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Theoretical modeling of infrared spectra of benzoic acid and its deuterated derivative

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Abstract

Theoretical simulation of the ν_s stretching band is presented for benzoic acid and its OD derivative at 300 K. The simulation takes into account an adiabatic coupling between the high-frequency O–H(D) stretching and the low-frequency intermolecular O···O stretching modes, linear and quadratic distortions of the potential energy for the low-frequency vibrations in the excited state of the O–H(D) stretching vibration, resonance interaction between the two hydrogen bonds in the dimer, and Fermi resonance between the fundamental ν OH(D) stretching and the overtone of the δ O–H(D) bending vibrations.

Infrared, far-infarared, Raman and low-frequency Raman spectra of the polycrystalline benzoic acid and its deuterated form have been measured. The geometry and experimental frequencies are compared with the results of our B3LYP/6-311++G** and B3LYP/cc-pVTZ calculations.

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1. Introduction

Vibrational spectra of hydrogen bonded dimers have been a subject of numerous experimental and theretical papers [1–13]. There have been also numerous studies of Fermi resonance in hydrogen bonded complexes and crystals [14–24]. In this paper, we present infrared and Raman spectra of polycrystalline benzoic acid and its OD derivative. We, also, compare the experimental frequencies with the results of our ab initio B3LYP/6-311++G** and B3LYP/cc-pVTZ calculations. The theoretical model was used to simulate O–H(D) stretching bands. Recent infrared spectra of hydrogen bonded benzoic acid crystals have been studied experimentally and interpreted theoretically within so-called 'strong coupling' model by Flakus et al. [10,25–28].

At room temperature benzoic acid is a crystal (its melting points is at 395 K). System which draws our attention in the present paper is benzoic acid dimer. Benzoic acid crystals are monoclinic, space group is $P2_1/c = C_{2h}^5$ and Z = 4. There are two centrosymmetric hydrogen bonded dimers in each unit cell, linked 2.645 Å long hydrogen bonds. All other intermolecular distances are over 3 Å, and correspond to normal van der Waals interactions. The identity periods are: a = 5.25 Å, b = 5.14 Å, c = 21.9 Å and $\beta = 97^\circ$. The closest contact between O of one dimer and O another dimer is 3.65 Å, related by a translation b[29–32].

An anharmonic coupling between the high frequency X–H stretching and low frequency intermolecular hydrogen bond vibrations, described by Maréchal and Witkowski [2] is an important mechanism shaping fine structure of v_s bands in hydrogen-bonded systems. The most important mechanism influencing the fine structure of vibratonal spectra of hydrogen bonded system is Fermi resonance. The theoretical model of this mechanism was published by Witkowski and Wójcik [15] and Wójcik [16]. In this paper, we present a theoretical interpretation of the fine structure of the v_s stretching band of benzoic acid and its deuterated derivative. For simulation of the fine structure we used an adiabatic coupling between

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the high-frequency O-H(D) stretching and the lowfrequency intermolecular $O \cdot \cdot O$ stretching modes, linear and quadratic distortions of the potential energies for these modes in the excited state of the O-H(D) stretching vibration, resonance interaction between the two hydrogen bonds in the dimer, and Fermi resonance between the fundamental ν OH(D) stretching and the overtone of the $\delta O-H(D)$ bending vibrations.

2. Methods

Policrystalline benzoic acid, which has been used in this investigation, was purchased from the Aldrich Chemical Corporation. The purity was 99%.

Infrared spectra of benzoic acid and deuterated benzoic acid (benzoic acid-D) presented in this paper were recorded on an Equinox 55 Brucker Fourier transform spectrometer. The samples were ground with KBr and pressed. The resolution of spectra was 2 cm^{-1} in the range from 400 to 4000 cm⁻¹. Far-infrared spectrum of polycrystalline benzoic acid in the range from 50 to 450 cm⁻¹ was recorded on a FTS Biorad 60 V spectrometer in the Regional Laboratory of Physico–Chemical Analyses and Structural Research in Kraków. The samples were mixtured with polyethylene and pressed. The resolution of spectra in this region was 2 cm⁻¹.

Raman spectra of benzoic acid were recorded on a Renishaw 2000 Micro Raman System. Samples were excited by a near-infrared diode laser generating light of wavelength 785 nm (30 mW) and Argon-Ion laser generating light of wavelenght 514 nm (50 mW). The resolution was 2 cm^{-1} .

Deuteration of the carboxylic group was done by dissolving the sample in D_2O (purchased from IBJ Świerk, 99.1% purity) then heating under a flux condensor, filtering and drying. The sample was deposite above zeolite-A.

The geometry of benzoic acid was optimized and the vibrational frequencies were computed using the GAUSSIAN 98 programs [33] at the B3LYP/6-311++G** and B3LYP/cc-pVTZ levels. Computations were carried out

in the Department of Materials Chemistry, Uppsala University in Sweden.

3. Theoretical model

The theoretical model of Fermi resonace in infrared spectra of hydrogen bonded carboxylic acid dimer, which we are going to use, has been first developed by Wójcik [16]. We used an extended version of this model, modified to encompass an adiabatic coupling between the high frequency O-H(D) stretching and low frequency hydrogen bond stretching vibrations, linear and quadratic distortions of the potential energies for these modes in the excited state of the O-H(D) stretching vibration, resonance interaction between the two hydrogen bonds in a dimer, and Fermi resonance interaction between the fundamental ν OH(D) stretching and the overtone of the $\delta O-H(D)$ bending vibrations.

