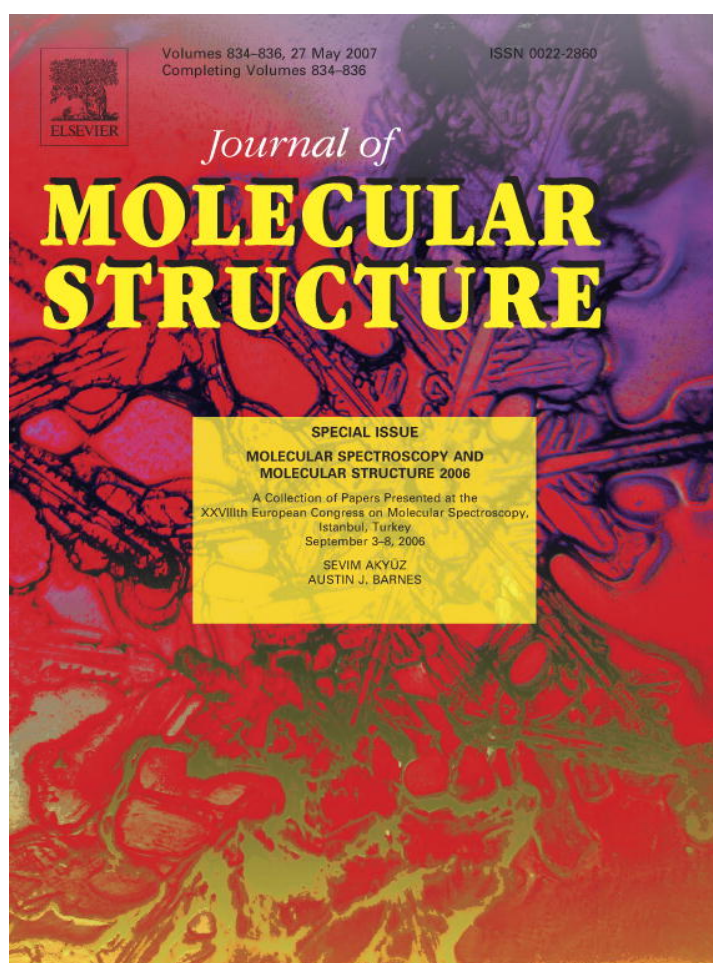


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Low temperature Raman study of bis(trimethylsilyl)acetylene

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Abstract

Low temperature Raman spectroscopy was applied in study of bis(trimethylsilyl)acetylene (BTMSA), a known catalyst with very low barrier for the internal rotation of methyl groups – less than 10 cal/mol (Sipachev et al. *J. Mol. Struct.*, 523 (2000) 1). Since crystals consisting of flexible molecules often show polymorphism, it was of interest to find out if it is the case of BTMSA.

Phonon Raman spectra recorded from 10 to 323 K were in complete agreement with previously determined crystal structure: for space group $P2_1/c$ with $Z=2$ six phonons are expected and six are observed below 100 cm^{-1} . BTMSA crystallizes in *trans* conformation, also the most stable one in gas phase. All observed bands could be attributed to crystal splitting of molecular g modes of D_{3d} symmetry into A_g and B_g modes of the point group C_{2h} of the crystal.

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Keywords: Raman; Bis(trimethylsilyl)acetylene; Methyl group; Vibrations; Phonons; Crystal

1. Introduction

Bis(trimethylsilyl)acetylene (BTMSA) often serves as a catalyst in organic synthesis [1–3], and it would be of use to know its temperature stability and crystalline phases. Our interest in BTMSA stems from the possibility to study how the ordering of methyl groups in solid affects the nature and stability of the given phase. BTMSA has altogether six methyl groups symmetrically placed in two groups of three and connected by two silicon atoms joined through an acetylenic bond. The barrier for internal rotation of one part of the molecule (three methyl groups together) with respect to the other was calculated by Sipachev et al. [4] to be very small. Their *ab initio* calculation was a restricted Hartree–Fock one, taking account of electron correlation as Møller–Plesset second order perturbations, with different basis sets. Total energies of D_{3d} and D_{3h} (*trans*- and *cis*-) conformers differed for less than 10 cal/mol, thus supporting the hypothesis of almost free internal rotation of methyl groups in the gas phase.

