Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

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Version of record first published: 21 Mar 2007.

To cite this article: Petros I. Ktorides & David L. Uhrich (1977): Orientation Dependence of an Unresolved Mössbauer Quadrupole Doublet in an Aligned Liquid Crystalline Glass, Molecular Crystals and Liquid Crystals, 40:1, 285-296

To link to this article: http://dx.doi.org/10.1080/15421407708084490

Mol. Cryst. Liq. Cryst., 1977, Vol. 40, pp. 285–296

Printed in Holland

Orientation Dependence of an Unresolved Mössbauer Quadrupole Doublet in an Aligned Liquid Crystalline Glass†

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(*Received December 8, 1976*)

In an aligned system, an unresolved Mössbauer quadrupole doublet will appear to be a broadened single line absorption with an orientation dependent line position (l.p.). Previously, we have reported an orientation dependent l.p. for the ^{119}Sn absorption for the solute, 4-trimethyltin-benzylidene-4′-*n*-butylaniline (Sn-BBA), in the smectic B glass of 4-*n*-butoxybenzylidene-4′-*n*-octylaniline (BBOA). The l.p. depended on the angle (θ) between the preferred molecular direction as determined by a 9 kG magnetic field and the direction of the γ-ray beam. In this report, we present a method of obtaining the isomer shift (I.S.), the quadrupole splitting (ΔE_Q) of the unresolved doublet, and the orientational order parameter [$S = \langle \frac{3}{2} \cos^2 \delta - \frac{1}{2} \rangle$] for the Sn-bearing molecules. The angle δ is the angle which a given molecule makes with the field direction and for the glass phase the brackets indicate a spatial average. The method consists of constructing a doublet spectrum for each θ based on initial guesses of I.S., ΔE_Q, S, and the single line linewidths. The constructed doublet spectrum is then computer fit with a single Lorentzian lineshape which shows a θ-dependent position and linewidth. The Mössbauer parameters are then adjusted to reproduce the θ variation of the line position and linewidth of the apparent singlet experimental spectrum. This method yields $\Delta E_Q = -0.33$ mm/sec and $S = 0.48$ for Sn-BBA in the BBOA glass at 77°K. This S-value is compared to other determinations of S for ^{57}Fe and ^{119}Sn bearing solutes which show resolved doublet spectra in liquid crystalline glasses.

INTRODUCTION

In recent years there have been several Mössbauer studies of liquid crystalline materials.[1–7] For the most part they have consisted of observing the orientation dependence of the Mössbauer parameters of solute molecules containing ^{57}Fe, ^{119}Sn, or ^{129}I. In particular, for ^{57}Fe and ^{119}Sn, the recoil-free fraction

† Presented at the Sixth International Conference on Liquid Crystals, Kent State University, Kent, Ohio 44242. August, 1976.

(f) and the relative intensities (A_π/A_σ) of the two quadrupole split absorption lines exhibit a dependence on the angle (θ) between the preferred molecular direction as determined by the external magnetic field and the gamma ray direction. To insure an observable f value the measurements are usually performed in the liquid crystalline glass phase which is produced by rapid cooling from the normal liquid crystalline phase.[1-4,6,7] In the rapid cooling, the molecular alignment evident in the normal liquid crystalline phase is preserved.

Recently, we observed the θ-dependence of the line position (l.p.) of an apparent singlet ^{119}Sn Mössbauer absorption from 4-trimethyltin-benzylidene-4′-*n*-butylaniline (Sn-BBA) in the smectic B glass of 4-*n*-butoxybenzylidene-4′-*n*-octylaniline (BBOA or 40.8).[6] The l.p. vs. θ data were interpreted in terms of an unresolved quadrupole doublet. That is, as the intensity ratio (A_π/A_σ) changed with θ, the observed result consisted of a slight change in the line position of an apparent singlet absorption. By assuming that Sn-BBA in BBOA had the same order parameter ($S = 0.17$) as triethytinpalmitate (Sn-Palm) in 4-*n*-hexoxybenzylidene-4′-*n*-propylaniline (HBPA or 60.3)[1] we were able to estimate a value for the quadrupole splitting (ΔE_Q) of the unresolved doublet.[6]

The aim of this paper is to give computer results as well as an analytical approximation for the law of variation of the apparent singlet l.p. vs. θ and computer results for the variation of the linewidth of the apparent singlet vs. θ. Further, we are able to determine ΔE_Q, S, and the isomer shift (I.S.) for Sn-BBA in BBOA by generating l.p. and linewidth vs. θ data which reproduce the experimental data to within the experimental error.

