the N$_1$-methyl group have slightly higher frequencies than the corresponding vibrations in the C$_5$-methyl group (Table 1). However, the calculated frequencies of some modes are very close (for example, modes Q5 and Q6), therefore, the corresponding bands probably overlap, in the experimental spectra.

Table 2
Bands observed in the infrared and Raman spectra of solid 1-MeT and their assignment

No[a]	IR[b]	Raman[b]	Assignment[c]
[d]	3150 w		ν^{as} (N3H)
[d]		ov	ν^{s} (N3H)
Q2	3066 w	3064 m	ν(C6H)
Q3	3019 w	3019 w	ν(Me2)$_N$
Q4		2989 w	ν(Me2)$_C$
Q5	2975 vw	2975 w	ν(Me3)$_N$
Q6	2953 vw	2954 m	ν(Me3)$_C$
Q7	2928 vw	2927ms	ν(Me1)$_N$
Q8	2905 vw	2901m	ν(Me1)$_C$
	2832 w	2838 vw	$2\nu_{17}$
	1766 sh		Combinations
	1750 sh		
Q9	1701 s	1706 w	ν(C2O)
[d]	1683 s	1685 w	ν^{as} (C4O)
	1657 s		Combinations
Q11	1640 s	1647 vs	ν(C5C6)
d		1635 sh	ν^{s} (C4O)
	1568 w		$2\nu_{31}$
	1515 w	1510 vw	$2\nu_{32}$
Q12	1490 m	1488 w	β(Me2)$_N$
Q13	1465 w	1467 w	β(Me4)$_N$
Q14	ov		β(Me2)$_C$
Q15	1450 br		β(Me4)$_C$
Q16	1434 sh	1433 m	β(Me2)$_N$, ν(C4C5)
Q17	1422 m		β(Me1)$_N$
Q18	1381 m	1383 m	β(Me1)$_C$
Q19	ov		β(N3H), β(C6H)
Q20	1367 m	1369 vs	ν(ring), β(N3H), β(C6H)
Q21	1336 s	1337 w	ν(C6N1), β(C6H), β(N3H)
Q22		1234 m	ν(C2N3), β(ring)
Q23	1211m	1212 sh	β(C6H),ν(N3C4), ν(N1C9)
Q24	1152 m	1153 w	ν(N3C4),ν(C5C14),(C2N3)
Q25		ov	β(Me5)$_N$
Q26	1067 m	1064 m	β(Me3)$_N$,ν(C6N1)
Q27	1047s	1048 vw	β(Me5)$_C$, γ(C5C14)
Q28	1009 w	1008 w	β(Me3)$_C$
Q29	898 m		γ(C6H)
Q30	ov	879 m	ν(N1C2),ν(C5C14)
Q35[e]	870 sh		γ(N3H)
Q31	787 m	788 vs	β(ring)
Q32	758 m	762 w	γ(C4O)
Q33	754 m		γ(C2O)
Q34	692 m	697m	β(ring, ν(C5C14) ν(N1C9)
Q36	650 w	648 w	β(CO)$_{rock}$
Q37	524 m	524 s	β(ring)
Q38	453 m	450 m	β(ring)
Q39	421w	427 m	τ(ring), γ(C4O)
Q40	395 sh	390 vw	β(CO)$_{sciss}$
Q41	325 w	325 w	β(N1C9), β(CO)$_{rock}$
Q42		284 w	γ(C5C14), γ(N1C9)
Q43	277 w		β(C5C14)
Q44	241 w	230 vw	τ(ring), γ(N1C9)
Q45		162 w	τ(Me)$_C$
Q46		139 w	τ(Me)$_C$, γ(N1C9)
Q47		109 w	τ(ring)
Q48			τ(Me)$_N$, γ(N1C9)