Fig. 1 present geometry of the benzoic acid dimer optimized at the B3LYP/cc-pVTZ level. In this case the two hydrogen bonds of this dimer are related by the symmetry operation C_2 corresponding to the two-fold symmetry axis.

The vibrational hamiltonian, *H*, can be written as:

$$H = T(Q_1) + T(Q_2) + h_{s,1} + h_{s,2} + h_{b,1} + h_{b,2} + V'_{1,ah} + V'_{2,ah} + V'_{res},$$
(1)

where $T(Q_i)$ is the kinetic energy operator of the lowfrequency vibration; $Q_i(i = 1, 2)$ are the coordinates of the two low frequency intermolecular $O \cdot O$ stretching modes, denote ν_{σ} ; $h_{s,i} = T(q_{s,i}) + V(q_{s,i}, Q_i)$ is the vibrational hamiltonians of the high frequency ν_s vibrations; $q_{s,i}(i = 1, 2)$ are the coordinates of the high frequency O-H stretching vibrations, in the first and second hydrogen bond; $h_{b,i} = T(q_{b,i}) + V(q_{b,i})$ is the vibrational hamiltonians of the high frequency ν_b vibrations; $q_{b,i}(i = 1, 2)$ are the coordinates of the in plane bending vibrations in the first or second hydrogen bond; $V'_{i,ah}(q_{s,i}, q_{b,i})$ is the anharmonic coupling terms between the hydrogen bond stretching and bending vibrations; $V'_{i,res}(q_{s,1}, q_{s,2})$ is the resonance



Fig. 1. Geometry of the benzoic acid dimer, optimized at the B3LYP/cc-pVTZ level.

interaction potential between the two equivalent hydrogen bonds; V is the potential energy. We neglect interactions of ν_s and ν_{σ} vibrations with the other vibrations of the system. Fermi resonance is considered between the fundamental vibration ν_s and the first overtone of the bending mode ν_b . With a suitable change of the anharmonic coupling parameter the in plane bending can be replaced by any other vibration of the system. We do not consider any coupling between the ν_b and ν_{σ} vibrations.

In the first exciting state of O–H stretching vibrations, the total vibrational wavefunction, $\Psi_{i'}^+$, has the form:

$$\Psi_{j}^{+} = \alpha_{1}\chi_{s,1}^{+}\chi_{b,1}\chi_{s,2}\chi_{b,2} + \beta_{1}\chi_{s,1}\chi_{b,1}^{+}\chi_{s,2}\chi_{b,2} + \alpha_{2}\chi_{s,1}\chi_{b,1}\chi_{s,2}^{+}\chi_{b,2} + \beta_{2}\chi_{s,1}\chi_{b,1}\chi_{s,2}\chi_{b,2}^{+}, \qquad (2)$$

where $\chi_{s,i}(q_{s,i}, Q_i)$ are the eigenfunctions of the hamiltonians $h_{s,i}$; $\chi_{b,i}(q_{b,i})$ the eigenfunctions of the hamiltonians $h_{b,i}$; $\alpha_i(Q)$, $\beta_i(Q)$ the wavefunctions of the hydrogen-bond vibrations ν_{σ} , not determined yet. Superscript '+' – marks the excited state of ν_s and of the first overtone of ν_b .

Applying the procedure of Longuet–Higgins [38] to the Schrödinger equation with hamiltonian (1) and the wavefunction (2), enables to find the $\alpha_i(Q)$, $\beta_i(Q)$ functions and the total vibrational energy. With the crude adiabatic approximation assumed for the ν_s and ν_b vibrations the effective hamiltonian H^{eff} for the low-frequency vibration ν_σ takes the four-dimensional matrix form: The energies $\varepsilon_{s,i}(Q_i)$ of the high-frequency hydrogen stretching vibration of individual hydrogen bonds determine the effective potential governing the low-frequency hydrogen bond vibrations. Those potentials are assumed harmonic and to have the same force constant in the upper and lower states of the hydrogen bond stretching vibrations:

$$\varepsilon_{s,i} = \frac{1}{2}KQ_i^2; \qquad \varepsilon_{s,i}^+ = R + LQ_i + \frac{1}{2}DKQ_i^2 + \frac{1}{2}KQ_i^2,$$
(5)

where R is vertical excitation energy; L the linear distortion parameter, DK the quadratic distortion parameter, K the quadratic force constant.

Introducing dimensionless quantities:

$$q_{i} = Q_{i}(M\Omega/\hbar)^{1/2}, \quad p_{i} = P_{i}/(\hbar M\Omega)^{1/2},$$

$$b = L/(\hbar M\Omega^{3})^{1/2}, \quad V_{ah} = V'_{ah}/\hbar\Omega, \quad r = R/\hbar\Omega,$$

$$r' = \varepsilon_{b,i}^{+}/\hbar\Omega, \quad dk = DK/M\Omega^{2}, \quad V_{res} = V'_{res}/\hbar\Omega,$$

