ISSN 1330–0008
CODEN FIZAE4

ASYMMETRIC PROFILE OF THE TOTALLY SYMMETRIC STRETCHING BAND IN RAMAN SPECTRA OF BIS(TRIMETHYLSILYL)ACETYLENE

VLASTA MOHAČEK-GROŠEV and KREŠIMIR FURIĆ

Ruđer Bošković Institute, POB 180, 10002 Zagreb, Croatia

Dedicated to the memory of Professor Vladimir Šips

Received 26 January 2005; Accepted 28 November 2005
Online 7 December 2005

The asymmetric band profile of the triple $C=C$ stretching Raman band in bis(trimethylsilyl)acetylene was decomposed into a higher and a lower wavenumber part, each described as one half of a Lorentzian bandshape with its own halfwidth ($\Gamma_{\rm high}$ and $\Gamma_{\rm low}$), but with common band centre and maximum point. $\Gamma_{\rm high}$ and $\Gamma_{\rm low}$ were fitted at seventeen different temperatures ranging from 110 K to 323 K (the melting point occurring roughly at 290 K). It was found that lower wavenumber side of the band was considerably broader than the higher wavenumber side, throughout the whole temperature interval chosen. This unexpected crystal-band asymmetry, present together with the "normal" phonon spectrum, seems to indicate a freezing of orientational disorder of methyl groups, while molecular centres of mass remain positioned on the Bravais lattice – like in the case of the so called glassy crystals. The asymmetry of the band above 290 K suggests the existence of a nonisotropic liquid state.

PACS numbers: 78.30.-j, 61.43.-j, 63.30.-e, 63.50.rx UDC 535.375.5, 532.74, 539.194

Keywords: Raman spectra, bis(trimethylsilyl)acetylene, low temperature, disorder, glassy crystal

1. Introduction

Bis(trimethylsilyl)acetylene (BTMSA, Fig. 1) is often used as a ligand in the synthesis of transition metal complexes [1, 2]. The barrier to internal rotation of three methyl groups of one half of the molecule with respect to the other three methyl groups is estimated to be very low (less than 45 J/mole [3]), whereas the minimum energy confirmation corresponds to D_{3d} (*trans*) form. The crystal struc-

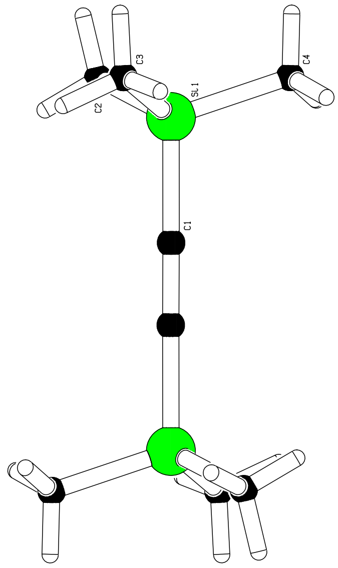

Fig. 1. Bis(trimethylsilyl)acetylene molecule in the lowest energy conformation [4].

ture of BTMSA was determined at 102 K to be monoclinic $P2_1c$ with two molecules in *trans* conformation per unit cell, and the melting point was reported to be at 293 K [4]. A Raman-scattering photon-correlation study on liquid BTMSA was reported in 1987 by Moses and Baghin who analyzed the profile of the very strong acetylenic stretching band at 2109 cm^{-1} and calculated the inhomogeneous dephasing and reorientational correlation functions for liquid at 296 K to 323 K [5]. The most striking observation occurrs in the tail of reorientational correlation functions where oscillations were reported above 3 psec, with the conclusion that BTMSA is a high-torque liquid. However, these authors used only one side (high wavenumbers, Stokes) of the band and the model that assumed the existence of a symmetric band profile [5]. As we shall see, this assumption is not appropriate for BTMSA. We recorded the 2050 − 2150 cm^{-1} Raman spectral interval of BTMSA in the temperature range from 100 K to 323 K and demonstrate the asymmetric nature of this A_{1g} band.

