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Effect of molecular shape on the dielectric relaxation in the glassy phase of rigid polar molecules—*cis*-decalin mixtures

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The effect of molecular shape on the α and β relaxations in the glassy phase of rigid polar molecules bromobenzene (planar), n-butyl chloride (linear), and t-butyl chloride (nearly spherical) in *cis*-decalin mixtures has been studied by measuring the dielectric parameters in the frequency range 0.1 to 100 kHz and over the temperatures from 77 to 300 K. The α-relaxation peaks are pronounced in all three systems, but the β-relaxation peaks are different. β peaks are almost absent in n-butyl chloride, while in bromobenzene they are of lower magnitude than the α peaks in agreement with the earlier reported results. However, in t-butyl chloride, the β peaks appear to be of higher magnitude than the α peaks. The present studies support the model proposed by Johari that in the amorphous phase above T_g the dielectric behavior is governed by the cooperative rearrangement of molecules, while in the glassy phase below T_g the β-relaxation process arises from the hindered rotation of polar molecules encaged in the glassy matrix. The static dielectric constant has been estimated in the amorphous phase from the temperature variation of ϵ' at a fixed frequency. The dipole moments have also been evaluated from the static dielectric constant in the amorphous phase as well as in the normal liquid.

I. INTRODUCTION

Dielectric relaxation loss peaks in the frequency region 0.1 to 100 kHz have been observed in a variety of glass forming systems. At a fixed frequency, loss peaks occur at two temperatures, one above the glass transition temperature T_g (amorphous phase) designated as α-relaxation process, and the other below T_g (glass phase) usually known as secondary or β-relaxation process. Such loss peaks have been known for a long time in complicated molecules like organic high polymers,[1] and have been attributed to the overall rotation of the molecules above T_g (α process) and hindered internal molecular modes of motion that remain active even when the molecule as a whole is frozen in place below T_g (β process). However, α- and β-relaxation processes are not limited to long chain molecules and polymers, but have been observed even in simple rigid molecules[2] like chlorobenzene in *cis*-decalin mixtures. Several studies[3-6] have been made to understand the mechanism of these processes in the mixtures of rigid polar molecules and glass forming solvents. It is well established[7] that (i) both α- and β-relaxation processes have wide distribution of relaxation times, (ii) the loss peaks for the α process are well defined, while for the β process they appear generally as shoulders with much lower magnitude as compared to the α peaks, and (iii) the activation energy for the α process is very much higher (20 to 100 kcal/mol) than that for the β process (5 to 10 kcal/mol) which is close to the activation energy of the solute in the normal liquid phase solution.

Detailed studies on supercooled liquids by Williams and co-workers[8-10] suggest that the α relaxation process is due to cooperative rearrangement of the molecules. This view has also been supported by Johari.[11] Goldstein[12] has suggested that the β process does not reflect the features of the individual molecules that compose the glass, but arises from common features of amorphous packing. Johari[11] on the other hand, has proposed that the β-relaxation process arises from the hindered rearrangement of the molecules encaged by a large region which have been made relatively immobile by the stringent requirement of cooperative motion. The features of the β-relaxation process should be independent of the shape of the solute molecules if it is due to amorphous packing, while it should depend on the molecular shape if it is due to orientation of the encaged molecules. To test this idea, we have chosen bromobenzene (planar), n-butyl chloride (linear) and t-butyl chloride (nearly spherical) as solute molecules, and *cis*-decalin as a nonpolar glass forming solvent. Dielectric constant and loss tangent $\tan\delta$ have been measured in the frequency range 0.1 to 100 kHz and at temperatures from 77 to 300 K, and the results are reported in this paper.

II. EXPERIMENTAL

A. Experimental setup

The dielectric constant ϵ' and $\tan\delta$ measurements have been made in the frequency range from 0.1 to 100 kHz using a General Radio 716 CS capacitance bridge in conjunction with a Hewlett-Packard 203A oscillator and a GR 1232 tuned-amplifier/null-detector. The details of the experimental setup and the accuracy of measurements have been reported earlier.[13] The values of ϵ' and $\tan\delta$ were measured at various temperatures and frequencies during both cooling and heating runs. The rate of heating was kept at about 0.5 °C/min and that of cooling at 1.5 °C/min.

