

Laser Raman and FT-IR spectroscopic study of antimony thiourea bromide crystals

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Abstract : Single crystals of orthorhombic antimony thiourea bromide (ATBO) and monoclinic antimony thiourea bromide (ATBM) have been grown in gels at ambient temperature using a controlled chemical reaction method. The laser Raman and FT-IR spectra of the gel grown ATBO and ATBM crystals have been recorded. The presence of thiourea ion, water molecules and normal mode vibrational frequencies are identified and discussed. The basic ideas regarding the normal modes of vibration, selection rules for Raman and IR spectra, hydrogen bonding effect are considered in brief.

Keywords : Laser Raman, FT-IR spectra, antimony thiourea bromide, crystal spectra.

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Spectroscopic investigations in different regions of the electromagnetic spectrum provide information regarding translational, rotational, vibrational and electronic energy levels of molecules. Information regarding molecular structure, stereo chemistry of complex molecules, hydrogen bonding and inter and intra molecular processes can be obtained from the vibrational spectra. The development of sophisticated experimental techniques in Fourier transform infra-red spectroscopy and Raman spectroscopy has simplified the problem of obtaining the vibrational spectra of even very complicated crystals [1]. In this paper the detailed analysis of the Raman and FT-IR vibrational spectra of the gel grown ATBO and ATBM crystals have been presented.

The FT-IR spectra of gel grown [2,3] ATBO and ATBM crystals in the micro crystalline form have been recorded on a BRUKER IFS FT-IR spectrometer in the region of 400–4000 cm^{-1} using KBr pellet technique. Laser Raman spectra of micro crystalline samples were recorded using BRUKER IFS 66V FT-IR spectrometer-FRA 106 Raman Module with YAG laser.

Figures 1 and 2 give the FT-IR and Raman spectra respectively, of the ATBO and ATBM crystals. The assignment for different vibrations of the ATBO and ATBM

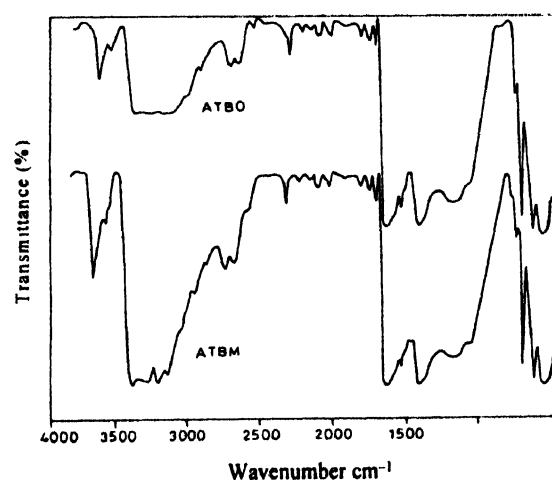


Figure 1. FT-IR spectra of ATBO and ATBM crystals.

crystals are given in Table 1. The existence of molecular units such as thiourea and water in the crystal facilitates the analysis of the vibration spectra in terms of the vibrations

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of these molecular groups, particularly in the internal mode region. A number of studies are available on the infrared and Raman spectra of thiourea [4–6]. The normal coordinate analysis of thiourea molecule has also been reported [7]. The structure of thiourea has been investigated. Wyckoff and

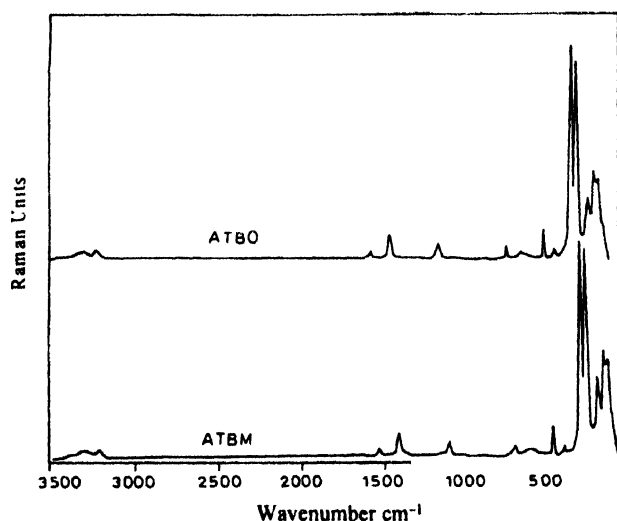


Figure 2. Laser Raman spectra of ATBO and ATBM crystals.

Corey [8] found that at room temperature the crystal belongs to the orthorhombic centro symmetric space group D_{2h} with four molecules per unit cell. The asymmetric crystal unit consists of half one molecule, the carbon and sulphur atoms lying in the mirror plane and the molecule was found to be planar. No hydrogen bonding was found presumably because of large thermal motion. The ATBO crystallize in the orthorhombic form with $a = 12.273 \text{ \AA}$, $b = 11.675 \text{ \AA}$, $c = 18.617 \text{ \AA}$, space group $Cmc2_1$, having eight molecules in the unit cell. ATBM crystal crystallize in monoclinic form with $a = 8.467(3) \text{ \AA}$, $b = 18.676(8) \text{ \AA}$, $c = 8.488(4) \text{ \AA}$, $\alpha = 90^\circ$, $\beta = 92^\circ 94'$, $\gamma = 90^\circ$, space group $P2_1/m$, having four molecules in the unit cell. The thiourea molecule in its free state has C_{2v} symmetry and the irreducible representation of the modes is : $T = 7A_1 + 2A_2 + 6B_1 + 3B_2$.