THEORY

As our starting point we will use previously derived formulae which give the variation of A_π/A_σ and f as a function of θ for transmission Mössbauer spectra.[1,2,6]

$$\frac{A_\pi(\theta)}{A_\sigma(\theta)} = \frac{1 + \frac{1}{4}(3\cos^2\theta - 1)S}{1 - \frac{1}{4}(3\cos^2\theta - 1)S} \tag{1}$$

$$\frac{f(\theta)}{f(\theta = 0)} = \exp(\varepsilon_L \sin^2\theta) \tag{2}$$

Here S is the spatial order parameter of the solute molecules in the host liquid crystalline glass and it is defined as $S = \langle\frac{1}{2}(3\cos^2\delta - 1)\rangle$ where δ is the angle between the preferred direction and the long axis of a particular molecule; $\varepsilon_L = (1/\hat{\kappa}^2)(\langle x_{\parallel}^2\rangle_L - \langle x_{\perp}^2\rangle_L)$ is the intermolecular contribution to the nuclear vibrational anisotropy of the Mössbauer nuclei. Equations 1 and 2 were derived assuming that the intermolecular vibrations and the

intramolecular vibrations are uncoupled as is usually assumed in molecular crystals.[8] Further, the intramolecular contribution to the vibrational anisotropy ε_M is assumed to be approximately zero[9] and the liquid crystalline glass is assumed to be either a nematic glass or an untilted smectic structure (e.g., smectic A or smectic B).

Experimentally, f in Eq. (2) is the total probability for a Mössbauer absorption and therefore the sum of probabilities for the π and σ transitions. For a true singlet the ratio of peak height to the background gives an adequate representation of f; however, for an unresolved doublet where the apparent singlet linewidth may have a slight θ-dependence the total area of the absorption should be used. That is $f(\theta)/f(\theta = 0)$ of Eq. (2) should be replaced with $A(\theta)/A(\theta = 0)$. The relationship between Eq. (2) and the areas for Lorentzian lineshapes is given by:

$$A(\theta) = A_\pi(\theta) + A_\sigma(\theta) = \frac{\pi}{2}\Gamma[f_\pi(\theta) + f_\sigma(\theta)] \tag{3}$$

Here, $f_\pi(\theta)$ and $f_\sigma(\theta)$ are the peak heights divided by the background for the π and σ transitions, respectively. $A_\pi(\theta)$ and $A_\sigma(\theta)$ are the areas of the π and σ transitions, respectively, and Γ is the linewidth at half height for each line. This latter assumption that $\Gamma = \Gamma_\pi = \Gamma_\sigma$ will be valid in the absence of a spread of electric field gradients at the site of Mössbauer nuclei. By using Eqs. (1) and (3), we obtain the amplitudes of the π and σ transitions as follows:

$$\begin{aligned} f_\pi(\theta) &= A(0)\exp(\varepsilon_L \sin^2\theta)\frac{1 + \tfrac{1}{4}(3\cos^2\theta - 1)S}{\pi\Gamma} \\ f_\sigma(\theta) &= A(0)\exp(\varepsilon_L \sin^2\theta)\frac{1 - \tfrac{1}{4}(3\cos^2\theta - 1)S}{\pi\Gamma}. \end{aligned} \tag{4}$$

When analyzing Mössbauer spectra one usually fits Lorentzian lineshapes to the experimental data. In particular, the resultant transmission spectrum is given by

$$y(\varepsilon) = \text{Background} - \sum_i \frac{f_i}{\left(\dfrac{\varepsilon - \varepsilon_{0i}}{\Gamma_i/2}\right)^2 + 1} \tag{5}$$

and ε_{0i}, Γ_i, and f_i are, respectively, the centroid, linewidth and amplitude of the ith absorption. Putting Eq. (4) into Eq. (5) we get:

$$\begin{aligned} y(\varepsilon) = \text{Background} &- \frac{A(0)}{\pi\Gamma}\exp(\varepsilon_L \sin^2\theta) \\ &\times \left\{\frac{1 + \tfrac{1}{4}(3\cos^2\theta - 1)S}{1 + (2/\Gamma)^2(\varepsilon - \varepsilon_{0\pi})^2} + \frac{1 - \tfrac{1}{4}(3\cos^2\theta - 1)S}{1 + (2/\Gamma)^2(\varepsilon - \varepsilon_{0\sigma})^2}\right\} \end{aligned} \tag{6}$$

To simulate the observed variation of the line position and linewidth of the apparent singlet, we can use Eq. (6) to generate n data points ($n \equiv$ number of channels used in the multichannel analyzer) for each θ. The constructed doublet spectrum may then be computer fit with a single Lorentzian lineshape. (Of course, this procedure is only useful if $(\Gamma_{exp}/2) \geq |\varepsilon_{0\pi} - \varepsilon_{0\sigma}| = |\Delta E_Q|$.) Then the l.p. vs. θ data and the $\Gamma/2$ vs. θ data for the constructed unresolved spectrum can be compared to experiment.

The respective effects of varying ΔE_Q, S and $\Gamma_\sigma = \Gamma_\pi$ on the l.p. and the linewidth of the constructed unresolved doublet spectrum are shown in Figures 1-6. An increase in the ΔE_Q or S have similar effects on the θ dependence of the l.p. To be noted, however, is that changes in $\Gamma_\sigma = \Gamma_\pi$ affect