(6)

where Ω is the angular frequency for ν_{σ} vibration and M is reduced mass for ν_{σ} vibration ($K = M\Omega^2$). We can re-write the hamiltonian (3) in a compact form, using the two orthogonal sets of Dirac matrices σ and ρ :

$$H^{\text{eff}} = \begin{bmatrix} \{T(Q_1) + T(Q_2) + \varepsilon_{s,1}^+(Q_1) \\ +\varepsilon_{s,2}(Q_2) + \varepsilon_{b,1} + \varepsilon_{b,2}; \} & V'_{ah}; & V'_{\text{res}}; & 0 \\ V'_{ah}; & \{T(Q_1) + T(Q_2) + \varepsilon_{s,1}(Q_1) \\ & +\varepsilon_{s,2}(Q_2) + \varepsilon_{b,1}^+ + \varepsilon_{b,2}; \} & 0; & 0 \\ V'_{\text{res}}; & 0; & \{T(Q_1) + T(Q_2) + \varepsilon_{s,1}(Q_1) \\ & & +\varepsilon_{s,2}^+(Q_2) + \varepsilon_{b,1} + \varepsilon_{b,2}; \} & V'_{ah} \\ 0; & 0; & 0; & V'_{ah}; & \{T(Q_1) + T(Q_2) + \varepsilon_{s,1}(Q_1) \\ & & +\varepsilon_{s,2}(Q_2) + \varepsilon_{b,1} + \varepsilon_{b,2}\} \end{bmatrix},$$
(3)

where $\varepsilon_{s,i}(Q_i)$ are eigenvalues of the hamiltonians $h_{s,i}$; $\varepsilon_{b,i}$ the eigenvalues of the hamiltonians $h_{b,i}$; V'_{ah} the matrix element of the anharmonic coupling between excited states of ν_s and ν_b ; V'_{res} the vibrational analogue of the exchange integral. The V'_{ah} and V'_{res} are defined as:

$$V_{ah}' = \langle \chi_{s,1}^{+} \chi_{b,1} \chi_{s,2} \chi_{b,2} | V_{1,ah} | \chi_{s,1} \chi_{b,1}^{+} \chi_{s,2} \chi_{b,2} \rangle_{q_{s},q_{b}},$$

$$= \langle \chi_{s,1} \chi_{b,1} \chi_{s,2}^{+} \chi_{b,2} | V_{2,ah} | \chi_{s,1} \chi_{b,1} \chi_{s,2} \chi_{b,2}^{+} \rangle_{q_{s},q_{b}}$$

$$V_{res}' = \langle \chi_{s,1}^{+} \chi_{b,1} \chi_{s,2} \chi_{b,2} | V_{res} | \chi_{s,1} \chi_{b,1} \chi_{s,2}^{+} \chi_{b,2} \rangle_{q_{s},q_{b}}.$$
(4)

$$H^{\text{eff}}/\hbar\Omega = \frac{1}{2}(p_1^2 + q_1^2)\mathbf{1} + \frac{1}{2}(p_2^2 + q_2^2)\mathbf{1} + \frac{1}{4}\left(bq_1 + bq_2 + \frac{1}{2}dkq_1^2 + \frac{1}{2}dkq_2^2\right)(\mathbf{1} + \sigma_3) + \frac{1}{4}\left(bq_1 - bq_2 + \frac{1}{2}dkq_1^2 - \frac{1}{2}dkq_2^2\right)(\mathbf{1} + \sigma_3)\rho_3 + \frac{1}{2}M'\sigma_3 + V_{ah}\sigma_1 + \frac{1}{2}V_{\text{res}}(\mathbf{1} + \sigma_3)\rho_1 + \frac{1}{2}(r + r')\mathbf{1}$$
(7)

The dimensionless parameter M' means the difference between the vertical excitation energy r of the hydrogen bond stretching vibration (to the first excited state) and the excitation energy to the first overtone of the proton bending vibration $r'(\varepsilon_{b,i} = 0, \varepsilon_{b,i}^+ = r')$. For exact Fermi resonace M' = 0. 1 is the unit matrix. The four-dimensional Dirac matrices have the following forms:

$$\sigma_{1} = \begin{bmatrix} 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{bmatrix}, \ \sigma_{3} = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \end{bmatrix},$$

$$\rho_{1} = \begin{bmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{bmatrix}, \ \rho_{3} = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{bmatrix}.$$
(8)

In the hamiltonians (3) and (7) we have neglected the resonance interaction between the two hydrogen bonds involving the overtone states of the bending ν_b vibrations.

Applying the symmetry operator C_2 , we can reduce the four-dimensional hamiltonian (7) to the two-dimensional hamiltonians h^+ and h^- . The hamiltonians h^+ and h^- are given by the formulas:

$$h^{\pm} = \frac{1}{2}(p_1^2 + q_1^2)\mathbf{1} + \frac{1}{2}(p_2^2 + q_2^2)\mathbf{1} + \frac{1}{2}\left(bq_1 + \frac{1}{2}dkq_1^2\right)\mathbf{1} + \frac{1}{2}\left(bq_1 + \frac{1}{2}dkq_1^2 + M'\right)\gamma_3 + V_{ah}\gamma_1 \pm \frac{1}{2}V_{res}(\mathbf{1} + \gamma_3)C_2 + \frac{1}{2}(r + r')\mathbf{1}$$
(9)

where γ_i are the two-dimensional Pauli matrices:

$$\gamma_1 = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}, \ \gamma_3 = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}.$$
(10)

The hamiltonians (9) describe the two low-frequency vibrations which are coupled through the high-frequency motions. The two mechanisms, i.e. Fermi resonance and exchange resonance interaction, which are not in general separable, contribute to the spectra, which are irregular and no longer exhibit Franck-Condon type progressions.

The IR intensities of the transitions from the ground state to the excited state of the hydrogen bond stretching vibrations are given by the formula:

$$I_{jj'} \sim |\langle \Psi_j | \mu | \Psi_j^+ \rangle|^2 \exp\left(\frac{-j\hbar\Omega}{kT}\right),\tag{11}$$

where ψ_j is the *j*th wavefunctions of the ground vibrational state of the ν_s and ν_b vibrations; $\psi_{j'}^+$ the *j'*th wavefunctions of the excited vibrational state, μ the dipole moment of the dimer.

