

Substituent Perturbation on Masked 1L_b - 1A_1 Transition of Anthracene Monosulphonates : Detection by Photoselection in Glycerol Glass at 77K

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Attempts are made to detect the long axis polarized weakly absorbing 1L_b bands in anthracene 1-sulphonate (1-AS) and anthracene 2-sulphonate (2-AS) in glycerol glass by the method of photoselection. The unpolarized fluorescence spectra and excitation (absorption) spectra are separated into two component spectra based on short and long axis polarized transition dipoles and detailed vibrational analysis is made. From a comparison of the Franck-Condon envelope it has been concluded that the vibration bands around 31746 cm^{-1} in 1-AS and 30395 cm^{-1} in 2-AS in excitation spectra are mainly due to 1L_b band. The perturbation of 1L_b band due to substitution in 1- and 2- positions of the anthracene moiety is discussed.

We have been engaged for quite some time in the study of photophysical and photochemical properties of anthracene sulphonates. It was found¹⁻³ that anthracene sulphonates exhibited interesting variations in their excited state properties depending upon the number and the position of sulphonate (SO_3^-) groups in the anthracene moiety. For example, in aqueous solution, anthracene 1-sulphonate (1-AS) gives structureless and anthracene 2-sulphonate (2-AS) gives nearly structureless fluorescence spectra. On the other hand, fluorescence spectra of anthracene 1,5-disulphonate (1,5-AS) and anthracene 1,8-disulphonate (1,8-AS) exhibit vibrational features, and mirror-image symmetry relationship between absorption and emission spectra is preserved. In aprotic solvents the vibrational structures in the emission spectra of monosulphonates are restored and are blue shifted¹. In the IR spectra also characteristic differences⁴ in C-H out-of-plane deformation modes appear depending on the position of SO_3^- group in anthracene skeleton. The $-\text{C}=\text{C}-$ skeletal modes which appear as progression in absorption and emission spectra of these compounds are similarly affected. The loss of structure in fluorescence spectra as well as the discrepancy between calculated and observed values of lifetime² in the case of monosulphonates indicates that the emitting state may not be the pure S_1 state of the compound. The differences in the excited state properties of anthracene sulphonates are expected if two very closely spaced electronic states of different symmetry exist. In anthracene the two states, 1L_a and 1L_b , lie in the region of their lowest absorption band and 1L_b is masked by the strong 1L_a band. In this paper attention is focussed to detect the long axis polarized weakly absorbing 1L_b band in anthracene monosulphonates by the method of photoselection using substituent

perturbation technique. There has been ever increasing search for the exact location of this hidden band.

Theoretical Considerations

The principle of photoselection spectroscopy has been fully discussed by Albercht¹⁰. In photo-selection technique, an anisotropic light beam selects a nonrandom arrangement of molecules from an isotropic or random sample¹¹. For experiments with anthracene sulphonates, the photoselection technique consists of two steps: (i) photoselection and (ii) detection of photoselected population by a radiative step such as emission or polarized absorption spectroscopy.

In two-step photoselection, a polarization ratio (N) of the fluorescence excited at a given wavelength λ_e in the absorption region is defined by expression(1),

$$N = \frac{I_V}{I_H} = \frac{2\Sigma + 1}{2 - \Sigma} \quad \dots(1)$$

where I_V and I_H are intensities of vertically and horizontally polarized emission respectively when the viewing axis is horizontal to the laboratory plane and 90° to the direction of excitation using vertically polarized light. Σ , the electronic anisotropy, is given by Eq. (2),

$$\Sigma = \Sigma_{\zeta} R_{\zeta} Q_{\zeta} = R_x Q_x + R_y Q_y + R_z Q_z = 1 \quad \dots(2)$$

where R_{ζ} is the intrinsic or true molecular fractional probability for absorption with the transition dipole directed along $\zeta(x,y,z)$ symmetry axis respectively in absorption. Similarly Q_{ζ} is the fractional probability for emission when the transition dipole in emission is directed along the $\zeta(x,y,z)$ axis. The polarized components R_{ζ} or Q_{ζ} in absorption or in

emission can be calculated from excitation or emission polarization spectra. The experimentally obtained data are the polarization ratio N . Possible depolarization due to causes such as, (i) rotational motion during the lifetime of the molecule, (ii) long range intermolecular energy transfer phenomenon and (iii) concentration depolarization, are taken into account using a randomisation factor ϵ , given by the expression (3)¹².

