Spectroscopic and theoretical study of vibrational spectra of hydrogen-bonded 2,4-dithiouracil

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Abstract

Theoretical simulation of the bandshape and fine structure of the ν_s stretching band is presented for 2,4-dithiouracil-H and 2,4-dithiouracil-D taking into account an adiabatic coupling between high-frequency N–H(D) stretching and low-frequency intermolecular N···S stretching modes, and linear and quadratic distortions of the potential energies for the low-frequency vibrations in the excited state of the N–H(D) stretching vibrations.

In order to determine the low-frequency vibrations, the experimental spectra of the polycrystalline 2,4-dithiouracil in the far infrared and the low-frequency Raman range have been recorded. The experimental frequencies in the low-frequency region are compared with the results of the HF/6-31 G** and Becke3LYP/6-31 G** calculations carried out for the 2,4-dithiouracil dimer. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Low-frequency vibrations; Spectroscopic and theoretical study; Hydrogen-bonded 2,4-dithiouracil

1. Introduction

The nucleic acids bases with sulphur atom instead of oxygen have been a subject of considerable interest since they were detected in natural tRNAs [1]. Thiouracils attract attention because they exhibit pharmacological activities. 2,4-dithiouracil analogues were tested for anti-conflict and anaesthetic activity in rats or mice [2]. The infrared spectra of 2,4-dithiouracil monomer in the N_2 matrices have been measured by Rostkowska et al. [3]. The infrared spectra of monomers in N_2 matrices were compared with the result of ab initio calculations at the HF/6-31G(d, p),

DFT(B3-LYP)/6-31G(d,p) and MP2/6-31G(d,p) by Lapinski et al. [4].

The crystal structure of 2,4-dithiouracil has been determined by Schefter and Mautner [5]. The crystals are monoclinic and adhere to the space group $P2_1/c$. The dimers of 2,4-dithiouracil are present in the structure. Every molecule is connected with two neighbouring molecules by means of two kinds of pair coupling hydrogen bonds. At the same time each molecule is a donor and an acceptor in four hydrogen bonds of the N–H···S type.

In this work, we present infrared and Raman spectra of the polycrystalline 2,4-dithiouracil in the far-infrared and the low-frequency Raman regions and compare the experimental frequencies with results of our ab initio HF/6-31 G** and Becke3LYP/6-31 G** calculations performed for the 2,4-dithiouracil dimer.

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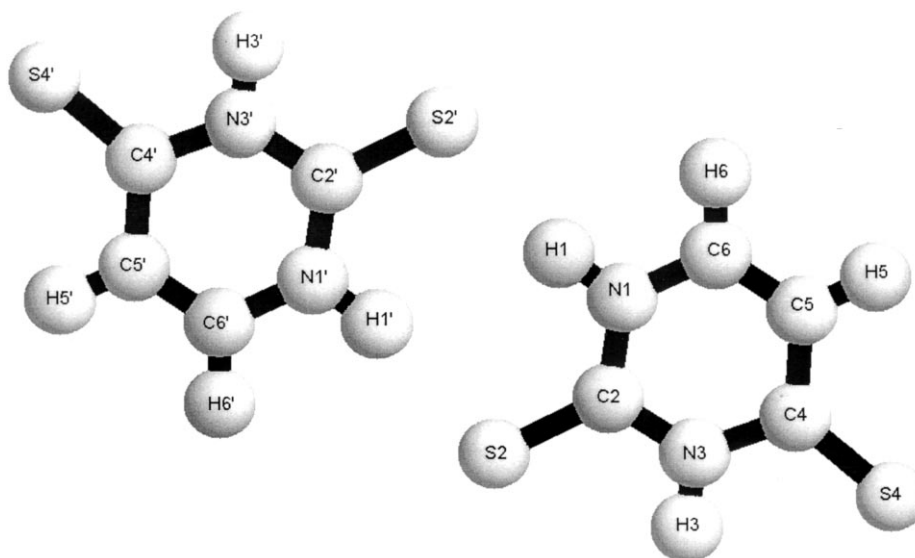*E-mail address:* wojcik@trurl.ch.uj.edu.pl (M.J. Wójcik).

Fig. 1. Geometry of the 2,4-dithiouracil dimer optimized at Becke3LYP/6-31G** level.

