



Hydrostatic pressure and temperature effect on the Raman spectra of the molecular crystal 2-amine-1,3,4-thiadiazole

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ABSTRACT

The structural, thermal and vibrational properties of the molecular crystal 2-amine-1,3,4-thiadiazole (ATD) were investigated combining X-ray diffraction, infrared spectroscopy, Raman scattering (in solid and in solution) and thermal analysis as experimental techniques and first principle calculations based on density functional theory using PZ, BLYP in condensed-phase and B3LYP/cc-pVTZ in isolated molecule methods. The structural stability and phonon anharmonicity were also studied using Raman spectroscopy at different temperatures and hydrostatic pressures. A reasonable agreement was obtained between calculated and experimental results. The main difference between experimental and computed structural and vibrational spectra occurred in the intermolecular bond distance N–H···N and stretching modes of NH₂. The vibrational spectra were interpreted and assigned based on group theory and functional group analysis assisted by theoretical results, which led to a more comprehensive knowledge about external and internal modes at different thermodynamic conditions. As temperature increases, it was observed the line-width increases and red-shifts, indicating a phonon anharmonicity without a temperature-induced phase transition in the range 10–413 K. However, ATD crystal undergoes a phase transition in the temperature range 413–475 K, as indicated by thermal analysis curve and Raman spectra. Furthermore, increasing pressure from ambient to 3.1 GPa, it was observed the splitting of the external Raman bands centered at 122 cm⁻¹ (at 0.2 GPa), 112 cm⁻¹ (1.1 GPa), 93 cm⁻¹ (2.4 GPa) in two components as well as the appearance of new band near 50 cm⁻¹ at 1.1 GPa, indicating a possible phase-transition. The blue-shift of the Raman bands was associated to anharmonicity of the interatomic potential caused by unit cell contraction.

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1. Introduction

Because of their biological properties [1–3] and potential application in electronic organic devices [4,5], 2-amine-1,3,4-thiadiazole (ATD) and its derivatives have been intensely studied in the last decades. The experimental [6–8] and theoretical [9] investigations on structural and vibrational properties of ATD are reported in the literature with the purpose of understand fundamental issues of this class of materials, since it is a relatively small and simple organic molecular crystal, which facilitates the comprehension of the relationship among molecular structures,

physical, chemical and biological properties. Once these properties are well learned, it is possible to design molecules with desired properties. However, to the best of our knowledge, there are neither Raman study concerning ATD vibrational properties in solid and solution at room conditions in the spectral range 10–4000 cm⁻¹, as a function of temperature and high hydrostatic pressure, nor consistent assignment of its external and internal Raman modes. Also, theoretical investigations of its structural and vibrational properties in the condensed phase, as well as discussion about its optical properties, are missing in the literature. It is well known that the material properties are influenced by temperature and pressure, therefore the investigation of thermal and hydrostatic compression responses may provide essential data on this structure and interaction, which are relevant for further research of new materials for technological applications [10–16]. In the case of pharmaceutical materials, it is interesting to say that the structural

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stability is an important characteristic because phase transitions may result in changes in the biological properties. On the other hand, information regarding thermal transformations is desirable for applications in organic electronics at different thermodynamic condition [17]. For these reasons, the temperature and pressure dependence on the Raman spectra of the molecular crystal ATD assisted by thermogravimetric (TG) and differential thermogravimetric (DTG) analysis were investigated to obtain information about anharmonicity, thermal stability, molecular packing revealed by crystal lattice mode region and expose some phase transition. Furthermore, the structural and vibrational properties are also studied at room conditions combining x-ray diffraction (XRD), infrared and Raman spectroscopy as experimental techniques and theoretical method based on DFT calculations to give a more precise knowledge about the intra- and inter-molecular bond and vibrational mode assignments. Finally, it is included in this investigation the Raman spectra of ATD in chloroform (CHCl₃) and acetonitrile solution (CH₃CN) to collect definitive evidence for a complete assignment of this material as well as study the influence of solvation effect on the Raman spectra of the organic molecule.

2. Experimental

The ATD was purchased from Sigma-Aldrich (U. S. A.) with state of purity of greater than 97% and was used without any further purification. The X-Ray powder diffraction pattern was collected at room temperature in Shimadzu LabX XRD-6100 using CuK α radiation and a monochromator in the 2-theta range (5–90°). The TG-DTA curves were taken on Shimadzu DTG-60H in the temperature range 300–1000 K, with a heating rate of 5 °C/min in a controlled nitrogen atmosphere. The infrared spectrum was recorded using potassium bromide (KBR) pellet method on Varian-660 in the spectral region 4000–400 cm⁻¹ with a spectral resolution of 4 cm⁻¹. The Raman spectra were acquired in backscattering geometry with a spectral resolution of 2 cm⁻¹ using T64000 Jobin Yvon micro-Raman system coupled to Olympus BX40 microscopy equipped with N2-cooled CCD detector. The 488-nm line from an argon laser was used as excitation source. The spectra were recorded using three accumulations and the acquisition time was 30 s. The low-temperature measurements were performed in cryogenic closed system in the temperature range from 10 to 290 K, while the high-temperature measurements are used a Linkan TS1500 micro furnace in the temperature range from ambient to 475 K. The pressure measurements were carried out at room temperature