B. Sample preparation

Bromobenzene was obtained from Veb (Germany) n-butyl chloride from Riedel (Germany), and t-butyl chlo-

ride was prepared by mixing[14] t-butyl alcohol (J. T. Baker, USA) and hydrochloric acid (BDH, England). The nonpolar solvent cis-decalin was procured from BDH (England). Although these chemicals were of high grade purity they were further dried and purified through fractional distillation before use. The measured boiling points, dielectric constants, and densities showed good agreement with the literature values. Three solutions of each solute were prepared in cis-decalin by weight and the measurements were made as reported earlier.[13]

III. RESULTS AND DISCUSSION

A. Variation of dielectric loss tangent tanδ with temperature

The variation of the loss tangent tan δ with temperature is plotted in Fig. 1.for three concentrations of each solute, bromobenzene (BB), n-butyl chloride (NBC), and t-butyl chloride (TBC) in cis-decalin in the heating run. The main peaks in NBC appear at much lower temperatures as compared to those in BB or TBC. It can be noted that the magnitude of the main peak increases with increasing concentration, and its temperature slightly shifts to higher values with the decreasing concentration. Additional peaks at a temperature higher than that of the main peak appear in BB and
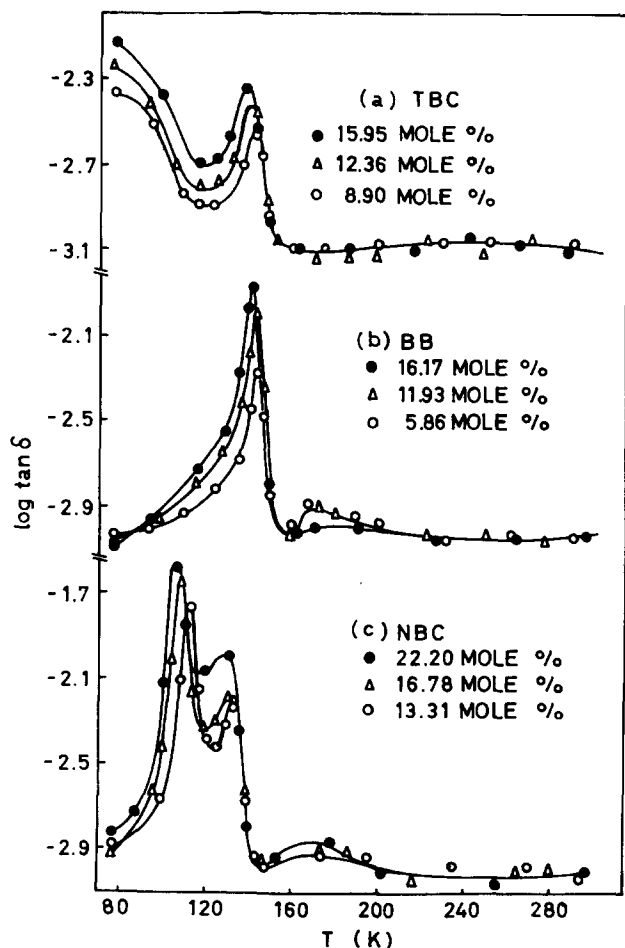
FIG. 2. Loss tangent tan δ vs temperature for 8.90 mol% TBC, 16.17 mol% BB, and 13.31 mol% NBC in cis-decalin solutions. o: 0.1 kHz, ●: 100 kHz.

