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Effect of molecular environment on the vibrational dynamics of pyrimidine bases as analysed by NIS, optical spectroscopy and quantum mechanical force fields

M. Ghomi[a,*], A. Aamouche[a], B. Cadioli[b], G. Berthier[c], L. Grajcar[d], M.H. Baron[d]

[a]*Laboratoire de Physicochimie Biomoléculaire et Cellulaire, CNRS URA 2056, Case courrier 138, Université Pierre et Marie Curie, 4 Place Jussieu, 75252 Paris Cedex 05, France.*
[b]*Dipartimento di Chimica, Università di Modena, 183 via Campi, 41100 Modena, Italy*
[c]*Institut de Biologie Physico-Chimique, 13 rue Pierre et Marie Curie, 75231 Paris Cedex 05 and Laboratoire de Radioastronomie Millimétrique, Ecole Normale Supérieure, 75231 Paris Cedex 05, France.*
[d]*Laboratoire de Spectrochimie Infrarouge et Raman, CNRS UPR 2631, 2 rue Henri Dunant, 94320 Thiais, France.*

Abstract

A complete set of vibrational spectra, obtained from several spectroscopic techniques, i.e. neutron inelastic scattering (NIS), Raman scattering and infrared absorption (IR), has been used in order to assign the vibrational modes of pyrimidine bases (uracil, thymine, cytosine) and their N-deuterated species. The spectra of solid and aqueous samples allowed us to analyse the effects of hydrogen bonding in crystal and in solution.

In a first step, to assign the observed vibrational modes, we have resorted to harmonic quantum mechanical force field, calculated at SCF + MP2 level using double-zeta 6-31G and D95V basis sets with non-standard exponents for d-orbital polarisation functions. In order to improve the agreement between the experimental results obtained in condensed phases and the calculated ones based on isolated molecules, the molecular force field has been scaled. In a second step, to estimate the effect of intermolecular interactions on the vibrational dynamics of pyrimidine bases, we have undertaken additional calculations with the density functional theory (DFT) method using B3LYP functionals and polarised 6-31G basis sets. Two theoretical models have been considered:

1. a uracil embedded in a dielectric continuum ($\varepsilon = 78$), and
2. a uracil H-bonded to two water molecules (through N1 and N3 atoms). © 1997 Elsevier Science B.V.

Keywords: Hydrogen bonding; Pyrimidine bases; Vibrational assignment

1. Introduction

Vibrational spectroscopy is an efficient method to study the structure of nucleic acids: it allows biomolecular conformational states to be understood by using vibrational marker bands arising from the various fragments as base, sugar or phosphate. The bases take a considerable part in stabilising the secondary and tertiary structures of nucleic acids. Consequently, the study of their structural and

* Corresponding author

dynamic properties is of primary importance. For this purpose, we have used several spectroscopic techniques in order to record and analyse the vibrational features of pyrimidine bases and their N-deuterated analogues, in both solid and aqueous phases. To refine our vibrational mode assignments, we have resorted to quantum-mechanical force-field calculations after full geometry optimisation of the pyrimidine bases considered first as isolated molecules (gas phase), then as interacting with implicit or explicit solvent.

2. Materials and methods

The preparation of the solid and aqueous samples as well as the whole experimental set-up, the data acquisition system and the data treatment for NIS, Raman and IR spectra, have been described in our recent papers on uracil [1,2]. To estimate structural parameters and harmonic fundamental vibrations in a state corresponding to the gas-phase, ab initio quantum mechanical calculations have been performed at the level of correlation normally used for molecules of medium size: self-consistent field (SCF) plus second-order Møller–Plesset perturbation treatment (MP2). Gaussian basis functions of double zeta form (6-31G and D95V basis sets) have been selected first. They have been enlarged by adding a non-standard set of d-polarisation functions with exponents equal to 0.75, 0.80 and 0.85 for carbon, nitrogen and oxygen, respectively. These special basis functions are referred to as $6\text{-}31G^{(*)}$ and $D95V^{(*)}$. However, in order to discuss further the hydrogen vibrational dynamics, responsible for intense NIS bands, we have undertaken additional calculations with standard basis functions 6-31G** and D95V** (involving p-polarisation functions of hydrogen atoms). We have also used the density functional theory (DFT) method for calculating the geometry and force field of pyrimidine bases with B3LYP functional and polarised basis sets. All computations were carried out by GAUSSIAN92 running on different machines in Modena and Paris. Post-processing of the vibrational modes (redundancy treatment, PED matrix calculation for assigning the normal modes) was achieved by using a home-made program (BORNS).