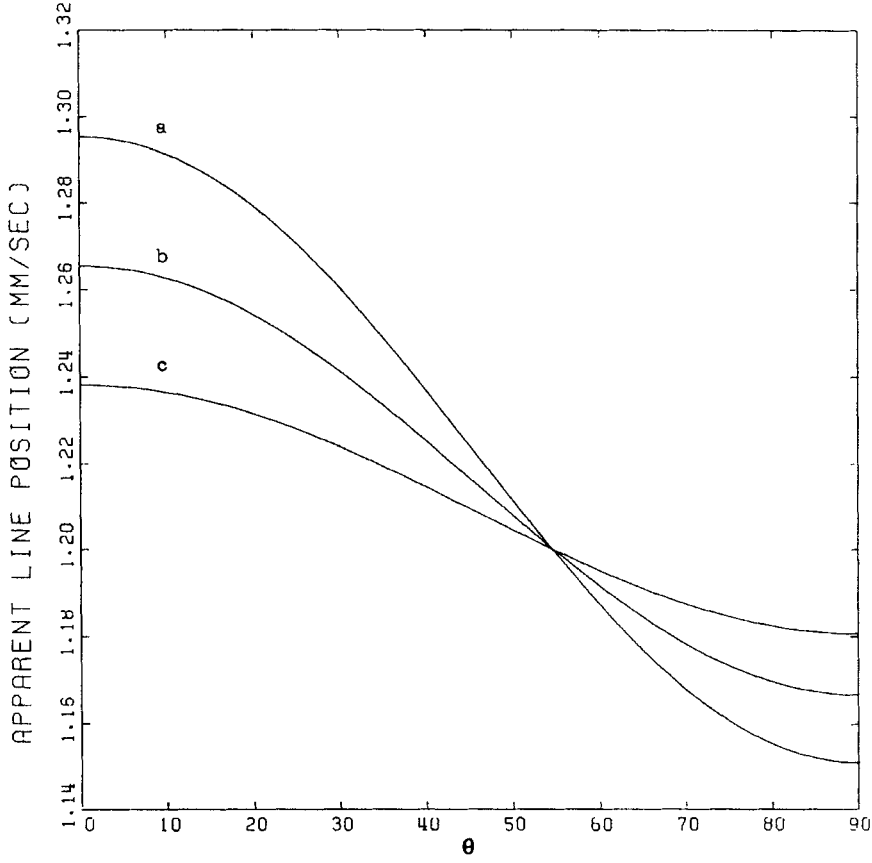

FIGURE 1 The θ variation of the l.p. of the constructed unresolved doublet spectrum for several values of ΔE_Q with fixed $S = 1.00$ and fixed $\frac{1}{2}\Gamma_\sigma = \frac{1}{2}\Gamma_\pi = 0.48$ mm/sec. Here the values of ΔE_Q (in mm/sec) are (a) 0.35, (b) 0.25, and (c) 0.15.

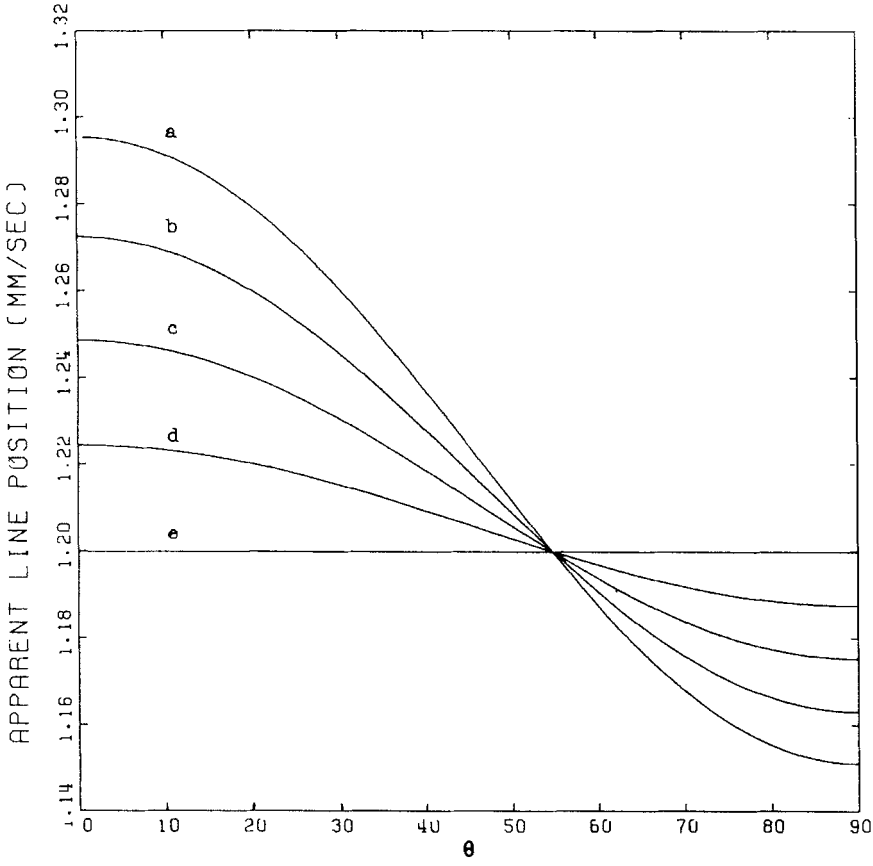

FIGURE 2 The θ variation of the l.p. of the constructed unresolved doublet spectrum for several values of S with fixed $\Delta E_Q = 0.35$ mm/sec and fixed $\frac{1}{2}\Gamma_\sigma = \frac{1}{2}\Gamma_\pi = 0.48$ mm/sec. Here the values of S are (a) 1.00, (b) 0.75, (c) 0.50, (d) 0.25, and (e) 0.00.

the variation to a lesser degree. Note, also, that the total θ variation of the unresolved doublet linewidth is very small for reasonable values of ΔE_Q, S, and $\Gamma_\pi = \Gamma_\sigma$. In fact, the total variation of the apparent singlet linewidth ($\sim$0.02 mm/sec) as shown in Figures 4–6 is of the order of the accuracy of the experimental measurements.

