

CHAPTER-3

**STRUCTURAL AND ASSOCIATIONAL
ASPECTS OF BINARY AND SINGLE POLAR
LIQUIDS IN NONPOLAR SOLVENT UNDER
HIGH FREQUENCY ELECTRIC FIELD**

STRUCTURAL AND ASSOCIATIONAL ASPECTS OF BINARY AND SINGLE POLAR LIQUIDS IN NONPOLAR SOLVENT UNDER HIGH FREQUENCY ELECTRIC FIELD

The dielectric relaxation mechanism of a polar-nonpolar liquid mixture under the microwave electric field is of special interest [1,2] for its inherent ability to predict the associational aspects of polar solutes in nonpolar solvents. An investigation was, however, made on ternary solution of binary polar liquids in which both or even one of them are aprotic [2,3] to study various types of weak molecular associations by polar liquids in nonpolar solvents. We are, therefore, tempted further to consider more mixtures of binary aprotic polar liquids like N, N. dimethyl formamide (DMF) and dimethyl sulphoxide (DMSO) together with a single aprotic polar liquid like N, N. diethyl formamide (DEF) and DMSO in C_6H_6 and CCl_4 [4-6] respectively. DMSO, DMF and DEF are very interesting liquids for their wide application in medicine and industry. They also act as building blocks of proteins and enzymes. The concentration variation of the measured real ϵ'_{ijk} , ϵ'_{ij} or ϵ'_{ik} and imaginary ϵ''_{ijk} , ϵ''_{ij} or ϵ''_{ik} parts of hf complex dielectric constants ϵ^*_{ijk} , ϵ^*_{ij} or ϵ^*_{ik} of jk , j or k polar solutes in nonpolar solvents are used to detect the weak molecular interactions among the molecules [7] at a single or different temperatures under nearly 3cm wavelength electric field. The τ_{jk} of jk polar mixtures as well as τ_j 's or τ_k 's of j or k polar solutes in a nonpolar solvent were estimated from :

$$K''_{ijk} = K_{\infty ij k} + \frac{1}{\omega \tau_{jk}} K'_{ijk} \quad (3.1)$$

where $K''_{ijk} = \frac{\omega}{4\pi} \epsilon''_{ijk}$ and $K'_{ijk} = \frac{\omega}{4\pi} \epsilon'_{ijk}$ are the imaginary and real parts of complex hf conductivity K^*_{ijk} [8]. The other terms carry usual significance as presented elsewhere [2]. The τ_{jk} 's are estimated from the slopes of the

linear variations of K''_{ijk} against K'_{ijk} of Eq. (3.1). The linearity of Eq. (3.1) is tested by the correlation coefficients and the errors involved in the measurement of τ 's are within 5%. τ_{jk} 's are then plotted with different mole fractions x_k 's of DMSO at various experimental temperatures as shown in Figure 3.1.