Here we present low temperature Raman results of the study of both internal and external parts of BTMSA vibra-

tional spectrum starting from 323 K and cooling to 10 K. Particular attention was paid to dynamics and changes in methyl modes, in order to elucidate ordering in solid. Rotations of methyl groups in solid monosubstituted neopentanes have been the subject of NMR [5,6], infrared [7,8], microwave [9,10] and Raman [11,12] studies. Szcześniak [5] pointed out that for solid $(\text{CH}_3)_3\text{COH}$, the barrier to internal rotation of a methyl group is larger (22.3 kJ/mol) than the barrier for *t*-butyl group (13.2 kJ/mol). On inspection of intra- and intermolecular distances in crystals containing *t*-butyl group, one finds that the shortest distance d between two methyl groups from the same molecule is smaller than the shortest distance D between two methyl groups from different molecules: $d < D$. This observation is valid for most of the compounds of the $(\text{CH}_3)_3\text{CX}$ type [13,14], but in case of $(\text{CH}_3)_3\text{SiX}$ compounds, the opposite, $d > D$, is true [15–17]. Tert-butyl compounds $(\text{CH}_3)_3\text{CX}$ have three solid phases [18]: in phase I dipole moments of molecules possess orientational freedom, in phase II there exist uniaxial rotations of molecules around their C–X axis, and in phase III there is freezing of all molecular orientations. For $(\text{CH}_3)_3\text{CNO}_2$ temperatures of phase transitions are: 216.4 K (solid III to solid II), 260.6 K (solid II to solid I) and 298.9 K (solid I to liquid).

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BTMSA is reported to have the melting point at 276 K [19]. We have found that it solidifies at 263 K on cooling. In the previous article [20] we reported the observation of an asymmetric band profile of the triple carbon–carbon stretching band at temperatures between 10 and 300 K, and tentatively suggested that the crystalline phase of BTMSA might be a glassy crystal. There, molecular centres of mass would be lying on the translationally ordered lattice, but orientation of six methyl groups would be disordered.

2. Experimental

Bis(trimethylsilyl)acetylene (BTMSA), 98% pure, produced by Sigma–Aldrich, was degassed and sealed in a cap-

illary under vacuum. The capillary was mounted on a cold finger of CTI CRYOGENICS model 21 closed cycle He cryostat operating with Lake Shore temperature controller. Temperature stability was about ± 0.1 K.

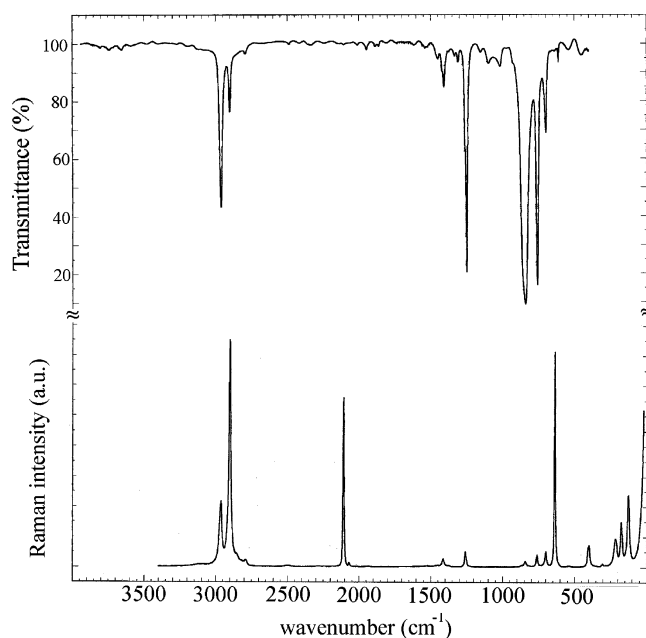


Fig. 1. Infrared and Raman spectra of liquid BTMSA.