An important mechanism for shaping fine structure of ν_s bands in hydrogen-bonded systems is an anharmonic coupling between the high-frequency X–H stretching and low-frequency intermolecular hydrogen bond vibrations [6–9]. In this paper, we present theoretical interpretation of the fine structure of the ν_s stretching band of 2,4-dithiouracil-H and 2,4-dithiouracil-D taking into account an adiabatic coupling between the high-frequency N–H(D) stretching and the experimental low Raman frequencies described as intermolecular N···S stretching vibrations, and linear and quadratic distortions of the potential energies for these modes in the excited state of the N–H(D) stretching vibration. A similar model has been recently used to describe infrared bandshapes of the crystalline tropolone-H and tropolone-D [10].

2. Methods

Polycrystalline 2,4-dithiouracil which has been used in this investigation came from the Sigma Chemical Corporation. The same was dried over zeolite-A. Deuteration of the hydroxyl group of 2,4-dithiouracil was done by dissolving the sample in D_2O followed by the fractional distillation. Sample was deposited above zeolite-A.

Infrared ν_s bands of the polycrystalline 2,4-dithiouracil presented in this work were recorded on a Brucker IPS 48 Fourier transform spectrophotometer. Polycrystalline sample was ground with KBr and pressed. Far-infrared spectra of 2,4-dithiouracil in the range from 50 to 450 cm^{-1} were recorded on an FTS Biorad Fourier transform spectrophotometer. The polycrystalline samples were mixed and pressed with polyethylene. Low-frequency Raman spectra of the 2,4-dithiouracil in the range 50–400 cm^{-1} were recorded on a Cary 82 dispersive spectrophotometer. The slit width was 5 cm^{-1}. The energy on the sample was 60 mW. The excitation line was 514.5 nm. An ILA 120-1 argon laser was used. All the spectra were recorded at room temperature.

The structure of the 2,4-dithiouracil dimer was optimized and the vibrational frequencies were computed using the GAUSSIAN 94 programs [11] at the HF/6-31 G** and Becke3LYP/6-31 G** levels. Computation was carried out at the Computer Center of the Institute for Molecular Science in Okazaki, Japan.

3. Theoretical model

The theoretical model of the X–H stretching vibrations in hydrogen bonded systems, which we are

going to use, has been first developed by Witkowski and Maréchal [6,7]. We present a version of this model devised for the 2,4-dithiouracil dimer modified to encompass an adiabatic coupling between the high-frequency N–H stretching and two low-frequency hydrogen-bond stretching vibrations, and linear and quadratic distortions of the potential energies for these modes in the excited state of the N–H stretching vibration.

Fig. 1 presents geometry of the 2,4-dithiouracil dimer optimized at the Becke3LYP/6-31 G** level. Let q_A and q_B be the coordinates of the high-frequency N–H stretching vibrations in the first and second hydrogen bond, and Q_A and Q_B coordinates of the two low-frequency intermolecular N···S stretching vibrations. Only coupling between these vibrations will be further considered.

The vibrational Hamiltonian can be written as

$$H = T(q_A) + T(q_B) + T(Q_A) + T(Q_B) + V_A(q_A, Q_A)$$
$$+ V_B(q_B, Q_B) + V_{int}(q_A, q_B), \tag{1}$$

where T and V_i $(i = A, B)$ denote kinetic and potential energies, respectively, V_{int} is the interaction term between bond A and bond B.

In the adiabatic approximation applied to the ground state of the N–H stretching vibrations, the total vibrational wave function Ψ^0 has the form

$$\Psi^0(q_A, q_B, Q_A, Q_B) = \chi(Q_A, Q_B)\phi_A^0(q_A, Q_A)\phi_B^0(q_B, Q_B), \tag{2}$$

where the wave functions of the proton stretching vibration ϕ_i are defined by

$$[T(q_i) + V_i(q_i, Q_i)]\phi_i(q_i, Q_i) = \varepsilon_i(Q_i)\phi_i(q_i, Q_i). \tag{3}$$

In the first excited state of the fast N–H stretching vibrations, the total vibrational wavefunction Ψ^+ has the form

$$\Psi^+(q_A, q_B, Q_A, Q_B) = \alpha(Q_A, Q_B)\phi_A^+(q_A, Q_A)\phi_B^0(q_B, Q_B)$$
$$+ \beta(Q_A, Q_B)\phi_A^0(q_A, Q_A)\phi_B^+(q_B, Q_B). \tag{4}$$

