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LOW-FREQUENCY RAMAN SPECTRUM OF CRYSTALLINE 2-(2'-HYDROXYPHENYL)BENZOXAZOLE

The normal mode density functional theory calculations for the isolated molecule of 2-(2'hydroxyphenyl)benzoxazole and atom-atom potential phonon calculations under the rigid molecule approximation are compared with the non-polarized Raman spectrum of a corresponding single crystal in the region 15-350 cm⁻¹. The isolated molecule demonstrates nine intramolecular vibrations in the considered region. The band corresponding to the out-of-plane intramolecular vibration with a calculated frequency of 161 cm⁻¹ is found to be splitted by 11 cm⁻¹ into two components that exhibite different intensity. The intense Raman bands observed below 130 cm⁻¹ are assigned to the intermolecular vibrations. The increase of temperature up to 393 K causes the decrease of the intensity of the Raman bands below 130 cm⁻¹ but there is no preferable disappearance of the bands attributed to the librations around the principal axis of inertia with the lowest moment. It might be concluded that reorientation of the molecules is hampered by crystal packing.

Keywords: molecular crystals, lattice vibrations, excited state proton transfer, atom-atom potential method.

Результати розрахунків нормальних мод для ізольованої молекули 2-(2'-гідроксифеніл) бензоксазолу на основі теорії функціонала густини і фононів на основі методу атом - атомних потенціалів у наближенні жорстких молекул зіставлені з неполяризованими спектрами комбінаційного розсіювання монокристала в області 15 - 350 см⁻¹. У розглянутій області спектра ізольована молекула має дев'ять внутрішньомолекулярних коливань. Встановлено, що смуга, яка відповідає неплоскому внутрішньомолекулярному коливанню з розрахованою частотою 161 см⁻¹, розщеплюється на величину 11 см⁻¹ на дві складові, які мають різні інтенсивності. Інтенсивні смуги, що спостерігаються в області частот нижче 130 см⁻¹, віднесені до міжмолекулярних коливань. Підвищення температури до 393 К призводить до зниження інтенсивності смуг комбінаційного розсіювання з частотами нижче 130 см⁻¹, але смуги, що відповідають лібраціям відносно головної вісі інерції з найменшим моментом, повністю не розмиваються. Це дозволяє зробити висновок, що кристалічна упаковка перешкоджає переорієнтації молекул.

Ключові слова: молекулярні кристали, граткові коливання, перенесення протона в збудженому стані, метод атом-атомних потенціалів.

Результаты расчетов нормальных мод для изолированной молекулы 2-(2'гидроксифенил)бензоксазола на основе теории функционала плотности и фононов на основе метода атом-атомных потенциалов в приближении жестких молекул сопоставлены с неполяризованными спектрами комбинационного рассеяния монокристалла в области 15 - 350 см⁻¹. В рассматриваемой области спектра изолированная молекула имеет девять внутримолекулярных колебаний. Обнаружено, что полоса, соответствующая неплоскому внутримолекулярному колебанию с расчетной частотой 161 см⁻¹ расщепляется на величину 11 см⁻¹ на две составляющие, которые имеют различные интенсивности. Интенсивные полосы, наблюдаемые в области частот ниже 130 см⁻¹, отнесены к межмолекулярным колебаниям. Повышение температуры до 393 К приводит к снижению интенсивности полос комбинационного рассеяния с частотами ниже 130 см⁻¹, однако, полосы, соответствующие либрациями относительно главной оси инерции с наименьшим моментом, полностью не размываются. Это позволяет сделать вывод, что кристаллическая упаковка препятствует переориентации молекул.

Ключевые слова: молекулярные кристаллы, решеточные колебания, перенос протона в возбужденном состоянии, метод атом-атомных потенциалов.

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1. Introduction

Organic molecules comprising proton donating and proton accepting sites, which are in close proximity, can demonstrate, upon photoexcitation, transfer of the proton from one group to another. 2-(2'-hydroxyphenyl)benzoxazole (HBO, Fig. 1a), which is an intramolecularly hydrogen-bonded compound that exhibit the excited state proton transfer, has been extensively studied for decades. In HBO, which has enol structure in the ground state, the excited state proton transfer occurs from the hydroxyl group to heterocyclic nitrogen atom resulting in keto tautomer [1]. Excited state proton transfer (ESIPT) as a fast unimolecular photoreaction have been studied mostly for molecues in gas phase, liquid solutions and solid matrices [1-3]. Low-frequency intramolecular vibrations were considered to play a prominent role in the proton transfer process changing the distance between the proton donor and acceptor [4]. Various substances with ESIPT have been probed for a number of applicatons some of them involve the photoreactive compounds in crystalline state [5].