For given ΔE_Q and $\Gamma_\pi = \Gamma_\sigma$ we see in Figure 5 that all of the unresolved doublet linewidth vs. θ curves coincide for θ such that $3\cos^2\theta - 1 = 0$. As a result, the linewidth of the constructed singlet is independent of S at $\theta \approx 55°$ as one could also conclude by noticing that at $\theta \approx 55°$, $y(\varepsilon)$ in Eq. (6) is independent of S. Therefore, for fixed $\Gamma_\pi = \Gamma_\sigma$ the experimental linewidth of the apparent singlet at $\theta = 55°$ is determined by ΔE_Q of the

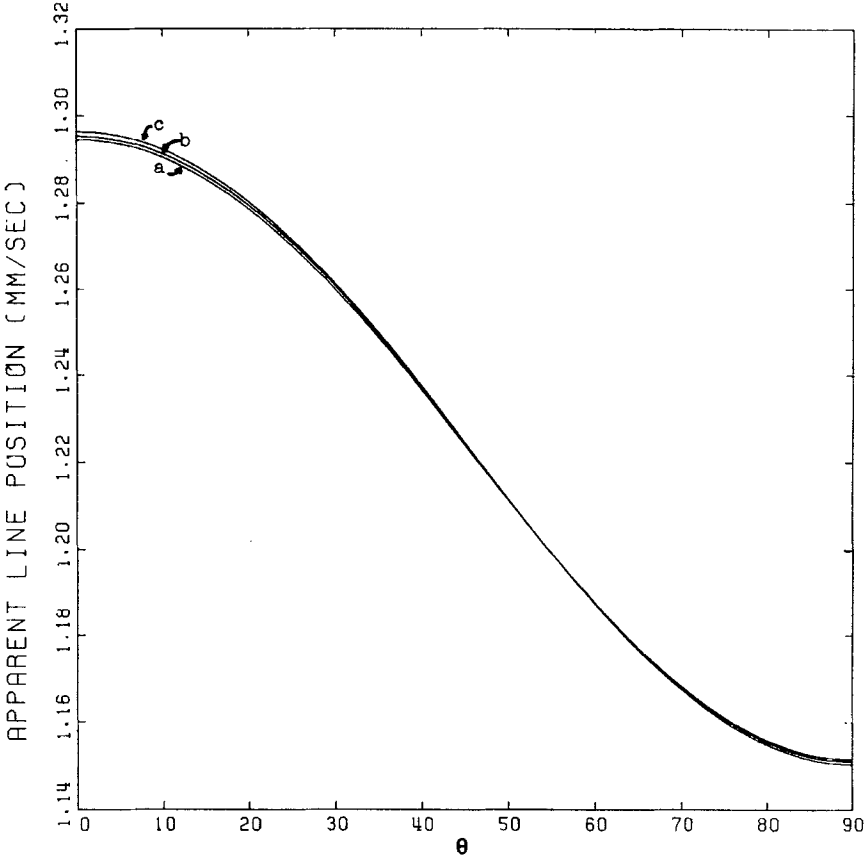

FIGURE 3 The θ variation of the l.p. of the constructed unresolved doublet spectrum for several values of $\frac{1}{2}\Gamma_\sigma = \frac{1}{2}\Gamma_\pi$ with fixed $\Delta E_Q = 0.35$ mm/sec and fixed $S = 1.00$. Here, the values of $\frac{1}{2}\Gamma_\sigma = \frac{1}{2}\Gamma_\pi$ (in mm/sec) are (a) 0.51, (b) 0.48, and (c) 0.45.

unresolved doublet. In practice, the linewidth of the singlet Lorentzian used to fit the constructed doublet spectra is adjusted to yield the experimental linewidth at $\theta = 55°$ by varying ΔE_Q.[10] Once ΔE_Q is determined, the I.S. and S are adjusted in Eq. (6) to reproduce the experimental l.p. vs. θ data for the apparent singlet.[11]

To get an analytical expression for the l.p. vs. θ variation for the case of $|\Delta E_Q| \ll \Gamma_{exp}$ one can minimize $y(\varepsilon)$ in Eq. (6) with respect to ε. To first order the result is:

$$\varepsilon = \frac{\varepsilon_{0\pi} + \varepsilon_{0\sigma}}{2} + \frac{(\varepsilon_{0\pi} - \varepsilon_{0\sigma})}{8}(3\cos^2\theta - 1)S. \tag{7}$$