The potential energies for the slow vibrations depend on the state of the fast N–H stretching vibrations. In this paper, we will assume the harmonic form

of these potentials. In the ground N–H state

$$\varepsilon_i(Q_i)/\hbar\Omega = \frac{1}{2} Q_i'^2, \tag{5}$$

where $Q_i' = Q_i\sqrt{M_i\Omega_i/\hbar}$ are expressed in dimensionless units; M_i and Ω_i denote the reduced masses and angular frequencies of the low-frequency modes.

Equilibrium values and force constants of the slow hydrogen-bond stretching coordinates Q_i' change when moving from the ground to the excited N–H state. In the excited N–H state

$$\varepsilon_i^+(Q_i)/\hbar\Omega_i = r_i + b_iQ_i' + \frac{1}{2} Q_i'^2 + dk_iQ_i'^2, \tag{6}$$

where r_i, b_i and dk_i denote vertical excitation energy, linear, and quadratic distortion parameters, respectively.

The change of equilibrium coordinates and force constants between the ground and excited states of the high-frequency vibrations are described by b_i and dk_i parameters. The values of these parameters are diminished when the hydroxylic proton is replaced by deuteron, by the ratio of square root of reduced masses for the N–H/N–D stretching vibrations [6,7].

By introducing symmetry coordinates

$$Q^\pm = \frac{1}{\sqrt{2}} (Q_A' \pm Q_B') \tag{7}$$

and using symmetry operator $\hat{C}_2$ [6,8] we obtain the effective Hamiltonians describing the total vibrational energy and eigenvectors of the low-frequency vibrations in the excited state of the N–H stretching vibration

$$H^\pm/\hbar\Omega = \frac{1}{2} (P^{+2} + P^{-2} + Q^{+2} + Q^{-2})$$
$$+ dk(Q^{+2} + Q^{-2}) + b(Q^+ + Q^-) \pm V_o\hat{C}_2, \tag{8}$$

where $P^\pm$ are the conjugate momenta of $Q^\pm$ and $V_0 = \langle \phi_A^+ \phi_B^0|V_{int}|\phi_A^0\phi_B^+\rangle_{qA,qB}/\hbar\Omega$.

The dipole moment of the complex, μ, can be expanded into a Taylor series in the vibrational coordinates

$$\mu = \mu_0 + \left(\frac{\partial\mu}{\partial q^-}\right)_0 q^- + \left(\frac{\partial\mu}{\partial Q^-}\right)_0 Q^- + \cdots \tag{9}$$

We assume that the dipole moment is independent of the slow hydrogen-bond vibrations, and neglect electrical anharmonicity. Then, we retain only two first
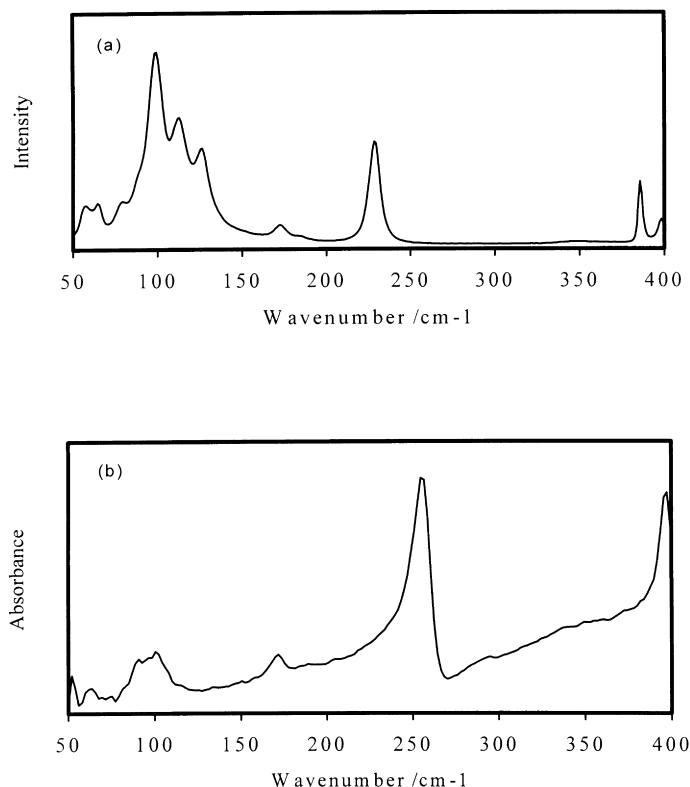
Fig. 2. (a) Raman spectrum of the polycrystalline 2,4-dithiouracil in the range from 50 to 400 cm^{-1}. (b) Infrared spectrum of the polycrystalline 2,4-dithiouracil in the range from 50 to 400 cm^{-1}.