$$\epsilon = \frac{3}{2} \left[\frac{3 - N_0^0}{N_0^0 + 2} \right] \quad \dots (3)$$

where N_0^0 is the experimental polarization ratio N , measured in the 0-0 band. Assuming that the value of ϵ is wavelength independent, the same value of ϵ is used at all other wavelengths. The electronic anisotropy is then calculated by the expression (4)^{5,10}.

$$\Sigma_{\mathbf{r}} R_{\mathbf{r}} Q_{\mathbf{r}} = \frac{3(2N - 1) - \epsilon(N + 2)}{3(1 - \epsilon)(N + 2)} \equiv f(N, \epsilon) \quad \dots (4)$$

To separate R and Q from one another the following photoselection technique is followed. In the case of emission polarization spectrum a wavelength (λ_e) corresponding to the 0-0 of the absorption band is selected for excitation and emission is observed at a wavelength (λ_v). Considering excitation along the X-axis or Y-axis of the molecule to be pure, X-axis or Y-axis polarised i.e. $R_x(0-0) = 1$ or $R_y(0-0) = 1$, we get,

$$\begin{aligned} \Sigma_{\mathbf{r}} R_{\mathbf{r}} Q_{\mathbf{r}} &= R_x(0-0) Q_x(\lambda_v) = Q_x(\lambda_v) \\ &\text{or } R_y(0-0) Q_y(\lambda_v) = Q_y(\lambda_v) \quad \dots (5) \end{aligned}$$

Similarly in the case of excitation polarization spectrum the molecule is excited at any wavelength (λ_e) and the emission is observed at a wavelength (λ_v) corresponding to 0-0 of the fluorescence band (Q_x or $Q_y = 1$). Then considering emission to be observable along the X-axis of the molecule, we get,

$$\Sigma_{\mathbf{r}} R_{\mathbf{r}} Q_{\mathbf{r}} = R_x(\lambda_e) Q_x(0-0) = R_x(\lambda_e) \quad \dots (6)$$

The values of N and Σ are not formally valid when the cartesian axes are not symmetry elements, for then cross-terms can appear. It is assumed that in all $\pi-\pi^*$ transitions of anthracene sulphonates there are no out-of-plane components. Though electronically they cannot, but vibronically, they may exist as in anthracene⁵. Therefore only x and y components of $R_{\mathbf{r}}$ and $Q_{\mathbf{r}}$ have been considered. Since the sums of the fractional components are unity, we have only one component remaining as an unknown. Choosing to focus on the short-axis (Y-axis), in-plane direction, R_x and Q_x can then be determined from R_y by the expression (7)

$$R_x = 1 - R_y; \quad Q_x = 1 - Q_y \quad \dots (7)$$

Actual excitation (absorption) and emission spectra polarized along long axis (X-axis) and short axis (Y-axis) are represented by A_x , A_y and F_x , F_y respectively. The A_x and A_y spectra are obtained by multiplying the observed unpolarized absorption intensity spectrum by R_x , i.e. $(1 - R_y)$ and R_y at every 3 nm intervals. Similarly F_x and F_y spectra are

obtained by multiplying the normalized fluorescence spectra by $(1 - Q_y)$ and Q_y .

Materials and Methods

Anthracene 1- and 2-sulphonates, 1-AS and 2-AS respectively, were prepared from corresponding quinones¹³. Glycerol (BDH) was distilled twice under reduced pressure and emission impurities were checked.