The wavefunctions ψ_{j}^{+} are given by Eq. (2) and the wavefunctions ψ_{j} , in the adiabatic approximation, have the form:

$$\Psi_{j} = \alpha_{0}^{(j)} \chi_{s,1} \chi_{b,1} \chi_{s,2} \chi_{b,2}.$$
(12)

Neglecting the dependence of the dipole moment μ on the coordinates Q of the low frequency hydrogen bond vibrations we obtain the intensity given as a combination of the Franck-Condon integrals between the wavefunctions $\alpha_0^{(j)}$ and the wavefunctions $\alpha_{\pm}^{(j')}$ and $\beta_{\pm}^{(j')}$. The intensity is given by following equation:

$$I_{jj'} \sim |\mu_{0s}|^2 \{ |\langle \alpha_0^{(j)}| 1 \pm C_2 |\alpha_{\pm}^{(j')} \rangle|^2 \\ + \delta^2 |\langle \alpha_0^{(j)}| 1 \pm C_2 |\beta_{\pm}^{(j')} \rangle|^2 \} \exp\left(\frac{-j \hbar \Omega}{kT}\right),$$
(13)

where:

 $\mu_{0s} = \langle \chi_{s,1}\chi_{b,1}\chi_{s,2}\chi_{b,2} | \mu | \chi^+_{s,1}\chi_{b,1}\chi_{s,2}\chi_{b,2} \rangle_{qs,qb}$

and δ^2 is the ratio of the intensities of the bending overtone to the fundamental stretching vibrations.

To obtain formula (13) from (11) we have used symmetrical form of the eigenfunctions of the hamiltonian (7):

$$\begin{bmatrix} \alpha_{\pm}^{(j')} \\ \beta_{\pm}^{(j')} \\ \pm C_2 \alpha_{\pm}^{(j')} \\ \pm C_2 \beta_{\pm}^{(j')} \end{bmatrix}$$
(14)

derived from the eigenfunctions of the two-dimensional hamiltonians (9):

$$\begin{bmatrix} \alpha_{\pm}^{(f)} \\ \beta_{\pm}^{(f)} \end{bmatrix}$$
(15)

The eigenenergies of the hamiltonians h^{\pm} (9) and eigenfunctions α_{\pm} and β_{\pm} (15) have been calculated numerically by expanding the eigenfunctions into series of harmonic oscillators and diagonalising the resulting energy matrices.

The parameters b, dk, V_{res} and M' of the hamiltonians (9) can be evaluated from the succesive moments M_k of the infrared band. These moments are defined as:

$$M_k = \frac{\sum_{j,j'} I_{jj'} (E_{j'}^+ - E_j)^k}{\sum_{j,j'} I_{jj'}},$$
(16)

where E_j are the eigenenergies of the ground state; E_j^+ the eigenenergies of the excited state.

The first and second transition moments describe the centre of gravity of the spectrum ω_0 and its theoretical

half-widths $\Delta \omega$:

$$\omega_0 = M_1 \qquad \Delta \omega = (M_2 - M_1^2)^{1/2}.$$
 (17)

Assuming, as previously, that the intensity of transitions to the overtone states is negligible compared to the fundamental transitions and applying formula (13) we obtain from (16) and (17):

$$\omega_0 = r - V_{\text{res}}$$
$$\Delta \omega = \left[\frac{1}{2} \left(b^2 + \frac{1}{2} dk^2 \right) \coth\left(\hbar \Omega / 2kT\right) + V_{ah}^2 \right]^{1/2}$$
(18)

We see that the anharmonic term V_{ah} increases the width of the spectrum but does not influence its position, whereas the exchange interaction, described by the parameter V_{res} , shifts the centre of gravity but does not change the width.

The formulas (18) can also be generalized for the case of non-negligible intensity of transitions to the overtone bending vibrations:

$$\omega_0 = r - V_{\rm res} + 2\delta V_{ah} \cos\varphi + \theta(\delta^2); \tag{19}$$

$$\Delta \omega = \left[\frac{1}{2} \left(b^2 + \frac{1}{2} dk^2 \right) \coth\left(\hbar \Omega/2kT\right) \right]^{1/2} + V_{ah}^2 - 2\delta V_{ah} M' \cos\varphi + \theta(\delta^2) \right]^{1/2}$$

where φ is the angle between the transition dipole moments to these states.

4. Results and discussion

Fig. 1 presents the geometry of the benzoic acid dimer optimized at the B3LYP/cc-pVTZ level. Optimized geometries, calculated at the B3LYP/cc-pVTZ and B3LYP/6-311++G** levels, are summarized in Table 1 and compared with the experimental data. This table contains also results of Alcolea Palafox et al. [34] ab initio B3LYP/6-31G** frequencies calculation for the benzoic acid dimer. The calculated values reproduce reasonably well the experimental bond lengths and angles. The largest differences are observed for the bonds which involve the hydrogen atoms. The agreement between the calculated and the experimental angles is slightly worse than for the bond lengths. The largest discrepancies are for the angles which involve the oxygen atoms, both in the carboxylic and ester groups. On the base on our calculations we can conclude that optimization at the B3LYP/cc-pVTZ level gives better resuls.