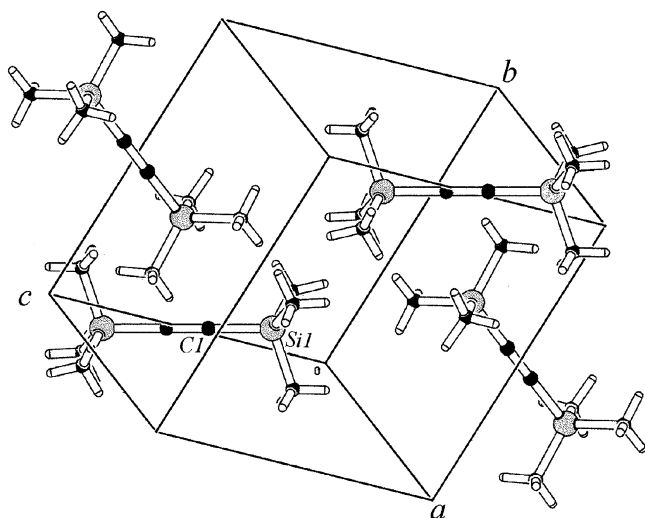


Fig. 2. Crystal packing of BTMSA. Space group is $P2_1/c$, $Z=2$. Figure prepared by PLATON [23].

Table 1

Calculated and observed frequencies of *trans*-bis(trimethylsilyl)acetylene

Symmetry	Mode No.	Calculated using B3lyp/6-311++G(d,p) unscaled	Observed Raman liquid
A_{1g}	1	3093	2966 s
	2	3023	2903 vs,as
	3	2195	2108 vs
	4	1477	1451 w
	5	1305	1260 m
	6	899	870 w,sh
	7	626	637 vs
	8	386	399 m
	9	166	127 s
A_{2g}	10	3099	–
	11	1453	–
	12	701	–
	13	148	–
E_g	14	3100	2966 s
	15	3090	2966 s
	16	3021	2903 vs,as
	17	1466	1413 mw
	18	1459	1382 w
	19	1294	1255 mw
	20	872	843 w
	21	784	760 w
	22	696	699 mw
	23	399	405 m
	24	209	216 m
	25	167	175 ms
	26	115	127 s
A_{1u}	27	3099	–
	28	1453	–
	29	701	–
	30	146	–
	31	6	–
A_{2u}	32	3092	2963 s
	33	3023	2900 m
	34	1477	1450 w,as
	35	1304	1260 s,sh
	36	879	864 s,sh
	37	765	759 vs
	38	600	609 mw
	39	235	*
	E_u	40	3100
41		3090	2963 s
42		3021	2900 m
43		1466	1409 m
44		1460	1421 mw
45		1294	1250 vs
46		874	843 vs,br
47		783	759 vs
48		696	699 ms
49		302	*
50		198	*
51		167	*
52		47	*

Asterisks denote frequencies falling in far infrared which we did not record. Short lines were put in places of inactive frequencies (A_{2g} and A_{1u}).

Table 2
Observed Raman and infrared bands for bis(trimethylsilyl)acetylene-*anti* D_{3d} at various temperatures

Raman 10 K phase I	Raman 303 K	Infrared 300 K	Mode No.	Symmetry	Assignment [4]
		3804 w			
		3737 w			
		3657 w			
		3589 w			
		3480 vw			
		3401 vw			
		3275 vw			
		3193 vw			
		3128 vw			
2968 s	2966 s		ν_1, ν_4, ν_5	A_{1g}, E_g, E_g	CH ₃ stretch. B and A
2960 s			$\nu_{32}, \nu_{40}, \nu_{41}$	A_{2u}, E_u, E_u	CH ₃ stretch. B and A
2901 s	2903 vs,as	2963 s	ν_2, ν_{16}	A_{1g}, E_g	CH ₃ symmetric stretching
2891 ms			ν_{33}, ν_{42}	A_{2u}, E_u	CH ₃ symmetric stretching
2850 mw	2856 mw,sh	2900 m			
2836 mw	2827 w				
2827 w					
2783 w	2793 w				
	2752 vw	2792 w			
	2507 vw				
	2491 vvw	2488 vw			
		2415 vw			
		2361 vw			
	2286 vvw	2335 vw			
		2246 vw			
2112 vvs	2108 vs		ν_3	A_{1g}	Triple bond stretching
2072 mw	2071 w	2103 vw			
	2015 vvw				
	1935 vvw	2009 vw			
		1949 w			
		1887 w			
		1863 w			
		1812 vw			
	1525 vvw	1617 vw			
1457 vw		1534 w			
1451 w	1451 w		ν_4	A_{1g}	CH ₃ deformation A
			ν_{34}	A_{2u}	CH ₃ deformation A
1427 vw		1450 w,as	ν_{43}	E_u	CH ₃ deformation B
1420 m		1421 mw			
1417 m	1413 mw		ν_{17}	E_g	CH ₃ deformation B
1411 w					
1406 w		1409 m	ν_{43}	E_u	CH ₃ deformation A, B
1395 vw	1382 w	1375 vw	ν_{18}	E_g	CH ₃ deformation A, B
1375 w		1335 w			
		1310 w,sh			
1279 vw	1260 m		ν_5	A_{1g}	CH ₃ symmetric deformation
1264 m		1260 s,sh	ν_{35}	A_{2u}	CH ₃ symmetric deformation
1258 w	1255 mw		ν_{19}	E_{2g}	CH ₃ symmetric deformation
1253 w		1250 vs	ν_{45}	E_u	CH ₃ symmetric deformation
1249 mw					
1246 w	1230 vw,sh				
		1155 w			
	1060 vw	1100 mw			
		1020 mw			
		981 w,sh			
	870 vw,sh		ν_6	A_{1g}	CH ₃ rocking parallel
862 w		864 s,sh	ν_{36}	A_{2u}	CH ₃ rocking parallel
855 mw					
846 w	843 w		ν_{20}	E_g	CH ₃ rocking perpendicular
843 w		843 vs,br	ν_{46}	E_u	CH ₃ rocking perpendicular
	816 w,sh				
811 vw					

