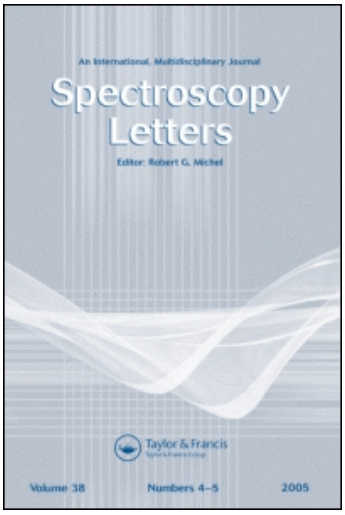

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Polarized Infrared and Raman Spectra and *Ab-Initio* Calculations of 2-(Methylthio)Benzothiazole

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POLARIZED INFRARED AND RAMAN SPECTRA AND *Ab-Initio* CALCULATIONS OF 2-(METHYLTHIO)BENZOTHIAZOLE

Key words: 2-(methylthio)benzothiazole, infrared, Raman, polarized spectra, *Ab-Initio* Calculations

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ABSTRACT

The infrared spectra of 2-(methylthio)benzothiazole have been measured from 4000 to 180 cm^{-1} for liquid and polycrystalline samples, polarized spectra of oriented films have also been obtained. The Raman spectra of polycrystalline and liquid samples have been investigated. The structural parameters, energies and vibrational frequencies have been calculated from *ab-initio* RHF calculations using the 6-31G** basis set for various conformations. A detailed assignment of most of the observed bands has been proposed on the basis of the infrared dichroism, Raman polarization data and frequency calculations.

INTRODUCTION

Besides applications in the fields of rubber technology and photography, shared with 2-mercaptobenzothiazole and its derivatives[1], the use of 2-(methylthio)benzothiazole (MTBT in the following) as a transparentizing agent for electrophotographic migration image members[2] and as a component of electrochromic materials[3] has been recently suggested. A thorough knowledge of

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the photophysical properties, in particular the optical spectra, could be of much help in understanding the behaviour of such systems. To this purpose we have undertaken an investigation of the optical spectra of MTBT and other parent compounds. At our best knowledge, an interpretation of the vibrational spectra has not yet been reported in the literature. Therefore, it was thought worthwhile to investigate the infrared and Raman spectra, also using the polarized light techniques, and to carry-out *ab-initio* calculations in order to have a firm theoretical basis for the assignment of the vibrational modes and to get information about the stable molecular conformations. We present here the vibrational assignments proposed on the basis of the infrared dichroic data and of the polarization of the Raman bands, keeping in mind the results of the theoretical calculations of the harmonic frequencies.

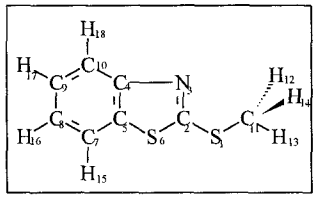
EXPERIMENTAL

MTBT from Aldrich was purified by repeated crystallizations from methanol. The trideuteromethyl-derivative was obtained from 2-mercaptobenzothiazole in alkaline solution by addition of CDI_3 following the method of Hofmann[4]. The infrared spectra were recorded on Perkin-Elmer 983G and System 2000 spectrophotometers. Polycrystalline samples were in the form of KBr pellets and Nujol mulls. Spectra of liquid films, obtained by melting the substance between CsI windows, were also obtained. Since the low melting-point of the substance prevented preparation of single crystals suitable for polarized light measurements, well oriented polycrystalline films were prepared by slow cooling of melts, between CsI plates, under a suitable temperature gradient. An area of the film which appeared uniform in orientation between crossed polarizers was chosen and the remaining was masked off. An investigation of the extinction peculiarities of the sample by means of the polarizing microscope[5] suggested that the optical symmetry plane **ac** was perpendicular to the plane developed by crystallization. The measurements of the polarized spectra were carried out using a wire-grid polarizer. The Raman spectra were obtained both with a SPEX Ramalog spectrometer, using the 488.0 nm line of a Spectra-Physics model 165 Ar^+ laser for the excitation, and with a Perkin-Elmer System 2000 FT-Raman instrument, with the excitation provided by the 1064 nm line of a diode-pumped Nd-Yag laser. The samples were enclosed in capillary cells. Depolarization ratios were measured for melted samples.