In crystalline state, HBO is strongly luminescent (quantum yield of 0.42) while in liquid solution at room temperature the quantum yield is much less (0.018). The major radiationless channel is considered to be large amplitude twisting of the molecule in the excited state [1,6,7]. In the ground state, HBO can exist in two rotameric forms with intramolecular hydrogen bonds (OH...N and OH...O); only the structure with the OH...N hydrogen bond undergoes ESIPT [3]. A high concentration (approximately 1:1 ratio) of OH...O rotamer has been determined by the X-ray study of HBO [8], however, only the tautomer fluorescence band was found for crystalline HBO [6]. Moreover, the study of IR spectra of HBO in the region of intramolecular vibrations has not found the bands which can be assigned to the vibrations of OH...O rotamer that implies a low number of this species [9].

Forming a molecular crystal, organic molecules tend to close packing [10] so that large amplitude intramolecular motions as well as reorientation of the whole molecule are substantially hindered. Increase in temperature can cause some molecular rotational degrees of freedom to experience melting when the molecules may either almost freely rotate or perform jumps between the restricted numbers of orientations. Fragments of molecules that are linked by a single bond can also demonstrate changes of orientations in relation to each other. This orientational melting can be observed in Raman measurements in the low-frequency region as gradual brodening, intensity decrease and disappearance of the Raman lines corresponding to the certain librational vibrations of the molecules under temperature increasing [11].

In the previous paper [12] we described temperature dependence of the Raman spectrum in the region $15 - 250 \text{ cm}^{-1}$ where all observed bands were considered as lattice vibrations. However, the resonance Raman study of HBO dissolved in non-polar solvent and semi-empirical calculations show that there is a number of intramolecular vibrations below 250 cm⁻¹ [4]. In the present work we compared the low-frequency Raman spectrum with the normal mode calculations for isolated molecule and rigid-body lattice phonon calculations.

2. Experimental details and theoretical models

The non-polarized Raman spectra were measured in the reflection geometry under excitation at 532 nm with the experimental setup described in [12]. The single crystal of HBO with dimensions of $2.0 \times 1.0 \times 0.5$ mm was used without polishing. Density functional theory (DFT) calculations were performed with the Gaussian 03 program package [13] using the B3LYP functional and 6-31++G(d,p) basis set. Optimization of the structure

and harmonic normal-mode calculations were carried out for the isolated molecule of HBO assuming the C_s symmetry, the frequencies were unscaled. The Raman bands were simulated with a model of damped harmonic oscillators:

$$I(\omega, T) = (n(\omega, T) + 1) \sum_{i=1}^{m_s} \frac{I_{0i} \omega \Gamma_i \omega_{0i}^2}{(\omega_{0i}^2 - \omega^2)^2 + \omega^2 \Gamma_i^2},$$

where I_{0i} , ω_{0i} , and Γ_i were the oscillator strength (integral intensity of the Raman line), frequency, and damping constant of the i-th damped harmonic oscillator (full width at half maximum of the spectral line), respectively; m_s - the number of vibrations, $n(\omega T)$ - Bose - Einstein factor. The width of all lines was 7 cm⁻¹ and integral intensity I_{0i} was proportional to the Raman activity yielded by the calculations.



Fig. 1. The structural formula of an HBO molecule (a), crystal cell (b) and principal axes of inertia of the molecule (c).

Frequencies of the lattice vibrations were calculated by atom-atom potential method implemented in the DMAREL program [14, 15] under approximation of rigid molecules. Dispersion and repulsion interaction were expressed by the Buckingham potential:

$$U_{rep-disp,MN} = \sum A_{ik} \exp\left(-B_{ik}R_{ik}\right) - \frac{C_{ik}}{R_{ik}^6},$$

using the FIT set of the parameters [16]. Electrostatic interaction was described by the distributed multipole model; the multipole expansion was derived with the GDMA program [17] from the MP2/6-31G(d,p) electron density. The initial structure of the crystal cell (Fig.1) was taken in accordance with the reported X-ray data [8]; all molecules in the cell were assumed to have the OH...N conformation (Fig. 1b).