Table 2 (continued)

Raman 10 K phase I	Raman 303 K	Infrared 300 K	Mode No.	Symmetry	Assignment [4]
764 ms	760 w		ν_{21}	E_g	CH ₃ rocking parallel
	699 mw	759 vs	ν_{17}, ν_{47}	A_{2u}, E_u	Si–C = stretch, CH ₃ rock paral.
701 s		699 ms	ν_{35}	E_g	SiC ₃ stretching A, B
697 m			ν_{48}	E_u	SiC ₃ stretch A, B, CH ₃ rock
641 vs	637 vs		ν_7	A_{1g}	SiC ₃ symmetric stretching
	551 vw,sh	609 mw	ν_{38}	A_{2u}	SiC ₃ symmetric stretching
530 vw	538 vw	538 w	$\nu_{23} + \nu_{30}$	E_u	combination
460 vw, br		451 w	$\nu_{24} + \nu_{39}$	E_u	combination
404 m	405 m		ν_{23}	E_g	linear bending X, Y
385 m	399 m		ν_8	A_{1g}	Si–C = stretch, SiC ₃ stretching
	356 vvw				
	305 vw		ν_{49}	E_u	SiC ₃ rocking A, B
235 mw			ν_{39}	A_{2u}	SiC ₃ symmetric deformation
227 s					
217 mw	216 m		ν_{24}	E_g	SiC ₃ deformation A, B
			ν_{51}	E_u	CH ₃ torsion A, B, CH ₃ symmetric torsion
200 m			ν_{50}	E_u	SiC ₃ deformation A, B
187 mw					
179 mw	175 ms		ν_{25}	E_g	CH ₃ symmetric torsion
171 mw					
164 mw					
161 m					
139 s			ν_9, ν_{26}	A_{1g}, E_g	SiC ₃ symmetric deformation, linear bending X, Y
129 s	127 s				
124 m					
75 ms					
66 ms ^b					
62 mw,sh			ν_{52}	E_u	linear bending X, Y
49 ms					
	38 ^a w				
43 s					
27 vw					

Assignment from [4].

^a The 38 cm⁻¹ band was obtained after correction with R(ν) function [24].^b Phonon line at 66 cm⁻¹ coincides with laser plasma line.

Raman spectra were recorded with DILOR Z24 triple monochromator, with Peltier cooled RCA C31034A2 photomultiplier, in sequential mode with slitwidth of 300 μ m, stepsize ranging from 0.5 to 4 cm⁻¹. The time constant was 1 s, except when multiscanning was done: there it was 4 s. COHERENT INNOVA 100 argon ion laser operating at 514.5 nm with 200 mW served as an excitation source.

Infrared spectrum of liquid BTMSA was recorded with Perkin Elmer 2000 instrument from 400 to 4000 cm⁻¹ with a resolution of 1 cm⁻¹ and 20 scans, using Perkin Elmer liquid cell with 0.025 mm thick Teflon spacers between KBr windows.