Details of calculations

The geometry of MTBT was optimized within the Hartree-Fock method using the 6-31G** basis set and allowing all the parameters to relax. Two structures, both with Cs symmetry, were found to correspond to energy minima, as revealed by the absence of imaginary values in the frequency calculations. In the more stable structure the S-CH_3 group has a *syn*- configuration with respect to the

C-N bond of the thiazole ring, whereas in the less stable structure, differing by 2.583 Kcal/Mole, the configuration is *anti-*. The *syn-* configuration is also found for the molecules in the crystal[6]. Since in the spectra of liquid samples there is no evidence of the presence of detectable amounts of different conformers, only the more stable configuration will be discussed in the following. The atom numbering is indicated in Scheme 1. The harmonic frequencies and the normal modes were calculated analytically at the same level of approximation using the following parameters obtained from the optimization step (distances in Å, angles in degrees): C_2S_1=1.7561; C_2N_3=1.2672; C_4N_3=1.3892; C_4C_5=1.392; C_5S_6=1.7499; C_2S_6=1.7605;C_5C_7=1.3875; C_7C_8=1.38; C_8C_9=1.3964; C_9C_{10}=1.3781;$C_{10}C_4$=1.3914; C_7H_{15}=1.0748; C_8H_{16}=1.0753; C_9H_{17}=1.0753; $C_{10}H_{18}$=1.0744; S_1C_{11}=1.8094; $C_{11}H_{12}$= $C_{11}H_{14}$=1.0794; $C_{11}H_{13}$=1.0819; $S_1C_2N_3$=124.8776; $N_3C_2S_6$=116.5002; $C_2N_3C_4$=111.0384; $N_3C_4C_5$= 115.3314; $C_4C_5S_6$=109.0249; $C_2S_6C_5$=88.1051; $C_4C_5C_7$=121.595; $C_5C_7C_8$=118.0399; $C_5C_7H_{15}$=121.1248; $C_7C_8C_9$=120.8169; $C_7C_8H_{16}$=119.5449; $C_8C_9C_{10}$=120.9182; $C_8C_9H_{17}$=119.4179; $C_9C_{10}C_4$=118.7843; $C_9C_{10}H_{18}$=121.6311; $N_3C_4C_{10}$=124.8229; $C_2S_1C_{11}$=100.3158; $S_1C_{11}H_{12}$= $S_1C_{11}H_{14}$=110.4861; $S_1C_{11}H_{13}$=105.9297; $H_{12}C_{11}H_{13}$= $H_{14}C_{11}H_{13}$=110.0381; $H_{12}C_{11}H_{14}$=109.801; $H_{14}C_{11}S_1C_2$=60.8551; $H_{12}C_{11}S_1C_2$=-60.8551; $H_{13}C_{11}$ S_1C_2=180.0



Scheme 1

Calculations were performed using the GAUSSIAN 94 program[7] . A semiquantitative description of vibrational modes in terms of internal coordinates was also obtained. To this purpose the cartesian force constants were transformed to the internal coordinate space using the relationship

$$\mathbf{F}_{int}=(\mathbf{B}^{-1})^t\mathbf{F}_{cart}(\mathbf{B}^{-1})$$

where the pseudo-inverse $\mathbf{B}^{-1}$ matrix was obtained following the procedure outlined by Boatz and Gordon[8] and using the optimized geometry. A redundant set of 66 internal coordinates was used: torsional coordinates were defined according to the suggestions of Keresztury *et al.* [9] .The $\mathbf{F}_{int}$ and **G** matrices built in the previous step were used to perform a standard zero-order **GF**-matrix treatment from which the vibrational frequencies and the Potential Energy Distribution (P.E.D.) were obtained. A uniform scaling of 0.81 was applied to the force constants. It is worth mentioning that the frequencies computed with $\mathbf{F}_{cart}$ and $\mathbf{F}_{int}$ were in complete agreement.

RESULTS AND DISCUSSION

Selection rules and spectral predictions

MTBT crystallizes in the monoclinic system, space group $P2_1/c$ (C_{2h}^5)[6].There are four molecules in the unit cell located on C_1 sites, and the molecular skeleton is planar with the exception of the S-CH_3 group, which lies 0.19 pm out of the molecular plane. So, keeping in mind the results of the *ab-initio* calculations, a C_s symmetry is assumed for the discussion of the spectra. The selection rules for the MTBT molecules and the crystal are given in Table 1.