The excitation and emission spectra at 77 K were recorded on a Perkin-Elmer fluorescence spectrophotometer model MPF-44B with recorder using phosphorescence attachment with the chopper removed. The excitation and emission band-pass were 3 and 2 nm, respectively. All the spectra recorded were uncorrected for spectral response. Polarization measurements were made with the polaroid polarizer and analyzer supplied with the instrument. For excitation below 275 nm Polacoat polarizers were used. The solutions of anthracene sulphonates were 10^{-5} M in pure glycerol (0.5% water) and formed rigid glass at 77 K.

Results and Discussion

When a substituent is attached to the anthracene ring, its ability to affect a given electronic transition depends on the position and nature of the substituent. Anthracene^{14,15} and its sulphonates^{16,17} are thought to contain two overlapping transitions in their long wavelength absorption region. The partially allowed ${}^1L_a \rightarrow {}^1A_1$ transition is short axis polarized and considerably more intense than the long axis polarized weakly absorbing forbidden ${}^1L_b \rightarrow {}^1A_1$ transition. Theoretically^{5,15} and experimentally⁵⁻⁹ the origin of 1L_b transition has been placed anywhere between 25000 and 30000 cm^{-1} . Recently Numukhametov and coworkers¹⁶ have attempted to locate latent 1L_b transition of anthracene sulphonic acids from the polarization spectra of oriented polymer films.

Emission spectra and emission polarization spectra (Q_y)—The unpolarized emission spectra and emission polarization spectra (Q_y) along the short axis for 1-AS and 2-AS are given in Fig. 1. The Q_y values are obtained from the fluorescence polarization data exciting the corresponding 1B_b bands. The λ_e for 1-AS is at 253 nm and that for 2-AS at 263 nm. Strong negative polarization establishes in-plane long X-axis polarized nature of 1B_b bands in these sulphonates similar to that in anthracene^{17,18}. However for asymmetrically substituted anthracene such as 2-methylantracene and 2-methoxyanthracene it has been shown by Albrecht³ that even for these molecules the 1B_b is completely X-axis polarized.

Excitation spectra and excitation polarization spectra (R_y)—The unpolarized excitation spectra and excitation polarization spectra R_y along the short axis for 1-AS and 2-AS are shown in Fig. 2. R_y values are obtained from the excitation polarization data by monitoring the fluorescence peak at 0-0 band, i.e. λ_v for 1-AS is at 394 nm and that for 2-AS at 388 nm. It is assumed that 0-0 band is totally free from vibronic coupling and Y-axis polarized^{19,20}. In the excitation spectrum the corresponding R_y values are unity near the 0-0 region after due correction is

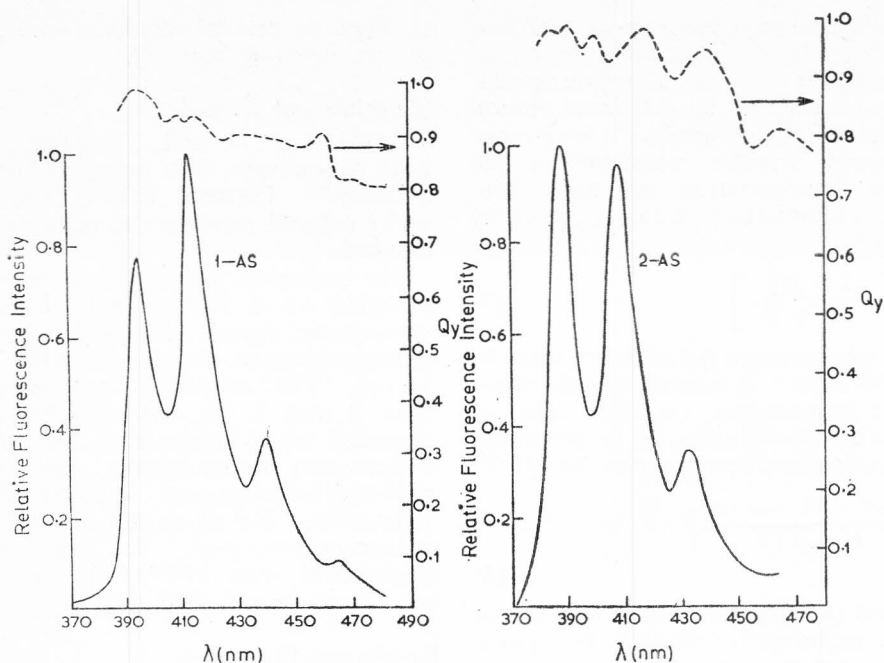


Fig. 1—Fluorescence spectra of 1-AS and 2-AS in glycerol at 77 K and experimental fractional emission intensity (Q_y) polarized along short axis [Excitation at 1B_b band 253 nm for 1-AS and 263 nm for 2-AS]