terms in the expansion (9). With this assumption, the N–H stretching band will be composed of the Franck–Condon type progression in the hydrogen-bond low-frequency modes.

The intensity $I_{m,n}$ of the individual transition $(1, n) \leftarrow (0, m)$ is expressed by the formula

$$I_{m,n} \propto |\langle 0|\mu|1\rangle|^2 |\langle \chi_m|1 \mp \hat{C}_2|\alpha_n^{\pm}\rangle|^2 \exp(-m\hbar\Omega_i/kT). \quad (10)$$

In our interpretation of the infrared bandshape of 2,4-dithiouracil, we consider homogeneous broadening of vibrational transitions. To describe bandshapes, we used Gaussian functions assuming uniform half-width for each transition.

4. Results and discussion

The experimental far-infrared and low-frequency

Raman spectra of the polycrystalline 2,4-dithiouracil in the range up to 400 cm^{-1} are presented in Fig. 2. The spectra of the solid tropolone in this range have never been published before. The experimental frequencies are listed in Table 1 which contains also results of our ab initio HF/6-31 G** and Becke3LYP/6-31 G** frequency calculations for the 2,4-dithiouracil dimer (shown in Fig. 1). The calculated Hartree–Fock (HF) frequencies were uniformly scaled by a factor of 0.9 as recommended to compensate for the neglect of electron correlation [12]; the density functional theory (DFT) frequencies were not scaled. Calculations for the 2,4-dithiouracil dimer have been previously reported by Piskorz [13] at the STO-3G and HF/3-21 G levels and for the 2,4-dithiouracil monomer by Lapinski et al. [4] at the HF/6-31 G(d, p), DFT(B3-LYP)/6-31 G(d, p) and MP2/6-31 G(d, p) levels.

The number of observed bands is smaller than the

Table 1
Observed and calculated far-infrared and low Raman frequencies for 2,4-dithiouracil (in cm^{-1}) (i.p., in-plane; o.p., out of plane)

Sym. C_s group	Experimental solid		Calculated-dimer							Description
			Becke3LYP/6-31 G**			HF/6-31 G**				
	IR	R	IR	Int[b]	R	IR[b]	Int[c]	R[b]	Int[a]	
au			7	0.1		7				o.p. wag.
au			34	8.8		31	13.2			o.p. wag.
bg					45			35	13.4	o.p. wag.
bu	52w		56	9.3		43	10.5			twist. i.p. N$_1$···S$'_2$strech. N$'_1$···S$_2$
		57w								
ag	65w	65w			69			56	0.1	strech. i.p. N$_1$···S$'_2$
		79sh								
	90sh									
ag	100w	100s			104			81	4.2	strech. i.p. N$_1$···S$'_2$
		112s								
		125s								
au			136	2.8		136	3.5			o.p. ring def.
bg		171vw			139			139	0.3	o.p. ring def.
bg					163			154	0.3	o.p. ring def.
au	172w		163	0.005		157	0.1			o.p. ring def.
ag		229s			221			213	18.7	i.p. bend.
bu	254s		235	27.9		221	31.2			i.p. bend.
ag		386s			391			379	5.6	i.p. bend.
bg					398			390	2.4	o.p. N$_3$–H$_3$, C$_6$–H$_6$
au			399	18.1		390	21.1			o.p. N$_3$–H$_3$, C$_6$–H$_6$
bu			400	0.2		384	1.3			i.p. bend.