According to Table 1, each molecular fundamental should give four components in the crystal spectrum for **k**=0, two being infrared active and two Raman active; one of the infrared active components is polarized along the **b** axis, the other in the **ac** plane. The A' and A" molecular fundamentals could be discriminated, to some extent, on the basis of the Raman polarization data of the liquid samples.

Information concerning the assignments of the infrared bands can also be obtained from the consideration of their dichroism. The oriented gas model may be used to predict the behaviour in polarized light. For the isolated molecule, only the direction of the transition moments of the A" vibrations is fixed by symmetry in a direction perpendicular to the molecular plane. The direction of transition moments of the A' modes are only being restricted in the plane of the molecule. Therefore, using the atomic coordinates given by Wheatley[6], the proportionality factors for the absorption intensities of A" modes, for light polarized along some significant crystallographic directions, as

	a*(⊥bc)	**b**	**c**
I(A")	0.540	0.456	0.003

From these values it can be argued that, in the polarized infrared spectra recorded on the **bc** crystal plane, the A" out-of-plane modes should give the strongest component when the electric vector of the light is parallel to the **b** crystal axis. Bands showing a strong component perpendicular to the **b** axis or components in both polarizations can be confidently assigned to A' in-plane modes. Since the orientation of the crystal axes with respect to the polarizer was not initially known, the following procedure was used to interpret the dichroic spectra. The strong infrared band at 756 cm^{-1}, whose assignment to an A" out-of-plane CH bending mode may be considered firmly settled on the basis of the Raman depolarization ratio, absorption intensity, and correlative arguments[10,13], was chosen as reference. A polarizer orientation giving the maximum intensity for this band was set up (β-spectrum): by 90° rotation of the polarizer the intensity of the band was reduced to a minimum value (α-spectrum). Keeping in mind the relative intensities predicted by the oriented-gas model and the extinction

TABLE I

Selection rules for the free molecule and the unit cell of MTBT

Molecule C_s	Site C_1	Unit cell C_{2h}
		A_g 54 (3T+3T) (R)
A' 32 (IR, R)		
	A 48 (IR, R)	B_g 54 (3T+3R) (R)
		A_u 53 (2T+3R)+T_b (IR)
A'' 16 (IR, R)		
		B_u 52 (1T+3R)+$T_{a,c}$ (IR)

T= Translatory lattice modes; R= Rotatory lattice modes

properties observed under the polarizing microscope, this behaviour is consistent with an orientation of the **b** and **c** axes parallel to the electric vector direction giving the β- and α-spectrum, respectively.

Vibrational assignments

The polarized infrared spectra are shown in Figure 1 and the relevant infrared and Raman data are collected in Table 2 together with the assignments. The approximate descriptions of the fundamentals are given with reference to the P.E.D. values obtained from the normal coordinate calculation.

Two CH stretching fundamentals for the benzene ring may be safely assigned to the polarized Raman bands observed at 3060 and 3028 cm^{-1} in the spectrum of the liquid, which correspond to the weak infrared absorption at 3064 and 3026 cm^{-1} , respectively. One of the remaining two fundamentals of this type may be associated to the α-polarized infrared band at 3053 cm^{-1} , whereas no obvious candidate for the fourth mode may be proposed on the basis of the available experimental data. The high-frequency component of the weak infrared doublet at 3011-3006 cm^{-1} is tentatively proposed on correlative grounds[11] and on the basis of the observation that a weak absorption at 3013 cm^{-1} is still present in the spectrum of the $-CD_3$ derivative. The assignment of one of the CH_3 stretching fundamentals of A' symmetry to the polarized Raman band at 2928 cm^{-1} is straightforward since it completely disappears after deuteration, the corresponding CD_3 stretching mode being observed at 2130 cm^{-1} .Likewise, the observation that the weak absorption at 3006 cm^{-1} is completely absent in the spectrum of the $-CD_3$ derivative suggests its assignment as another $-CH_3$ stretching fundamental. This choice is also supported by the disappearance, after deuteration, of a weak Raman