using Diamond Anvil Cells (DACs) with Nujol oil as pressure-transmitting medium. A stainless-steel gasket with a drilled hole of 100 μm in diameter was used as the sample chamber. The pressure inside of the DAC was monitored by the shift of the ruby fluorescence line.

3. Theoretical procedures

DFT quantum chemistry calculation on the isolated ATD molecule (in gas-phase and in CHCl₃ and CH₃CN solution) were performed using B3LYP [18] method with Dunning cc-pVTZ basis sets [19] on Gaussian 09 [20] software package to predicted the optimized structure and vibrational spectra. To investigate the intermolecular interaction and its effect in the physical and chemical properties of ATD, the first-principle calculations based on plane-wave DFT (PW-DFT) method using Perdew-Zunger local density approximation (LDA) [21] and generalized-gradient approximation (GGA) with Becke-Lee-Yang-Parr correlation hybrid functional (BLYP) [18] were performed on the Plane-Wave-Self-Consistent-Functions (PWSCF) code from Quantum Espresso (QE) package [22]. The initial structure of ATD was modeled using the atomic coordinates reported in crystallographic information file (CIF) given in Ref. [7], since the calculation was performed with the harmonic model at 0 K. The unit cell dimension vectors were conserved during the optimization process. To calculate IR spectrum, the structure was optimized, then calculated IR frequencies and intensities using BLYP functional applying the norm-conserving pseudo-potentials generated with Bachelet–Haman–Schlüter [23] method to H, N, C, and S atom. To calculate the Raman spectrum, the structure was reoptimized applying LDA functional following by frequencies and intensities calculation. In the latter, it was used Von Barth-Car type [24] approach applied to H, N and C atoms as well as Bachelet–Haman–Schlüter type employed to S atom. Both methodologies were performed to help in the interpretation of the fundamental properties of the ATD crystal and because Raman intensity was not properly implemented in QE with GGA, but the Raman mode was computed and tabulated in Table 1. The PW-DFT calculations were carried out by using 50 Ry kinetic energy cut-off and potential energy density of 400 Ry. Brillouin zone integrations were performed following the Monkhorst-Pack scheme [25] with 3 \times 3 \times 3 K-point mesh. No scaling factors were applied to PW-DFT calculated frequencies, whereas dual scaling factor of 0.958 and 0.983 was used to shift-down the computed stretching mode of CH, NH₂ and the others frequency. The

Table 1
Selected experimental and theoretical geometrical parameters of ATD: bond distance and bond angle (Å, °) at room temperature (RT) [6], at 120 K (LT) [7] and calculated with PZ, BLYP and B3LYP functional.

Atoms	RT [6]	LT [7]	PZ	BLYP	B3LYP/cc-pVTZ		
					In gas-phase	In CHCl ₃ solution	In CH ₃ CN solution
C5–S1	1.718	1.735	1.709	1.783	1.751	1.747	1.745
S1–C2	1.729	1.745	1.736	1.803	1.755	1.755	1.755
C5–N4	1.280	1.293	1.306	1.306	1.287	1.288	1.289
C2–N3	1.328	1.323	1.340	1.338	1.300	1.305	1.301
N4–N3	1.378	1.390	1.380	1.406	1.366	1.370	1.372
C2–N2	1.331	1.345	1.333	1.346	1.370	1.363	1.360
C5–H5	0.931	0.948	1.100	1.082	1.078	1.078	1.078
N2–H21	0.860	0.868	1.056	1.032	1.010	1.009	1.008
N2–H22	0.860	0.890	1.049	1.023	1.006	1.006	1.006
N2–H21...N3	2.176	2.133	1.818	1.936	–	–	–
N2–H22...N4	2.148	2.085	1.805	1.931	–	–	–
C5–S1–C2	86.76	86.6	88.15	85.90	85.63	85.94	86.05
S1–C2–N3	113.77	113.8	112.51	114.43	113.86	113.65	113.58
S1–C5–N4	114.85	114.8	114.12	113.44	114.22	114.22	114.24
H21–N2–H22	120	124.5	124.04	122.79	114.14	114.46	114.65
N4–C5–H5	122.58	127.1	123.24	123.93	123.40	124.04	124.05

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