FIG. 1. Loss tangent tanδ vs temperature for different concentrations of (a) TBC, (b) BB, and (c) NBC in cis-decalin solutions at 1.0 kHz.
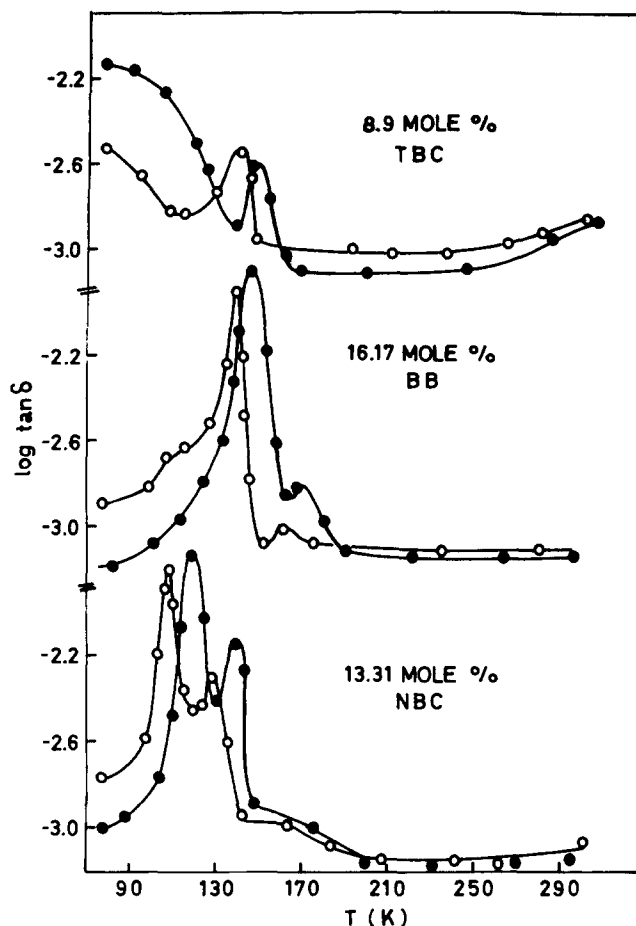
NBC. These (premelting) peaks have very low magnitudes in BB but are well defined in NBC, and their origin may be attributed to the presence of a liquid-crystal mixture caused by nonhomogeneity of temperature before melting, or the absence of a sharp melting point in these systems.

As the frequency of the applied field is increased, the main tanδ peak shifts to the higher temperature side. This is shown in Fig. 2 were tan δ is plotted as a function of temperature for two extreme frequencies (0.1 and 100 kHz) of our measurement for all three systems. It may be clearly observed that the effect of frequency on the magnitude of the main peaks is insignificantly small in all three systems. The temperature of the main peak at 0.1 kHz is close to, but slightly higher than the glass transition temperature T_g. The exact value of T_g, however, could not be determined as the relaxation frequency at T_g appears to be much lower than the lowest measuring frequency of 0.1 kHz.[13]

In Fig. 2, the secondary relaxation β process is shown in BB as a shoulder at the lowest frequency of 0.1 kHz below T_g, while no evidence for its presence is observed in NBC. No clear β peak in TBC is observed but the trend of the measured tan δ indicates that a well defined peak for the β process may appear
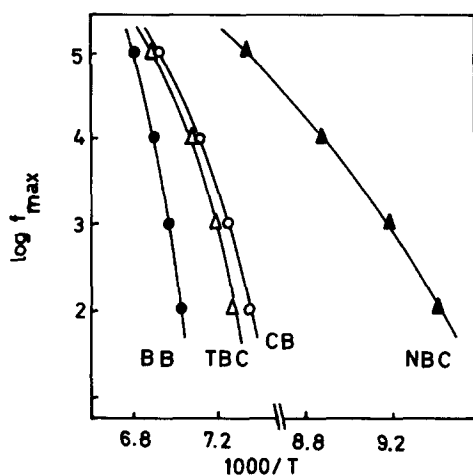
FIG. 3. Arrhenious plots for cis-decalin solutions of — •: 11.93 mol % BB; △: 15.95 mol % TBC; ○: 21.99 mol% CB (chlorobenzene from our previous studies) and ▲: 22.20 mol% NBC.

at a temperature lower than 77 K. It is interesting to note that below T_g the magnitude of loss in BB and NBC is much smaller, while in TBC it is much higher than the loss above T_g. The lower magnitude of loss above T_g than that below T_g in TBC may be attributed to the broader distribution of relaxation times above T_g. The fact that the β peaks in TBC appear much broader than the α peaks may be attributed to the higher activation energy for the α process as compared to that for the β process.

The activation energy for the α-relaxation process can be estimated from the plot of log f_m against reciprocal temperature (Fig. 3). It can be noted that all the plots are nonlinear and give activation energies ranging between 20 to 100 kcal/mol for the α-relaxation process in agreement with those reported by Johari.[7] It may be pointed out that the premelting peaks of NBC also show activation energy in the same range.

The behavior of tanδ with temperature clearly shows that the α-relaxation process is almost independent of molecular shape, while the β-relaxation process is dependent on the shape of the molecule. The activation energies for the α process are indicative of the cooperative rearrangement of molecules which is independent of the molecular shape.