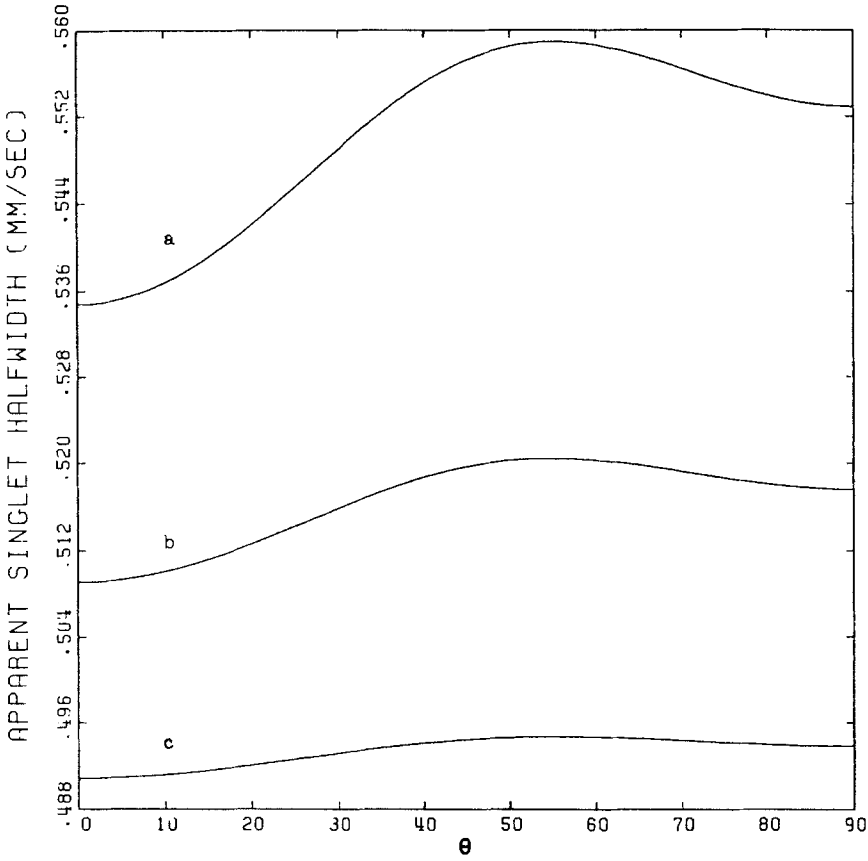

FIGURE 4 The θ variation of the half-width of the constructed unresolved doublet spectrum for several values of ΔE_Q with fixed $S = 1.00$ and fixed $\frac{1}{2}\Gamma_a = \frac{1}{2}\Gamma_\pi = 0.48$ mm/sec. Here, the values of ΔE_Q (in mm/sec) are (a) 0.35, (b) 0,25, and (c) 0.15.

or

$$\varepsilon = \text{I.S.} + \frac{\Delta E_Q}{8}(3\cos^2\theta - 1)S. \tag{8}$$

Note that for $\theta \approx 55°$ the approximate expression for ε yields the I.S. Eq. (8) gives the general shape of the l.p. vs. θ curves which are generated with the computer. For $|\Delta E_Q| < 0.5$ mm/sec Eq. (8) yields results which are very close to the results obtained using Eq. (6). Furthermore, Eq. (8) can be used to obtain initial values of ΔE_Q and S for use in the computer analysis using Eq. (6).

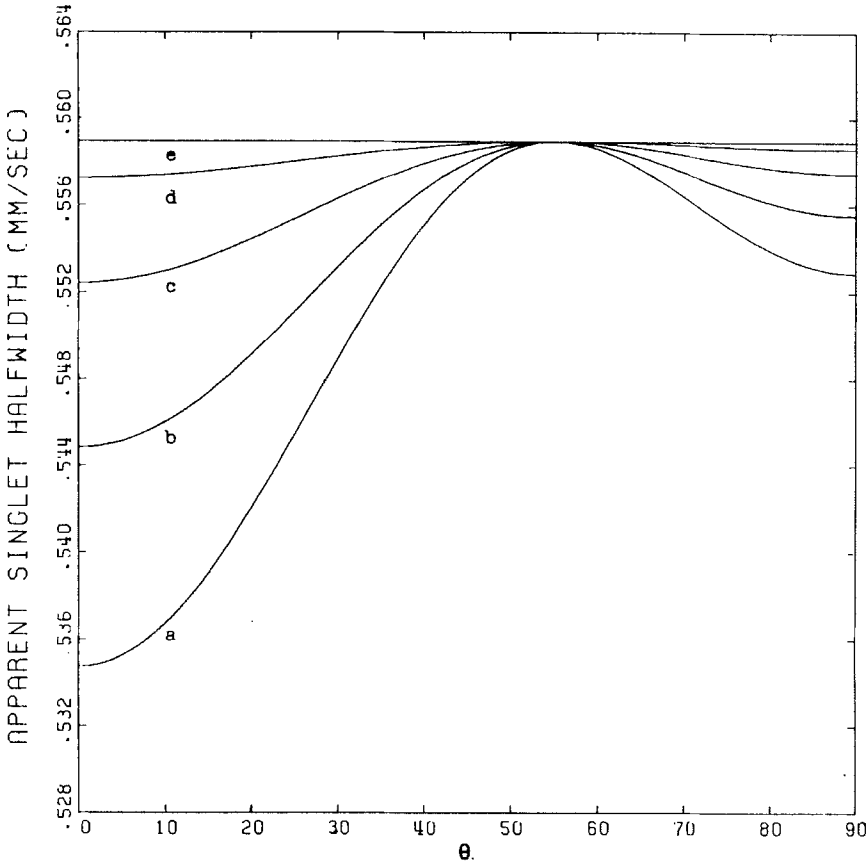

FIGURE 5 The θ variation of the half-width of the constructed unresolved doublet spectrum for several values of S with fixed $\Delta E_Q = 0.35$ mm/sec and fixed $\frac{1}{2}\Gamma_\sigma = \frac{1}{2}\Gamma_\pi = 0.48$ mm/sec. Here, the values of S are (a) 1.00, (b) 0.75, (c) 0.50, (d) 0.25, and (e) 0.00.