The experimental far-infrared spectrum of the polycrystalline benzoic acid in the range $50-450 \text{ cm}^{-1}$ and its standard infrared spectrum in the range $400-4000 \text{ cm}^{-1}$, recorded by us, are presented in Fig. 2. Fig. 3 presents a far-Raman spectrum in the range $50-400 \text{ cm}^{-1}$ and Raman spectrum in the range $400-4000 \text{ cm}^{-1}$. The experimental IR and Raman frequencies are shown in Table 2. This table

Table 1 Optimized geometries of benzoic acid dimer by the B3LYP/6-311++G** and B3LYP/cc-pVTZ methods

	Calculated		Experimental	B3LYP/ 6-31G***	
_	B3LYP/ 6-311++G**	B3LYP/ cc-pVTZ			
Bond leng	ths (Å)				
$O_1 \! \cdots \! O_2{'}$	2.663	2.638	2.64 ^b ; 2.629 ^c ; 2.633 ^d	2.625	
$O_1 - H_1'$	1.663	1.635	1.64 ^c	1.617	
O_2-H_1	1.000	1.003	0.988 ^c	1.006	
$C_1 - O_1$	1.230	1.229	1.24 ^b ; 1.268 ^c ; 1.263 ^d	1.237	
$C_1 - O_2$	1.323	1.318	1.29 ^b ; 1.275 ^c ; 1.275 ^d	1.320	
$C_2 - C_1$	1.486	1.485	1.48 ^b ; 1.484 ^d	1.487	
$C_2 - C_3$	1.400	1.396	1.39; 1.390 ^c	1.402	
$C_3 - C_4$	1.391	1.388	1.42 ^b ; 1.387 ^d	1.393	
$C_4 - C_5$	1.395	1.391	1.36 ^b ; 1.379 ^d	1.397	
$C_5 - C_6$	1.395	1.392	1.37 ^b ; 1.384 ^c	1.397	
$C_6 - C_7$	1.390	1.386	1.41 ^b ; 1.401 ^d	1.392	
$C_7 - C_2$	1.400	1.396	1.39 ^b ; 1.392 ^c	1.402	
C ₃ -H ₃	1.082	1.080	0.79 ^b	1.084	
$C_4 - H_4$	1.084	1.082	0.96 ^b	1.086	
C ₅ -H ₅	1.084	1.082	0.91 ^b	1.086	
$C_6 - H_6$	1.084	1.082	0.96 ^b	1.086	
C_7-H_7	1.083	1.080	0.79 ^b	1.084	
Bond angl	es (°)				
$O_1H_1'O_2'$	177.14	178.73			
$C_1O_1H_1'$	126.84	124.79		124.63	
$C_1O_2H_1$	110.27	110.50		110.41	
$O_1C_1O_2$	123.26	123.44	$122^{b}; 123.2^{d}$	123.72	
$O_2 C_1 C_2$	114.50	114.59	118 ^b ; 119.9 ^c	114.62	
$C_2C_1O_1$	122.24	121.97	$122^{\rm b}; 120.2^{\rm d}$	121.66	
$C_1C_2C_3$	121.40	121.42	122 ^b ; 118.0 ^c	121.68	
$C_{3}C_{2}C_{7}$	119.90	119.82	119 ^b ; 119.9 ^d	119.95	
$C_7 C_2 C_1$	118.70	118.76	119 ^b ; 118.8 ^c	118.73	
$C_2C_3C_4$	119.86	119.91	118 ^b ; 120.1 ^d	119.84	
$C_3C_4C_5$	120.02	120.07	123 ^b ; 119.9 ^c	120.08	
$C_4C_5C_6$	120.15	120.13	118 ^b ; 120.3 ^d	120.17	
$C_5C_6C_7$	119.98	119.97	122 ^b ; 119.7 ^c	119.97	
$C_6C_7C_2$	120.02	120.08	120 ^b ; 119.8 ^d	119.99	
$C_2C_3H_3$	119.48	119.46		119.36	
$H_3C_3C_4$	120.66	120.63		120.80	
$C_3C_4H_4$	119.85	119.84		119.84	
$H_4C_4C_5$	120.07	120.07		120.08	
$C_4C_5H_5$	119.91	119.92		119.91	
$H_5C_5C_6$	119.94	119.95		119.92	
$C_5C_6H_6$	120.09	120.09		120.10	
$H_6C_6C_7$	119.93	119.94		119.93	
$C_6C_7H_7$	121.12	121.10		121.29	
$H_7C_7C_2$	118.86	118.82		118.72	
^a Ref. [3	34].				

^b Ref. [29].

^c Ref. [30].

^d Ref. [31].

contains also results of our ab initio B3LYP/cc-pVTZ and B3LYP/6-311++G** frequencies calculations for the benzoic acid dimer. To compensate for partial neglect of electron correlation [39], the calculated frequencies were uniformly scaled by a factor of 0.9754 and 0.9786 for B3LYP/6-311++G** and B3LYP/cc-pVTZ, respectively. The scaling factor has been determined as the slope of



Fig. 2. Far-infrared spectra (a) and infrared spectra (b) of the polycrystalline benzoic acid.

the correlation diagram for experimental versus computed frequencies. We used the MOLEKEL program [37] to visualize the amplitudes of the normal modes. The corespondence between the experimental and calculated frequencies was based on the comparison of frequencies and intensities and on the assignment of calculated normal modes. The differences between the calculated and experimental frequencies are due to anharmonicity, intermolecular interactions, correlation effects and the limited basis set.

The experimental ν_s stretching bands of benzoic acid and its O–D derivative are shown in Figs. 4–5. All spectra exhibit fine structure. To explain the fine structure we applied a theoretical model presented in the preceding section. The intermolecular O···O stretching vibration observed in the far-Raman spectrum has a frequency 114 cm⁻¹ (Table 2). The calculated frequencies for this mode are 119 and 114 cm⁻¹ in B3LYP/cc-pVTZ and B3LYP/6-311++G**, respectively. There is another mode involving intermolecular hydrogen bond stretching observed in the far-Raman spectrum at 420 cm⁻¹.