B. Dielectric constant and dipole moment

The temperature dependence of dielectric constant ϵ' at a fixed frequency for one concentration of each solute in the cooling and heating runs is given in Fig. 4. A small thermal lag is observed in all three systems. Apart from the fact that an additional peak due to premelting is observed in NBC and the rise in ϵ' on transition from glass to amorphous phase is not very sharp in TBC, the behavior of ϵ' during heating, recooling, and reheating (Fig. 4) is similar to that reported for chlorobenzene.[13,15] It may be noted that the peak value of ϵ' near T_g during heating and cooling runs is approximately the same for BB and TBC, while it is considerably lower for NBC in the heating run. This suggests that during heating, some crystallization occurs in

NBC, and in the amorphous phase not all the dipoles are rendered free but some remain inactive due to crystallization. The phase above T_g in NBC is thus not a true amorphous one but a mixture of amorphous and crystalline, which then changes to a crystal-liquid mixture phase.

The variation of ϵ' and ϵ'' with frequency at a fixed temperature above T_g is shown in Fig. 5 for BB. Similar curves were obtained for NBC and TBC. It is obvious from Fig. 5 that the dielectric dispersion is characterized by a wide distribution of relaxation times.[4] The extraction of static dielectric constant ϵ_0 in presence of wide distribution of relaxation times is difficult. However, ϵ_0 can be easily estimated from Fig. 4, because values of ϵ', at temperatures higher than the tempera-

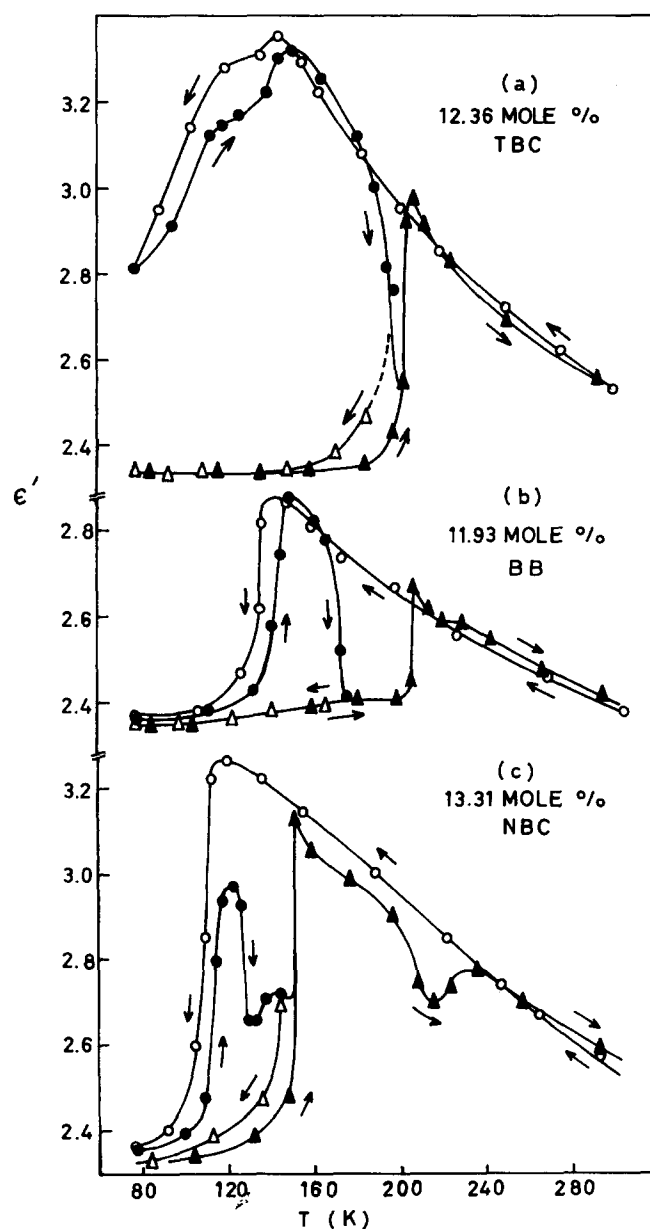FIG. 4. ϵ' vs temperature during cooling and heating runs for (a) 12.36 mol % TBC at 100 kHz, (b) 11.93 mol % BB at 1.0 kHz, and (c) 13.31 mol % NBC at 1.0 kHz in cis-decalin solutions— ○: cooling; •: heating; △: recooling, and ▲: reheating.
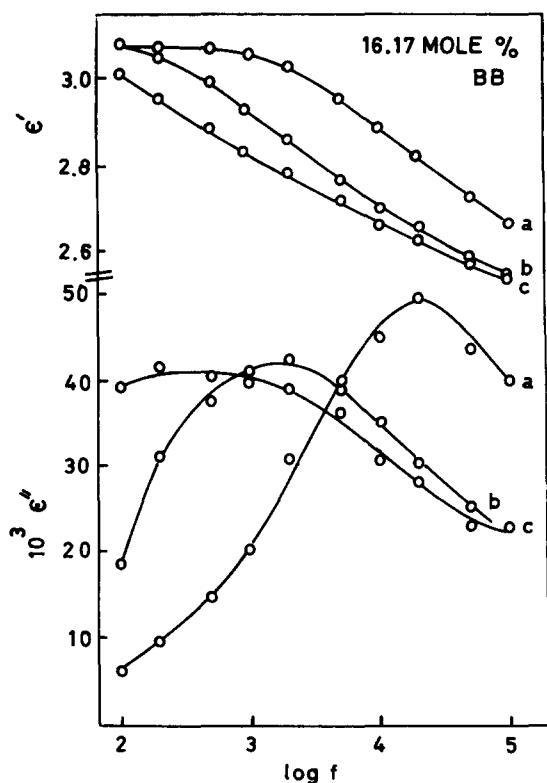
FIG. 5. Frequency dependence of permittivity (ϵ') and loss (ϵ'') for 16.17 mol% BB in cis-decalin solution at (a) 143.3 K, (b) 140.0 K, and (c) 138.8 K.