RESULTS AND DISCUSSION

The experimental spectra[12] were analyzed using a modified version of a program entitled PARLORS MF which fits a sum of independent Lorentzians plus a curved background to the data.[13] The data analyzed here were from folded spectra obtained using a triangle wave Doppler velocity drive system. As a result, the curved background was very small.

For Sn-BBA in BBOA at 77°K the experimental half width of the apparent singlet was $\Gamma_{exp}/2 = 0.55$ mm/sec and independent of θ. Assuming that $\Gamma_\sigma/2 = \Gamma_\pi/2 = 0.48$ mm/sec which was the half-width of true singlets for

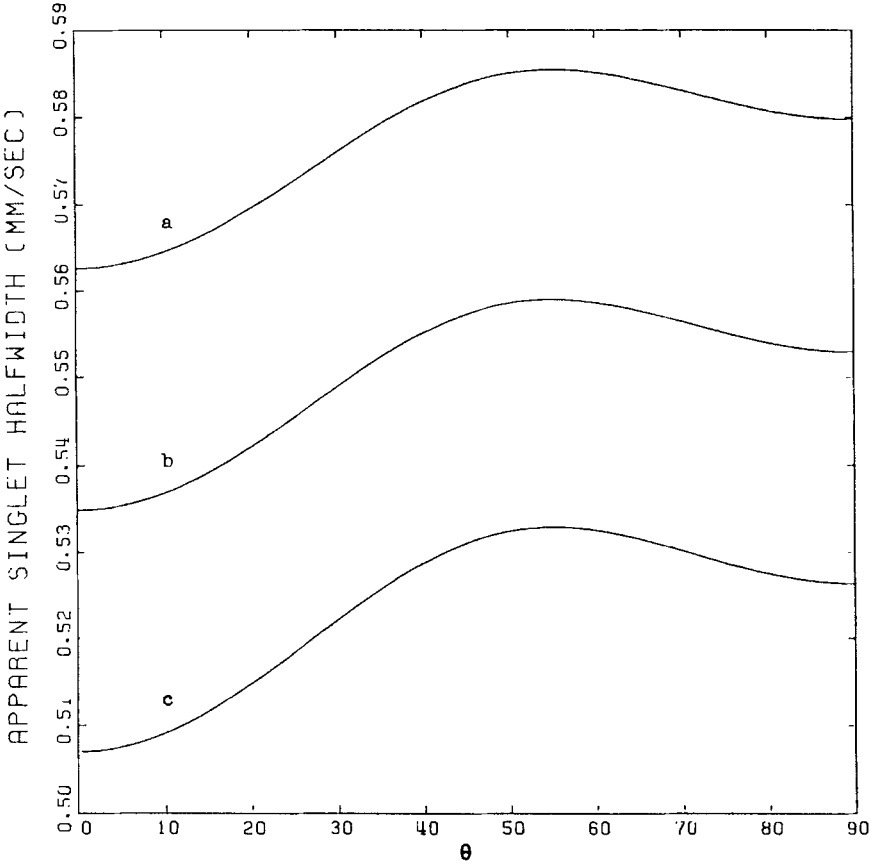

FIGURE 6 The θ variation of the half-width of the constructed unresolved doublet spectrum for several values of $\frac{1}{2}\Gamma_\sigma = \frac{1}{2}\Gamma_\pi$ with fixed $\Delta E_Q = 0.35$ mm/sec and fixed $S = 1.00$. Here the values of $\frac{1}{2}\Gamma_\sigma = \frac{1}{2}\Gamma_\pi$ (in mm/sec) are (a) 0.51, (b) 0.48, and (c) 0.45.

the same $BaSnO_3$ source and similar solutions of Sn-bearing molecules in BBOA,[14] then the method described in the previous section yielded $\Delta E_Q = -0.33$ mm/sec, $S = 0.48$, and I.S. $= 1.24$ mm/sec.[15] The apparent singlet l.p. vs. θ variation obtained using Eq. (6) with the above results is compared to the experimental data in Figure 7. Table I shows how ΔE_Q and S depend on the initial estimates of the individual linewidths of the σ and π transitions.