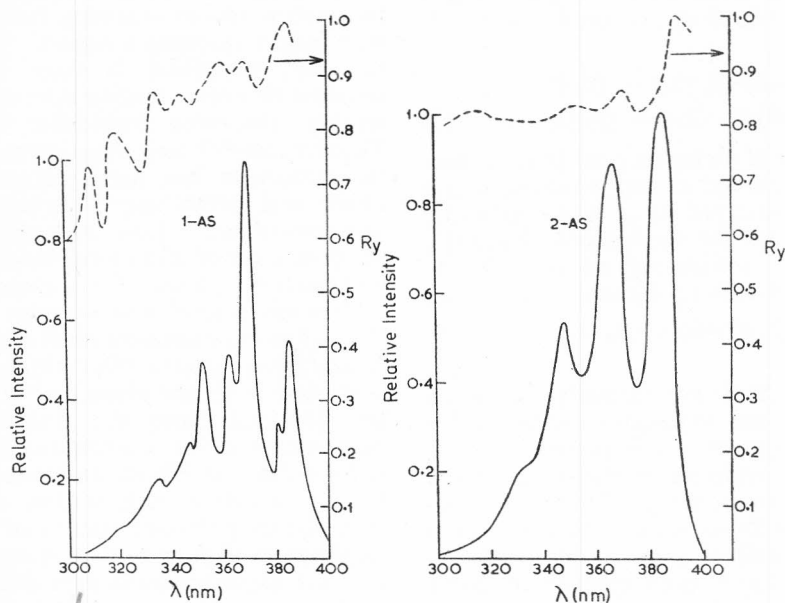


Fig. 2—Excitation spectra (absorption spectra) of 1-AS and 2-AS in glycerol at 77 K and experimental fractional transition intensity R_y polarized along short axis [Emission observed at 0-0 band of the corresponding fluorescence spectra]

made for the randomization factor (ϵ). This indicates that the 0-0 vibration peaks of the two monosulphonates are mainly due to short axis polarized 1L_a band. The observed values of randomization factor for 1-AS are much greater than those for 2-AS in both excitation and emission polarization spectra.

From Fig. 3 it is observed that the first peak in Q_y spectrum blue-shifts by about 125 cm^{-1} for 1-AS, but it is red-shifted by 132 cm^{-1} for 2-AS when compared with the corresponding fluorescence spec-

trum. These shifts indicate that a low frequency promoting mode is superimposed on the original vibronic bands of the spectrum for these partially forbidden transitions. At the same time the values of R_y decrease towards shorter wavelength and opposite is observed for Q_y in mirror image relationship. These changes in R_y and Q_y values could be due to vibronic coupling of X-axis polarized transition with 1L_a vibrational modes. The vibronic pattern of R_y (excitation polarization spectrum) of

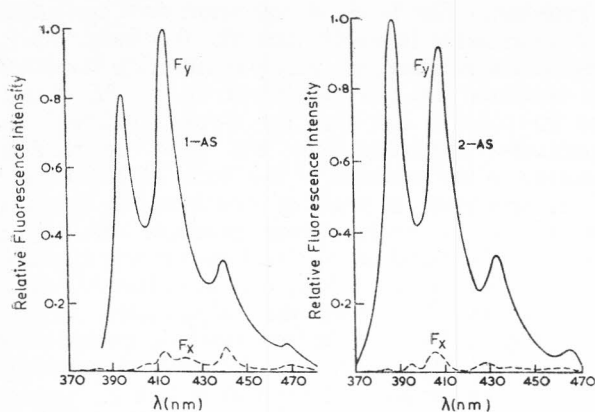


Fig. 3—Polarized fluorescence spectra of 1-AS and 2-AS in glycerol at 77 K. [F_y is Q_y times the fluorescence spectrum and F_x is $(1-Q_y)$ times the fluorescence spectrum]