ture at which its peak appears in the amorphous phase, correspond to the static value ϵ_0.[13,15] The estimated ϵ_0 at different temperatures from Fig. 4 is reported in Table I.

The dipole moment μ in the amorphous phase and the normal liquid phase has been computed by the following relation[4]:

$$\mu^2 = 0.4923 \frac{(\epsilon_0 - \epsilon_s)}{(\epsilon_0 + 2)(\epsilon_s + 2)} \frac{T}{C} \quad , \tag{1}$$

where ϵ_0 and ϵ_s are the static dielectric constants of the solution and the solvent, respectively, at the temperature T, and C is the solute concentration in moles per liter. In order to evaluate ϵ_s, the dielectric constant of the solvent cis-decalin was measured as a function of temperature. It was noted that this variation was not linear with temperature. The value of ϵ_s at room temperature (293 K) was 2.150. In the range from 100 to 150 K, the variation was less than 0.3% and, therefore, an average value of 2.320 (independent of temperature) was taken for evaluating the dipole moment in the amorphous phase. The density of cis-decalin at these temperatures was obtained by extrapolation of the literature values[16] in order to evaluate C. The values of dipole moment in the normal liquid region were also calculated at 20°C using the above formula. The values of the static permittivity ϵ_0, the permittivity ϵ', the temperature and frequency f_{max} corresponding to maximum loss ϵ''_{max}, the dipole moment μ in the amorphous

TABLE I. Static dielectric permitivity ϵ_0 of the solution, the maximum loss ϵ''_{max}, the permittivity ϵ'_m, the temperature T, and the frequency f_{max} corresponding to the maximum loss, and the apparent dipole moments μ (amorphous) and μ_{liq} for CB, BB, NBC, and TBC molecules in cis-decalin solutions.

T (K)	f_{max} (kHz)	ϵ_0	ϵ'_m	ϵ''_{max}	μ (D)	μ_{liq}[a] (D)	μ_{11t}[b] (D)
12.98 mol% chlorobenzene							
138.8	0.1	2.991	2.853	0.027	1.47	1.52	(1.50–1.62)
141.6	1.0	2.970	2.835	0.026	1.47		
143.7	10.0	2.953	2.804	0.026	1.47		
146.2	100.0	2.936	2.765	0.029	1.46		
11.93 mol% bromobenzene							
142.4	0.1	2.916	2.813	0.028	1.51	1.59	(1.50–1.56)
143.6	1.0	2.910	2.745	0.027	1.51		
145.2	10.0	2.900	2.669	0.028	1.51		
149.7	100.0	2.874	2.689	0.033	1.51		
13.31 mol% n-butyl chloride							
108.5	0.1	3.026	2.660	0.043	1.28	1.94	(1.94–2.05)
113.0	1.0	2.987	2.805	0.048	1.28		
116.0	10.0	2.960	2.750	0.046	1.28		
118.5	100.0	2.940	2.603	0.048	1.28		
12.36 mol% t-butyl chloride							
138.5	0.1	3.458	3.420	0.014	1.86	1.96	(1.96–2.17)
140.0	1.0	3.440	3.406	0.013	1.86		
142.3	10.0	3.420	3.370	0.012	1.87		
144.0	100.0	3.403	3.220	0.010	1.87		