In Table II the computed value of $S = 0.48$ for Sn-BBA in BBOA is compared to the S values for several ^{57}Fe-bearing solutes[16] in the smectic B glass of BBOA and in one case the solute Sn-Palm in the smectic H glass of HBPA.[1] All these samples were aligned in a 9 kG field and the Mössbauer

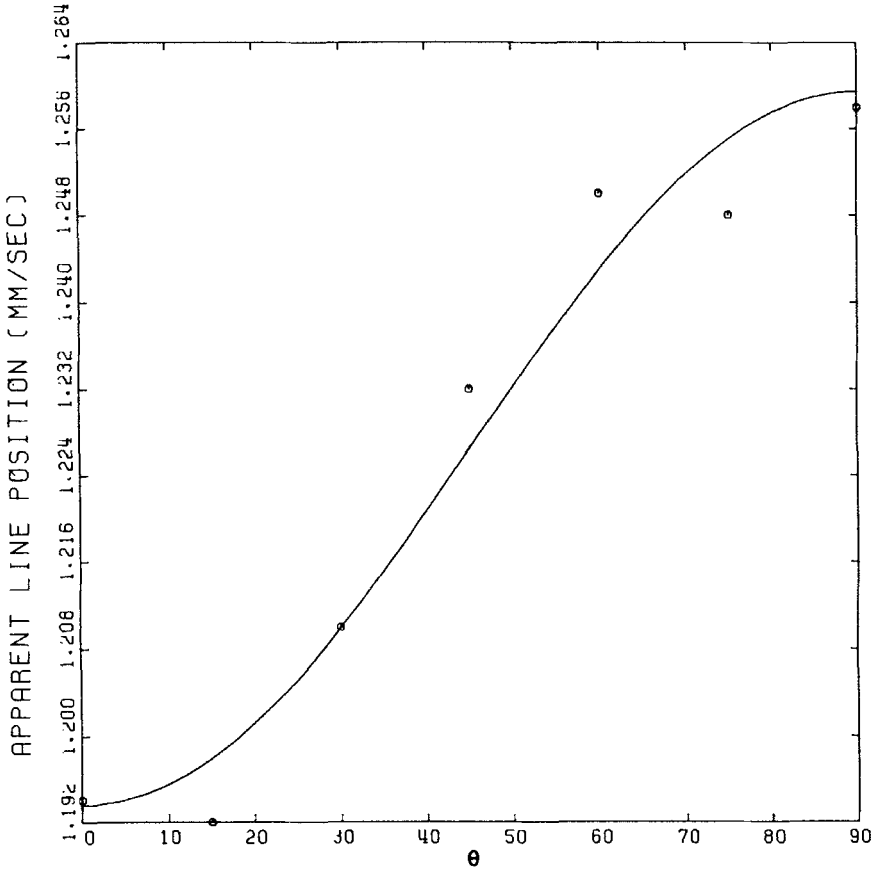

FIGURE 7 The apparent singlet l.p. vs. θ variation as obtained from Eq. 6 with $\Delta E_Q = -0.33$ mm/sec, $S = 0.48$, and $\frac{1}{2}\Gamma_a = \frac{1}{2}\Gamma_\pi = 0.48$ mm/sec (solid line) is compared to the experimental data points for Sn-BBA in the smectic B glass of BBOA at 77° K. The experimental points are average values obtained from several Mössbauer runs at each θ. The mean deviation for each point is ± 0.02 mm/sec. For Sn-BBA, $\Delta E_Q = \varepsilon_{0\pi} - \varepsilon_{0a} < 0$ so the l.p. increases with increasing θ in contrast to the curves in Figures 1–3 where $\Delta E_Q > 0$ was assumed in the computed curves and the l.p. decreases with increasing θ. From Eq. 8 one sees that the range in the l.p. variation is independent of the sign of ΔE_Q.

runs taken at 77°K. Of all the solutes the molecular shape of Sn-BBA is most like that of the liquid crystalline host molecules and its flat central core will pack well with the central cores of the BBOA molecules and produce fairly good alignment of the Sn-BBA molecules. Furthermore, the Sn-atom in Sn-BBA is bonded directly to the rigid core (the benzylidene group) and thus experiences the order characteristic of the central core portion of the

TABLE I

A comparison of ΔE_Q, S, and I.S. values as determined from the θ dependence of the apparent singlet line position for Sn-BBA in BBOA for different input values of the half-widths of the σ and π transitions. Here, we assume that $\Gamma_\pi = \Gamma_\sigma$ and $\varepsilon_m = 0$. Each set of data listed here, when used in Eq. 6 essentially reproduces the smooth curve in Figure 7.

$\Gamma_\pi/2 = \Gamma_\sigma/2$ (mm/sec)	ΔE_Q (mm/sec)	S	I.S.[a] (mm/sec)
0.45	−0.38	0.41	1.24
0.47	−0.35	0.45	1.24
0.48	−0.33	0.48	1.24
0.49	−0.31	0.53	1.24
0.51	−0.25	0.66	1.24

[a] The isomer shift values are with respect to a $BaSnO_3$ source.

host molecules. In contrast, the Mössbauer probe nucleus in the other four molecules resides in the end-chain region of the host liquid crystal molecules. The positioning of the ^{57}Fe-bearing probe molecules has been discussed in detail, previously.[16] The relatively large S values obtained for FMA and FBA are due to the attraction between the polarizable benzine rings in their end-chains and the polarizable central-core regions of the BBOA molecules. This aligning mechanism is absent in DOF which lacks benzine rings in its end-chains. Sn-Palm has a very long flexible chain which lacks polarizable units. The result is that the Sn-end of the molecule probably resides in the host end-chain region and the flexible tail is only weakly aligned by the central cores of the liquid crystal molecules. Therefore, that S for the Sn-Palm molecule is less than S for the Sn-BBA molecule is not unreasonable.