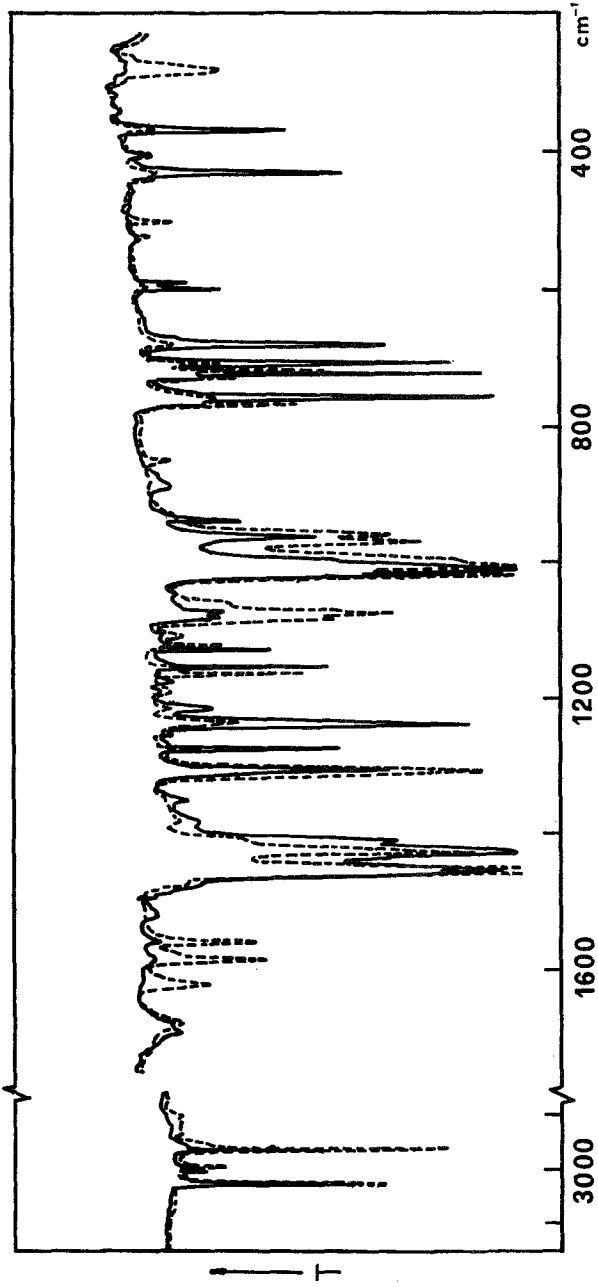


FIG. 1. Polarized infrared spectra of 2-(methylthio)benzothiazole.
Solid line:β-spectrum; dashed line:α-spectrum

band in the same range. Moreover, the β-polarization of the infrared band is consistent with the attribution to the A" symmetry. According to the *ab-initio* calculations the remaining CH_3 stretching fundamental of A' symmetry should fall at wavenumbers slightly lower than that of the A" fundamental. The band at 2990 cm^{-1}, which is not affected by the deuteration of the methyl group, must be ruled out, but a careful comparison of the infrared spectra of $-CH_3$ and $-CD_3$ derivatives reveals that a shoulder on the low-frequency side of this band is present at 2981 cm^{-1} only in the spectrum of the normal derivative and so it can be tentatively assigned to this mode.

Two A' skeletal stretching fundamentals can be safely assigned to the infrared bands found at 1589 and 1558 cm^{-1} in the spectrum of the liquid compound, their attribution being supported by the Raman polarization data and by the dichroism. Calculations suggest the presence of another A' mode in the range1650-1600 cm^{-1}: although no Raman bands are present in this range, it appears reasonable to assign this fundamental to the shoulder observed at 1615 cm^{-1} in the infrared spectrum of the liquid sample, with an α-polarized counterpart at 1620 cm^{-1} in the spectrum of the oriented sample. Skeletal stretching fundamentals as well as methyl bending modes[12] are expected in the region 1500-1290 cm^{-1}, but deuteration does not cause appreciable effects on the spectra in this range, excepting a change in the relative intensities of the two strong polarized Raman bands at 1460 and 1426 cm^{-1} and a noticeable reduction of the intensity of the low-frequency shoulder of the last band. So, it appears reasonable to assign these bands to the skeletal stretching fundamentals calculated between 1500 and 1400 cm^{-1} and to assume that the methyl bending fundamentals have low intensity. That one corresponding to the A" component of the degenerate bending very likely contributes to the intensity of the shoulder at 1412 cm^{-1}. This hypothesis is in agreement with the β-polarization of the infrared band observed at 1411 cm^{-1} in the dichroic spectrum. That one corresponding to the A' component is probably hidden by the strong skeletal band at higher frequency.