3. Results and discussion

Bis(trimethylsilyl)acetylene is a non-rigid molecule, for which proper symmetry group is a permutation-inversion group. Its character table has not been worked out yet, but suffice it to say that the group for B(CH₃)₃ is G_{324} and has 324 elements [21], and for (CH₃)₃GeCCH is G_{162} with 162 elements [22]. Because we are focused mainly on the Raman spectra of solid, we shall use D_{3d} symmetry group for the assignment of *trans*-BTMSA bands. In particular, we are

interested in the possible appearance of methyl internal rotation transitions.

An overview of the whole infrared and Raman spectrum of liquid is given in Fig. 1. Relatively small number of observed bands indicates lack of splitting of methyl bands (there are three methyl groups attached to each of two silicon atoms as shown in Fig. 2 [23]). Seventy eight normal modes of BTMSA *trans* are distributed among the irreducible representations of D_{3d} as follows: $9A_{1g} \oplus 4A_{2g} \oplus 13E_g \oplus 5A_{1u} \oplus 8A_{2u} \oplus 13E_u$. Vibrations A_{2g} and A_{1u} are inactive.

In Table 1 are listed all fundamental modes of BTMSA D_{3d} , together with calculated frequencies of normal modes. We undertook an independent calculation using B3LYP functional and 6-311++G(d,p) basis set [25] in order to check if more sophisticated *ab initio* calculation would produce any infrared fundamentals falling in the interval between 400 and 600 cm⁻¹, because we observed two infrared bands at 451 and 538 cm⁻¹ (see Table 2. for complete listing) and none were calculated to be close by Sipachev et al. [4]. It turned out that our unscaled values below 1000 cm⁻¹ are very close to those scaled from [4]. We found

no *ungerade* fundamentals between 400 and 600 cm^{-1} , therefore the two mentioned bands were assigned as combinations. Our numeration of modes followed the convention from Wilson [26]. Optimized geometrical parameters were: $C_{ac}-C_{ac}$ 122.04 pm, $Si-C_{ac}$ 184.82 pm, $C_{meth}-Si$ 188.50 pm, angle $C_{meth}SiC_{ac}$ 108.4888°, angle $H_1C_{meth}Si$ 110.7446°, angle $H_{2,3}C_{meth}Si$ 111.2098°.

In Raman spectrum of liquid BTMSA below 600 cm^{-1} there are six bands that correspond to normal modes of the *trans* conformer: at 405 cm^{-1} , (linear bending, E_g) at 399 cm^{-1} ($Si-C_{ac}$ and $Si-C_{meth}$ stretching, A_{1g}), at 216 cm^{-1} (SiC_3 deformation, E_g), at 175 cm^{-1} (CH_3 torsion, E_g) and two at 127 cm^{-1} (SiC_3 symmetric deformation, A_{1g} , and a linear bending, E_g). From Table 1, we note that there is another methyl torsion mode of A_{2g} symmetry calculated at 148 cm^{-1} , but inactive for free molecule in liquid. There are no Raman active internal modes predicted below 100 cm^{-1} .

Crystal structure of BTMSA was determined to belong to $P2_1/c$ space group with $Z=2$, $a=602.5$ pm, $b=1051.9$ pm, $c=958.4$ pm, $\beta=105.91^\circ$, each molecule lying on a site with the centre of inversion [17]. From correlation tables between D_{3d} and C_{2h} point groups, one finds that vibrations belonging to inactive A_{2g} under D_{3d} become B_g under C_{2h}

and thus Raman active. We thus expect six bands around 400 cm^{-1} (from $Z=2$ splitting of E_g and A_{1g} modes), four bands around 216 cm^{-1} (splitting of E_g mode of SiC_3 deformation), four bands around 175 cm^{-1} (from crystal splitting of E_g CH_3 torsion), two bands around 148 cm^{-1} from crystal splitting of A_{2g} mode becoming active, and six bands around 127 cm^{-1} (two from A_{1g} and four from E_g mode). Methyl torsion bands are expected at approximately 175 and 148 cm^{-1} .