Of which, sixteen vibrations with symmetries A_1 , B_1 and B_2 are allowed in the IR spectrum by the selection rules and all eighteen vibrations are allowed in the Raman spectrum. Thiourea like other thioamides, thiosemicarbazones and dithioamides exhibit bands in the region 940–1140, 1260–1420 and 1375–1570 cm^{-1} [9]. These bands arise

Table 1. Spectral assignment of ATBO and ATBM crystals (spectral lines in cm^{-1}).

FTIR	Raman	Symmetry	FTIR	Raman	Symmetry	Assignment
ATBO	ATBO		ATBM	ATBM		
3644		A_1	3645		A_1	H_2O stretching
3556		A_1	3557		A_1	(γ_s and γ_l)
3285	3306	A_1	3370	3374	B_1	γ_{as} and γ_l vibrations
3201	3210	B_1	3279	3304	A_1	of NH
3127		B_1	3127	3210	B_1	
2928		B_1	2930		B_1	
2750 to 1700		A_1	2800 to 1700		A_1	Combinations and overtones
1639		A_1	1631		A_1	NH δ
1614		A_1	1612		A_1	H_2O bending (γ_2)
	1619	A_1		1618	A_1	(253X2 + 1112)
1524	1526	A_2	1524	1525	A_2	(SCN) bending
1050		B_2	1040		B_2	(NH) ρ
731		A_2	729		A_2	(CN) γ_s
688	689	B_2	687	688	B_2	(CN) γ_{as}
607	595	B_1	607	595	A_1	Librational modes of H_2O
457	457	A_1	456	458	A_1	(CN) δ
	387	B_1		387	B_1	(253 + 139) (253 + 138)
	283	A_2		282	A_2	(Sb–S) stretching
	253	A_1		253	A_1	(Sb–Br) stretching
	179, 139	B_2		181, 138	B_1	(S–Sb–Br) bending
	118	A_1		118	A_1	(Sb–Br) ρ

ρ -rocking; γ -stretching; s -symmetric; as -asymmetric; δ -deformation.

because of the strong coupling between C=S and C-N vibrations.

In the high wave number region 3000–3400 cm⁻¹, there are several peaks due to N-H stretching. NH₂ stretching modes are observed at lower wave number than for free ion [7]. This effect is observed in ATBO and ATBM crystals, being the highest in ATBO. This indicates that the hydrogen atoms of NH₂ take part in intermolecular/intramolecular hydrogen bonds. Another possible reason for the bands in this region is the existence of thiourea in the resonance configuration [10]. The vibration between about 1700 to about 2800 cm⁻¹ is considered as overtones/combination.

Earlier workers [11–13] did infrared studies on metal coordination compounds of thiourea. Swaminathan *et al* [12] have studied the effects of metal complexation of the type M(Tu)₂X₂ where M = Mn, Co, Ni, Zn, Cu, Hg, Ti and Pt; Tu is thiourea and X is a halogen. All metals except Ti form complexes *via* sulphur. (Ti forms bond *via* nitrogen). It is expected that on formation of metal-sulfur bond, the vibrations at 1412 cm⁻¹ and 730 cm⁻¹ would be down shifted. A comparison of our results with the infrared spectra of thiourea, Zn(tu)₃SO₄ is made in Table 2. These studies corroborate the crystal structure data of thiourea complexes, establishing the metal complexation *via* sulfur atoms.

Table 2. Comparison of vibrations (cm⁻¹) of thiourea with metal complexes

Species	Thiourea*	Zn(tu) ₃ SO ₄ '	ATB (ortho)	ATB (mono)**
γ(NH)	3385	3329	3285	3370
δNH ₂	1618	1635	1639	1631
γCS	1412	1408	1405	1404
ρNH ₂	1087	1083	1050	1040
γCN	730	713	731	729

* Ref [12]

' Ref [13]

** Present work

The stretching frequencies of H₂O are slightly down shifted and the bending frequencies are slightly uplifted. This shows that the water of crystallization does not take part in forming hydrogen bonds [14]. This inference is in support of the structure analysis of the crystals. The free H₂O molecule vibration is compared with that of the water of crystallization of ATBO and ATBM crystals in Table 3. The comparison result shows that the H₂O molecules are weakly bonded in these crystals.

Raman spectra obtained at lower wave number region helps in assigning the vibrations, which involve heavy atoms. The vibrations of metal-sulfur stretching mode appear

Table 3. Comparison of H₂O mode vibrations

Free H ₂ O molecule vibrations cm ⁻¹	H ₂ O mode vibrations in the grown crystals (cm ⁻¹)	
	ATB (ortho)	ATB (mono)
(A ₁) 3657 γ ₁	3356	3557
(B ₂) 3756 γ ₃	3644	3645
(A ₁) 1595 γ ₂	1614	1612

around 273 cm⁻¹ in Zn thiourea complexes [13,15]. On complex formation with various ligands, the metal-sulfur vibration wave number was observed not to change appreciably [16]. The Sb/Bi-S stretching and bending modes are compared with that of the study made on antimony sulfobromide and on antimony sulfochloride [17]. Depending on the atomic mass, the bond distance and the bond angle the vibration frequencies vary. During complex formation, it is observed that thiourea is coordinated to the antimony through sulfur in ATBO and ATBM crystals. Intermolecular/intramolecular hydrogen bonds are observed in these new crystals. Molecules of water of crystallization are weakly bonded in the crystals *i.e.*, they do not take part in hydrogen bond formation.

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