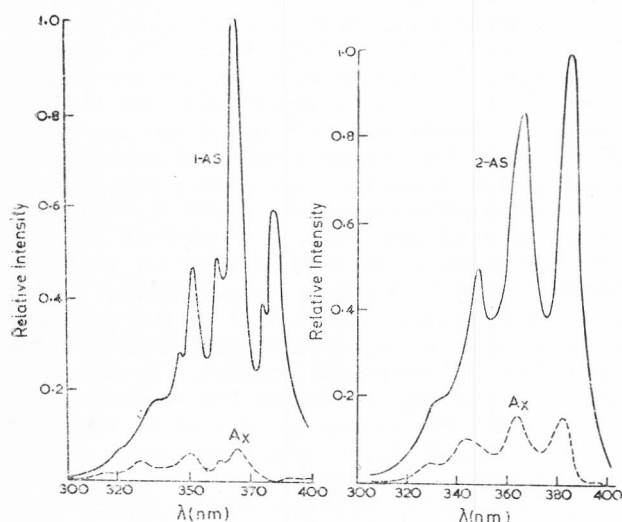


Fig. 4—Polarized excitation spectra (absorption spectra) of 1-AS and 2-AS in glycerol at 77 K. [A_y is R_y times the excitation spectrum and A_x is $(1-R_y)$ times the excitation spectrum]

1-AS is quite similar in nature to that of anthracene⁵. For 2-AS the vibronic contribution of R_y on high energy side, away from 0-1 band is much lower but it does not decrease sharply with increasing energy as observed for 1-AS.

Albrecht⁵ identified two vibronic origins in the polarized absorption and fluorescence spectra of anthracene, a 1630 cm^{-1} , b_{1g} molecular vibration and a weak 60 cm^{-1} , b_g type of lattice vibration. The R_x structures in the near UV absorption have been assigned to Franck-Condon (FC) progressions built upon these vibronic origins in the 1L_a band. Koyanagi *et al*²¹ recently reported an important nontotally symmetric 1655 cm^{-1} , b_{3g} ring vibration in fluorescence polarization spectra of anthracene. Comparing the vibrational structures of R_y and Q_y spectra for these AS it is to be noted that the R_y is more structured and regular than Q_y spectrum for 1-AS and opposite is observed for 2-AS. Such structured R_y spectrum for 1-AS is expected due to the symmetric FC progression in absorption polarization spectrum. A sharp

decrease in Q_y value from 0.92 to 0.8 for 1-AS is observed between the 10833 and 21739 cm^{-1} regions. Onset of such sharp changes in R_y and Q_y values for these two compounds in this frequency range is suggestive of a probable perturbation of 1L_a band by the long axis polarized mode, active in this region.

Short axis (A_y, F_y) and long axis (A_x, F_x) polarized components in absorption (A) and emission spectra (F)—The Y-axis polarized and X-axis polarized intensity components in the excitation and emission spectra are shown in Figs 3 and 4 for 1-AS and 2-AS respectively. A_y is R_y times and A_x is $(1-R_y)$ times the corresponding excitation spectrum and F_y is Q_y times and F_x is $(1-Q_y)$ times the corresponding emission spectrum. The vibrational analysis of A_y and A_x excitation (absorption) intensity spectra and F_y and F_x emission intensity spectra are presented in Tables 1 and 2. The 0-0 peaks in excitation spectra observed at 25984 cm^{-1} for both 1-AS and 2-AS do not depend on the position of SO_3 group⁴. These peaks are the coupling-free 0-0 band of 1L_a transition. The vibronic progression in A_y is 1200 and 1400 cm^{-1} respectively for 1-AS and 2-AS. These frequencies correspond to vibrations which are mixtures of $-\text{C}=\text{C}-$ skeletal and in-plane C-H bending modes as indicated in the IR spectra of these sulphonates⁴. The progression for 1-AS is built upon a low frequency promoting mode of 450 cm^{-1} which is not observed for 2-AS, and is likely to be a skeletal distortion mode as observed for anthracene^{22,23}. The lower frequency vibrational progression of 1200 cm^{-1} for 1-AS compared to 2-AS could be the ring angle bending mode, excited