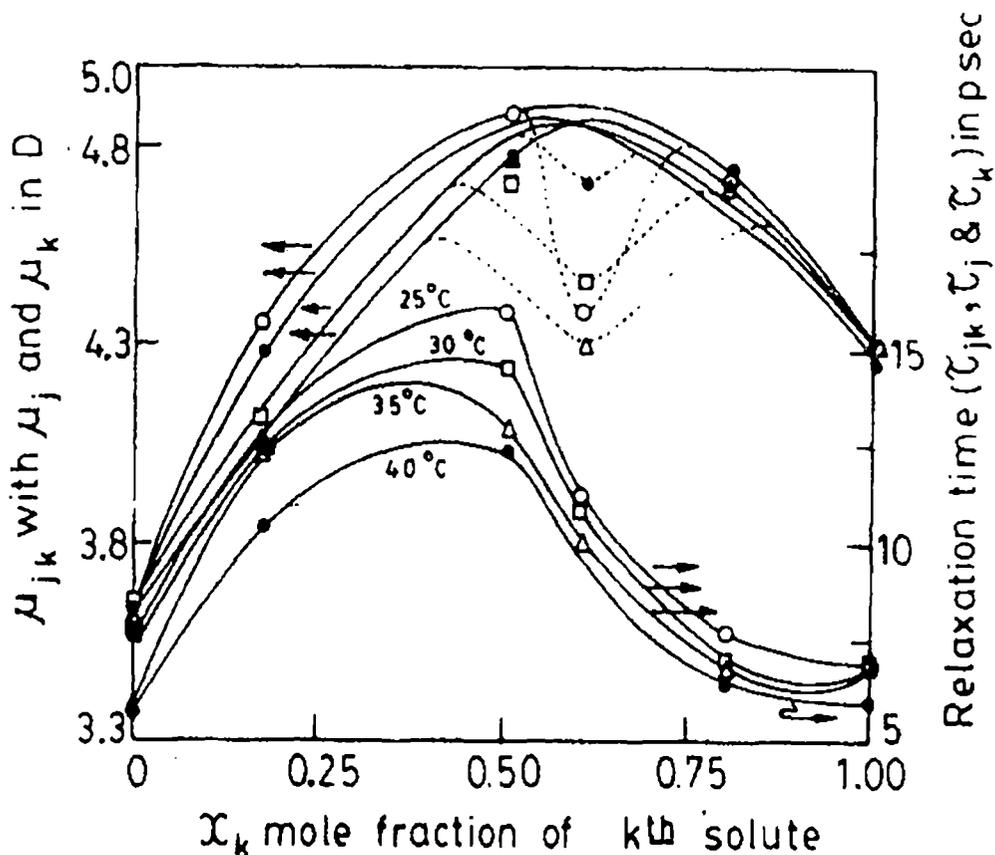


Figure 3.1 : Variation of τ_{jk} and μ_{jk} of DMF-DMSO mixture in C_6H_6 against mole fraction x_k of DMSO with τ_j and τ_k and μ_j and μ_k of DMF and DMSO respectively at different temperatures : (O) at 25°C, (□) at 30°C, (Δ) at 35°C and (●) at 40°C

The formation of dimer is responsible for the gradual rise of τ_{jk} from τ_j of DMF at $x_k = 0$ to $x_k = 0.5$ and then its rapid fall to τ_k due to rupture of dimerisation and self association [4]. The estimated τ 's are slightly larger than those of Gopalakrishna's method [9]. But τ 's from conductivity measurement are much more reliable as they provide microscopic relaxation times [10].

The energy parameters due to dielectric relaxation process were then obtained in terms of measured τ from the rate process equation of Eyring *et al* [11] :

$$\tau_s = \frac{A}{T} e^{(\Delta F_\tau/RT)}$$

$$\text{or } \ln(\tau_s T) = \ln A' + \frac{\Delta H_\tau}{RT} \quad (3.2)$$

where $A' = Ae^{-\Delta S_\tau/R}$.

Eq. (3.2) is a straight line of $\ln(\tau_s T)$ against $1/T$ as seen in Figure 3.2 having intercepts and slopes to yield the entropy of activation ΔS_τ enthalpy of activation ΔH_τ and free energy of activation ΔF_τ due to dielectric relaxation.