3. Results and discussion

The non-polarized Raman spectrum of the single crystal of HBO consists of prominent narrow bands at 33, 40 with a shoulder at 46 cm⁻¹, 6 overlapping bands with approximately equal intensities in the range 50 - 130 cm⁻¹, broad bands at 141, 185, 196, 262, and 286 cm⁻¹ and narrow weak bands at 300 and 316 cm⁻¹ (Fig. 1). The calculated spectral pattern for an isolated molecule demonstrates good correspondence in intensity with the measured spectrum in the region above 130 cm⁻¹ but the calculated frequencies

are than the observed ones lower by about 24 cm⁻¹, except the band at 315 cm⁻¹. The calculated frequencies for the three in-plane modes are in good agreement with those reported [4] for the bands in the resonance Raman measurements in solution (Table 1). Correspondence of the relative intensities of the observed bands to the calculated values allows assigning them to the intramolecular vibrations with the forms that are similar to the normal modes of the isolated molecules with a shift of the frequencies. The shift of the frequencies of internal vibrations in molecular crystal in comparison with the ones in gas phase is caused by interaction of the molecule with all surrounding molecules (static force field of a crystal) and vibrational interaction of translationally equivalent molecules [11]. The presence of two bands at 185 and 196 cm⁻¹ can be treated as Davydov splitting of the internal vibration. Assignment of the band observed in the Raman spectrum of the single crystal in the range 130 - 150 cm⁻¹ to the internal vibrations of the isolated molecule is presented in Table 1.



Fig. 2. The low-frequency Raman spectrum of the single crystal and simulated Raman spectrum of an isolated molecule of HBO.

The DFT calculations yield eight out-of-plane vibration and three in-plane internal vibrations of molecule of HBO with an OH...N hydrogen bond in the spectral range studied (Table 1). The approximate description of the normal vibration can be done using Varsanyi's notation for vibrations of benzene derivatives [18]. The two lowest are twisting motions of the benzoxazole and phenol moieties relatively to each other, they are calculated to have low Raman activity so that the observed bands at 62 and 71 cm⁻¹ are caused by rather changing the position and orientation of the molecule in relation to the surrounding molecules than deformation of the molecule. The mode at 117 cm⁻¹ is an inplane bending vibration, which involves the angles between the CC bond, linking the benzoxazole and phenol moieties, and the bonds that constitute the oxazole ring. The vibration changes the distance between hydrogen-donating and hydrogen-accepting centers. The vibrations 161, 246 and 263 cm⁻¹ are out-of-plane deformation of the benzoxazole and phenol moieties that can be described as Varsanyi's modes 10b. The

vibration with a frequency of 276 cm⁻¹ is an in-plane bending vibration that involves the angles between the CC bond, linking the benzoxazole and phenol moieties, and the bonds that constitute phenolic aromatic ring as well as deformation of the phenolic aromatic ring. This mode changes the distance between the C and N atoms of the hydrogen bond site as well as the next vibration with a frequency of 315 cm⁻¹.

Table 1

Calculated parameters		Descriptio	Experimental solution [4]	Experimental crystal	
Frequency, cm ⁻¹	Raman activity, arb. un.	In-plane	Out-of-plane	Frequency, cm ⁻¹	Frequency, cm ⁻¹
57	0.04	0.802	twist		
66	0.13	0.863	twist		
117	1.00	δ (benzoxazole-CCO)+ δ (benzoxazole-CCN)		121	141
161	4.60		$\rho(\text{phO-10b})+$ $\rho(\text{ph-10a})$		185 196
246	1.30		$\rho(\text{phO-10b})+$ $\rho(\text{ph-10b})$		262
263	0.68		ρ(ph-10b)		286
276	2.24	δ(phO-CCC)+δ(phO- CCCring)+ δ(benzoxazole-CCO)+ δ(benzoxazole-CCN)		280	300
315	1.65	$\delta(phO-CCC)+\delta(ph-9b)$		310	316
338	0.09		ρ(ph-10a)+ ρ(phO-16b)		

The low-frequency internal vibrations of an isolated molecule of HBO

Table 2

The lattice vibrations of the crystal of HBO calculated under the rigid molecules approximation