2. Experimental

Bis(trimethylsilyl)acetylene produced by Aldrich, 99% pure, was used without further purification.

Raman spectra were recorded with a DILOR Z24 triple monochromator in sequential mode, stepsize 1 cm^{-1} and time constant 1 sec, with slitwidth equal to 2 cm^{-1}. As the excitation source, a COHERENT INNOVA 100 Argon laser operating at 514.5 nm and laser power of 200 mW at the sample was used. Thermal equilibration of the sample, sealed into a capillary tube under vacuum, was achieved with CTI Cryogenics model 21 cryostat coupled with a Lake Shore temperature controller. Temperature stability was better than 1 K.

3. Results and discussion

Figure 2 shows two Raman spectra recorded at 323 K (liquid) and 210 K (solid) each shown together with its theoretical curve fitted to an expression

$$I(\tilde{\nu}) = DINT\left(\frac{\tilde{\nu}_0}{\tilde{\nu}}\right)\frac{I_0}{1+\left(\dfrac{2(\tilde{\nu}-\tilde{\nu}_0)}{\Gamma_{\mathrm{low}}}\right)^2} + DINT\left(\frac{\tilde{\nu}}{\tilde{\nu}_0}\right)\frac{I_0}{1+\left(\dfrac{2(\tilde{\nu}-\tilde{\nu}_0)}{\Gamma_{\mathrm{high}}}\right)^2} + b \quad (1)$$

for wavenumbers $\tilde{\nu}$ from 2050 − 2150 cm^{-1}. The function $DINT(x)$ is the integer number of the real x, and for $\tilde{\nu} < \tilde{\nu}_0$ from our spectral interval $DINT(\tilde{\nu}_0/\tilde{\nu})$ is equal to 1, while $DINT(\tilde{\nu}/\tilde{\nu}_0)$ is equal to 0. The reverse holds if $\tilde{\nu} > \tilde{\nu}_0$.

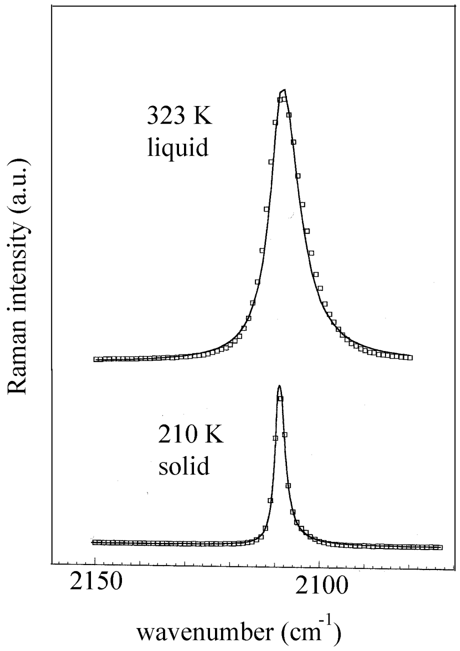

Fig. 2. Raman 2109 cm^{-1} *band of BTMSA observed in liquid and solid state. Experimental data (squares) are compared to curves obtained by fitting of expression (1).*

In this way, there are five parameters that are fitted using MINUIT program [6] at each temperature: I_0, ν_0, $\Gamma_{\rm low}$, $\Gamma_{\rm high}$ and b (background). $\Gamma_{\rm low}$ is the halfwidth of the low-frequency wing of the band centered at ν_0, measured at the intensity of $0.5\,I_0$, and $\Gamma_{\rm high}$ the corresponding quantity for the high-frequency ($\nu > \nu_0$) side.

The temperature dependence of $\Gamma_{\rm low}$ and $\Gamma_{\rm high}$ is shown in Fig. 3. At 100 K, the total bandwidth of the 2109 $\rm cm^{-1}$ band is 2 $\rm cm^{-1}$ and equals the spectral slitwidth of the spectrometer. With the temperature rise, we observe a more rapid increase of $\Gamma_{\rm low}$ than of $\Gamma_{\rm high}$, which proceeds in a likewise manner even after melting has taken place (vertical dashed line).