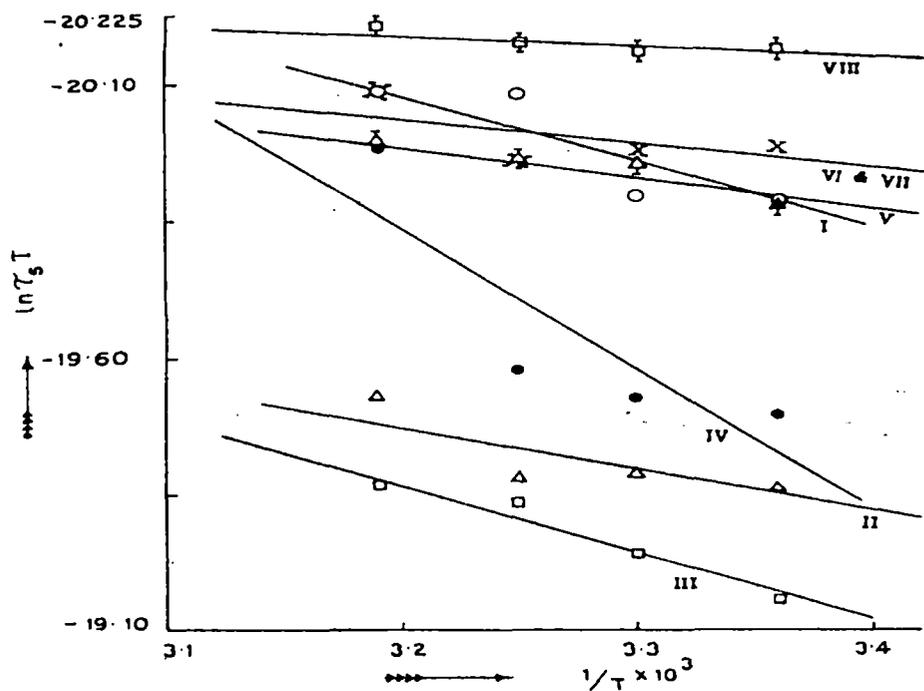


Figure 3.2: Variation of $\ln(\tau_s T)$ against $\frac{1}{T}$ of binary and single polar solutes in nonpolar solvent. I-DMF + 0 mole% DMSO in C_6H_6 (O), II-DMF + 17 mole% DMSO in C_6H_6 (Δ), III-DMF + 50 mole% DMSO in C_6H_6 (\square), IV-DMF + 60 mole% DMSO in C_6H_6 (\bullet), V-DMF + 80 mole% DMSO in C_6H_6 (∇), VI-DMF + 100 mole% DMSO in C_6H_6 (X), VII-DMF + 100 mole% DMSO in C_6H_6 (X), VIII-DMSO in CCl_4 (\odot).

The values of $\gamma (= \Delta H_\tau / \Delta H_\eta)$ for all the liquids except DMSO in CCl_4 are greater than 0.55, as obtained from the slope of the linear relation of $\ln(\tau_s T)$ with $\ln \eta$ indicating them as solid phase rotators in solvent environment. η is the coefficient of viscosity of solvent. ΔH_η due to viscous flow of the solvent is obtained from slope of $\ln(\tau_s T)$ against $1/T$ and known γ . Again, ΔH_η are greater than ΔH_τ for all the mixtures except 0,50 and 60 mole % DMSO in DMF and C_6H_6 . The difference in ΔH_τ and ΔH_η is due to the involvement of various types of bondings which are either formed or broken to some extent, depending on the temperature and concentration of the system. The negative values of ΔS_τ 's for all the system except 0 and 60 mole% DMSO in DMF and C_6H_6 indicate the existence of cooperative orientation of the molecules arising out of steric forces to yield more ordered states while the reverse is true for positive ΔS_τ 's. Although, ΔF_τ 's in all cases are almost constant at all temperatures, they increase with x_k of DMSO from $x_k = 0.0$ to $x_k = 0.5$ and then decrease gradually to $x_k = 1.0$ signifying the maximum dimerisation of DMF-DMSO mixture around $x_k = 0.5$. The formation of dimer causes larger molecular size and hence, the energy needed for rotation in the relaxation process is higher.

The hf conductivity K_{ijk} as a function of weight fraction w_{jk} is given by

$$K_{ijk} = \frac{\omega}{4\pi} (\epsilon'_{ijk} + \epsilon''_{ijk})^{1/2} \quad (3.3)$$

Since $\epsilon'_{ijk} \gg \epsilon''_{ijk}$ Eq. (3.1) can be written as

$$K_{ijk} = K_{\infty ij k} + \frac{1}{\omega \tau_{jk}} K'_{ijk}$$

or
$$\left(\frac{dK'_{ijk}}{dw_{jk}} \right) w_{jk} \rightarrow 0 = \omega \tau_{jk} \beta \quad (3.4)$$

Here β 's are the slopes of $K_{ijk} - w_{jk}$, $K_{ij} - w_j$ or $K_{ik} - w_k$ curves respectively, which are linear with almost identical intercepts probably due to same polarity

of the molecules [2]. The real part of *hf* conductivity, K'_{ijk} is again related to w_{jk} of *jk* polar solute dissolved in a nonpolar solvent (i) at temperature TK [12] as

$$K'_{ijk} = \frac{\mu_{jk}^2 N \rho_{ijk} F_{ijk}}{3M_{jk} kT} \left(\frac{\omega^2 \tau_{jk}}{1 + \omega^2 \tau_{jk}^2} \right) w_{jk} \quad (3.5)$$