Fig. 3. Far-Raman spectra (a) and Raman spectra (b) of the polycrystalline benzoic acid. Samples were excited by light of wavelenght (a) 785 nm and (b) 514 nm.

The calculated frequencies are 419 and 413 cm^{-1} in B3LYP/cc-pVTZ and B3LYP/6-311++G**, respectively.

In our theoretical calculations we used these two experimental Raman frequencies v_{σ} , 114 and 420 cm⁻¹, for the intermolecular O···O stretching vibrations. The coupling between the O–H(D) stretching and the intermolecular O···O modes produces bandshapes of the main v_s bands as presented in Figs. 4–5. We were unable to reproduce the observed infrared bandshapes of the O–H(D) stretching vibrations in benzoic acid using in our model other low-frequency modes.

To determine the optimum parameters we performed a series of calculations of the ν_s stretching band to minimize the square root deviation between the experimental and theoretical spectra. All parameters which were determined in minimization procedure were increased by 0.01.

The theoretical spectra of benzoic acid and its deuterated derivative are shown and compared with the experimental ones in Figs. 4 and 5. The values of the optimized parameters are given in Table 3. δ^2 denotes the ratio of the intensities of the bending overtone to the fundamental stretching vibrations. The theoretical spectra are shown as δ functions and as bandshapes calculated with Gaussian functions of the half-width. For benzoic acid-H the positions and the fine structure of the theoretical ν_s bands agree well with the experimental spectrum (Fig. 4). The positions of the major bands are well reproduced, but the calculated intensities are too small. The theoretical bandshape is underestimated. As showed by Flakus [10], bandshapes of the spectra of C₆H₅COOH and C₆D₅COOH are different.

In Table 4 we showed the calculated total atomic charges in the benzoic acid. The calculated partial charges of the hydrogen atom H₃ are equal 0.168 e and 0.128 e, and of the oxygen atom O_2 are equal $-0.393 \ e$ and $-0.282 \ e$, in B3LYP/6-311++G** and B3LYP/cc-pVTZ, respectively. The calculated bond lenght $O_2 \cdots H_3$ is equal 2.426 and 2.424 Å, in B3LYP/6-311++G** and B3LYP/cc-pVTZ, respectively. The $O_2 \cdots H_3$ bond lenght is slightly shorter than hydrogen bond O···O lenght, equal 2.64 Å. This might probably be the source of another resonance mechanism between the fundamental $\nu OH(D)$ stretching and the $\delta C - H(D)$ bending vibrations. The effect of deuteration (Fig. 5) is reproduced correctly. In all cases the ν_s bandshapes are formed as a result of the complex mechanism of coupling between the O-H(D) stretching vibration and the hydrogen bond stretching intermolecular O···O vibrations, with linear and quadratic distortions of the potential energies for these modes in the excited state. This coupling involves resonance interaction between the two hydrogen bonds and Fermi resonance between the O-H(D) stretching and the overtone of the O-H(D) bending vibrations, all acting at the same time.

The ratios of b and dk parameters used in our calculation of the ν_s bands in benzoic acid-H and benzoic acid-D are: $b_{1H}/b_{1D} \approx 1.83, b_{2H}/b_{2D} \approx 1.60, dk_{1H}/dk_{1D} \approx 1.25, dk_{2H}/dk_{2D} \approx 1.30$. The harmonic value of these