Table 1—Vibrational Analysis of Excitation Spectra of Anthracene Monosulphonates in Glycerol Glass at 77 K, Polarized along Short Axis (A_y) and Long Axis (A_x)

Intensity	$\bar{\nu}(\text{cm}^{-1})$	$\bar{\nu}(\text{cm}^{-1})$	Analysis
Anthracene 1-Sulphonate; polarized component, A_y			
S	25974	0	0,0
VW	26385	411	0,411
VVS	27174	1196	0,1200
W	27628	1650	0,1200 + 450
MS	28409	2435	0,2(1200)
VW	28818	2844	0,2(1200) + 450
W	29674	3700	0,3(1200)
VVW	31250	5776	0,4(1200) + 450
Polarized component, A_x			
MS	27027	0	0,0
VW	27546	521	0,521
MS	28571	1544	0,1544
W	30303	3276	0,2(1544) + 188
VVW	31746	4719	0,3(1544) + 87
Anthracene 2-sulphonate; polarized component, A_y			
VVS	25974	0	0,0
S	27397	1423	0,1400
MS	28818	2844	0,2(1400)
W	30211	4237	0,3(1400)
Polarized component, A_x			
S	26178	0	0,0
S	27548	1370	0,1370
MS	29240	3062	0,2(1370) + 322
W	30395	4217	0,3(1370)

Table 2—Vibrational Analysis of Emission Spectra of Anthracene Monosulphonates in Glycerol Glass at 77 K, Polarized along Short Axis (F_y) and Long Axis (F_x)

Intensity	$\bar{\nu}$ (cm^{-1})	$\bar{\nu}$ (cm^{-1})	Analysis
Anthracene 1-sulphonate;		polarized	component, F_y
S	25381	00	0,0
VVS	24096	1285	0,2(1300)
MS	22727	2654	0,2(1300)
W	21413	3968	0,3(1300)
		Polarised component, F_x	
VVW	24691	0	0,0
MS	24213	460	0,460
W	23697	994	0,994
MS	22727	1964	0,1504 + 460
Anthracene 2-sulphonate;		polarized	component, F_y
VVS	25773	0	0,0
VS	24450	1323	0,1350
S	23095	2678	0,2(1350)
W	21598	4175	0,3(1350) + 125
		Polarized component, F_x	
VW	25316	0	0,0
MS	24691	625	0,625
W	23364	1952	0,1350 + 625

due to distortion along the short axis by SO_3^- group in 1-position which encounters considerably more steric hindrance from *peri*-hydrogen than the substituent in 2-position. The group frequencies of $-\text{SO}_3^-$ also lie in this range ($1000\text{--}1250\text{ cm}^{-1}$) and are strongly affected by the symmetry properties of the molecule⁴. McGlellan *et al.*²⁴ have assigned 1161 and 1262 cm^{-1} frequencies of anthracene in the Raman spectrum, to skeletal breathing and C-H bending modes, respectively.

The emission intensity spectra (F_y) progress by skeletal frequency modes of 1300 and 1350 cm^{-1} for 1-AS and 2-AS, respectively. The vibrational frequency difference of 1-AS in F_y spectra are larger compared to that in A_y spectra because in the absorption spectra the gamma-C stretch and skeletal bending modes play an important role in vibrational progression. There appears a stronger lattice vibronic coupling in absorption than that in emission.