[a]Liquid phase values in cis-decalin solution calculated at 20°C.
[b]Literature values in benzene solution (10 to 50°C), taken from Ref. 17.

phase, and μ_{11q} in normal liquid are given in Table I. These parameters for chlorobenzene have also been included from our previous publication.[15] The literature values[17] of the dipole moment are also given for comparison. It can be noted in this table that the estimated μ values at room temperature in *cis*-decalin are close to the values in benzene. It can further be noted that the measured μ values for CB (chlorobenzene) and BB in the amorphous phase are close to those reported by Johari and Smyth[4] who used Cole–Cole plots to estimate ϵ_0. The dipole moments in the amorphous phase are slightly lower than the normal liquid values in the case of CB, BB, and TBC, but the difference is within 5%. However, in the case of NBC the amorphous values are more than 25% lower than those in the liquid phase. This suggests that the number of free dipoles in the amorphous phase of NBC is considerably lower than that in the liquid phase; and the amorphous phase has some inactive dipoles probably due to crystallization. This is in agreement with the information obtained from heating and cooling runs of the dielectric constant.

IV. CONCLUSIONS

The dielectric relaxation above T_g or the α-relaxation process is independent of the molecular shape because the dielectric dispersion behavior of all three systems is similar. However, it may be pointed out that the linear molecule NBC does not show a true amorphous phase but an amorphous–crystalline mixture phase. Still the free dipoles in the amorphous phase show the same relaxation behavior as that of the other two systems. The dielectric relaxation in the glassy phase below T_g, or the β-relaxation process, shows a pronounced effect of molecular shape. The β peaks for the linear molecule NBC are nonexistent. For the planar molecule BB they appear only as a shoulder at 100 Hz, while for the nearly spherical molecule TBC the β peaks are well defined for all the frequencies. Contrary to the general conclusion arrived at by Johari and Goldstein,[2] the β peak in nearly spherical molecule TBC appears to be higher than that of α peak. Hence on the basis of the present studies it may be concluded that the α-relaxation process is governed by the cooper-

ative rearrangement of molecules and is independent of the molecular shape, while the β-relaxation process arises from the hindered rotation of polar molecules encaged in the glassy matrix. As expected, this rotational freedom (β-process) depends on the shape of the molecule, the maximum freedom being shown by a nearly spherical molecule.

[1]N. G. McCrum, B. E. Read, and G. Williams, *Inelastic and Dielectric Effects in Polymeric Solids* (Wiley, New York, 1967).

[2]G. P. Johari and M. Goldstein, J. Chem. Phys. **53**, 2372 (1970).

[3]M. Goldstein, *Amorphous Materials*, edited by R. Douglas and B. Elis (Wiley, New York, 1972), pp. 23.

[4]G. P. Johari and C. P. Smyth, J. Chem. Phys. **56**, 1411 (1972).

[5]M. Goldstein, J. Chem. Phys. **64**, 4767 (1976).

[6]L. Hayler and M. Goldstein, J. Chem. Phys. **66**, 4736 (1977).

[7]G. P. Johari, Ann. N. Y. Acad. Sci. **279**, 117 (1976).

[8]G. Williams and P. J. Hains, Chem. Phys. Lett. **10**, 585 (1971).

[9]G. Williams and P. J. Hains, Faraday Symp. Chem. Soc. **6**, 14 (1972).

[10]M. F. Shears and G. Williams, J. Chem. Soc., Faraday Trans. 2 **69**, 609 (1972).

[11]G. P. Johari, J. Chem. Phys. **58**, 1766 (1973).

[12]M. Goldstein, Ann. N. Y. Acad. Sci. **279**, 68 (1976).

[13]A. Mansingh, C. B. Agarwal, and R. Singh, Indian J. Pure Appl. Phys. **18**, 583 (1980).

[14]S. Urban, J. Lenik, and S. Wrobel, Acta Phys. Pol. A **41**, 91 (1972).

[15]A. Mansingh, C. B. Agarwal, and R. Singh, Chem. Phys. Lett. **69**, 101 (1980).

[16]W. E. Seyer and C. H. Davenport, J. Am. Chem. Soc. **63**, 2425 (1941).

[17]A. L. McClellan, *Tables of Experimental Dipole Moments* (Freeman, San Francisco, 1963).