Differentiating Eq. (3.5) with respect to w_{jk} and comparing the result at $w_{jk} \rightarrow 0$ to Eq. (3.4), one obtains the following relation

$$\mu_{jk} = \left[\frac{27M_{jk} kT}{N \rho_i (\epsilon_i + 2)^2} \cdot \frac{\beta}{\omega b} \right]^{1/2} \quad (3.6)$$

to estimate μ_{jk} , μ_j or μ_k of the respective solutes. b is a dimensionless parameter in terms of estimated τ_{jk} , τ_j or τ_k given by :

$$b = \frac{1}{1 + \omega^2 \tau_{jk}^2} \quad (3.7)$$

The other terms in Eq. (3.6) carry usual significance [2]. All the μ 's are then plotted against different x_k 's of DMSO at each temperature as shown in Figure 3.1. It shows the gradual rise of μ_{jk} in the range $0 < x_k \leq 0.5$. It then decreases slowly in order to exhibit the convex nature of each curve with an abnormally low value of μ_{jk} around $x_k = 0.6$. This sort of behaviours of $\mu_{jk} - x_k$ curves (Figure 3.1) is explained by the fact that dimers are being formed from $x_k \geq 0$ to $x_k = 0.6$, causing increase of μ . The rupture of dimerisation *i.e.* self association occurs in higher concentrations in the range $0.6 \leq x_k < 1.0$ to yield lower values of μ 's. But around $x_k = 0.6$ all μ_{jk} 's are minimum indicating the possible occurrence of double relaxation phenomena in such mixtures. μ_{jk} together with μ_j and μ_k for each mixture of a fixed concentration are shown graphically only to observe their temperature dependence like $\mu_{jk} = a + bt + ct^2$ with coefficients a , b and c as seen in Figure 3.3. The variation is concave with maximum depression at 17 mole% DMSO in DMF mixture. The depression gradually decreases upto $x_k = 0.6$ of DMSO in DMF and C_6H_6

probably due to solute-solute molecular association in the range $0 < x_k < 0.6$. The maximum dimerisation is, however, inferred from low μ 's because of the larger molecular sizes as confirmed by high values of $\tau_s T / \eta'$ (being proportional to volume of the rotating unit) for 60 mole% DMSO in DMF and C_6H_6 . As temperature increases the dipole-dipole interaction is weakened and the absorption of hf electric energy increases resulting in the rupture of dimer to yield high μ 's for smaller molecular species [10]. The slight convex nature of curves for 0 mole% DMSO in DMF and C_6H_6 and DMSO in C_6H_6 along with almost straight line variation of 100 mole% DMSO in DMF and C_6H_6 and DMSO in CCl_4 (Figure 3.3) is probably due to solute-solvent molecular interaction of either DMF with C_6H_6 or DMSO with C_6H_6 and CCl_4

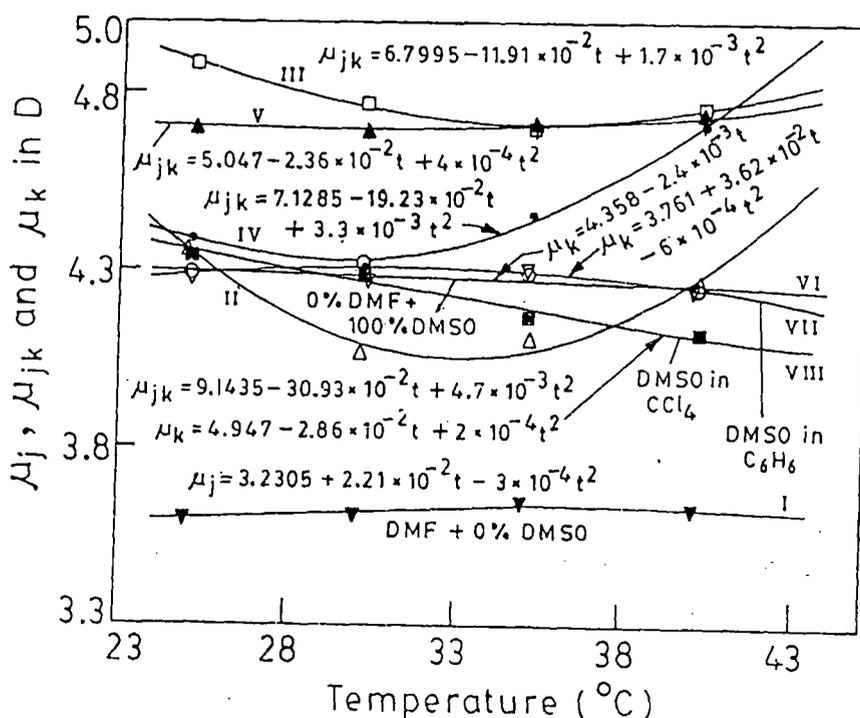


Figure 3.3 : Variation of μ_j , μ_{jk} and μ_k of binary and single polar solutes in nonpolar solvent with temperature t in $^{\circ}C$.