[a] Corresponding normal modes in the monomer (from Table 1).
[b] Abbreviations, br: broad; m: medium; ov: overlapped; s: strong; sh: shoulder; v: very; w: weak.
[c] From PED calculated for the 1-MeT monomer, except for the N3-H and C4-O stretching modes.
[d] The effect of hydrogen bond in dimers.
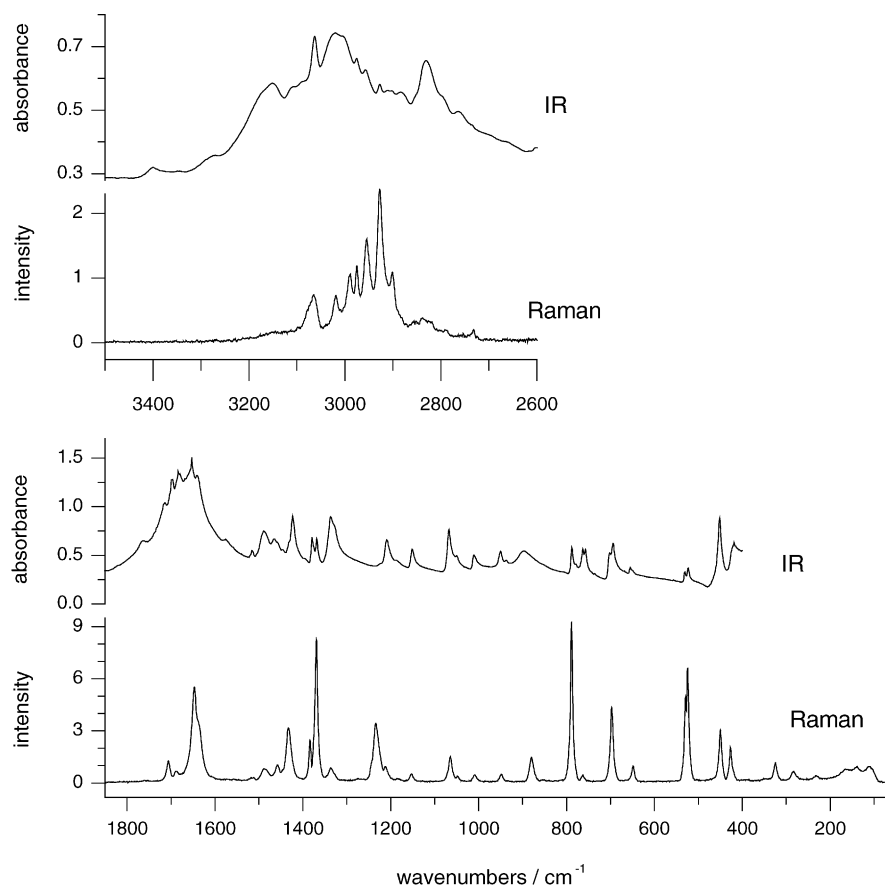[e] Reordered modes.

Fig. 4. The infrared and Raman spectra of polycrystalline 1-methylthymine.

The frequencies of the CH_3 antisymmetric bending vibrations in the N-methyl group (modes Q12 and Q13) have been calculated at 1479 and 1476 cm^{-1}, respectively. The theoretical frequency of the CH_3 symmetric bending (umbrella vibration, mode Q17), 1419 cm^{-1}, almost reproduces the experimental frequency (Table 1). The rocking vibrations (modes Q25 and Q26) have the theoretical frequencies of 1125 and 1071 cm^{-1}, respectively. In the case of mode Q25 (perpendicular rocking) the predicted IR intensity is zero, therefore this vibration cannot be detected in the experimental infrared spectra.