[a] Raman scattering activities in Å/amu.
[b] Calculated frequencies are uniformly scaled by a factor of 0.9.
[c] Infrared intensities in km/mol.

number of calculated normal modes. The correspondence between the experimental and calculated frequencies was based on comparison of frequencies and intensities and on the assignment of the calculated normal modes. The calculated frequencies agree reasonably well with the experimental ones; the results obtained with the BeckeLYP method are slightly better. The differences between the calculated and experimental frequencies are partly due to anharmonicity and crystal field interactions.

The experimental ν_s stretching bands of 2,4-dithiouracil-H and 2,4-dithiouracil-D, shown in Fig. 3, exhibit fine structures. The comparison between the spectra in the range from 2350 to 3250 cm^{-1} recorded without and after partial isotopic exchange (shown in Fig. 4) shows, that part of the bands recorded in the higher-frequency range of this region is not related to coupling of the N–H vibrations. The sub-bands observed at 3193, 3138, 3091 and 3052 cm^{-1} in the spectrum of the 2,4-dithiouracil-H are slightly shifted to lower frequencies in the 2,4-dithiouracil-D (to 3173, 3094, 3073 and 3032 cm^{-1}). In our interpretation, these bands originate from the C–H stretching vibrations. Calculated frequencies of the C–H stretching vibrations are equal 3270 and 3232 cm^{-1}. They can be assigned to observed bands 3193 cm^{-1} and 3091 cm^{-1}.

To explain the fine structures of the experimental ν_s stretching bands of 2,4-dithiouracil-H and 2,4-dithiouracil-D, we applied a theoretical model presented in Section 3. The model assumes an adiabatic coupling between the high-frequency N–H stretching and the two intermolecular low-frequency N...S stretching modes. The calculated Raman N...S
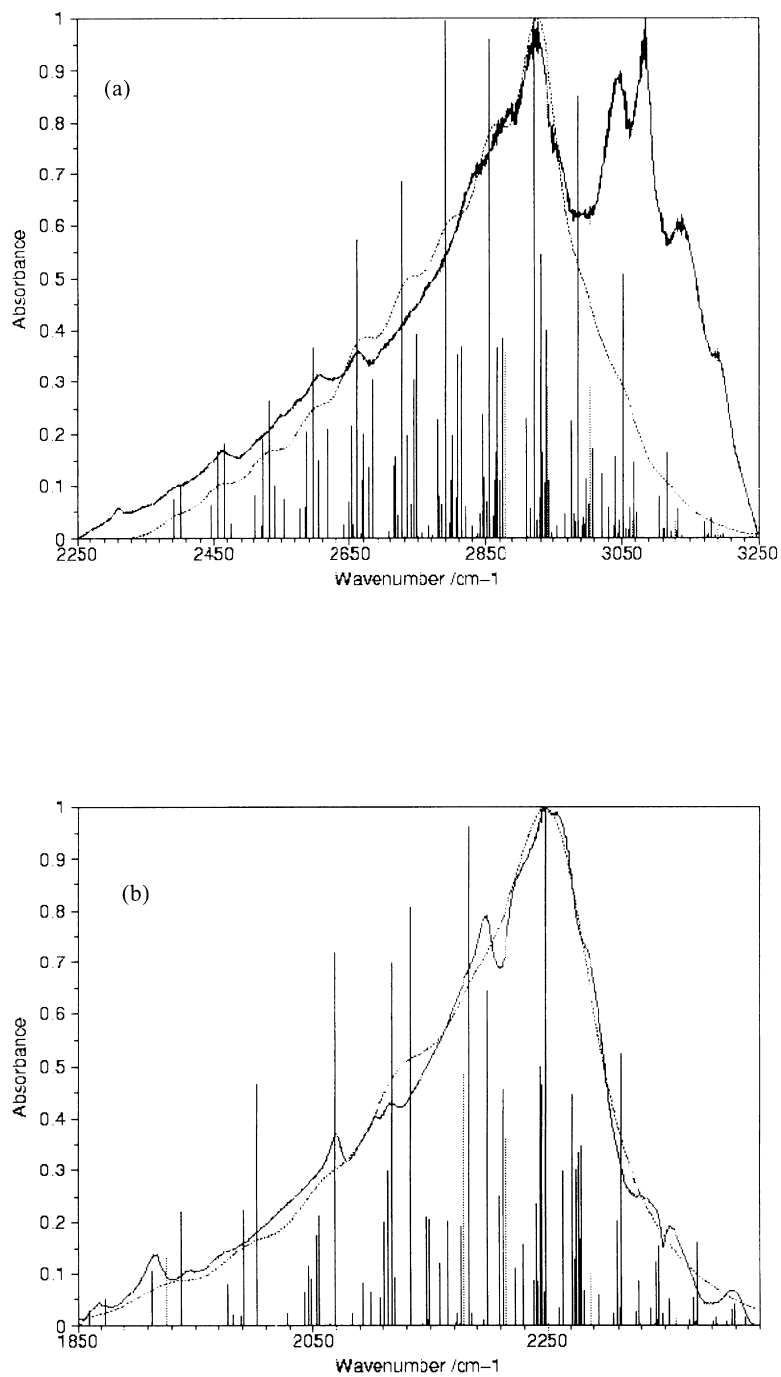
Fig. 3. Comparison between the experimental (solid line) and theoretical (dotted line) ν_s spectra for: (a) 2,4-dithiouracil-H and (b) 2,4-dithiouracil-D.
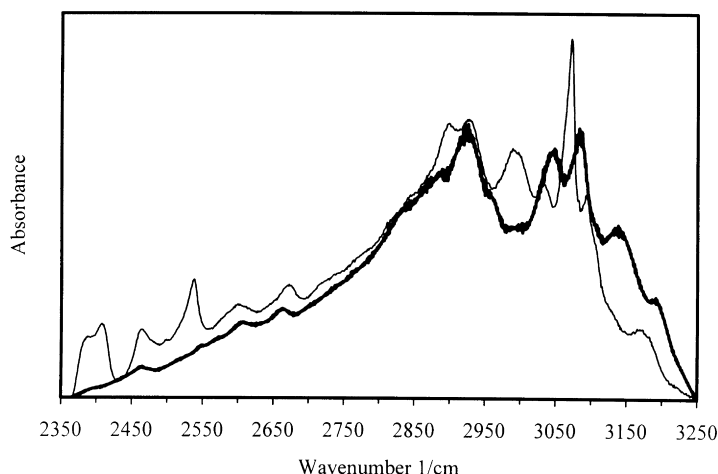
Fig. 4. Comparison between the 2,4-dithiouracil without (bold line) and after partial isotopic exchange (thin line) spectra in the range from 2350 to 3250 cm^{-1}.