3. Results and discussion

In order to test the reliability of the ab initio force-field (obtained at SCF + MP2 level), and the effect of the basis functions on the vibrational wavenumbers, theoretical values are compared [1,3] with those obtained for gas phase [4–6] and Ar-matrix [7–9]. Most of the values of the ν_{exp}/ν_{calc} ratios were close to unity: this shows the suitability of the theoretical methodologies used for calculating the molecular force-fields. The addition of the p-orbitals on hydrogen atoms (6-31G** and D95V**) does not change very much the agreement between the experimental and calculated values for the vibrational wavenumbers and the NIS intensities. In order to improve the agreement between the experimental and calculated wavenumbers, as well as the NIS band intensities, the force fields of uracil [1] and thymine [2,3] have been scaled. The scaling procedure of the ab initio force fields has been fully described elsewhere [1].

Although good agreement has been obtained between the experimental and simulated NIS intensities (calculated with scaled force-fields) for the major part of the vibrational modes of pyrimidine bases some particular difficulties still exist. For instance, in our work on solid-state uracil we have shown that N–H wagging motions, especially $\omega(N1\text{–}H)$, cannot be interpreted by the scaled force fields, whereas the non-scaled (initial) force fields provide wavenumbers and assignments for both N–H waggings, in agreement with the experimental measurements in the gas phase (Table 1).

As X-ray diffraction patterns show, carbonyl and N–H groups are involved in an intermolecular H-bond network. These groups should also be H-bonded to water molecules in solution. Consequently, the spectral regions involving the vibrational modes: $\nu(N\text{–}H)$ $(3300\text{–}2700\ cm^{-1})$, $\nu(C\text{=}O)$ $(1750\text{–}1600\ cm^{-1})$, $\delta(N\text{–}H)$ $(1530\text{–}1250\ cm^{-1})$, $\omega(N\text{–}H)$ and $\omega(C\text{=}O)$ $(850\text{–}550\ cm^{-1})$ are the most sensitive to the molecular environment. Table 1 shows the experimental wave numbers of these characteristic vibrational modes for uracil.

In order to account for these effects on the uracil vibrations, we have carried out a series of calculations with DFT method as follows:

Table 1
Comparison between the calculated (non-scaled force-field) and experimental wavenumbers (cm^{-1}) for the most characteristic vibrational modes of uracil

Modes	Calculated		Experiment gas [5]	Calculated		Experiment	
	Isolated uracil MP2/6-31G$^{(*)}$	Isolated uracil DFT/6-31G$^{(*)}$		Uracil + dielectric DFT/6-31G$^{(*)}$	Uracil + 2H$_2$O DFT/6-31G$^{(\dagger)}$	Solution [1]	Solid [1]
ν(N1–H)	3655	3637	3450	3623	3413		Broad band
ν(N3–H)	3611	3598	3427	3609	3386		2700–3200
ν(C2=O2)	1868	1846	1734	1833	1784	1708	1718
ν(C4=O4)	1825	1809	1688	1784	1750	1674	1681
δ(N1–H)	1536	1511	1480	1512	1548	1506	1527
δ(N3–H)	1413	1389	1380	1385	1473	1416	1417
ω(C2=O2)	738	759			758	762	771
ω(C4=O4)	722	730			733	718	741
ω(N3–H)	698	687	672	671	859		850
ω(N1–H)	567	554	556	583	797		807

ν: bond-stretch, δ: angle-deformation, ω: wagging modes.

1. To verify first the suitability of the DFT results, the non-scaled vibrational wavenumbers obtained with this method have been compared with those issued from MP2 calculations [1]. Table 1 shows that DFT and MP2 computations provide very close wave numbers.

2. Further DFT calculations have been performed by using the Onsager model in the framework of the self-consistent reaction-field theory (SCRF) [10]. The dielectric constant and the radius of the spherical cavity used in our calculations were taken as $\varepsilon = 78$ and $a_0 = 3.92$ Å, respectively, and the basis sets were 6-31G$^{(*)}$. The wave numbers issued from this step are also reported in Table 1 and compared with those related to the isolated molecule. As can be seen, small changes in vibrational wavenumbers are produced by the continuum solvent model. This fact has also

been remarked recently in other DFT calculations [11]. The maximum wave number deviation in going from isolated to embedded uracil, does not exceed 29 cm^{-1} in our calculations (Table 1).