The calculated frequencies of the CH_3 antisymmetric bending vibrations in the C_5-methyl group (modes Q14 and Q15) are 1466 and 1437 cm^{-1}. Since the theoretical infrared intensities of these bands are low, they can overlap with the neighboring bands (Q13 and Q16). It should be noted that the theoretical frequency of the CH_3 symmetric bending (umbrella) vibration, 1394 cm^{-1} (mode Q18) is in excellent agreement with the experimental frequency of 1391 cm^{-1} in Ar (Table 1). The corresponding umbrella vibration in thymine has been assigned at very similar frequency, 1388 cm^{-1} (in Ar matrix) [3]. The CH_3 rocking vibrations (modes Q27 and Q28) are attributed to the weak bands at 1047 and 1006 cm^{-1} in the infrared spectrum of 1-MeT in argon matrix.

In contrast to several pyrimidine bases, in which the out-of-plane C_6H bending vibration is strongly coupled with other vibrations [9,11,17], in 1-MeT the corresponding normal mode Q29 is almost pure $\gamma(C_6H)$, as shown in Table 1. It is assigned to the medium intensity split band at 895/891 cm^{-1} in the infrared spectrum of 1-MeT in Ar matrix. It should be noted that both the frequency and the infrared intensity of this mode are quite well predicted by the B3LYP method. However, in calculations with the MP2 method the frequency of $\gamma(C_6H)$ vibration is underestimated by about 80 cm^{-1}, whereas at the HF level of theory it is overestimated, by about 30 cm^{-1}, in comparison to experiment (supplementary information).

3.2.4. Ring vibrations

The $\nu(C_5{=}C_6)$ stretching vibration predominantly contributes to the mode Q11 (the other components of this normal mode are C_6H in-plane bending, $C_4{=}O$ stretching and N_1–C_6 stretching vibrations, the contribution of each being lower than 10%). This mode is observed as a very weak absorption at 1665 cm^{-1} in the infrared spectrum of 1-MeT in an Ar matrix (and at 1667 cm^{-1} in a nitrogen matrix). The calculated frequency, 1669 cm^{-1}, supports this assignment. The corresponding band for thymine was observed at very similar position, 1668 cm^{-1} (Ar matrix) [3,9]. It is interest-

ing to note that in 1-MeT and thymine, the $\nu(C_5{=}C_6)$ stretching frequency is higher than in 1-methyluracil (1638 cm^{-1} in Ar) [17] and in uracil (1643 cm^{-1} in Ar) [7–9]. This effect can be attributed to electron donation from the CH$_3$ group to the adjacent $C_5{=}C_6$ bond, which strengthens the double bond character of $C_5{=}C_6$ in 1-MeT and T, in comparison to 1-MeU and U.

The strong bands at 1371/1366 and 1320 cm^{-1} in the infrared spectra of 1-MeT (Ar) are assigned to the modes Q20 and Q21, respectively. These modes involve predominant contribution from the ring stretching vibrations coupled with the in-plane bending vibrations of the C$_6$H and N$_3$H groups. The calculated Raman scattering activity of mode Q20 is the highest among all the modes in the range of frequencies of 1500–1000 cm^{-1}. According to these results, the very strong band at 1369 cm^{-1} in the Raman spectrum of solid 1-MeT can be assigned to mode Q20. It should be noted that the frequency of this mode is very similar in the monomer of 1-MeT (1371 cm^{-1}, argon and nitrogen matrices) and in solid 1-MeT.

The strongest band at 788 cm^{-1} in the Raman spectrum of solid 1-methylthymine (Fig. 4) is assigned to the ring bending mode, Q31, which can be described as the "ring breathing" vibration or the in-plane trigonal deformation of the ring. This is confirmed by the calculated high Raman scattering activity of this mode (Table 1). The next two strong bands, at 697 and 524 cm^{-1}, in the Raman spectrum of solid 1-MeT, are assigned to modes Q34 and Q37, respectively, and they arise mainly from the in-plane ring bending vibrations. The corresponding frequencies in the infrared spectrum of 1-MeT in nitrogen matrix are observed at very similar frequencies, 692 and 518 cm^{-1} in Ar (694 and 520 cm^{-1} in nitrogen), as shown in Table 1.