In the long axis (X-axis) component spectra of anthracene and its sulphonates, both in absorption and emission, two antisymmetric vibronic origins are seen, one at very low frequency and the other corresponding to skeletal vibration. In the fractional absorption intensity spectra of 1-AS the FC envelope of A_x coincides with that of A_y from the 0-1 member of the A_y series, only slightly shifted towards lower energy. But for 2-AS there exists a considerable difference between the FC envelope for short axis and long axis polarized component from the 0-2 member of the A_y series. Anthracene-2-sulphonate(2-AS) shows a greater expression of intensity in the A_x spectrum compared to 1-AS. This is the likely region for the existence of 1L_b band. For substitution of SO_3^- group in the 2-position, which is the least electron rich position, the substituent axis is more closely aligned with the axis of ${}^1A_1\text{--}{}^1L_b$ transition. Therefore a greater perturbation of 1L_b band

is expected. For 1-AS, A_x spectrum does not show any appreciable intensity near the 0-0 band of A_y spectrum which suggests that 0-0 vibration bands of the molecule are not perturbed due to 1L_b band. But the same is not true for 2-AS. Although A_x component spectrum does not show appreciable intensity in the position of 0-0 band at 25974 cm^{-1} of A_y spectrum, a peak of considerable intensity appears at its neighbouring position. Therefore, for 2-AS, 0-0 band of A_y (1L_a band) is not expected to be totally free from long axis polarized 1L_b band perturbation. For both the sulphonates, in the 1L_b band the Y-axis polarized vibronic components are considerably weaker than the allowed spectrum built on true origin and for this reason F_x spectra due to long axis consist of a superposition of F_y (short axis) type of bands having different origins and different intensities. For this coincidence the forbidden 1L_b intensity is not clearly detectable in the ordinary vibration analysis. The 0-0 vibration bands of A_x component spectra are observed at 27027 cm^{-1} for 1-AS and 26178 cm^{-1} for 2-AS. The red shift of 1L_b band of 2-AS is expected because substitution in the 2-position has a greater effect on the 1L_b transition. Similar red shifts and greater expression of 1L_b band for naphthalene²⁵ and anthracene²⁶, substituted at position -2 are already reported.

On further comparison of the A_x and A_y component spectra of 1-AS and 2-AS, it is observed that the vibration bands of A_x at 31746 cm^{-1} for 1-AS and 30395 cm^{-1} for 2-AS in long axis polarization spectra are very prominent and there does not exist any vibronic band at the corresponding position in the short axis A_y component spectra. Therefore, it can be tentatively concluded that corresponding regions in the FC envelope are due to 1L_b band and X-axis polarized 1L_b components begin around these regions. Zimmerman and coworkers^{27,28} using photoselection technique suggested the possible origin of 1L_b band of anthracene at 28300 cm^{-1} but later Albrecht *et al.*⁵ ruled out this proposition and suggested that 1L_b band may be contributing to the X-axis polarized absorption beginning around 30500 cm^{-1} . From our observation the 0-0 levels of 1L_b band for both 1-AS and 2-AS are higher in energy than 1L_a band. So emission is expected from the lowest energy 1L_a state of these sulphonates. The energy gap between 1L_a and 1L_b states being approximately 1053 cm^{-1} for 1-AS and 231 cm^{-1} for 2-AS which are greater than kT (50 cm^{-1} at liq. N_2 temp.). Therefore in these cases there is no possibility of two level fluorescence^{29,30} nor fluorescence level inversion as already inferred from concentration depolarization studies³¹.

The F_x component of emission intensity spectra of 1- and 2-AS exhibit 1504 and 1350 cm^{-1} progression respectively and are built up on low frequency modes of 460 and 944 cm^{-1} for 1-AS and 625 cm^{-1} for 2-AS. The FC envelope of F_x component spectrum decreases in intensity in a manner similar for both 1-AS and 2-AS. The 0-0 bands of F_x component are at 24691 cm^{-1} for 1-AS and 25316 cm^{-1} for 2-AS. From the nature of emission polarization spectra of anthracene sulphonates it is clear that only 1L_a excited electronic state is involved in emission to the

ground state. But in polarized excitation spectra both, 1L_a and 1L_b are involved and hence the greater complexity of the polarized excitation spectra as compared to the polarized emission spectra.

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