Some support to this interpretation is supplied by the polarized infrared spectra, where a number of crystal components exceeding those estimated on the basis of the selection rules of Table 1 is observed in the region between 1450 and 1460 cm^{-1}. No satisfactory candidate may be proposed for the $-CH_3$ symmetric bending mode calculated at 1351 cm^{-1}, since all the weak features observed in the range 1400-1300 cm^{-1} are present both in the spectra of the normal compound and in those of the deuterated derivative. As to the methyl rocking modes, which are expected between 1030 and 960 cm^{-1} on correlative basis[12], two infrared bands are observed at 970 and 960 cm^{-1}, which disappear on deuteration, may be safely chosen for this assignment; the A" component has been chosen on the basis of the Raman polarization data rather than considering the infrared dichroism. Also, the assignment of ν_{42} to the α-polarized band at 523 cm^{-1} has to be considered as tentative and mainly suggested by the calculations.

Calculations reveal that the C_2-S_1 stretching contributes to several modes, the largest P.E.D. element being that calculated for the frequency at 357 cm^{-1},

TABLE 2
Experimental spectral data, calculated frequencies (scaled values) and assignments for 2(methylthio)-Benzothiazole

infrared frequencies and polarizations(P)			Raman shift and polarizations (P)		Calc.		Assignments and P.E.D. (>10%)
solid	P	liquid	solid	liquid			
3064 vw		3060 m	3063 w	3060 mw,p	3046 A'	ν_1	$20r_{9,17}$,$68r_{10,18}$
3052 mw	α		3054 mw		3038 A'	ν_2	$46r_{7,15}$, 34 $r_{16,8}$, $18r_{10,18}$
3025 vw	β	3028 w	3022 w	3028 vw,p	3027 A'	ν_3	$38r_{7,15}$, $38r_{17,9}$,$13r_{16,8}$, $10r_{10,18}$
3011 vw					3014 A'	ν_4	$12r_{7,15}$, $45r_{16,8}$,$39r_{17,9}$
3006 vw	β		3009 vw		3004 A"	ν_{33}	50 $r_{11,12}$, $50r_{11,14}$
2990 w	α=β	2994 w	2991 vw	2993 vw,dp			
2981 sh					2990 A'	ν_5	23 $r_{11,12}$, $54r_{11,13}$, $23r_{11,14}$
2925 mw	α=β	2926 m	2925 mw	2927 mw,p	2904 A'	ν_6	27 $r_{11,12}$, $46r_{11,13}$, $27r_{11,14}$
...		...	...	...			
1676 m	α=β	1680 m					
1617 w	α	1620 sh			1620 A'	ν_7	$13r_{5,7}$, $15r_{7,8}$,$18r_{9,10}$, $16r_{4,10}$
1584 w	α	1589 w	1589 mw	1591 mw,p	1588 A'	ν_8	$13r_{4,5}$, $24r_{8,9}$,$10r_{4,10}$
1556 w	α	1558 m	1560 mw	1559 w,p	1548 A'	ν_9	$71r_{2,3}$
1522 vw	β						
1475 w	α=β						
1458 s	α	1459 s	1459 vs	1460 vs,p	1458 A'	ν_{10}	$11r_{7,8}$, $12r_{4,10}$,$14\alpha_{9,8,17}$, $12\alpha_{10,9,17}$
1454 sh	α,β		1448 sh		1445 A'	ν_{11}	$13\alpha_{12,11,13}$, $64\alpha_{12,11,14}$, $13\alpha_{13,11,14}$
1424 vs	β>α	1426 vs	1429 vs	1426 vs,p	1452 A'	ν_{12}	$10r_{4,5}$,$13\alpha_{5,7,15}$, $13\alpha_{8,7,15}$
1412 sh	β		1413 sh	1410 sh	1431 A"	ν_{34}	$47\alpha_{12,11,13}$, $64\alpha_{13,11,14}$
1387 sh	β		1384 vw				
1355 sh	β	1340 vw	1348 vw	1350 vw,p			
					1351 A'	ν_{13}	$17\alpha_{1,11,12}$, $19\alpha_{1,11,13}$, $17\alpha_{1,11,14}$, $17\alpha_{12,11,13}$,$10\alpha_{12,11,14}$, $17\alpha_{13,11,14}$
1308 ms	α>β	1309 ms	1307 m	1310 mw,p	A'		
1272 m	β>α	1273 m	1272 ms	1274 m,p	1272 A'	ν_{14}	$10r_{4,10}$,$12\alpha_{4,10,18}$, $14\alpha_{5,10,18}$
1234 ms	β>α	1238 ms	1235 s	1238 s,p	1233 A'	ν_{15}	$34r_{3,4}$,$14r_{5,7}$, $12\alpha_{5,7,15}$
1215 w	β>α	1215 sh	1216 w	1216 sh	1212 A'	ν_{16}	$11r_{4,5}$, $12r_{5,7}$,$10r_{4,10}$, $10\alpha_{7,8,16}$
1195 vw	α		1192 vw				
1176 vw	β	1174 w	1177 vw	1178 vw,p			
1162 w	α						
1153 w	β	1157 mw	1155 w	1157 w,?			
1129 mw	β						
1121 mw	α	1125 m	1123 mw	1125 m,p	1122 A'	ν_{17}	$36r_{7,8}$,$12\alpha_{7,8,16}$, $10\alpha_{9,8,16}$
1110 w	α	1106 vw	1109 vw	1107 vw,p			
1082 sh	α						
1076 m	α	1079 ms	1075 w	1077 w,p	1098 A'	ν_{18}	$12r_{5,7}$, $17r_{8,9}$,$25r_{9,10}$, $10\alpha_{8,9,17}$
1064 sh	α	1068 ms					
1050 sh	α=β	1045 w	1048 vw	1047 vw,p	1066 A'	ν_{19}	$17r_{5,6}$, $10r_{4,10}$,$10\alpha_{8,7,15}$
		1024 sh	1026 sh	1027 sh,?			
1020 m	α>β	1019 ms	1019 w	1018 sh,?	1019 A'	ν_{20}	$20r_{1,2}$, $13r_{2,6}$,$10\alpha_{3,2,6}$