stretching vibrations have frequencies 69 and 104 cm^{-1} at the Becke3LYP/6-31 G** and 56 and 81 cm^{-1} at the HF/6-31 G** levels, compared with the experimental values 65 and 100 cm^{-1}.

In our theoretical calculations, we used the experimental frequencies 65 and 100 cm^{-1} for the intermolecular N...S stretching vibrations. The coupling between the N–H stretching and the two intermolecular S···N modes, with the frequencies 65 and 100 cm^{-1}, produces the bandshape of the main ν_s band, centered for the 2,4-dithiouracil-H at 2921 cm^{-1} and for the 2,4-dithiouracil at 2248 cm^{-1}. We were unable to reproduce the observed infrared bandshapes of the N–H/N–D stretching vibrations in the crystalline 2,4-dithiouracil using in our model other low-frequency modes.

Table 2
Calculated parameters (theoretical bandshapes were calculated with the Gaussian functions with the uniform half-width equal 62 cm^{-1})

Low-frequencies S...N (exp)		2,4-Dithiouracil-H	2,4-Dithiouracil-D
$\nu_1 = 65$ cm^{-1}	b_1	1.38	1.00
	dk_1	−0.25	−0.15
	V_{01}	−0.78	−0.55
$\nu_2 = 100$ cm^{-1}	b_2	0.18	0.15
	dk_2	0.00	0.00
	V_{02}	−0.65	−0.45

To calculate energies and intensities of transitions between the ground and excited states of the N–H stretching vibrations, we had to solve the Schrödinger equation with the Hamiltonians (Eq. (8)). For the ground state eigenenergies E_m^0 and eigenfunctions χ_m are the solutions of the equations for the harmonic oscillators, and for the excited state the eigenenergies E_n^+ and eigenfunctions α_n have been calculated variationally by approximating the wavefunction of the excited state as a linear combination of the harmonic wavefunctions. Subsequently, the intensities of transitions were calculated by using Eq. (10). The calculations were done separately for the two low-frequency modes 65 and 100 cm^{-1} and the calculated bands were convoluted. To calculate bandshapes, the Gaussian functions were used assuming uniform half-width for each transition.