No. Sym.		Calculated B3LYP ν (cm ⁻¹)		Experimental ν (cm ⁻¹)		Literature Infrared $u(cm^{-1})$	Approximate description	
		6-311++G**	cc-pVTZ	IR	Raman	ν (cm)		
1	A	21	23			25 ^a	'Butterfly'	
2	A.	32	32			35 ^a	Torsion ('twist')	
3	B_{a}^{u}	40	69			41 ^a	oop monomers rocking	
4	B_{μ}^{g}	59	62	63		71 ^a	Cogwheel	
5	B_{-}	62	63			79 ^a	π (Ph-COOH) twisting	
6	-g A_{μ}	85	85	80		94 ^b	τ (-COOH)	
7	$A_{a}^{''}$	103	106	110	98	110 ^a	H-bond shearing	
8	Å	111	116		114	127^{a}	$\nu_{\rm c}(0\cdots0)$	
9	A.	168	166			146 ^b	γ (Ph-COOH)	
10	B.	175	183				γ (Ph-COOH)	
11	A_{a}	253	257				$\delta(CO \cdots O) + \delta(CC)$	
12	B.	276	285	283			$\delta(CO \cdots O) + \delta(CC)$	
13	- u B.,	379	383	387			$\nu(CC) + \delta(CC)_{rings}$	
14	B	404	409	413			$\gamma(CC)_{rince}$	
15	A	405	409	110			$\gamma(CC)_{rings}$	
16	A	413	419		420		$v(0,,0) + \delta(CC)$	
17	A	435	440	432	420	421 ^b	$\gamma(CC)$	
18	R R	433	443	452		721	$\gamma(CC)$	
10	D_g	400	503				8(CC)	
20	R R	533	541	552		401 ^b	$\delta(CC) \pm \chi(0,, 0)$	
20	D_u	616	621	552	617	491	$\delta(CC) + \lambda(0.00)$	
21	Ag P	616	621	610	017	615 ^b	S(CC)	
22	\mathbf{D}_{u}	652	621	019	660	015	$\delta(CC)_{rings}$	
25	Ag D	033	038	660	000	660b	$\partial(CC)_{rings} + \partial(COOH)$ series	
24	D_u	002	008	008	(9(009	$\partial(CC)_{rings} + \partial(COOH)$ setss.	
25	B_g	0//	692	(95	080	cont	$\gamma(CC)_{rings} + \gamma(CC)$	
20	A _u	679	092	085	710	087	$\gamma(CC)_{rings} + \gamma(CC)$	
27	B_g	690 700	/13	709	/12	711b	$\gamma(CH)_{rings} + \gamma(CC)$	
28	A _u	706	/12	/08	70/	/11	$\gamma(CH)_{rings} + \gamma(CC)$	
29	B_g	784	813		/96		$\gamma(CH)_{rings} + \gamma(CC)_{rings}$	
30	A_g	/84	791	007	813	acab	$\nu(CC)_{rings} + \delta(COOH)$ sciss.	
31	B_u	/96	804	806		/0/~	$\nu(CC)_{rings} + \delta(COOH)$ sciss.	
32	Au	811	813	810		813	$\gamma(CH)_{rings} + \gamma(CC)_{rings}$	
33	A_u	845	853			orch	γ (CH) _{rings}	
34	B_g	845	853			856	γ (CH) _{rings}	
35	B_g	864	949				γ(OH)	
36	B_g	937	952			oorth	$\gamma(CH)_{rings}$	
37	A_u	939	952	920		937 ⁸	γ (CH) _{rings}	
38	A_u	958	989	936		960°	γ(OH)	
39	B_g	975	985		992	a – ch	$\gamma(CH)_{rings} + \gamma(OH)$	
40	A_u	975	984	945		974 ⁸	$\gamma(CH)_{rings} + \gamma(OH)$	
41	B_g	985	1002		1002	998°	$\gamma(CH)_{rings}$	
42	A_u	986	1002	1000		tooph	$\gamma(CH)_{rings}$	
43	B_u	993	1001	1000		10025	$\nu(CC)_{rings}$	
44	A_g	993	1002			100-	$\nu(CC)_{rings}$	
45	B_u	1020	1028	1026		10276	$\nu(\text{CC})_{\text{rings}} + \delta(\text{CH})$	
46	A_g	1020	1029		1028		$\nu(CC)_{rings} + \delta(CH)$	
47	A_g	1074	1081			L.	$\nu(CC)_{rings} + \delta(CH)$	
48	B_u	1074	1081	1073		1066 ^b	$\nu(CC)_{rings} + \delta(CH)$	
49	B_u	1118	1127	1129		1027 ^b	ν (Ph-COOH) + ν (CC) _{rings} + δ (CH)	
50	A_g	1122	1130		1135	L	ν (Ph-COOH) + ν (CC) _{rings} + δ (CH)	
51	B_u	1155	1162	1181		1164 ^b	$\nu(\text{CC})_{\text{rings}} + \delta(\text{CH})$	
52	A_g	1155	1162		1158		$\nu(CC)_{rings} + \delta(CH)$	
53	B_u	1169	1176	1187		1185 ^b	$\nu(CC)_{rings} + \delta(CH)$	
54	A_g	1170	1177		1182		$\nu(CC)_{rings} + \delta(CH)$	
55	A_g	1277	1288		1290	1316 ^b	ν (Ph-COOH) + δ (OH) + δ (CH)	
56	B_u	1285	1296	1275		1322 ^b	ν (CC) _{rings} + δ (OH) + δ (CH)	
57	A_g	1311	1317		1323		$\nu(CC)_{rings} + \delta(OH) + \delta(CH)$	
58	B_u	1313	1320	1294		1297 ^b	$\nu(CC)_{rings} + \delta(OH) + \delta(CH)$	
59	A_g	1317	1327				$\nu(\text{CC})_{\text{rings}} + \delta(\text{CH})$	

Table 2
Observed and calculated vibrational frequencies for benzoic acid dimer (ν , stretching; δ , in-plane bending; γ , out-of-plane bending; τ , torsion)

(continued on next page)

Table 2 (continued)

No.	Sym.	Calculated B3LYP ν (cm ⁻¹)		Experimental ν (cm ⁻¹)		Literature Infrared ν (cm ⁻¹)	Approximate description	
		6-311++G**	cc-pVTZ	IR	Raman	, ()		
60	B_{μ}	1317	1327	1327		1380 ^b	$\nu(\text{CC})_{\text{rings}} + \delta(\text{CH})$	
61	B_{μ}	1417	1437	1426		1430 ^b	δ(OH)	
62	A_{g}	1438	1453		1447		$\delta(OH) + \delta(CH)$	
63	B_u	1444	1456	1454		1456 ^b	δ(CH)	
64	A_{g}	1449	1471				$\delta(OH) + \delta(CH)$	
65	A_{g}^{o}	1487	1498				δ(CH)	
66	B_{u}°	1487	1499	1497		1496 ^b	δ(CH)	
67	B_{ρ}	1580	1589	1584		1590 ^b	$\nu(CC)_{rings} + \delta(CH)$	
68	A_{g}°	1581	1590		1605		$\nu(CC)_{rings} + \delta(CH)$	
69	B_{u}°	1603	1612	1603		1606 ^b	$\nu(CC)_{rings}$	
70	A_{ρ}	1603	1612		1639		$\nu(CC)_{rings}$	
71	A_{g}°	1645	1646			1699 ^b	ν (C=O) + δ (OH)	
72	B_{μ}°	1688	1696	1688		1738 ^b	$\nu(C = O) + \delta(OH)$	
						2605 ^b		
73	A_{ρ}	3026	2937		3010		$\nu(OH)$	
74	B_{u}°	3088	3100	3073			$\nu(CH)_{rings}$	
75	A_{g}	3088	3100		3040		$\nu(CH)_{rings}$	
76	B_{u}°	3101	3113			3041 ^b	$\nu(CH)_{rings}$	
77	A_{g}	3101	3113				$\nu(CH)_{rings}$	
78	B_{u}°	3109	3122			3068 ^b	$\nu(OH) + \nu(CH)_{rings}$	
79	A_{g}	3110	3122		3073		ν (CH) _{rings}	
80	B_{u}°	3118	3045	3012		3012 ^b	ν(OH)	
81	A_{g}	3124	3138				$\nu(CH)_{rings}$	
82	B_{u}°	3124	3138			3079 ^b	$\nu(OH) + \nu(CH)_{rings}$	
83	B_{μ}	3131	3144			3098 ^b	$\nu(CH)_{rings}$	
84	A_g	3131	3144				v(CH) _{rings}	