TABLE II

A comparison of order parameters for Fe and Sn bearing solutes in smectic liquid crystalline glasses at 77°K.

Host Liquid Crystal	Mössbauer Probe Molecule	S
BBOA (smectic B)	Sn-BBA	0.48
BBOA	ferrocenyl-4′-methoxyaniline (FMA)	0.37
BBOA	ferrocenyl-4′-butylaniline (FBA)	0.27
BBOA	1,1′-di-*n*-octanol ferrocene (DOF)	0.11
HBPA (smectic H)	triethyltin palmitate (Sn-Palm)	0.17

CONCLUSION

The analysis techniques presented here enable the determination of ΔE_Q, I.S. and S from the orientation dependence of an apparent single line absorption from aligned solute molecules in liquid crystalline glasses. The resulting S-value for the molecule Sn-BBA in the smectic B glass of BBOA is consistent with S-values found for probe molecules exhibiting well-resolved quadrupole doublets. Furthermore, for unresolved doublets, we have a sensitive way of determining ΔE_Q and the I.S.

References

1. D. L. Uhrich, Y. Y. Hsu, D. L. Fishel, and J. M. Wilson, *Mol. Cryst. Liq. Cryst.*, **20**, 349 (1973).
2. D. L. Uhrich, R. E. Detjen, and J. M. Wilson, in *Mössbauer Effect Methodology*, Vol. 8, edited by I. J. Gruverman and C. W. Seidel (Plenum, New York,,1973), p. 175.
3. D. L. Uhrich, J. Stroh, R. D'Sidocky, and D. L. Fishel, *Chem. Phys. Lett.*, **24**, 349 (1973).
4. R. E. Detjen and D. L. Uhrich, in *Mössbauer Effect Methodology*, Vol. 9, edited by I. J. Gruverman, C. W. Seidel, and D. K. Dieterly (Plenum, New York, 1974), p. 113.
5. V. I. Goldanskii, O. P. Kevdin, N. K. Kivrina, E. F. Makarov, V. Ya. Rochev, and R. A. Stukan, *Zh Eksp. Teor. Fiz.*, **63**, 2323 (1972), [*Sov. Phys. -JETP* **36**, 1226 (1973)].
6. D. L. Uhrich, V. O. Aimiuwu, P. I. Ktorides, and W. J. LaPrice, *Phys. Rev.*, **A12**, 211 (1975).
7. M. J. Potasek, P. G. Debrunner, and G. DePasquali, *Phys. Rev.*, **A13**, 1605 (1976).
8. V. I. Goldanskii and E. F. Makarov, in *Chemical Applications for Mössbauer Spectroscopy*, edited by V. I. Goldanskii and R. H. Herber (Academic Press, New York, 1968).
9. The assumption that $\varepsilon_M \sim 0$ for Sn-BBA has been discussed extensively in reference 6. In particular, based on Sn-C vs. Sn-O bond strengths it is quite likely much less than $|\varepsilon_M| = 0.8$ which was measured for Sn-Palm (reference 1). We have found, however, that if one includes the effect of ε_M into Eqs. 1 and 2 that for $-1 \leq \varepsilon_M \leq 1$ there is only a very small effect on the resulting ΔE_Q and S values.
10. A method similar to the bisection method for solving equations numerically was employed.
11. An iteration method similar to the Gauss–Seidel method for the solution of a system of simultaneous equations was used.
12. Due to a systematic error the l.p. values reported for Sn-BBA in reference 6 are 0.04 mm/sec too high
13. The program used is a modified version of the Parlors MF Computer Program by A. Polinger, J. J. Spijkerman, and B. W. Crist, (N. B. S., unpublished report). R. E. Detjen modified the original program for use on a Burroughs 5500 system.
14. The value of $\Gamma_\pi/2 = \Gamma_\sigma/2$ used will depend on the individual sources and detector characteristics.
15. The sign of $\Delta E_Q = \varepsilon_{0\pi} - \varepsilon_{0\sigma} = eQq/2$ is simply determined. (Q is the quadrupole moment and q is the e.f.g.). Eq. 1 shows, that for positive S, $A_\pi/A_\sigma > 1$ at $\theta = 0$ and $A_\pi/A_\sigma < 1$ at $\theta = 90°$. Thus, the σ-transition must grow with respect to the π-transition as θ increases. Consequently, as θ goes from $0° \rightarrow 90°$, if the apparent line position shifts to more positive (negative) velocities, the σ-transition must occur at the more positive (negative) velocity. For Sn-BBA in BBOA, $\varepsilon_{0\pi} - \varepsilon_{0\sigma} < 0$ and thus $q < 0$ (see reference 6) since $Q > 0$ for the first excited state in ^{119}Sn.
16. V. O. Aimiuwu, Ph.D. dissertation, Kent State University, 1976 (unpublished); and V. O. Aimiuwu and D. L. Uhrich, to be published.