To determine parameters b_i, dk_i and V_{0i}, we performed series of calculations of the ν_s spectra and found minimum of calculated square deviation between the theoretical and experimental bands. The b_i, dk_i and V_{0i} parameters were determined with the accuracy of 0.01. To determine the optimum half-width of the Gaussian bands, we performed a series of calculations with the half-widths in the range from 40 to 80 cm^{-1}.

The theoretical spectra are shown and compared with the experimental spectra of the crystalline 2,4-dithiouracil-H and 2,4-dithiouracil-D in Fig. 3. The

values of the parameters b_i, dk_i and V_{0i} are given in Table 2. The theoretical spectra are shown booth as the Dirac peak spectra (vertical lines) and bandshapes (dotted lines) calculated with the uniform Gaussian half-width equal 62 cm^{-1}. The agreement between the theoretical and experimental ν_s bands for 2,4-dithiouracil-D is good. For the 2,4-dithiourcail-H, the agreement between the theoretical and experimental ν_s bands appears worse, but it is caused by the presence in the spectrum of the C–H stretching vibrations not involved in the N–H fine structure. The ν_s bandshape is formed as a result of the coupling between the N–H stretching vibrations and the two hydrogen-bond stretching intermolecular S···N vibrations. The ratios of b_i, dk_i and V_{0i} parameters used in our calculations of the ν_s bands in 2,4-dithiouracil-H and 2,4-dithiouracil-D are equal:

$$\frac{b_{1_H}}{b_{1_D}} = 1.38, \quad \frac{dk_{1_H}}{dk_{1_D}} = 1.67, \quad \frac{V_{01_H}}{V_{01_D}} = 1.42$$

and

$$\frac{b_{2_H}}{b_{2_D}} = 1.2, \quad \frac{V_{02_H}}{V_{02_D}} = 1.44.$$

The values are closed to the harmonic value $\sqrt{2}$ (there is a small deviation for the parameter dk_1 and b_2). The ratio $\nu_{s_H}/\nu_{s_D} = 1.30$.

The calculated spectra reproduce the experimentally observed asymmetry of the ν_s bands in which most of the combination transitions are located at the low-frequency side of the N–H(D) band. It should be stressed that our simulation shows that the couplings between the N–H and the low-frequency N...S stretching vibrations in the 2,4-dithiouracil produce important quadratic distortions in the potentials of the low-frequency vibrations in the excited state of the N–H vibrations. It implies that the linear distortion model used in previous simulations of infrared bands of hydrogen-bonded systems (see for example Refs. [6–9]) is not adequate for 2,4-dithiouracil and in order to explain the spectra of 2,4-dithiouracil, the quadratic dependence of the frequency of the N–H(D) vibration on coordinates of the low-frequency modes must be taken into account.

5. Conclusions

Theoretical ab initio calculations of the vibrational spectra of the 2,4-dithiouracil dimer in the low-frequency range, presented in this paper, are compared with the far-infared and low-frequency Raman spectra of the polycrystalline 2,4-dithiouracil, published for the first time. The calculated frequencies agree well with the experimental ones. The differences between the calculated and experimental are partly due to anharmonicity and crystal field interactions.

The experimental infrared frequencies assigned to intermolecular N...S stretching vibrations were used in our theoretical model calculations of the fine structure of the ν_s bands of the polycrystalline 2,4-dithiouracil-H and 2,4-dithiouracil-D, presented in this paper. The theoretical model used for these calculations was based on the Witkowski and Maréchal model [6,7] modified to encompass an adiabatic coupling between the high-frequency N–H stretching and two low-frequency hydrogen-bond stretching vibrations, and linear and quadratic distortions of the potential energies for these modes in the excited state of the N–H stretching vibrations. The calculated spectra are in good agreement with the experimental ones. Our results confirm that the linear distortion model previously used in theoretical simulations of infrared bands of hydrogen-bonded systems is inadequate for 2,4-dithiouracil, and in order to explain the spectra of 2,4-dithiouracil the quadratic dependence of the frequency of the N–H(D) vibration on coordinates of the low-frequency modes must be taken into account.

Acknowledgements

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