The calculated frequencies were uniformly scaled by a factor of 0.9754 and 0.9786 for B3LYP/6-311++ G^{**} and B3LYP/cc-pVTZ, respectively. ^a Ref. [36].

^b Ref. [35].

ratios is close to $\sqrt{2}$. It should be stressed that our simulation shows that the coupling between the O-H(D) and O···O stretching vibrations in benzoic acid gives rise to important linear and quadratic distortions in the potentials of the low-frequency O···O stretching vibrations in the excited states of the O-H(D) vibrations. The resonance interaction between the two hydrogen bonds in the benzoic acid-H dimer is large, but in this



Fig. 4. Comparison between the experimental (bold solid line), theoretical (δ functions and thin line) ν_s spectra for benzoic acid-H.

case, the Fermi resonance interaction between the fundamental ν OH stretching and the overtone of the δ O-H bending vibrations is small. In the case of benzoic acid-D the situation is reversed. The resonance interaction parameter $V_{\rm res}$ in the benzoic acid-D dimer is small, but the Fermi resonance interaction parameter V_{ah} is large.

The present model allows to reproduce main features of the experimental spectra, but it is unable to explain all



Fig. 5. Comparison between the experimental (bold solid line), theoretical (δ functions and thin line) ν_s spectra for benzoic acid-D.

Table 3

Optimized parameters (the frequencies of the O–H and O–D stretching vibrations were taken as 3012 and 2231 cm⁻¹, respectively; they represent the parameter 1/2(r + r') in Eq. (9), the frequencies of the O–H and O–D bending vibrations were taken as 1471 and 1088 cm⁻¹, respectively)

Low frequencies (exp	.)	Benzoic acid-H	Benzoic acid-D	
	V _{res} M	-1.10 0.0	-0.11 0.0	
	$V_{ah} \delta^2$	0.1 0.2	1.9 0.2	
$\nu_1 = 114 \text{ cm}^{-1}$	$b_1 \\ dk_1$	1.280 0.250	0.701 0.200	
$v_2 = 420 \text{ cm}^{-1}$	b ₂ dk ₂ Half-width	0.0016 - 0.390 100 cm^{-1}	$0.001 - 0.300 \\ 100 \text{ cm}^{-1}$	

Table 4

To	tal	atomic	charges	in	the	benzoic	acid	dimer
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Atoms	Calculated charge, e						
	B3LYP/6-311++G**	B3LYP/cc-pVTZ					
O ₁ , O ₁ '	-0.337	-0.385					
O_2, O_2'	-0.393	-0.282					
C_1, C_1'	- 1.226	0.334					
C_2, C_2'	2.490	0.001					
C ₃ , C ₃	-0.817	-0.109					
C_4, C'_4	-0.010	-0.104					
C ₅ , C ₅	-0.529	-0.094					
C ₆ , C ₆	0.097	-0.108					
C ₇ , C ₇	-0.745	-0.096					
$\mathrm{H}_{1},\mathrm{H}_{1}^{'}$	0.592	0.250					
H ₃ , H ₃	0.168	0.128					
H_4, H_4'	0.189	0.111					
$H_{5}, H_{5}^{'}$	0.159	0.114					
$H_{6}, H_{6}^{'}$	0.190	0.112					
$\mathrm{H}_{7},\mathrm{H}_{7}^{'}$	0.168	0.129					

fine details. Further improvements of the model require taking into account interactions between hydrogenbonded dimers within unit cell and an harmonic potentials for $O \cdots O$ modes, and are planned in future.

Recently a similar model for three deuterated isotopomers of benzoic acid dimer with computed cubic anharmonic constants has been published by Florio et al. [40].

5. Conclusions

The ab initio calculated geometries and frequencies agree well with the experimental ones. The differences between the calculated and experimental frequencies are partly due to anharmonicity, to intermolecular interactions, the correlation effects and the limited basis set.

The experimental Raman frequencies assigned to the intermolecular $O \cdots O$ stretching vibrations were used in our calculations of the fine structure of the ν_s stretching bands.

The theoretical model used for these calculations was based on the Fermi resonance in the carboxylic acid dimer. The model was modified to encompass an adiabatic coupling between the high-frequency O–H(D) stretching and the low-frequency intramolecular O···O stretching modes. The linear and quadratic distortions of the potential energy for the low-frequency vibration in the excited state, a resonance interaction between the two hydrogen bonds in the dimer and Fermi resonance between the fundamental ν O–H(D) and the overtone of the δ O–H(D) vibrations was done.

The calculated spectra are in fairly good agreement with the experimental ones. The effect of deuteration was well reproduced by our model calculations. Our results show that spectra of benzoic acid and its deuterated analogue can be successfully simulated by our model.

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