TABLE 2 (cont.)

infrared frequencies and polarizations(P)			Raman shift and polarizations (P)		Calc.		Assignments and P.E.D. (>10%)
solid	P	liquid	solid	liquid			
1007 vs	α=β	1004 s	1007 m	1007 m,p	1004 A'	ν_{21}	$35r_{8,9}$, $10r_{9,10}$,$10r_{7,8}$
997 sh	?	998 sh	995 sh	995 sh,?	1003 A"	ν_{35}	$21\gamma_{16}$, $27\gamma_{17}$, $13\gamma_{18}$, $16\tau_{8,9}$, $10\tau_{9,10}$
970 m	α	968 sh	973 w	971 vw,?	981 A'	ν_{22}	$13r_{1,2}$,$10\alpha_{1,11,12}$, $43\alpha_{1,11,13}$, $10\alpha_{1,11,14}$
960 ms	α>β	959 m	960 vw	961 vw,?	974 A"	ν_{36}	$47\alpha_{1,11,12}$, $47\alpha_{1,11,14}$
936 w	β	932 w	930 vw		966 A"	ν_{37}	$26\gamma_{15}$, $15\gamma_{16}$, $23\gamma_{18}$, $12\tau_{7,8}$, $10\tau_{9,10}$
889 w	β	882 w	890 vw		878 A"	ν_{38}	$30\gamma_{15}$, $10\gamma_{17}$, $28\gamma_{18}$, $13\tau_{8,9}$
874 vw	β	870 vw	870 w,p				
852 w	α	850 w	849 w	860 w,p	841 A'	ν_{23}	$11r_{1,2}$, $17r_{3,4}$,$10r_{4,10}$, $14\alpha_{7,8,9}$
763 s	α						
756 s	β	753 vs	759 w	758 vw,dp	770 A"	ν_{39}	$17\gamma_{15}$, $34\gamma_{16}$, $13\gamma_{17}$, $12\gamma_{18}$, $12\tau_{5,7}$
726 m	α						
722 m	β	725 s	724 vw	...	735 A"	ν_{40}	$15\gamma_{15}$, $28\gamma_{17}$, $12\tau_{7,8}$, $13\tau_{4,10}$, $10\tau_{2,3}$
716 sh	α		715 w				
705 ms	β	704 mw	705 m	705 ms,p	700 A'	ν_{24}	$94r_{1,11}$
			688 w				
676 m	β	671 m	678 w	676 vw,p	694 A'	ν_{25}	$28r_{5,6}$,$14\alpha_{8,9,10}$, $10\alpha_{4,10,9}$
650 sh	β	665 sh	646 vw		664 A'	ν_{26}	$45r_{2,6}$, $10\alpha_{2,3,4}$
592 w	β	597 mw	596 w	597 vw,dp	594 A"	ν_{41}	$35\gamma_{1}$, $10\tau_{8,9}$, $18\tau_{3,4}$, $14\tau_{2,3}$
588 w	β	586 w	589 vw	587 vw,p?	590 A'	ν_{27}	$18r_{1,2}$,$13\alpha_{7,8,9}$, $12\alpha_{5,4,10}$
533 vw	α=β	528 sh					
523 vw	α>β	523 vw	521 vw	...	525 A"	ν_{42}	$35\gamma_{1}$, $28\tau_{8,9}$
504 vw	α=β	502vw	502 m	502 m,p	494 A'	ν_{28}	$18r_{5,6}$, $11\alpha_{4,5,6}$, $14\alpha_{2,6,5}$
436 sh	α						
429 m	β	428 mw	436 vw	428 vw,?	434 A"	ν_{43}	$15\tau_{7,8}$, $10\tau_{5,7}$, $19\tau_{9,10}$, $10\tau_{3,4}$, $11\tau_{5,6}$