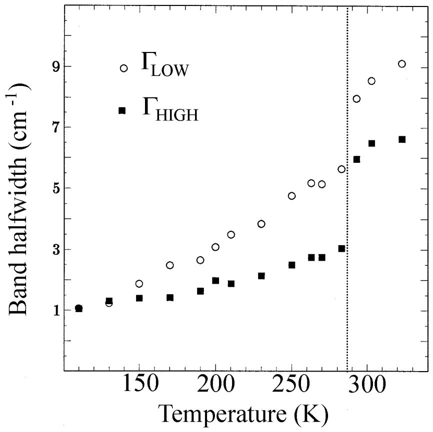

Fig. 3. Temperature dependence of the $\Gamma_{\rm low}$ *and* $\Gamma_{\rm high}$ *halfwidth of the triple* C – C *Raman stretching vibration. Vertical dotted line denotes approximately the melting transition.*

What causes the observed band asymmetry? According to Rotschild's interpretation of the shape of the quinoline glass bands [7], it is the existence of a limited number of neighbouring interaction sites that the active oscillator senses which causes the observed asymmetry. In this study, we have not observed a pure glassy state, which would be characterized by a low frequency asymmetric band called Boson peak [8], but a "normal" Raman phonon spectrum at all temperatures between 100 K and 290 K (see Fig. 4.). However, there exists a class of compounds known as glassy crystals [9] of which the primary example is cyclohexanol. In these systems, molecular centres of mass are distributed on a regular crystal lattice, but orientational order is frozen. What is the most probable reason for the existence of orientational disorder in BTMSA?

If we compare methyl-methyl distances both intra-(d) and intermolecular (D), found in a series of trimethyl compounds such as $(CH_3)_3COH$ [10], $(CH_3)_3CCl$ [11], $(CH_3)_3N$ [12, 13], and a number of trimethyl compounds attached to a silicon atom such as $(CH_3)_3SiC{=}CH$ [14], $(CH_3)_3SiCl$ [15] and $(CH_3)_3SiC{=}CSi(CH_3)_3$ (BTMSA) [4], we find the following. For all compounds, when the methyl groups are attached to a carbon atom, d is less than D, that is each methyl group has

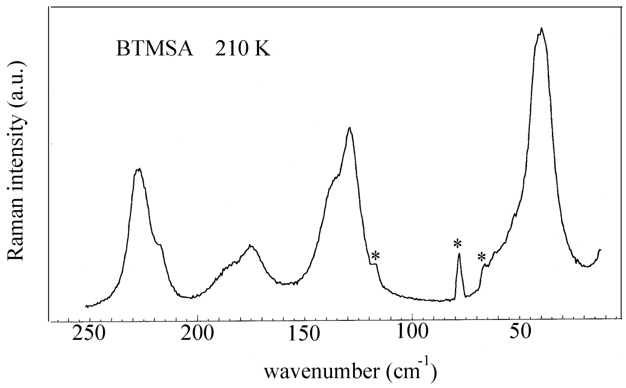

Fig. 4. Phonon Raman spectrum of BTMSA at 210 K *(12–252* cm^{-1}*). Laser plasma lines are denoted by asterisks.*

the closest neighbouring methyl group inside the molecule. In the $(CH_3)_3N$ case, both $d < D$ [12] and $d > D$ [13] occurr, depending on the crystal phase. When the three methyl groups are attached to a silicon atom, $d > D$, because C–Si bond is in all compounds 183 pm or greater. In BTMSA in particular, we find $d = 302.0$ pm and $D = 283.0$ pm.

For $(CH_3)_3COH$ and similar compounds with $d < D$, Szczesniak and coworkers found that the barrier to overall molecular rotation around the axis passing through C–O bond is nearly two times smaller than the barrier to internal rotation of an individual methyl group [16]. If this line of reasoning is true, for the opposite case of BTMSA with $d > D$, it is to be expected that the barrier to overall molecular rotation around the axis passing through the acetylenic bond is greater than the barrier for the internal rotation of an individual methyl group. That is, for BTMSA molecule in the solid, the overall rotation around the long axis is perturbed due to the presence of very close neighbouring molecules. Such systems often produce incommensurate phases, but there are at present no reports of any such phase in the case of BTMSA.