3. We have attempted to reproduce the environment effect by the explicit intermolecular H-bonds. The simplest and least CPU-time-consuming theoretical model which can be considered is a supermolecule constituted by a uracil H-bonded to two water molecules through N1 and N3 atoms (Fig. 1). The basis sets 6-31G$^{(\dagger)}$ used for this complex include both valence polarisation d functions on heavy atoms, as previously, and semi-diffuse s, p, d functions on atoms of uracil and water molecules involved in H-bonds. Optimised geometrical parameters of this model (not reported here) show that the uracil ring deviates slightly from planar symmetry. Another effect emerging from this

Table 2
Characteristic calculated values of interatomic distances (donor–acceptor) (/Å) and interatomic angles (donor–hydrogen–acceptor) (/°) involved in the H-bond networks of uracil

Parameters	Calc.	Parameters	Calc.
N1$\cdots$O$_W$	2.843	N3$\cdots$O$_W$	2.872
O$_W\cdots$O2	2.784	O$_W\cdots$O4	2.780
N1–H1$\cdots$O$_W$	144.41	N3–H3$\cdots$O$_W$	147.18
O$_W$–H$_W\cdots$O2	147.10	O$_W$–H$_W\cdots$O2	148.13

O$_W$ and H$_W$ are the oxygen and hydrogen, respectively, of the water molecules.
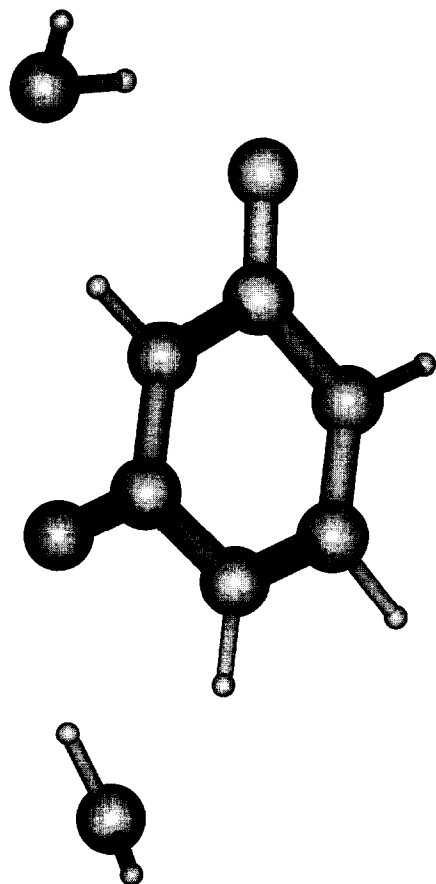H1 and H3 are the hydrogens covalently connected to N1 and N3 atoms, respectively, of uracil.

Fig. 1. Graphical representation of the geometry-optimised super-molecule (uracil + $2H_2O$) by DFT method using 6-31G$^{(+)}$ basis sets.

theoretical model is that one of the hydrogens of each water molecule is involved in an H-bond with the oxygen of the adjacent carbonyl group in the uracil ring (Fig. 1, Table 2). Moreover, the distances separating donors and acceptors, i.e. (N···O) and (O···O) distances, are well estimated by the present calculations. Computed donor–hydrogen–acceptor angles are also indicated in Table 2 for the above-mentioned hydrogen bonding between uracil and water molecules.

The calculated wavenumbers in the supermolecule model have larger deviations (from the isolated molecules) compared with those obtained from the continuum solvent model (max. deviation 243 cm^{-1}) (Table 1). At last the behaviour of N–H wagging modes upon the environmental changes is well explained by this series of calculations. The wave

numbers of these modes undergo drastic shifts from gas to condensed phases in uracil. In the gas phase and in the Ar-matrix [5,6], their values are located between 550 and 665 cm^{-1}, whereas in the solid state they are found in the 800–850 cm^{-1} range (Table 1). Our new results, based on the explicit hydrogen bonds on N1 and N3 sites, clearly reflect the important upshift of the N–H wagging wavenumbers, compared with those issued from an isolated uracil model (gas phase). The improvement of the other characteristic wavenumbers as a consequence of the H-bonding should also be emphasised.

Acknowledgements

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