402 w	α=β	397 w	403 w	401 w,p	396 A'	ν_{29}	$12r_{5,6}$,$17\alpha_{6,5,7}$, $15\alpha_{2,1,11}$
		371 sh		371 sh,p			
365 m	β	365 m	364 vw	365 w,p	357 A'	ν_{30}	$34r_{1,2}$,$10\alpha_{3,4,10}$
		300 vw	295 vw	300 vw,dp	297 A"	ν_{44}	$13\gamma_{1}$, $13\tau_{4,10}$, $24\tau_{2,3}$, $23\tau_{2,6}$
279 w	α	272 w	279 w	273 mw,p	263 A'	ν_{31}	$10r_{2,6}$,$54\alpha_{2,1,11}$
			207 w	203 w,dp	189 A"	ν_{45}	$14\tau_{4,5}$, $29\tau_{5,7}$, $29\tau_{3,4}$
			166 vw	151 vw,dp	166 A"	ν_{46}	$88\tau_{1,11}$
			125 m	120 w,dp	137 A'	ν_{32}	$24\alpha_{1,2,3}$, $25\alpha_{1,2,16}$, $34\alpha_{2,1,11}$
					99 A"	ν_{47}	$25\tau_{2,3}$, $40\tau_{2,6}$, $15\tau_{5,6}$
			86 s				lattice mode
					58 A"	ν_{48}	$97\tau_{1,2}$
			46 vs				lattice mode
			26 s				lattice mode

s=strong; m=medium;w=weak;r=stretch; α=i.p.bend; γ=o.o.p.bend; τ=torsion

which corresponds to the weak polarized Raman band at 365 cm^{-1} . On the contrary, only the mode calculated at 700 cm^{-1} is an almost pure S_1-CH_3 stretching.

Besides the previously discussed CH out-of-plane fundamental at 756 cm^{-1}, another γCH mode may be associated to the absorption band observed at 932 cm^{-1} in the spectrum of the liquid, on the basis of the prevailing β-polarization shown by its counterpart in the polarized spectra. Another γCH fundamental is tentatively assigned to the weak infrared band at 889 cm^{-1} which shows a clear β-type polarization and has only a very weak counterpart in the Raman spectra of solids. As to the remaining γCH fundamental, which is predicted at 1003 cm^{-1} by the calculations and near 970 cm^{-1} by correlative arguments[10,13] , it is possible that this mode is hidden by the strong absorption band with a maximum at 1007 cm^{-1} , which shows both α- and β- polarized components. No obvious candidate may be proposed for the assignment and the choice of the shoulder at 997 cm^{-1} , of uncertain polarization, must be considered as tentative.

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