3.2.5. Comparison of the IR and Raman spectra of polycrystalline 1-methylthymine

The infrared and Raman spectra of polycrystalline 1-methylthymine are illustrated in Fig. 4, and the frequencies are listed in Table 2 along with their assignment. The theoretically predicted intensity pattern of the IR and Raman bands has proved to be of great help in assigning the experimental spectra.

In this part, we focus our attention on the hydrogen bonding effect in the spectra of polycrystalline 1-methylthymine. Hoogsteen [38] reported the X-ray single crystal structure of 1-methylthymine (monoclinic system, space group P2$_1$(c) C_{2h}^5 and $z = 4$). According to his results, each two molecules are arranged in centrosymmetric dimer, involving the N$_3$-H and C$_4{=}$O$_8$ groups, linked by two hydrogen bonds at the N$\cdots$O distance of 2.83 Å, while the oxygen atom from the C$_2{=}$O$_7$ group is not hydrogen bonded at all [38]. Because the major intermolecular interaction arises from hydrogen bonding within each cyclic dimer, we may expect a splitting of the C$_4{=}$O$_8$ stretching frequency into two modes, one symmetric (g) and one antisymmetric (u) with respect

to the center of symmetry in the dimer. Thus, the infrared and Raman frequencies of $\nu(C_4{=}O_8)$ should be different. A similar effect should be observed for the $\nu(N_3{-}H)$ stretching vibrations.

Thus, in the infrared spectrum of solid 1-MeT, the broad band at 3150 cm^{-1} can be assigned to the antisymmetric $\nu(N_3{-}H)$ stretching vibrations in the dimer. In the Raman spectrum of solid 1-MeT the corresponding $\nu(N_3{-}H)$ stretching vibration is probably hidden under the stronger band at 3064 cm^{-1}, which has been assigned to the $\nu(C_6{-}H)$ stretching vibration. It should be noted that in the matrix-isolated 1-MeT, the $\nu(N_3{-}H)$ vibration occurs at 3434 cm^{-1} (Ar).

The NH out-of-plane vibration is particularly susceptible to the strength of hydrogen bonding. In the infrared spectrum of crystalline 1-MeU the corresponding $\gamma(N_3H)$ vibration was assigned at 865 cm^{-1} [15], while in solid uracil it was assigned at 850 cm^{-1} [7]. For 1-MeT the assignment of this vibration is quite difficult, because there are three modes of similar frequencies, in the range of frequencies between 900 and 870 cm^{-1}. In the infrared spectrum of crystalline 1-MeT we observe a strong and broad band with a maximum at 898 cm^{-1} and two shoulders, at about 880 and 870 cm^{-1}. The former band is assigned to the out-of-plane C$_6$H bending vibration in 1-MeT (mode Q29, observed at 895/891 cm^{-1} in Ar matrix). The shoulder at about 880 cm^{-1} in IR and its strong counterpart at 879 cm^{-1} in the Raman spectrum of solid 1-MeT are attributed to the ring stretching mode (Q30). Thus, a shoulder at about 870 cm^{-1} is probably due to $\gamma(N_3H)$ in solid 1-MeT. In this assignment we were guided by the fact that the predicted Raman scattering activity of the out-of-plane $\gamma(N_3H)$ vibration is very weak. This vibration is usually not observed in the Raman spectra of cyclic imides [20]. Furthermore, the shoulder at 870 cm^{-1} disappears from the infrared spectra of the N$_3$-deprotonated 1-methylthyminate complexes with Hg(II) and K(I) [5], which confirms our assignment. A similar frequency of the $\gamma(N_3H)$ vibration in solid 1-MeT and 1-MeU (865 cm^{-1}) indicates that the strength of hydrogen bonding is similar, in both the molecules. For the monomers of 1-MeT and 1-MeU isolated in Ar matrices, the corresponding out-of-plane N$_3$H vibration is observed at 658 cm^{-1} (1-MeT, this work) and at 659 cm^{-1} (1-MeU) [17].