Low frequency Raman spectra and the dependence of bands positions on temperature are shown in Figs. 3 and 4, respectively. Positions of all observed bands at 10 K are given in the first column of Table 2. There is a good agreement between the number of observed and expected number of phonons, since $2a_g + 4b_g$ phonons are Raman active and six bands observed below 100 cm^{-1} at 10 K. As for internal observed modes, in general, there are less bands than expected by group theory. Specifically, for methyl torsion bands [4], there are six bands at 200, 187, 179, 171, 164 and 161 cm^{-1} . They are assigned as ν_{25} and ν_{13} modes that split in the crystal. In Fig. 4, a band at 38 cm^{-1} observed in Raman spectrum of liquid after the correction with $R(\nu)$ function [24] is indicated. It probably corresponds to

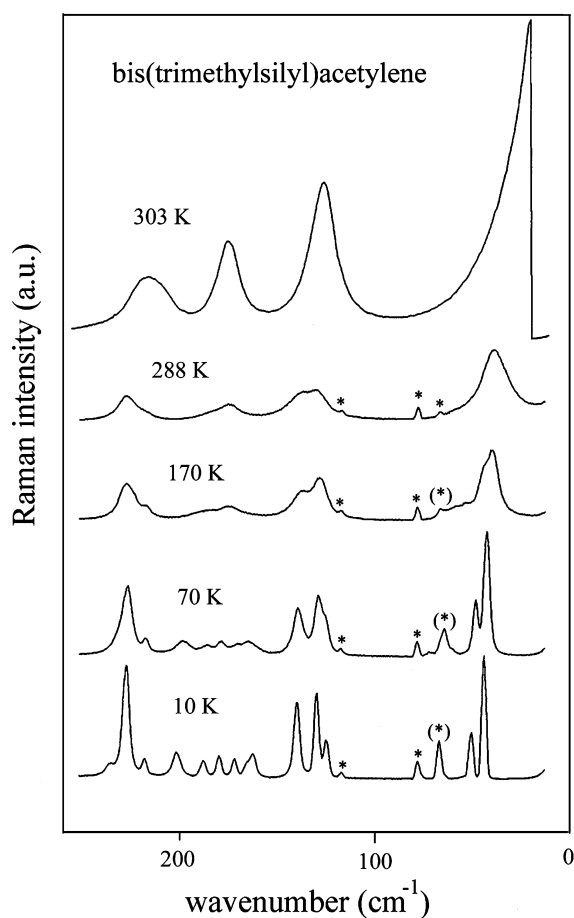


Fig. 3. Evolution of low frequency Raman spectra of BTMSA with temperature.

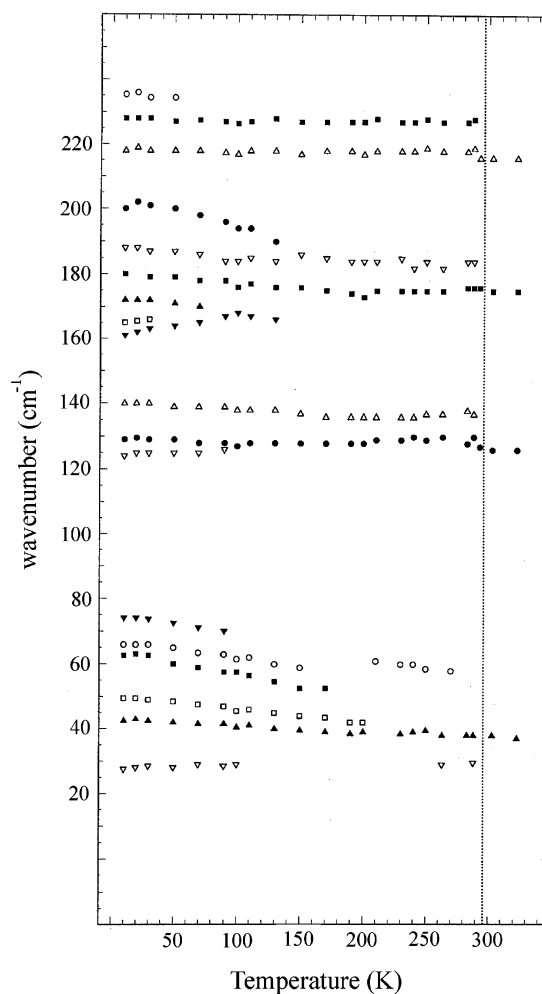


Fig. 4. Temperature dependence of the BTMSA bands below 250 cm^{-1} . Phonon bands lie below 100 cm^{-1} .

damped motions of the lowest linear bending normal modes of all BTMSA conformers present in liquid.

In conclusion, Raman spectra of BTMSA solid at low temperatures completely agree with predictions based on space group $P2_1/c$ with $Z=2$, with *trans* conformer present.

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