I-DMF + 0 mole% DMSO in C_6H_6 (\blacktriangledown), II-DMF+17 mole % DMSO in C_6H_6 (Δ), III-DMF+50 mole % DMSO in C_6H_6 (\square), IV-DMF +60 mole % DMSO in C_6H_6 (\bullet), V-DMF+80 mole % DMSO in C_6H_6 (\blacktriangle), VI-DMF+100 mole % DMSO in C_6H_6 (∇), VII-DMSO in C_6H_6 (\circ), VIII-DMSO in CCl_4 (\blacksquare).

respectively as illustrated in Figure 3.4. The associations of DMF, DEF and DMSO in C_6H_6 can arise due to interactions of fractional positive charges of N and S atoms of the molecules with the π delocalised electron cloud of C_6H_6 ring as seen in Figure 3.4 (i), (iii) and (iia) respectively. Again, one of C-Cl dipoles of CCl_4 , owing to more -ve charge on Cl atom, interacts with the

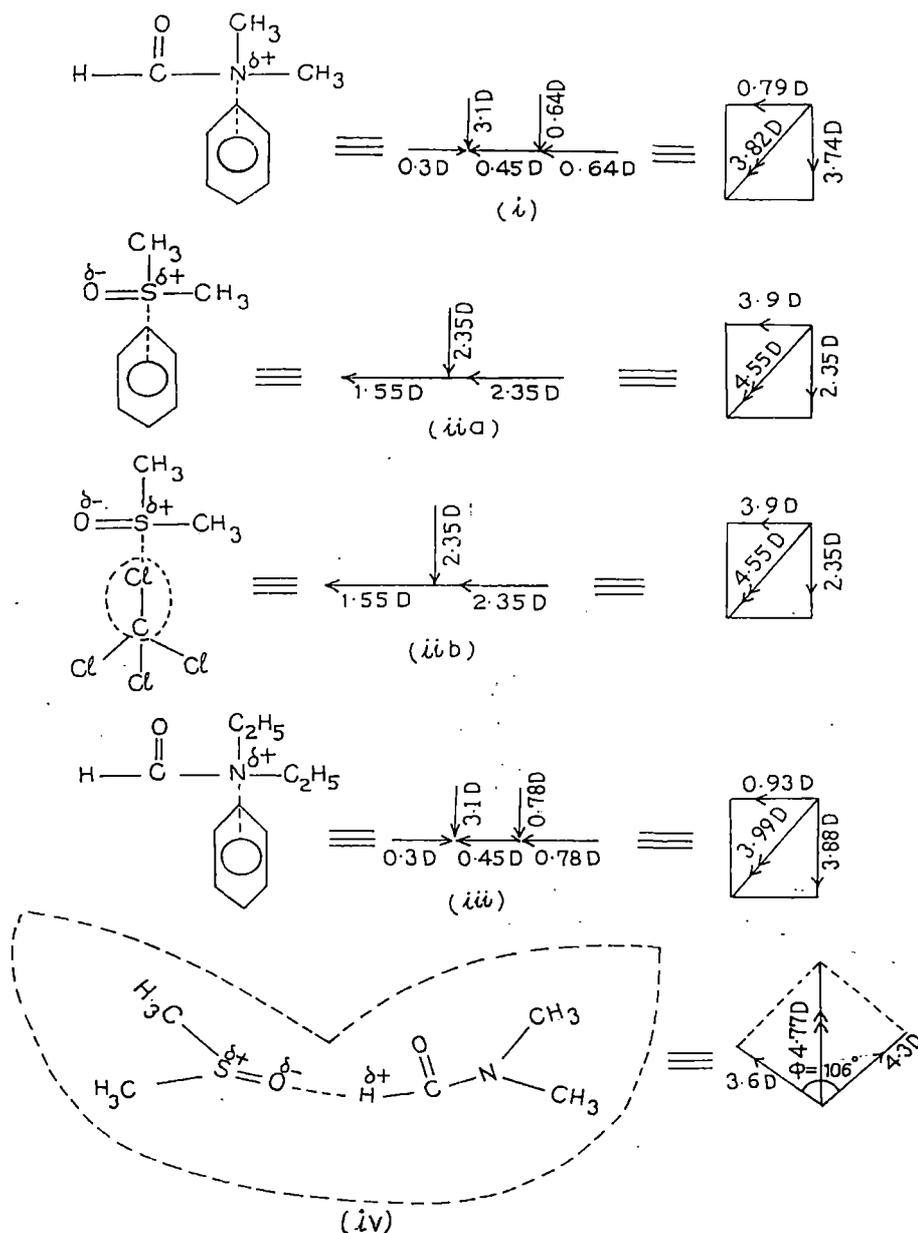


Figure 3.4 : Conformational structures along with solute-solvent and solute-solute interaction of molecules. (i) DMF in C_6H_6 , (iia) DMSO in C_6H_6 (iib) DMSO in CCl_4 , (iii) DEF in C_6H_6 , (iv) DMSO-DMF dimer.

fractional +ve charge of S-atom of DMSO (Figure 3.4 (iib)). The $\mu_{\text{theo}} = 4.55$ D of DMSO is, however, computed from available bond moments of 2.35 D and 1.55 D for $\text{S} \leftarrow \text{CH}_3$ and $\text{O} = \text{S}$ respectively, assuming the molecule to be planer one. The major contributions to μ_{theo} for DMF and DEF are due to 0.64 D and 0.78 D for $\text{N} \leftarrow \text{CH}_3$ and $\text{N} \leftarrow \text{C}_2\text{H}_5$ since the other common bond moments in them are the same with values of 0.3 D, 0.45 D and 3.10D for $\text{C} \leftarrow \text{H}$, $\text{C} \leftarrow \text{N}$ and $\text{C} \leftarrow \text{O}$ respectively. Figure 3.4 (iv), however, shows a certain angle $\phi (= 106^\circ)$ between monomeric μ 's of DMF and DMSO to have $\mu_{\text{theo}} = 4.77$ D of dimer below $x_k = 0.6$.