Acknowledgements

This work is submitted to the special edition of Fizika A, dedicated to the memory of late Professor Vladimir Šips.

References

[1] M. Horacek, J. Hiller, U. Thewalt, P. Stepnicka and K. Mach, J. Organomet. Chem. **571** (1998) 77.

[2] D. Thomas, N. Peulecke, V. V. Burlakov, P. Heller, W. Baumann, A. Spannenberg, R. Kempe and U. Rosenthal, Zeit. Anorg. Allgem. Chem. **624** (1998) 919.

[3] V. A. Sipachev, L. S. Khaikin, O. E. Grikina, V. S. Nikitin and M. Traetteberg, J. Mol. Struct. **523**(2000) 1.

[4] J. Bruckmann and C. Krüger, Acta Crystallogr. C **53** (1997) 1845.

[5] D. G. Moses and F. G. Baghin, J. Phys. Chem. **91** (1987) 1942.

[6] F. James and M. Roos, Comp. Phys. Commun. **10** (1975) 343.

[7] W. G. Rotschild, *Dynamics of Molecular Liquids*, J. Wiley & Sons (1984) p. 282.

[8] V. Mohaček and K. Furić, Croat. Chem. Acta **65** (1992) 119.

[9] H. Suga, J. Chim. Phys. **82** (1985) 275.

[10] D. Mootz and D. Staben. Z. Naturforsch. B **48** (1993) 1325.

[11] J. L. Tamarit, D. O. Lopez, X. Alcobe, M. Basrio, J. Salud and L. C. Pardo, Chem. Mater. **12** (2000) 555.

[12] A. J. Blake, E. A. V. Ebsworth and A. J. Welch Acta Crystallogr. C **40** (1984) 413.

[13] R. Boese, D. Blaser, M. Y. Antipin, V. Chaplinski and A. de Meijere, Chem. Commun. (1998) 781.

[14] A. D. Bond and J. E. Davies, Acta Crystallogr. E **58** (2002) 777.

[15] J. Buschmann, D. Lentz, P. Luger and M. Rottger, Acta Crystallogr. C **56** (2000) 121.

[16] S. Glowinkowski, S. Jurga, W. Suchanski and E. Szczesniak, Mol. Phys. Rep. **14** (1996) 83.

ASIMETRIČAN OBLIK POTPUNO SIMETRIČNE VRPCE ISTEZANJA U RAMANOVOM SPEKTRU BIS(TRIMETILSILIL)ACETILENA

Asimetričan oblik Ramanove vrpce trostrukog C = C istezanja bis(trimetilsilil)acetilena rastavili smo u visoko- i niskofrekventni dio, i svaki dio opisali polovicom Lorentzovog profila vlastite poluširine ($\Gamma_{\rm high}$ i $\Gamma_{\rm low}$), zajedničkog središta i jednakog maksimalnog intenziteta. Točke Ramanovog spektra u području trostrukog istezanja zabilježene su u intervalu temperature od 110 K do 323 K (do taljenja dolazi oko 290 K). Proveli smo postupak prilagodbe parametara ($\Gamma_{\rm high}$ i $\Gamma_{\rm low}$) na opažene točke. Našli smo da je niskofrekventna strana vrpce značajno šira od visokofrekventne strane i to u čitavom istraživanom području temperature. Čini se da je ova neočekivana asimetrija vrpce kristala, uz istovremeno opažen fononski spektar, znak zamrzavanja orijentacijskog nereda metilnih grupa, dok su središta masa molekula raspoređena pravilno na Bravaisovoj rešetci, kao u slučaju staklastih kristala. Asimetrija vrpce iznad 290 K ukazuje na postojanje neizotropne tekućine.