Frequency, cm-1	Eigenvector							
	а	b	с	u	v	W		
21	0.0411	0.0000	0.2832	0.3971	-0.0039	0.1020		
21	0.0444	-0.1073	-0.3422	0.1672	-0.0078	0.3023		
32	0.3590	-0.3261	0.0000	-0.0090	0.0950	0.0756		
35	0.0000	0.4352	0.0083	-0.0509	-0.2339	-0.0572		
36	-0.0430	0.0045	0.2461	-0.1837	-0.0683	0.3862		
38	-0.0957	-0.2057	0.0000	0.3326	-0.2958	-0.0212		
43	0.4764	0.0000	-0.0399	-0.0180	-0.1443	-0.0168		
44	-0.2977	0.3785	-0.1093	0.0308	-0.0626	0.0357		
47	0.0475	0.1218	0.0000	0.3640	0.3128	-0.0506		
52	0.0000	0.0101	0.1712	0.4319	-0.1060	0.1512		
61	0.0697	0.0236	-0.2436	-0.4285	0.0033	-0.0405		
71	0.0746	0.0000	-0.3234	0.2132	0.3032	0.0496		
71	0.1351	0.0208	0.0000	-0.0356	-0.0641	-0.4753		
75	0.0000	-0.0187	0.4666	-0.1773	0.0216	-0.0054		
78	-0.1255	0.0000	-0.2491	0.1930	-0.3667	-0.0232		
78	0.3867	0.3054	0.0287	0.0587	0.0155	0.0518		
79	0.3024	0.2934	0.0000	0.0746	-0.2270	0.1238		
85	0.0000	0.2368	0.0270	0.0990	0.4272	-0.0295		
90	-0.0559	0.0374	0.0156	-0.0180	0.4910	0.0617		
105	0.0000	0.0640	-0.0467	-0.1403	0.0325	0.4722		
119	-0.0057	0.0000	-0.0397	-0.0965	-0.0526	0.4861		

According to the X-ray data [8] a crystal of HBO belongs to the structure class Pna2₁ with four molecules per unit cell, adjacent molecules are stacked into chains with interplanar distance of 3.58 Å. Under the approximation of rigid molecules, theory group analysis predicts 21 external fundamental vibrations that are active in the Raman spectrum for the Pna2₁ (C_{2v}^{9}) space group, the modes are classified as $5A_1+6A_2+5B_1+5B_2$ [19]. Since the molecules of HBO occupy general positions in the crystal cell, the eigenvectors of the external normal vibrations have 6 components, that is, translation and libration motions are not strictly separated in harmonic approximation [10]. The symmetry of the molecule in the crystal lattice is C₁ (position symmetry) and each internal vibration of the isolated molecule is splitted into four by correlation field effect (Davydov splitting). The observed splitting of the band at 185 cm⁻¹ into only two distinguishable components can be caused by overlapping of the individual lines.



Fig. 3. The temperature dependence of the Raman spectrum of single crystal HBO in the region of 15-250 cm⁻¹.

The rigid-molecules phonon calculations predict that lattice vibrations lie in the region of 21 - 120 cm⁻¹ and the adjacent frequencies of vibrations are close (Table 1). The calculations performed for the model structure consisting of the OH...O conformations yield the frequencies that differ by about 2 cm⁻¹ from the obtained for the model structure consisting of the OH...N conformations. Despite translational and librational modes are not strictly separated in case of the HBO crystal, the calculations show that some of the vibrations are predominantly either translations or librations. Although the small difference of the frequencies does not allow unambiguous assignment of the observed bands, position of the narrow bands observed at 33, 40 and shoulder at 46 cm⁻¹ is found to correspond to the calculated modes with frequencies of 32, 35, 43 and 44 cm⁻¹ that have predominantly translational forms, while three observed bands at 100, 105 and 116 cm⁻¹ correspond to the modes with calculated frequencies of 90, 105 and 119 cm⁻¹ that have predominantly librational forms. The last two vibrations are librational motions around the lowest moment of inertia main axis, i.e. the long axis of the molecule. Reorientation of the molecule around the long axis is expected to have the lowest barrier due to the free

volume required for the reorientation is minimal in comparison with the volume needed for rotations around the two other principal axes of inertia.

The temperature evolution of the Raman spectrum in the range $15 - 250 \text{ cm}^{-1}$ is presented in Fig. 3. The increase of the temperature leads to the decrease of the intensity of all observed Raman lines. The decrease and broadening of the Raman lines point to the high concentration of structure defects at 393 K. At the same time the bands corresponding to the librations at 105 and 119 cm⁻¹ remain detectable, so that the complete rotational disorder is not reached even at 393 K.

4. Conclusions

The vibrational spectrum of crystalline HBO in the low-frequency region 15 - 350 cm⁻¹ contains both intra- and intermolecular modes. Although the external and internal vibrational motions are not separated, the modes below 130 cm⁻¹ are predominantly intermolecular vibration and the modes above 130 cm⁻¹ are predominantly internal vibrations with the forms similar to the normal modes of the free molecule with an OH...N intramolecular hydrogen bond. This means that Raman tensor of the crystal for the internal vibrations can be described within the oriented gas model. The presence in the spectrum of intense narrow lines corresponding to translational modes show that the oriented gas model, where only librations are Raman-active, is not suitable for the calculations of intensity of the bands caused by the external vibrations. Reorientation of the molecules in the crystal lattice and, consequently, dynamic orientational disorder are prohibited by close packing.

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