The slight deviations of the μ 's from the μ_{theo} 's occur probably due to the presence of inductive and mesomeric moments of such molecules. This is also observed elsewhere [13]. The corrected μ 's obtained from the reduced bond moments of the substituent groups by factors $\mu_{\text{cal}} / \mu_{\text{theo}}$ establish the above facts at different temperatures, too. Thus the dielectric relaxation parameters from *hf* conductivity measurements offer a useful tool to arrive at the structural and associational aspects of the non-spherical polar liquids.

References

- [1] C R. Acharyya, A.K. Chatterjee, P K Sanyal and S Acharyya *Indian J. Pure & Appl. Phys.* **24** (1986). 234.
- [2] A K Chatterjee, U Saha, N Nandi, R C Basak and S Acharyya *Indian J. Phys.* **66B** (1992) 291.
- [3] U Saha and S Acharyya *Indian J. Pure & Appl. Phys.* **3** (1993), 181.
- [4] A Sharma D R Sharma and M S Chauhan *Indian J. Pure & Appl. Phys.* **31**(1993) 841.
- [5] A Sharma and D R Sharma *J. Phys. Soc. Japan.* **61** (1992),1049.
- [6] A R Saksena *Indian J. Pure & Appl. Phys.* **16** (1978).1079.
- [7] U Saha and S Acharyya *Indian J. Pure & Appl. Phys.* **32** (1994).346.
- [8] F J Murphy and S O Morgan *Bell. Syst. Tech. J.* **18** (1939).502.
- [9] K V. Gopalakrishna *Trans. Faraday Soc.* **53** (1957):767.

- [10] S K Sit and S Acharyya *Indian J. Phys.* **70B** (1996), 19
- [11] H Eyring, S Glasstone and K J Laidler *The Theory of Rate Process* (New York : McGraw Hill) (1941).
- [12] C P Smyth *Dielectric Behaviour and Structure* (New York : McGraw Hill) (1955).
- [13] R C Basak, S K Sit, N Nandi and S Acharyya *Indian J. Phys.* **70B** (1996), 37.