Examination of the infrared and Raman spectra of solid 1-MeT shows that the region of the double bond stretching vibrations is complicated by Fermi resonances with several combination bands and overtones. In the Raman spectrum of solid 1-MeT the weak band at 1706 cm^{-1} can be assigned to $\nu(C_2{=}O_7)$ vibration, since the predicted Raman scattering activity of this vibration (mode Q9) is weak, as shown in Table 1. In the infrared spectrum of solid 1-MeT the corresponding strong band is observed at 1701 cm^{-1}. It is worth mentioning that the O$_7$ atom is not involved in hydrogen bonding.

The calculated Raman scattering activities of modes Q10 and Q11 are the highest, in this range of the spec-

tra. Therefore, the very strong band at $1647\,cm^{-1}$ in the Raman spectrum of solid 1-MeT can be assigned to the $\nu(C_5=C_6)$ stretching vibration. The next strong Raman band (observed as the shoulder at $1635\,cm^{-1}$) can be assigned to the symmetric $\nu(C_4=O_8)$ stretching vibration in centrosymmetric hydrogen-bonded dimer of crystalline 1-MeT.

The presented assignment of the C=O and C=C stretching vibrations in solid 1-MeT is similar to that reported for polycrystalline 1-MeU [25]. However, it differs substantially from that reported earlier for solid 1-MeT [21,23]. For example, Lagant et al. [23] assigned the Raman band at $1647\,cm^{-1}$ to the $\nu(C_2=O)$ stretching vibration. Furthermore, Susi and Ard [21] and Lagant et al. [23] assigned the very weak bands at about 1575 and $1516\,cm^{-1}$, in the IR spectrum of solid 1-MeT, to the ring stretching and the $\nu(C_4=O)$ stretching vibration, respectively. According to our results, these assignments are wrong. It is clear that the weak bands observed at 1568 and $1515\,cm^{-1}$ in the IR spectrum of crystalline 1-MeT (this work) can be assigned to the overtones of the modes Q31 and Q32, respectively ($2\nu_{31} = 1574$ and $2\nu_{32} = 1516\,cm^{-1}$), as shown in Table 2.

4. Conclusions

The clear-cut assignment of the vibrational spectra of 1-MeT has been obtained on the basis of the calculated PED at the three levels of theory (B3LYP, MP2 and HF). Comparison of the experimental matrix isolation spectra with the theoretical results has revealed that the B3LYP method is superior to both the MP2 and HF methods in predicting the frequencies of uracil derivatives. The MP2 method consistently underestimates the frequencies of the out-of-plane $\gamma(C=O)$ and $\gamma(C=H)$ bending modes, while the HF method yields the reverse order of the frequencies of the two $\nu(C=O)$ stretching vibrations.

The theoretically predicted intensity pattern of the IR and Raman bands has proved to be of great help in assigning the experimental spectra. Investigation of the frequency shift of several bands, on passing from matrix isolation to solid state spectra, provided information on the strength of intermolecular hydrogen bonding in crystal.

Our work substantially revises the earlier assignment of the IR and Raman spectra of solid 1-MeT reported by Susi and Ard [21] and Lagant et al. [23]. It is shown that prediction of the spectra on the basis of the constrained valence force field calculation [21] or semiempirical (AM1) calculations [23] can be misleading. Several discrepancies in the earlier assignment of the spectra of 1-MeT, have been clarified.

The results obtained will aid considerably in further investigation of the intermolecular interactions of 1-MeT with other biomolecules or metal ions, by using vibrational spectroscopic methods.

5. Supporting information

The table containing the theoretical frequencies, infrared intensities and Raman scattering activities calculated by HF and MP2 methods using different basis sets for A and B conformers of 1-MeT have been deposited with the British Library at Boston Spa, Wetherly, West Yorks, UK as Supplementary Publication No. SUP 13150 (6 p.).

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